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(71) Applicant: **Dow Global Technologies Llc**
Midland, MI 48674 (US)

(72) Inventors:
- **NIETO, Jesús**
  43006 Tarragona Sur (ES)
- **ALVAREZ, Eduardo**
  43006 Tarragona Sur (ES)
- **SANTINI, Luis Alberto**
  43006 Tarragona Sur (ES)
- **SHAH, Viraj K.**
  Freeport, TX Texas TX 77541 (US)

(74) Representative: **Elzaburu S.L.P.**
Miguel Angel 21, 2nd floor
28010 Madrid (ES)

(54) FLEXIBLE CONTAINER WITH THREE-DIMENSIONAL RANDOM LOOP MATERIAL

(57) The present disclosure provides a flexible container (10). In an embodiment, the flexible container comprises a first multilayer film (12) and a second multilayer film (14). Each multilayer film comprises a seal layer. The multilayer films are arranged such that seal layers oppose each other and the second multilayer film is superimposed on the first multilayer film. The films are sealed along a common peripheral edge (16) to form a closed chamber (18). In one embodiment, a free moving sheet (28) of three-dimensional random loop material (3DRLM) is located the closed chamber. In another embodiment, an oversized sheet (128) of 3DRLM is located in the closed chamber.

FIG. 1

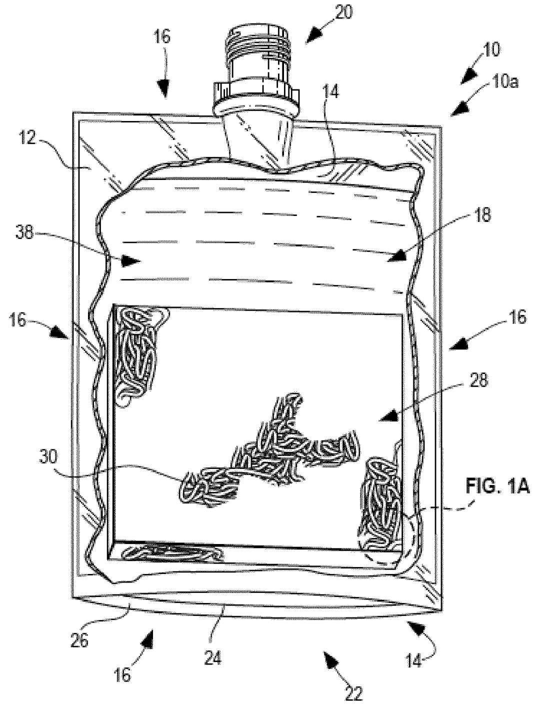

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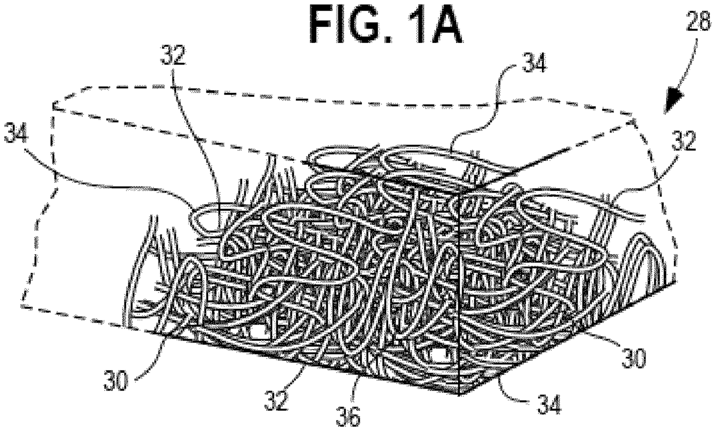
FIG. 1A



Description

BACKGROUND

[0001] Liquids, such as consumer liquids (beverages, cleaning solutions, health care liquids, etc.) are frequently packaged in flexible containers made from flexible polymeric films. Common structures for these flexible containers include pillow pouches and stand-up pouches.

[0002] Problematic with SUPs is that as the liquid is removed therefrom, the SUP collapses. Pouch collapse traps the remaining liquid in folds and crevices of the deformed SUP, impeding-and oftentimes preventing-removal of the entire volume of the stored liquid. Pouch collapse also robs the SUP of its ability to stand upright, making the SUP unstable and difficult to handle by the consumer.

[0003] A need exists for a flexible container-and an SUP in particular-that enables complete extraction of the liquid stored therein. A need further exists for an SUP that maintains its shape regardless whether the SUP is full, partially full, or empty.

SUMMARY

[0004] The present disclosure provides a flexible container. In an embodiment, the flexible container comprises a first multilayer film and a second multilayer film. Each multilayer film comprises a seal layer. The multilayer films are arranged such that seal layers oppose each other and the second multilayer film is superimposed on the first multilayer film. The films are sealed along a common peripheral edge to form a closed chamber. A free moving sheet of three-dimensional random loop material (3DRLM) is located the closed chamber.

[0005] The present disclosure provides another flexible container. In an embodiment, the the flexible container comprises a first multilayer film and a second multilayer film. Each multilayer film comprises a seal layer. The multilayer films are arranged such that seal layers oppose each other and the second multilayer film is superimposed on the first multilayer film. The films are sealed along a common peripheral edge to form a closed chamber. The closed chamber has opposing inner surfaces. An oversized sheet of three-dimensional random loop material (3DRLM) is located in the closed chamber. The oversized sheet of 3DRLM has a first end and an opposing second end. The first end and the second end of the oversized sheet of 3DRLM compressively engage opposing surfaces of the closed chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006]

FIG. 1 is a break-away perspective view a flexible container in accordance with an embodiment of the present disclosure.

FIG. 1A is an enlarged perspective view of Area 1A of FIG. 1.

FIG. 2 is a perspective view of a consumer squeezing the flexible container of FIG. 1 to discharge liquid therefrom.

FIG. 3 is a front perspective view of a flexible container and a sheet of three dimensional random loop material in accordance with another embodiment of the present disclosure.

FIG. 4 is a break-away front elevational view of the flexible container of FIG. 3 with the sheet of three dimensional random loop material installed therein.

FIG. 5 is a perspective view of a consumer squeezing the flexible container of FIG. 4 to discharge liquid therefrom.

DEFINITIONS AND TEST METHODS

[0007] All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2003. Also, any references to a Group or Groups shall be to the Groups or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. Unless stated to the contrary, implicit from the context, or customary in the art, all components and percents are based on weight. For purposes of United States patent practice, the contents of any patent, patent application, or publication referenced herein are hereby incorporated by reference in their entirety (or the equivalent US version thereof is so incorporated by reference).

[0008] The numerical ranges disclosed herein include all values from, and including, the lower value and the upper value. For ranges containing explicit values (e.g., 1, or 2, or 3 to 5, or 6, or 7) any subrange between any two explicit values is included (e.g., 1 to 2; 2 to 6; 5 to 7; 3 to 7; 5 to 6; etc.).

[0009] Unless stated to the contrary, implicit from the context, or customary in the art, all components and percents are based on weight, and all test methods are current as of the filing date of this disclosure.

[0010] Apparent density. A sample material is cut into a square piece of 38 cm x 38 cm (15 in x 15 in) in size. The volume of this piece is calculated from the thickness measured at four points. The division of the weight by the volume gives the apparent density (an average of four measurements is taken) with values reported in grams per cubic centimeter, g/cc.

[0011] Bending Stiffness. The bending stiffness is measured in accordance with DIN 53121 standard, with compression molded plaques of 550 μm thickness, using a Frank-PTI Bending Tester. The samples are prepared by compression molding of resin granules per ISO 293 standard. Conditions for compression molding are chosen per ISO 1872 - 2007 standard. The average cooling rate of the melt is 15°C/min. Bending stiffness is measured in 2-point bending configuration at room temperature with a span of 20 mm, a sample width of 15 mm, and a bending angle of 40°. Bending is applied at 6°/second (s) and the force readings are obtained from 6 to 600 s, after the bending is complete. Each material is evaluated four times with results reported in Newton millimeters ("Nmm").

[0012] "Blend," "polymer blend" and like terms is a composition of two or more polymers. 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. Blends are not laminates, but one or more layers of a laminate can comprise a blend.

^{13}C Nuclear Magnetic Resonance (NMR)

Sample Preparation

[0013] The samples are prepared by adding approximately 2.7 g of a 50/50 mixture of tetrachloroethane-d2/orthodichlorobenzene that is 0.025M in chromium acetylacetonate (relaxation agent) to 0.21 g sample in a 10 mm NMR tube. The samples are dissolved and homogenized by heating the tube and its contents to 150°C.

Data Acquisition Parameters

[0014] The data is collected using a Bruker 400 MHz spectrometer equipped with a Bruker Dual DUL high-temperature CryoProbe. The data is acquired using 320 transients per data file, a 7.3 sec pulse repetition delay (6 sec delay+1.3 sec acq. time), 90 degree flip angles, and inverse gated decoupling with a sample temperature of 125°C. All measurements are made on non-spinning samples in locked mode. Samples are homogenized immediately prior to insertion into the heated (130°C) NMR Sample changer, and are allowed to thermally equilibrate in the probe for 15 minutes prior to data acquisition.

[0015] "Composition" and like terms is a mixture of two or more materials. Included in compositions are pre-reaction, reaction and post-reaction mixtures, the latter of which will include reaction products and by-products as well as unreacted components of the reaction mixture and decomposition products, if any, formed from the one or more components of the pre-reaction or reaction mixture.

[0016] 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.

Crystallization Elution Fractionation (CEF) Method

[0017] Comonomer distribution analysis is performed with Crystallization Elution Fractionation (CEF) (PolymerChar in Spain) (B Monrabal et al, Macromol. Symp. 257, 71-79 (2007)). Ortho-dichlorobenzene (ODCB) with 600 ppm antioxidant butylated hydroxytoluene (BHT) is used as solvent. Sample preparation is done with autosampler at 160°C for 2 hours under shaking at 4 mg/ml (unless otherwise specified). The injection volume is 300 μm. The temperature profile of CEF is: crystallization at 3°C/min from 110°C to 30°C, the thermal equilibrium at 30°C for 5 minutes, elution at 3°C/min from 30°C to 140°C. The flow rate during crystallization is at 0.052 ml/min. The flow rate during elution is at 0.50 ml/min. The data is collected at one data point/second. CEF column is packed by the Dow Chemical Company with glass beads at 125 μm + 6% (MO-SCI Specialty Products) with 1/8 inch stainless tubing. Glass beads are acid washed by MO-SCI Specialty with the request from The Dow Chemical Company. Column volume is 2.06 ml. Column temperature calibration is performed by using a mixture of NIST Standard Reference Material Linear polyethylene 1475a (1.0 mg/ml) and Eicosane (2 mg/ml) in ODCB. Temperature is calibrated by adjusting elution heating rate so that NIST linear polyethylene 1475a has a peak temperature at 101.0°C, and Eicosane has a peak temperature of 30.0°C. The CEF column resolution is calculated with a mixture of NIST linear polyethylene 1475a (1.0 mg/ml) and hexacontane (Fluka, purum, >97.0 , 1 mg/ml). A baseline separation of hexacontane and NIST polyethylene 1475a is achieved. The area of hexacontane (from 35.0 to 67.0°C) to the area of NIST 1475a from 67.0 to 110.0°C is 50 to 50, the amount of soluble fraction below 35.0°C is <1.8 wt%. The CEF column resolution is defined in the following equation:

$$Resolution = \frac{Peak\ temperature\ of\ NIST\ 1475a - Peak\ Temperature\ of\ Hexacontane}{Half\ -\ height\ Width\ of\ NIST\ 1475a\ +\ Half\ -\ height\ Width\ of\ Hexacontane}$$

where the column resolution is 6.0.

[0018] Density is measured in accordance with ASTM D 792 with values reported in grams per cubic centimeter, g/cc.

[0019] Differential Scanning Calorimetry (DSC). Differential Scanning Calorimetry (DSC) is used to measure the melting and crystallization behavior of a polymer over a wide range of temperatures. For example, the TA Instruments Q1000 DSC, equipped with an RCS (refrigerated cooling system) and an autosampler is used to perform this analysis. During testing, a nitrogen purge gas flow of 50 ml/min is used. Each sample is melt pressed into a thin film at about 175°C; the melted sample is then air-cooled to room temperature (approx. 25°C). The film sample is formed by pressing a "0.1 to 0.2 gram" sample at 175°C at 1,500 psi, and 30 seconds, to form a "0.1 to 0.2 mil thick" film. A 3-10 mg, 6 mm diameter specimen is extracted from the cooled polymer, weighed, placed in a light aluminum pan (ca 50 mg), and crimped shut. Analysis is then performed to determine its thermal properties. The thermal behavior of the sample is determined by ramping the sample temperature up and down to create a heat flow versus temperature profile. First, the sample is rapidly heated to 180°C, and held isothermal for five minutes, in order to remove its thermal history. Next, the sample is cooled to -40°C, at a 10°C/minute cooling rate, and held isothermal at - 40°C for five minutes. The sample is then heated to 150°C (this is the "second heat" ramp) at a 10°C/minute heating rate. The cooling and second heating curves are recorded. The cool curve is analyzed by setting baseline endpoints from the beginning of crystallization to -20°C. The heat curve is analyzed by setting baseline endpoints from -20°C to the end of melt. The values determined are peak melting temperature (Tm), peak crystallization temperature (Tc), onset crystallization temperature (Tc onset), heat of fusion (Hf) (in Joules per gram), the calculated % crystallinity for polyethylene samples using: % Crystallinity for PE = ((Hf)/(292 J/g)) x 100, and the calculated % crystallinity for polypropylene samples using: % Crystallinity for PP = ((Hf)/165 J/g)) x 100. The heat of fusion (Hf) and the peak melting temperature are reported from the second heat curve. Peak crystallization temperature and onset crystallization temperature are determined from the cooling curve.

[0020] Elastic Recovery. Resin pellets are compression molded following ASTM D4703, Annex A1, Method C to a thickness of approximately 5-10 mil. Microtensile test specimens of geometry as detailed in ASTM D1708 are punched out from the molded sheet. The test specimens are conditioned for 40 hours prior to testing in accordance with Procedure A of Practice D618.

[0021] The samples are tested in a screw-driven or hydraulically-driven tensile tester using flat, rubber faced grips. The grip separation is set at 22 mm, equal to the gauge length of the microtensile specimens. The sample is extended to a strain of 100% at a rate of 100%/min and held for 30s. The crosshead is then returned to the original grip separation at the same rate and held for 60s. The sample is then strained to 100% at the same 100%/min strain rate.

[0022] Elastic recovery may be calculated as follows:

$$Elastic\ Recovery = \frac{(Initial\ Applied\ Strain - Permanent\ Set)}{Initial\ Applied\ Strain}\ x\ 100\%$$

[0023] An "ethylene-based polymer" is a polymer that contains more than 50 weight percent polymerized ethylene monomer (based on the total weight 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. Nonlimiting examples of ethylene-based polymer (polyethylene) include low density polyethylene (LDPE) and linear polyethylene. Nonlimiting examples of linear polyethylene include linear low density polyethylene (LLDPE), ultra low density polyethylene (ULDPE), very low density polyethylene (VLDPE), multi-component ethylene-based copolymer (EPE), ethylene/α-olefin multi-block copolymers (also known as olefin block copolymer (OBC)), single-site catalyzed linear low density polyethylene (m-LLDPE), substantially linear, or linear, plastomers/elastomers, and high density polyethylene (HDPE). Generally, polyethylene may be produced in gas-phase, fluidized bed reactors, liquid phase slurry process reactors, or liquid phase solution process reactors, using a heterogeneous catalyst system, such as Ziegler-Natta catalyst, a homogeneous catalyst system, comprising Group 4 transition metals and ligand structures such as metallocene, non-metallocene metal-centered, heteroaryl, heterovalent aryloxyether, phosphinimine, and others. Combinations of heterogeneous and/or homogeneous catalysts also may be used in either single reactor or dual reactor configurations.

[0024] "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 C_4-C_8 α-olefin comonomer and a density from greater than 0.94 g/cc, or 0.945 g/cc, or 0.95 g/cc, or 0.955 g/cc to 0.96 g/cc, or 0.97 g/cc, or 0.98 g/cc. The HDPE can be a monomodal copolymer or a multimodal copolymer. A "monomodal ethylene copolymer" is an ethylene/C_4-C_{10} α-olefin copolymer that has one distinct peak in a gel permeation chromatography (GPC) showing the molecular weight distribution. A "multimodal ethylene copolymer" is an ethylene/C_4-C_{10} α-olefin copolymer that has at least two distinct peaks in a GPC showing the molecular weight distribution. Multimodal includes copolymer having two peaks (bimodal) as well as copolymer having more than two peaks. Nonlimiting examples of HDPE include DOW™ High Density Polyethylene (HDPE) Resins (available from The Dow Chemical Company), ELITE™ Enhanced Polyethylene Resins (available from The Dow Chemical Company), CONTINUUM™ Bimodal Polyethylene Resins (available from The Dow Chemical Company), LUPOLEN™ (available from LyondellBasell), as well as HDPE products from Borealis, Ineos, and ExxonMobil.

[0025] An "interpolymer" is a polymer prepared by the polymerization of at least two different monomers. This generic term includes copolymers, usually employed to refer to polymers prepared from two different monomers, and polymers prepared from more than two different monomers, e.g., terpolymers, tetrapolymers, etc.

[0026] "Low density polyethylene" (or "LDPE") consists of ethylene homopolymer, or ethylene/α-olefin copolymer comprising at least one C_3-C_{10} α-olefin, preferably C_3-C_4 that has a density from 0.915 g/cc to 0.940 g/cc and contains long chain branching with broad MWD. LDPE is typically produced by way of high pressure free radical polymerization (tubular reactor or autoclave with free radical initiator). Nonlimiting examples of LDPE include MarFlex™ (Chevron Phillips), LUPOLEN™ (LyondellBasell), as well as LDPE products from Borealis, Ineos, ExxonMobil, and others.

[0027] "Linear low density polyethylene" (or "LLDPE") is 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 comonomer or at least one C_4-C_8 α-olefin comonomer, or at least one C_6-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, or 0.915 g/cc, or 0.920 g/cc, or 0.925 g/cc to 0.930 g/cc, or 0.935 g/cc, or 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).

[0028] "Ultra low density polyethylene" (or "ULDPE") and "very low density polyethylene" (or "VLDPE") each is 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 comonomer, or at least one C_4-C_8 α-olefin comonomer, or at least one C_6-C_8 α-olefin comonomer. ULDPE and VLDPE each has a density from 0.885 g/cc, or 0.90 g/cc to 0.915 g/cc. Nonlimiting examples of ULDPE and VLDPE include ATTANE™ ultra low density polyethylene resins (available form The Dow Chemical Company) and FLEXOMER™ very low density polyethylene resins (available from The Dow Chemical Company).

[0029] "Multi-component ethylene-based copolymer" (or "EPE") comprises units derived from ethylene and units derived from at least one C_3-C_{10} α-olefin comonomer, or at least one C_4-C_8 α-olefin comonomer, or at least one C_6-C_8 α-olefin comonomer, such as described in patent references USP 6,111,023; USP 5,677,383; and USP 6,984,695. EPE resins have a density from 0.905 g/cc, or 0.908 g/cc, or 0.912 g/cc, or 0.920 g/cc to 0.926 g/cc, or 0.929 g/cc, or 0.940 g/cc, or 0.962 g/cc. Nonlimiting examples of EPE resins include ELITE™ enhanced polyethylene (available from The Dow Chemical Company), ELITE AT™ advanced technology resins (available from The Dow Chemical Company), SURPASS™ Polyethylene (PE) Resins (available from Nova Chemicals), and SMART™ (available from SK Chemicals Co.).

[0030] "Single-site catalyzed linear low density polyethylenes" (or "m-LLDPE") are linear ethylene/α-olefin copolymers containing homogeneous short-chain branching distribution comprising units derived from ethylene and units derived from at least one C_3-C_{10} α-olefin comonomer, or at least one C_4-C_8 α-olefin comonomer, or at least one C_6-C_8 α-olefin comonomer. m-LLDPE has density from 0.913 g/cc, or 0.918 g/cc, or 0.920 g/cc to 0.925 g/cc, or 0.940 g/cc. Nonlimiting examples of m-LLDPE include EXCEED™ metallocene PE (available from ExxonMobil Chemical), LUFLEXEN™ m-LLDPE (available from LyondellBasell), and ELTEX™ PF m-LLDPE (available from Ineos Olefins & Polymers).

[0031] "Ethylene plastomers/elastomers" are substantially linear, or linear, ethylene/α-olefin copolymers containing homogeneous short-chain branching distribution comprising units derived from ethylene and units derived from at least one C_3-C_{10} α-olefin comonomer, or at least one C_4-C_8 α-olefin comonomer, or at least one C_6-C_8 α-olefin comonomer. Ethylene plastomers/elastomers have a density from 0.870 g/cc, or 0.880 g/cc, or 0.890 g/cc to 0.900 g/cc, or 0.902 g/cc, or 0.904 g/cc, or 0.909 g/cc, or 0.910 g/cc, or 0.917 g/cc. Nonlimiting examples of ethylene plastomers/ elastomers include AFFINITY™ plastomers and elastomers (available from The Dow Chemical Company), EXACT™ Plastomers (available from ExxonMobil Chemical), Tafmer™ (available from Mitsui), Nexlene™ (available from SK Chemicals Co.), and Lucene™ (available LG Chem Ltd.).

[0032] Melt flow rate (MFR) is measured in accordance with ASTM D 1238, Condition 280°C/2.16 kg (g/10 minutes).

[0033] Melt index (MI) is measured in accordance with ASTM D 1238, Condition 190°C/2.16 kg (g/10 minutes).

[0034] "Melting Point" or "Tm" as used herein (also referred to as a melting peak in reference to the shape of the plotted DSC curve) is typically measured by the DSC (Differential Scanning Calorimetry) technique for measuring the melting points or peaks of polyolefins as described in USP 5,783,638. It should be noted that many blends comprising two or more polyolefins will have more than one melting point or peak, many individual polyolefins will comprise only one melting point or peak.

[0035] Molecular weight distribution (Mw/Mn) is measured using Gel Permeation Chromatography (GPC). In particular, conventional GPC measurements are used to determine the weight-average (Mw) and number-average (Mn) molecular weight of the polymer and to determine the Mw/Mn. The gel permeation chromatographic system consists of either a Polymer Laboratories Model PL-210 or a Polymer Laboratories Model PL-220 instrument. The column and carousel compartments are operated at 140°C. Three Polymer Laboratories 10-micron Mixed-B columns are used. The solvent is 1,2,4 trichlorobenzene. The samples are prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent containing 200 ppm of butylated hydroxytoluene (BHT). Samples are prepared by agitating lightly for 2 hours at 160°C. The injection volume used is 100 microliters and the flow rate is 1.0 ml/minute.

[0036] Calibration of the GPC column set is performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000, arranged in 6 "cocktail" mixtures with at least a decade of separation between individual molecular weights. The standards are purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards are prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards are dissolved at 80°C with gentle agitation for 30 minutes. The narrow standards mixtures are run first and in order of decreasing highest molecular weight component to minimize degradation. The polystyrene standard peak molecular weights are converted to polyethylene molecular weights using the following equation (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)):

$$M_{\text{polypropylene}}=0.645(M_{\text{polystyrene}}).$$

[0037] Polypropylene equivalent molecular weight calculations are performed using Viscotek TriSEC software Version 3.0.

[0038] An "olefin-based polymer," as used herein, is a polymer that contains more than 50 weight percent polymerized olefin monomer (based on total amount of polymerizable monomers), and optionally, may contain at least one comonomer. Nonlimiting examples of olefin-based polymer include ethylene-based polymer and propylene-based polymer.

[0039] A "polymer" is a compound prepared by polymerizing monomers, whether of the same or a different type, that in polymerized form provide 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 has being based on "units" that are the polymerized form of a corresponding monomer.

[0040] A "propylene-based polymer" is a polymer that contains more than 50 weight percent polymerized propylene monomer (based on the total amount of polymerizable monomers) and, optionally, may contain at least one comonomer.

Creep Zero Shear Viscosity Measurement Method

[0041] Zero-shear viscosities are obtained via creep tests that were conducted on an AR-G2 stress controlled rheometer (TA Instruments: New Castle, Del.) using 25-mm-diameter parallel plates at 190°C. The rheometer oven is set to test temperature for at least 30 minutes prior to zeroing fixtures. At the testing temperature a compression molded sample disk is inserted between the plates and allowed to come to equilibrium for 5 minutes. The upper plate is then lowered down to 50 μm above the desired testing gap (1.5 mm). Any superfluous material is trimmed off and the upper plate is lowered to the desired gap. Measurements are done under nitrogen purging at a flow rate of 5 L/min. Default creep time is set for 2 hours.

[0042] A constant low shear stress of 20 Pa is applied for all of the samples to ensure that the steady state shear rate is low enough to be in the Newtonian region. The resulting steady state shear rates are in the range of 10^{-3} to $10^{-4}s^{-1}$

for the samples in this study. Steady state is determined by taking a linear regression for all the data in the last 10% time window of the plot of log (J(t)) vs. log(t), where J(t) is creep compliance and t is creep time. If the slope of the linear regression is greater than 0.97, steady state is considered to be reached, then the creep test is stopped. In all cases in this study the slope meets the criterion within 2 hours. The steady state shear rate is determined from the slope of the linear regression of all of the data points in the last 10% time widow of the plot of E vs. t, where E is strain.

[0043] The zero-shear viscosity is determined from the ratio of the applied stress to the steady state shear rate.

[0044] In order to determine if the sample is degraded during the creep test, a small amplitude oscillatory shear test is conducted before and after the creep test on the same speciment from 0.1 to 100 rad/s. The complex viscosity values of the two tests are compared. If the difference of the viscosity values at 0.1 rad/s is greater than 5%, the sample is considered to have degraded during the creep test, and the result is discarded.

[0045] Zero-shear viscosity ratio (ZSVR) is defined as the ratio of the zero-shear viscotity (ZSV) of the branched polyethylene material to the ZSV of the linear polyethylene material at the equivalent weight average moleculasr weight (Mw-gpc) according to the following Equation:

$$ZSVR = \frac{\eta_{0B}}{\eta_{0L}} = \frac{\eta_{0B}}{2.29^{-15} M_{w-gpc}^{3.65}}$$

[0046] The ZSV value is obtained from creep test at 190°C via the method described above. The Mw-gpc value is determined by the HT-GPC method. The correlation between ZSV of linear polyethylene and its Mw-gpc was established based on a series of linear polyethylene reference materials. A description for the ZSV-Mw relationship can be found in the ANTEC proceeding: Karjala, Teresa P.; Sammler, Robert L.; Mangnus Marc A.; Hazlitt, Lonnie G.; Johnson, Mark S.; Hagen, Charles M., Jr.; Huang, Joe W.L.; Reichek, Kenneth N. Detection of low levels of long-chain branching in polyolefins. Annual Technical Conference - Society of Plastics Engineers (2008), 66th 887-891.

DETAILED DESCRIPTION

[0047] The present disclosure provides a flexible container. The flexible container includes a first multilayer film and a second multilayer film. Each multilayer film includes a seal layer. The multilayer films are arranged such that the seal layers oppose each other and the second multilayer film is superimposed on the first multilayer film. The multilayer films are sealed along a common peripheral edge to form a closed chamber. The flexible container includes a free moving sheet of three-dimensional random loop material (3DRLM) in the closed chamber.

1. Multilayer Films

[0048] The present flexible container includes a first multilayer film and a second multilayer film. In an embodiment, a flexible container 10 includes a first multilayer film 12 (a front film) and a second multilayer film 14 (a rear film) as shown in FIG. 1. The term 'first multilayer film" and the term "front film" are used interchangeably. The term "second multilayer film" and the term "rear film" are used interchangeably.

[0049] Each multilayer film is flexible and has at least two, or at least three layers. The multilayer film is resilient, flexible, deformable, and pliable. The structure and composition for each multilayer film may be the same or different. For example, each of two opposing multilayer films can be made from a separate web, each web having a unique structure and/or unique composition, finish, or print. Alternatively, each multilayer film can be the same structure and the same composition.

[0050] In an embodiment, each multilayer film 12, 14 is a flexible multilayer film having the same structure and the same composition.

[0051] Each flexible multilayer film 12, 14 may be (i) a coextruded multilayer structure or (ii) a laminate, or (iii) a combination of (i) and (ii). In an embodiment, each flexible multilayer film 12, 14 has at least three layers: a seal layer, an outer layer, and a core layer (which may be a tie layer) therebetween. When the core layer is a tie layer, the tie layer adjoins the seal layer to the outer layer. The flexible multilayer film may include one or more optional inner layers disposed between the seal layer and the outer layer.

[0052] In an embodiment, the flexible multilayer film is a coextruded film having at least two, or three, or four, or five, or six, or seven to eight, or nine, or 10, or 11, or more layers. Some methods, for example, used to construct films are by cast co-extrusion or blown co-extrusion methods, adhesive lamination, extrusion lamination, thermal lamination, and coatings such as vapor deposition. Combinations of these methods are also possible. Film layers can comprise, in addition to the polymeric materials, additives such as stabilizers, slip additives, antiblocking additives, process aids, clarifiers, nucleators, pigments or colorants, fillers and reinforcing agents, and the like as commonly used in the packaging industry. It is particularly useful to choose additives and polymeric materials that have suitable organoleptic and or optical properties.

[0053] Nonlimiting examples of suitable polymeric materials for the seal layer include olefin-based polymer (including any ethylene/C_3-C_{10} α-olefin copolymers linear or branched), propylene-based polymer (including plastomer and elastomer, random propylene copolymer, propylene homopolymer, and propylene impact copolymer), ethylene-based polymer (including plastomer and elastomer, high density polyethylene ("HDPE"), low density polyethylene ("LDPE"), linear low density polyethylene ("LLDPE"), medium density polyethylene ("MDPE"), ethylene-acrylic acid or ethylene-methacrylic acid and their ionomers with zinc, sodium, lithium, potassium, magnesium salts, ethylene vinyl acetate copolymers and blends thereof.

[0054] Nonlimiting examples of suitable polymeric material for the outer layer include those used to make biaxially or monoaxially oriented films for lamination as well as coextruded films. Some nonlimiting polymeric material examples are biaxially oriented polyethylene terephthalate (OPET), monoaxially oriented nylon (MON), biaxially oriented nylon (BON), and biaxially oriented polypropylene (BOPP). Other polymeric materials useful in constructing film layers for structural benefit are polypropylenes (such as propylene homopolymer, random propylene copolymer, propylene impact copolymer, thermoplastic polypropylene (TPO) and the like, propylene-based plastomers (e.g., VERSIFY™ or VISTAMAX™)), polyamides (such as Nylon 6, Nylon 6,6, Nylon 6,66, Nylon 6,12, Nylon 12 etc.), polyethylene norbornene, cyclic olefin copolymers, polyacrylonitrile, polyesters, copolyesters (such as PETG), cellulose esters, polyethylene and copolymers of ethylene (e.g., LLDPE based on ethylene octene copolymer such as DOWLEX™, blends thereof, and multilayer combinations thereof.

[0055] Nonlimiting examples of suitable polymeric materials for the tie layer include functionalized ethylene-based polymers such as ethylene-vinyl acetate ("EVA"), polymers with maleic anhydride-grafted to polyolefins such as any polyethylene, ethylene-copolymers, or polypropylene, and ethylene acrylate copolymers such an ethylene methyl acrylate ("EMA"), glycidyl containing ethylene copolymers, propylene and ethylene based olefin block copolymers (OBC) such as INTUNE™ (PP-OBC) and INFUSE™ (PE-OBC) both available from The Dow Chemical Company, and blends thereof.

[0056] The flexible multilayer film may include additional layers which may contribute to the structural integrity or provide specific properties. The additional layers may be added by direct means or by using appropriate tie layers to the adjacent polymer layers. Polymers which may provide additional mechanical performance such as stiffness or opacity, as well polymers which may offer gas barrier properties or chemical resistance can be added to the structure.

[0057] Nonlimiting examples of suitable material for the optional barrier layer include copolymers of vinylidene chloride and methyl acrylate, methyl methacrylate or vinyl chloride (e.g., SARAN™ resins available from The Dow Chemical Company); vinylethylene vinyl alcohol (EVOH), metal foil (such as aluminum foil). Alternatively, modified polymeric films such as vapor deposited aluminum or silicon oxide on such films as BON, OPET, or OPP, can be used to obtain barrier properties when used in laminate multilayer film.

[0058] In an embodiment, the flexible multilayer film includes a seal layer selected from LLDPE (sold under the trade name DOWLEX™ (The Dow Chemical Company)), single-site LLDPE (substantially linear, or linear, olefin polymers, including polymers sold under the trade name AFFINITY™ or ELITE™ (The Dow Chemical Company) for example, ethylene vinyl acetate (EVA), ethylene ethyl acrylate (EEA), propylene-based plastomers or elastomers such as VERSIFY™ (The Dow Chemical Company), grafted olefin-based polymer (MAH-grafted), and blends thereof. An optional tie layer is selected from either ethylene-based olefin block copolymer PE-OBC (sold as INFUSE™) or propylene-based olefin block copolymer PP-OBC (sold as INTUNE™). The outer layer includes greater than 50 wt% of resin(s) having a melting point, Tm, that is from 25°C to 30°C, or 40°C or higher than the melting point of the polymer in the seal layer wherein the outer layer polymer is selected from resins such as AFFINITY™, LLDPE (DOWLEX™), VERSIFY™ or VISTAMAX, ELITE™, MDPE, HDPE or a propylene-based polymer such as propylene homopolymer, propylene impact copolymer or TPO.

[0059] In an embodiment, the flexible multilayer film is co-extruded.

[0060] In an embodiment, flexible multilayer film includes a seal layer selected from LLDPE (sold under the trade name DOWLEX™ (The Dow Chemical Company)), single-site LLDPE (substantially linear, or linear, olefin polymers, including polymers sold under the trade name AFFINITY™ or ELITE™ (The Dow Chemical Company) for example, propylene-based plastomers or elastomers such as VERSIFY™ (The Dow Chemical Company), grafted olefin-based polymer (MAH-grafted), and blends thereof. The flexible multilayer film also includes an outer layer that is a polyamide.

[0061] In an embodiment, the flexible multilayer film is a coextruded and/or laminated film, the seal layer is composed of an ethylene-based polymer, such as a linear or a substantially linear polymer, or a single-site catalyzed linear or substantially linear polymer of ethylene and an alpha-olefin monomer such as 1-butene, 1-hexene or 1-octene, having a Tm from 55°C to 115°C and a density from 0.865 to 0.925 g/cm^3, or from 0.875 to 0.910 g/cm^3, or from 0.888 to 0.900 g/cm^3. The outer layer is composed of a material selected from LLDPE, OPET, OPP (oriented polypropylene), BOPP, polyamide, and combinations thereof.

[0062] In an embodiment, the flexible multilayer film is a coextruded and/or laminated film having at least five layers, the coextruded film having a seal layer composed of an ethylene-based polymer, such as a linear or substantially linear polymer, or a single-site catalyzed linear or substantially linear polymer of ethylene and an alpha-olefin comonomer such as 1-butene, 1-hexene or 1-octene, the ethylene-based polymer having a Tm from 55°C to 115°C and a density from 0.865 to 0.925 g/cm^3, or from 0.875 to 0.910 g/cm^3, or from 0.888 to 0.900 g/cm^3 and an outermost layer composed of a material selected from LLDPE, OPET, OPP (oriented polypropylene), BOPP, polyamide, and combinations thereof.

[0063] In an embodiment, the flexible multilayer film is a coextruded and/or laminated film having at least seven layers. The seal layer is composed of an ethylene-based polymer, such as a linear or substantially linear polymer, or a single-site catalyzed linear or substantially linear polymer of ethylene and an alpha-olefin comonomer such as 1-butene, 1-hexene or 1-octene, the ethylene-based polymer having a Tm from 55°C to 115°C and density from 0.865 to 0.925 g/cm^3, or from 0.875 to 0.910 g/cm^3, or from 0.888 to 0.900 g/cm^3. The outer layer is composed of a material selected from LLDPE, OPET, OPP (oriented polypropylene), BOPP, polyamide, and combinations thereof.

[0064] In an embodiment, the flexible multilayer film is a coextruded (or laminated) five layer film, or a coextruded (or laminated) seven layer film having at least two layers containing an ethylene-based polymer. The ethylene-based polymer may be the same or different in each layer.

[0065] In an embodiment, the flexible multilayer film is a coextruded and/or laminated five layer, or a coextruded (or laminated) seven layer film having at least one layer containing a material selected from LLDPE, OPET, OPP (oriented polypropylene), BOPP, and polyamide.

[0066] In an embodiment, the flexible multilayer film is a coextruded and/or laminated five layer, or a coextruded (or laminated) seven layer film having at least one layer containing OPET or OPP.

[0067] In an embodiment, the flexible multilayer film is a coextruded (or laminated) five layer, or a coextruded (or laminated) seven layer film having at least one layer containing polyamide.

[0068] In an embodiment, the flexible multilayer film is a seven-layer coextruded (or laminated) film with a seal layer composed of an ethylene-based polymer, or a linear or substantially linear polymer, or a single-site catalyzed linear or substantially linear polymer of ethylene and an alpha-olefin monomer such as 1-butene, 1-hexene or 1-octene, having a Tm from 90°C to 106°C. The outer layer is a polyamide having a Tm from 170°C to 270°C. The film has an inner layer (first inner layer) composed of a second ethylene-based polymer, different than the ethylene-based polymer in the seal layer. The film has an inner layer (second inner layer) composed of a polyamide the same or different to the polyamide in the outer layer. The seven layer film has a thickness from 100 micrometers to 250 micrometers.

[0069] The rear film 14 opposes the front film 12, such that the rear film 14 is superimposed on the front film 12. The front film 12 and the rear film 14 are sealed around a common peripheral edge 16 to form a closed chamber 18.

[0070] The present flexible container 10 can be a box pouch, pillow pouch, spout k-sealed pouch, spout side gusseted pouch, or a stand-up pouch. The flexible container may or may not have a fitment (i.e., a spout). If a fitment is present, the location of the fitment installed into the container can be anywhere a seal exists between two films, i.e., on top, side or even on bottom in the seal of bottom gusset to front panel, for example. In other words, the fitment can be located, or otherwise formed, on the flexible container anywhere where two films meet and are heat sealed together. Nonlimiting examples of suitable locations for the fitment to be sealed include top, bottom, side, corner, gusset areas of the flexible container.

[0071] The present flexible container can be formed with or without handles.

[0072] In an embodiment, the flexible container 10 includes a fitment 20. The fitment 20 is sandwiched between the front film and the rear film, with a base of the fitment sealed along a portion of the common peripheral edge 16. The fitment may or may not include a closure. The fitment 20 dispenses the contents held within the closed chamber 18.

[0073] In an embodiment, present flexible container is a stand-up pouch 10a, or "SUP," as shown in FIGS. 1-2. The SUP 10a includes a gusset 22. The gusset 22 is attached to, or otherwise extends from, a lower portion of the front film 12 and/or a lower portion of the rear film 14. The gusset 22 includes a gusset film 24 and a gusset rim 26. The gusset 22 may be formed by way of heat seal, weld (ultrasonic or high frequency or radio frequency), adhesive bond, and combinations thereof. The gusset 22, the films 12, 14, and the fitment define a closed and hermetically sealed chamber for holding a flowable substance, such as liquid, for example.

[0074] The gusset 22 is made of a flexible polymeric material. In an embodiment, the gusset 22 is made from a multilayer film with the same structure and composition as the front film 12 and the rear film 14. The gusset 22 provides (1) the structural integrity to support the SUP and its contents without leakage, and (2) the stability for the SUP to stand upright (i.e., base on a support surface, such as a horizontal surface, or a substantially horizontal surface), without tipping over. In this sense, the pouch is a self-standing upright pouch, or a "stand-up pouch".

[0075] In an embodiment, the gusset 22 is an extension of one or both multilayer films 12, 14. A folding procedure forms the gusset 22 from one, or both, of the multilayer films 12,14.

[0076] The gusset rim 26 defines a footprint for the SUP. The footprint can have a variety of shapes. Nonlimiting examples of suitable shapes for the footprint include circle, square, rectangle, triangle, oval, ellipsoid, eye-shape, and teardrop. In a further embodiment, the shape of the footprint is ellipsoid.

[0077] In an embodiment, the flexible container includes a closure. Although FIGS. 1-2 show fitment 20 with threads to accommodate a screw-on type closure (for use with a mated screw-on cap), it is understood that the fitment 20 may embody other closure systems. Nonlimiting examples of suitable fitments and closures, include, screw cap, flip-top cap, snap cap, liquid or beverage dispensing fitments (stop-cock or thumb plunger), Colder fitment connector, tamper evident pour spout, vertical twist cap, horizontal twist cap, aseptic cap, vitop press, press tap, push on tap, lever cap, conro fitment connector, and other types of removable (and optionally reclosable) closures. The closure and/or fitment may or may not include a gasket.

[0078] In an embodiment, the SUP 10a has a volume from 0.25 liters (L), or 0.5L, or 0.75L, or 1.0L, or 1.5L, or 2.5L, or 3L, or 3.5L, or 4.0L, or 4.5L, or 5.0L to 6.0L, or 7.0L, or 8.0L, or 9.0L, or 10.0L, or 20L, or 30L.

[0079] In an embodiment, the present flexible container is made from 90 wt% to 100 wt% ethylene-based polymer-the films 12, 14 and gusset 22 being composed of flexible multiple layer film with layer materials selected from ethylene-based polymer such as LLDPE, LDPE, HDPE, and combinations thereof, and the fitment 10 composed of HDPE or ethylene/α-olefin multi-block copolymer. Weight percent is based on total weight of the flexible container (without content). The flexible container made from 90 wt% to 100 wt% ethylene-based polymer is advantageous as it is readily recyclable.

2. 3-dimensional random loop material

[0080] The present flexible container includes a sheet of 3-dimensional random loop material located in the closed chamber. A "3-dimensional random loop material" (or "3DRLM") is a mass or a structure of a multitude of loops formed by allowing continuous fibers, to wind, permitting respective loops to come in contact with one another in a molten state and to be heat-bonded, or otherwise melt-bonded, at most of the contact points. FIGS. 1-1A show 3DRLM 30 having loops 32 of continuous fibers 34, the continuous fibers 34 coming in contact with one another at contact points 36. Even when a great stress to cause significant deformation is given, the 3DRLM 30 absorbs the stress with the entire net structure composed of three-dimensional random loops melt-integrated, by deforming itself; and once the stress is lifted, elastic resilience of the polymer manifests itself to allow recovery to the original shape of the structure. When a net structure composed of continuous fibers made from a known non-elastic polymer is used as a cushioning material, plastic deformation is developed and the recovery cannot be achieved, thus resulting in poor heat-resisting durability. When the fibers are not melt-bonded at contact points, the shape cannot be retained and the structure does not integrally change its shape, with the result that a fatigue phenomenon occurs due to the concentration of stress, thus unbeneficially degrading durability and deformation resistance. In certain embodiments, melt-bonding is the state where all contact points are melt-bonded.

[0081] A nonlimiting method for producing 3DRLM 30 includes the steps of (a) heating a molten olefin-based polymer, at a temperature 10°C-140°C higher than the melting point of the polymer in a typical melt-extruder; (b) discharging the molten interpolymer to the downward direction from a nozzle with plural orifices to form loops by allowing the fibers to fall naturally (due to gravity). The polymer may be used in combination with a thermoplastic elastomer, thermoplastic non-elastic polymer or a combination thereof. The distance between the nozzle surface and take-off conveyors installed on a cooling unit for solidifying the fibers, melt viscosity of the polymer, diameter of orifice and the amount to be discharged are the elements which decide loop diameter and fineness of the fibers. Loops are formed by holding and allowing the delivered molten fibers to reside between a pair of take-off conveyors (belts, or rollers) set on a cooling unit (the distance therebetween being adjustable), bringing the loops thus formed into contact with one another by adjusting the distance between the orifices to this end such that the loops in contact are heat-bonded, other otherwise melt-bonded, as they form a three-dimensional random loop structure. Then, the continuous fibers, wherein contact points have been heat-bonded as the loops form a three-dimensional random loop structure, are continuously taken into a cooling unit for solidification to give a net structure. Thereafter, the structure is cut into a desired length and shape. The method is characterized in that the olefin-based polymer is melted and heated at a temperature 10°C-140°C higher than the melting point of the interpolymer and delivered to the downward direction in a molten state from a nozzle having plural orifices. When the polymer is discharged at a temperature less than 10°C higher than the melting point, the fiber delivered becomes cool and less fluidic to result in insufficient heat-bonding of the contact points of fibers.

[0082] Properties, such as, the loop diameter and fineness of the fibers constituting the cushioning net structure provided herein depend on the distance between the nozzle surface and the take-off conveyor installed on a cooling unit for solidifying the interpolymer, melt viscosity of the interpolymer, diameter of orifice and the amount of the interpolymer to be delivered therefrom. For example, a decreased amount of the interpolymer to be delivered and a lower melt viscosity upon delivery result in smaller fineness of the fibers and smaller average loop diameter of the random loop. On the contrary, a shortened distance between the nozzle surface and the take-off conveyor installed on the cooling unit for solidifying the interpolymer results in a slightly greater fineness of the fiber and a greater average loop diameter of the random loop. These conditions in combination afford the desirable fineness of the continuous fibers of from 100 denier to 100000 denier and an average diameter of the random loop of not more than 100 mm, or from 1 millimeter (mm), or 2 mm, or 10 mm to 25 mm, or 50 mm. By adjusting the distance to the aforementioned conveyor, the thickness of the structure can be controlled while the heat-bonded net structure is in a molten state and a structure having a desirable thickness and flat surface formed by the conveyors can be obtained. Too great a conveyor speed results in failure to heat-bond the contact points, since cooling proceeds before the heat-bonding. On the other hand, too slow a speed can cause higher density resulting from excessively long dwelling of the molten material. In some embodiments the distance to the conveyor and the conveyor speed should be selected such that the desired apparent density of 0.005-0.1 g/cc or 0.01-0.05 g/cc can be achieved.

[0083] In an embodiment, the 3DRLM 30 has, one, some, or all of the properties (i) - (iii) below:

(i) an apparent density from apparent density from 0.016 g/cc, or 0.024 g/cc, or 0.032 g/cc, or 0.040 g/cc, or 0.050 g/cc, or 0.060 to 0.070, or 0.080, or 0.090, or 0.100, or 0.150; and/or
(ii) a fiber diameter from 0.1 mm, or 0.5 mm, or 0.7 mm, or 1.0 mm or 1.5 mm to 2.0 mm to 2.5 mm, or 3.0 mm; and/or
(iii) a thickness (machine direction) from 1.0 cm, 2.0 cm, or 3.0, cm, or 4.0 cm, or 5.0 cm, or 10 cm, or 20 cm, to 50 cm, or 75 cm, or 100 cm, or more. It is understood that the thickness of the 3DRLM 30 will vary based on the type of product to be packaged.

[0084] The 3DRLM 30 is formed into a three dimensional geometric shape to form a sheet (*i.e.,* a prism). In an embodiment the 3DRLM 30 is formed into a regular geometric shape. Nonlimiting examples of suitable regular geometric shapes include prism, pyramid, cone, cylinder, and disk.

[0085] The 3DRLM 30 is an elastic material which can be compressed and stretched and return to its original geometric shape. An "elastic material," as used herein, is a rubber-like material that can be compressed and/or stretched and which expands/retracts very rapidly to approximately its original shape/length when the force exerting the compression and/or the stretching is released. The three dimensional random loop material 30 has a "neutral state" when no compressive force and no stretch force is imparted upon the 3DRLM 30. The three dimensional random loop material 30 has "a compressed state" when a compressive force is imparted upon the 3DRLM 30. The three dimensional random loop material 30 has "a stretched state" when a stretching force is imparted upon the 3DRLM 30.

[0086] The three dimensional random loop material 30 is composed of one or more olefin-based polymers. The olefin-based polymer can be one or more ethylene-based polymers, one or more propylene-based polymers, and blends thereof.

[0087] In an embodiment, the ethylene-based polymer is an ethylene/α-olefin polymer. Ethylene/α-olefin polymer may be a random ethylene/α-olefin polymer or an ethylene/α-olefin multi-block polymer. The α-olefin is a C_3-C_{20} α-olefin, or a C_4-C_{12} α-olefin, or a C_4-C_8 α-olefin. Nonlimiting examples of suitable α-olefin comonomer include propylene, butene, methyl-1-pentene, hexene, octene, decene, dodecene, tetradecene, hexadecene, octadecene, cyclohexyl-1-propene (allyl cyclohexane), vinyl cyclohexane, and combinations thereof.

[0088] In an embodiment, the ethylene-based polymer is a homogeneously branched random ethylene/α-olefin copolymer.

[0089] "Random copolymer" is a copolymer wherein the at least two different monomers are arranged in a non-uniform order. The term "random copolymer" specifically excludes block copolymers. The term "homogeneous ethylene polymer" as used to describe ethylene polymers is used in the conventional sense in accordance with the original disclosure by Elston in U.S. Pat. No. 3,645,992, the disclosure of which is incorporated herein by reference, to refer to an ethylene polymer in which the comonomer is randomly distributed within a given polymer molecule and wherein substantially all of the polymer molecules have substantially the same ethylene to comonomer molar ratio. As defined herein, both substantially linear ethylene polymers and homogeneously branched linear ethylene are homogeneous ethylene polymers.

[0090] The homogeneously branched random ethylene/α-olefin copolymer may be a random homogeneously branched linear ethylene/α-olefin copolymer or a random homogeneously branched substantially linear ethylene/α-olefin copolymer. The term "substantially linear ethylene/α-olefin copolymer" means that the polymer backbone is substituted with from 0.01 long chain branches/1000 carbons to 3 long chain branches/1000 carbons, or from 0.01 long chain branches/1000 carbons to 1 long chain branches/1000 carbons, or from 0.05 long chain branches/1000 carbons to 1 long chain branches/1000 carbons. In contrast, the term "linear ethylene/α-olefin copolymer" means that the polymer backbone has no long chain branching.

[0091] The homogeneously branched random ethylene/α-olefin copolymers may have the same ethylene/α-olefin comonomer ratio within all copolymer molecules. The homogeneity of the copolymers may be described by the SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) and is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described in U.S. Pat. No. 4,798,081 (Hazlitt et al.), or in U.S. Pat. No. 5,089,321 (Chum et al.) the disclosures of all of which are incorporated herein by reference. The SCBDI or CDBI for the homogeneously branched random ethylene/α-olefin copolymers is preferably greater than about 30 percent, or greater than about 50 percent.

[0092] The homogeneously branched random ethylene/α-olefin copolymer may include at least one ethylene comonomer and at least one C_3 -C_{20} α-olefin, or at least one C_4-C_{12} α-olefin comonomer. For example and not by way of limitation, the C_3-C_{20} α-olefins may include but are not limited to propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-

1-pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene, or, in some embodiments, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

[0093] The homogeneously branched random ethylene/α-olefin copolymer may have one, some, or all of the following properties (i) - (iii) below:

(i) a melt index (1_2) from 1 g/10 min, or 5 g/10 min, or 10 g/10 min, or 20 g/10 min to 30 g/10 min, or 40 g/10 min, or 50 g/10 min, and/or
(ii) a density from 0.075 g/cc, or 0.880 g/cc, or 0.890 g/cc to 0.90 g/cc, or 0.91 g/cc, or 0.920 g/cc, or 0.925 g/cc; and/or
(iii) a molecular weight distribution (Mw/Mn) from 2.0, or 2.5, or 3.0 to 3.5, or 4.0.

[0094] In an embodiment, the ethylene-based polymer is a heterogeneously branched random ethylene/α-olefin copolymer.

[0095] The heterogeneously branched random ethylene/α-olefin copolymers differ from the homogeneously branched random ethylene/α-olefin copolymers primarily in their branching distribution. For example, heterogeneously branched random ethylene/α-olefin copolymers have a distribution of branching, including a highly branched portion (similar to a very low density polyethylene), a medium branched portion (similar to a medium branched polyethylene) and an essentially linear portion (similar to linear homopolymer polyethylene).

[0096] Like the homogeneously branched random ethylene/α-olefin copolymer, the heterogeneously branched random ethylene/α-olefin copolymer may include at least one ethylene comonomer and at least one C_3-C_{20} α-olefin comonomer, or at least one C_4-C_{12} α-olefin comonomer. For example and not by way of limitation, the C_3-C_{20} α-olefins may include but are not limited to, propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene, or, in some embodiments, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene. In one embodiment, the heterogeneously branched ethylene/α-olefin copolymer may comprise greater than about 50% by wt ethylene comonomer, or greater than about 60% by wt., or greater than about 70% by wt. Similarly, the heterogeneously branched ethylene/α-olefin copolymer may comprise less than about 50% by wt α-olefin monomer, or less than about 40% by wt., or less than about 30% by wt.

[0097] The heterogeneously branched random ethylene/α-olefin copolymer may have one, some, or all of the following properties (i) - (iii) below:

(i) a density from 0.900 g/cc, or 0.0910 g/cc, or 0.920 g/cc to 0.930 g/cc, or 0.094 g/cc;
(ii) a melt index (I_2) from 1 g/10 min, or 5 g/10 min, or 10 g/10 min, or 20 g/10 min to 30 g/10 min, or 40 g/10 min, or 50 g/10 min; and/or
(iii) an Mw/Mn from 3.0, or 3.5 to 4.0, or 4.5.

[0098] In an embodiment, the 3DRLM 30 is composed of a blend of a homogeneously branched random ethylene/α-olefin copolymer and a heterogeneously branched ethylene/α-olefin copolymer, the blend having one, some, or all of the properties (i) - (v) below:

(i) a Mw/Mn from 2.5, or 3.0 to 3.5, or 4.0, or 4.5; and/or
(ii) a melt index (I_2) from 3.0 g/10 min, or 4.0 g/10 min, or 5.0 g/10 min, or 10 g/10 min to 15 g/10 min, or 20 g/10 min, or 25 g/10 min; and/or
(iii) a density from 0.895 g/cc, or 0.900 g/cc, or 0.910 g/cc, or 0.915 g/cc to 0.920 g/cc, or 0.925 g/cc; and or
(iv) an I_{10}/I_2 ratio from 5 g/10 min, or 7 g/10 min to 10 g/10 min, or 15 g/10 min; and/or
(v) a percent crystallinity from 25%, or 30%, or 35%, or 40% to 45%, or 50%, or 55%.

[0099] According to Crystallization Elution Fractionation (CEF), the ethylene/α-olefin copolymer blend may have a weight fraction in a temperature zone from 90°C to 115°C or 5% to 15% by wt., or 6% to 12%, or 8% to 12%, or greater than 8%, or greater than 9%.

[0100] The present ethylene/α-olefin copolymer blend may have at least two, or three melting peaks when measured using Differential Scanning Calorimetry (DSC) below a temperature of 130°C. In one or more embodiments, the ethylene/α-olefin copolymer blend may include a highest temperature melting peak of at least 115°C, or at least 120°C, or from about 120°C to about 125°C, or from about from 122 to about 124°C. Without being bound by theory, the heterogeneously branched ethylene/α-olefin copolymer is characterized by two melting peaks, and the homogeneously branched ethylene/α-olefin copolymer is characterized by one melting peak, thus making up the three melting peaks.

[0101] Additionally, the ethylene/α-olefin copolymer blend may comprise from 10 to 90% by weight, or 30 to 70% by weight, or 40 to 60% by weight of the homogeneously branched ethylene/α-olefin copolymer. Similarly, the ethylene/α-olefin copolymer blend may comprise from 10 to 90% by weight, 30 to 70% by weight, or 40 to 60% by weight of the heterogeneously branched ethylene/α-olefin copolymer. In a specific embodiment, the ethylene/α-olefin copolymer blend may comprise from 50% to 60% by weight of the homogeneously branched ethylene/α-olefin copolymer, and 40% to 50% of the heterogeneously branched ethylene/α-olefin copolymer.

[0102] Moreover, the strength of the ethylene/α-olefin copolymer blend may be characterized by one or more of the following metrics. One such metric is elastic recovery. Here, the ethylene/α-olefin copolymer blend has an elastic recovery, Re, in percent at 100 percent strain at 1 cycle of between 50-80%. Additional details regarding elastic recovery are provided in US Patent 7,803,728, which is incorporated by reference herein in its entirety.

[0103] The ethylene/α-olefin copolymer blend may also be characterized by its storage modulus. In some embodiments, the ethylene/α-olefin copolymer blend may have a ratio of storage modulus at 25° C, G' (25°C) to storage modulus at 100°C, G' (100°C) of about 20 to about 60, or from about 20 to about 50, or about 30 to about 50, or about 30 to about 40.

[0104] Moreover, the ethylene/α-olefin copolymer blend may also be characterized by a bending stiffness of at least about 1.15 Nmm at 6 s, or at least about 1.20 Nmm at 6 s, or at least about 1.25 Nmm at 6 s, or at least about 1.35 Nmm at 6 s. Without being bound by theory, it is believed that these stiffness values demonstrate how the ethylene/α-olefin copolymer blend will provide cushioning support when incorporated into 3DRLM fibers bonded to form a cushioning net structure.

[0105] In an embodiment, the ethylene-based polymer is an ethylene/α-olefin interpolymer composition having one, some, or all of the following properties (i)-(v) below:

(i) a highest DSC temperature melting peak from 90.0°C to 115.0°C; and/or
(ii) a zero shear viscosity ratio (ZSVR) from 1.40 to 2.10; and/or
(iii) a density in the range of from 0.860 to 0.925 g/cc; and/or
(iv) a melt index (I_2) from 1 g/10 min to 25 g/10 min; and/or
(v) a molecular weight distribution (Mw/Mn) in the range of from 2.0 to 4.5.

[0106] In an embodiment, the ethylene-based polymer contains a functionalized commoner such as an ester. The functionalized comonomer can be an acetate comonomer or an acrylate comonomer. Nonlimiting examples of suitable ethylene-based polymer with functionalized comonomer include ethylene vinyl acetate (EVA), ethylene methyl acrylate EMA, ethylene ethyl acrylate (EEA), and any combination thereof.

[0107] In an embodiment, the olefin-based polymer is a propylene-based polymer. The propylene-based polymer can be a propylene homopolymer or a propylene/α-olefin polymer. The α-olefin is a C_2 α-olefin (ethylene) or a C_4-C_{12} α-olefin, or a C_4-C_8 α-olefin. Nonlimiting examples of suitable α-olefin comonomer include ethylene, butene, methyl-1-pentene, hexene, octene, decene, dodecene, tetradecene, hexadecene, octadecene, cyclohexyl-1-propene (allyl cyclohexane), vinyl cyclohexane, and combinations thereof.

[0108] In an embodiment, the propylene interpolymer includes from 82 wt% to 99 wt% units derived from propylene and from 18 wt% to 1 wt% units derived from ethylene, having one, some, or all of the properties (i) - (vi) below:

(i) a density of from 0.840 g/cc, or 0.850 g/cc to 0.900 g/cc; and/or
(ii) a highest DSC melting peak temperature from 50.0°C to 120.0°C; and/or
(iii) a melt flow rate (MFR) from 1 g/10 min, or 2 g/10 min to 50 g/10 min, or 100 g/10 min; and/or
(iv) a Mw/Mn of less than 4; and/or
(v) a percent crystallinity in the range of from 0.5 % to 45%; and/or
(vi) a DSC crystallization onset temperature, Tc-Onset, of less than 85°C.

[0109] In an embodiment, the olefin-based polymer used in the manufacture of the 3DRLM 30 contains one or more optional additives. Nonlimiting examples of suitable additives include stabilizer, antimicrobial agent, antifungal agent, antioxidant, processing aid, ultraviolet (UV) stabilizer, slip additive, antiblocking agent, color pigment or dyes, antistatic agent, filler, flame retardant, and any combination thereof.

3. Sheets

[0110] Returning to FIGS. 1-2, the SUP 10a includes a free moving sheet 28 made of 3DRLM 30. A "free moving sheet of 3DRLM," as used herein, is a sheet of 3DRLM 30 located in the closed chamber 18, the sheet of 3DLRM detached from the surfaces of the closed chamber so that the sheet of 3DRLM moves freely within the volume of the closed chamber. In other words, the free moving sheet 28 of 3DRLM is sized and shaped to have a volume that is less than the volume of the closed chamber, and the free moving sheet of 3DRLM is not connected to any surface which defines the closed chamber, thereby enabling the sheet to move about the closed chamber. The free moving sheet 28 of 3DRLM 30 is loose within the closed chamber 18, enabling the free moving sheet 28 to move freely within the confines of the closed chamber 18.

[0111] In an embodiment, the SUP 10a holds a liquid 38 in the closed chamber. The free moving sheet 28 of 3DRLM

30 moves freely within the liquid 38.

[0112] As shown in FIG. 2, when a squeezing force is imparted upon the front and rear multilayer films 12, 14 (such as a squeezing force from a hand of a consumer 40), the squeezing force compresses the free moving sheet 28 to dispense the liquid 38 (such as a beverage, for example) from the fitment 20. In FIG. 2, the free moving sheet 28 is shown in dashed lines within the SUP 10a. The squeezing force moves the 3DRLM 30 to a compressed state. When the squeezing force is removed from the multilayer films 12, 14, the 3DRLM 30 returns to the neutral state.

4. Oversized sheet

[0113] The present disclosure provides another flexible container. In an embodiment, the flexible container includes a first multilayer film and a second multilayer film. Each multilayer film includes a seal layer. The multilayer films are arranged such that the seal layers oppose each other and the second multilayer film is superimposed on the first multilayer film. The multilayer films are sealed along a common peripheral edge to form a closed chamber. The closed chamber has opposing inner surfaces. An oversized sheet of three-dimensional random loop material (3DRLM) (or "oversized sheet") is located in the closed chamber. The term "oversized sheet of 3DRLM" (or "oversized sheet"), as used herein, is defined as follows. When the oversized sheet (in the neutral state) and the closed chamber are compared in the same axis dimension (e.g., comparing the height of the oversized sheet to the height of the closed chamber), the oversized sheet (in the neutral state) has an extent that is greater than the extent of the closed chamber in the same axis dimension (e.g., the oversized sheet has a height that is greater than the height of the closed chamber). The oversized sheet has a first end and an opposing second end. The first end and the second end of the sheet compressively engage opposing inner surfaces of the closed chamber.

[0114] In an embodiment, a flexible container 110 is provided. Flexible container 110 includes a front film 112 and a rear film 114. Front/rear films 112, 114 can be any multilayer film as previously disclosed for respective front film and rear film. Rear film 114 opposes the front film 112, such that the rear film 114 is superimposed on the front film 112. The front film 112 and the rear film 114 are sealed around a common peripheral edge 116 to form a closed chamber 118.

[0115] The present flexible container 110 can be a box pouch, pillow pouch, spout k-sealed pouch, spout side gusseted pouch, or a stand-up pouch as previously disclosed above. The flexible container may or may not have a fitment (i.e., a spout). The flexible container 110 can be formed with or without handles.

[0116] In an embodiment, the flexible container 110 includes a fitment 120. The fitment 120 is sandwiched between the front film and the rear film, with a base of the fitment sealed along a portion of the common peripheral edge 116. The fitment may or may not include a closure. The fitment 120 dispenses the contents held within the closed chamber 118 as previously disclosed herein.

[0117] In an embodiment, present flexible container is a stand-up pouch 110a, or "SUP," as shown in FIGS. 3-5. The SUP 110a includes a gusset 122. The gusset 122 is attached to, or otherwise extends from, a lower portion of the front film 112 and/or a lower portion of the rear film 114 as previously disclosed above. The gusset 122 includes a gusset film 124 and a gusset rim 126 as previously disclosed herein. The gusset 122, the films 112, 114, and the fitment 120 define a closed and hermetically sealed chamber 118 for holding a flowable substance, such as liquid, for example.

[0118] The SUP 110a includes a sheet 128 of 3DRLM 130. The sheet 128 is sized and shaped to compressively engage opposing inner surfaces of the closed chamber 118. The term "compressively engage" as used herein, is the sheet of 3DRLM has at least one of (i) a length, (ii) a width, and/or (iii) a height that is greater than a respective length, width, or height of closed chamber 118.

[0119] FIG. 3 shows the closed chamber 118 having opposing surfaces 119a and 119b. The distance between surface 119a and 119b is the width, X, of the closed chamber 118. The width X for closed chamber 118 is best seen in FIG. 4.

[0120] Returning to FIG. 3, FIG. 3 shows oversized sheet 128 prior to installation into the SUP 110a. Oversized sheet 128 has a first end 129a and an opposing second end 129b. The distance between first end 129a and second end 129b when the 3DRLM 130 is in a neutral state is the width, Y, of the oversized sheet 128. As best seen in FIG. 4, the width Y of oversized sheet 128 (in the neutral state) is greater than the width, X, of the closed chamber 118. In other words, when in the same axis (in this instance the width axis), the sheet 128 has a length (length Y) that is greater than the length of closed chamber along the same axis for the closed chamber (length X). In this sense, the sheet 128 is an "oversized sheet" with respect to the same axis dimension of the closed chamber 118.

[0121] The oversized sheet 128 is placed into a compressed state in order to fit into the closed chamber 118. The oversized sheet 128 is compressed so that the width Y (neutral state) is reduced to the length of closed chamber width X (distance between first and second sides 119a and 119b). When in the closed chamber 118, oversized sheet 128 of 3DRLM 30 is in a constant compressed state. As the nature of the 3DRLM 30 is to move to the neutral state, the first end 129a and the second end 129b impart a constant outward force upon respective sides 119a, 119b of the closed chamber 118. The first end and the second end 129a, 129b impinge upon, and compressively engage, opposing sides 119a, 119b of the closed chamber 118. The compressive engagement onto respective sides 119a, 119b holds the oversized sheet 128 in a stationary position within the closed chamber 118. In this way, the compressive engagement of oversized sheet 128 maintains, or otherwise holds, the full shape of the SUP 110a, regardless of the amount of liquid (full, partially full, partially empty, or empty) present in the closed chamber 118.

[0122] It is understood that the oversized sheet 128 can be configured to compressively engage opposing sides of the closed chamber 118 in one, some, or all of the following axes: width axis, length axis, and/or height axis. Oversized sheet 128 maintains the size, shape, volume, and stand-up feature of the SUP 110a, regardless of the amount of liquid present in the closed chamber 118.

[0123] In an embodiment, the oversized sheet 128 is removable from the closed chamber 118. The oversized sheet 128 is thereby reusable and/or recyclable.

[0124] As shown in FIG. 5, when a squeezing force is imparted upon the front and rear multilayer films 112, 114 (such as a squeezing force from the hand of a consumer 140), the squeezing force compresses the oversized sheet 128 to dispense a liquid 138 (such as a cleaning solution, for example) from the fitment 120 and onto an object 142, or a surface thereof.

[0125] The present flexible container(s) 10, 10a, 110, 110a is/are suitable for storage of flowable substances including, but not limited to, liquid comestibles (such as beverages), oil, paint, grease, chemicals, suspensions of solids in liquid, and solid particulate matter (powders, grains, granular solids). Nonlimiting examples of suitable liquids include liquid personal care products such as shampoo, conditioner, liquid soap, lotion, gel, cream, balm, and sunscreen. Other suitable liquids include household care/cleaning products and automotive care products. Other liquids include liquid food such as condiments (ketchup, mustard, mayonnaise) and baby food.

[0126] The present flexible container(s) 10, 10a, 110, 110a is/are suitable for storage of flowable substances with higher viscosity and requiring application of a squeezing force to the container in order to discharge. Nonlimiting examples of such squeezable and flowable substances include grease, butter, margarine, soap, shampoo, animal feed, sauces, and baby food.

[0127] The present container(s) 10, 10a, 110, 110a provide many performance improvements versus the current package designs, such as improved pouch stand-up stability, film downgauging, higher package dimensions enabled by the higher stability from the sheet of 3DRLM, static mixing, improved SUP handling and consumer perception, and higher mechanical resistance (e.g. drop test). Also, bursting issues can be minimized when SUPs 10, 10a, 110, 110a with sheet of 3DRLM thereon, are submitted to pressure while packed together in big bags or boxes. As a further advantage, flexible containers 10, 10a, 110, and 110a reduce the use of secondary package by means of a high performance (e.g. via shock absorbing) primary package, offering cost savings and carbon footprint reduction.

[0128] 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 with the scope of the following claims.

Claims

1. A flexible container comprising:

a first multilayer film and a second multilayer film, each multilayer film comprising a seal layer, the multilayer films arranged such that seal layers oppose each other and the second multilayer film is superimposed on the first multilayer film, the films sealed along a common peripheral edge to form a closed chamber; and
a free moving sheet of three-dimensional random loop material (3DRLM) in the closed chamber.

2. The flexible container of claim 1 wherein the flexible container comprises
a fitment comprising a base; and
the base is located between the multilayer films and the base is sealed to each multilayer film at a portion of the common peripheral edge.

3. The flexible container of claim 2 comprising a liquid in the closed chamber, wherein the sheet of 3DRLM contacts the liquid.

4. The flexible container of claim 3 wherein a squeezing force on the multilayer films compresses the sheet of 3DRLM and discharges the liquid through the fitment.

5. A flexible container comprising:

a first multilayer film and a second multilayer film, each multilayer film comprising a seal layer, the multilayer films arranged such that the seal layers oppose each other and the second multilayer film is superimposed on

the first multilayer film, the films sealed along a common peripheral edge to form a closed chamber, the closed chamber having opposing inner surfaces;
an oversized sheet of three-dimensional random loop material (3DRLM) in the closed chamber, the oversized sheet having a first end and an opposing second end;
the first end and the second end of the oversized sheet of 3DRLM compressively engaging opposing surfaces of the closed chamber.

6. The flexible container of claim 5 wherein the oversized sheet of 3DRLM is in a compressed state.

7. The flexible container of claim 6, wherein the flexible container comprises a fitment comprising a base, the base is located between the multilayer films; and
the base is sealed to each multilayer film at a portion of the common peripheral edge.

8. The flexible container of claim 7, comprising a liquid in the closed chamber.

9. The flexible container of claim 8 wherein a squeezing force on the multilayer films further compresses the sheet of 3DRLM and discharges the liquid through the fitment.

FIG. 1

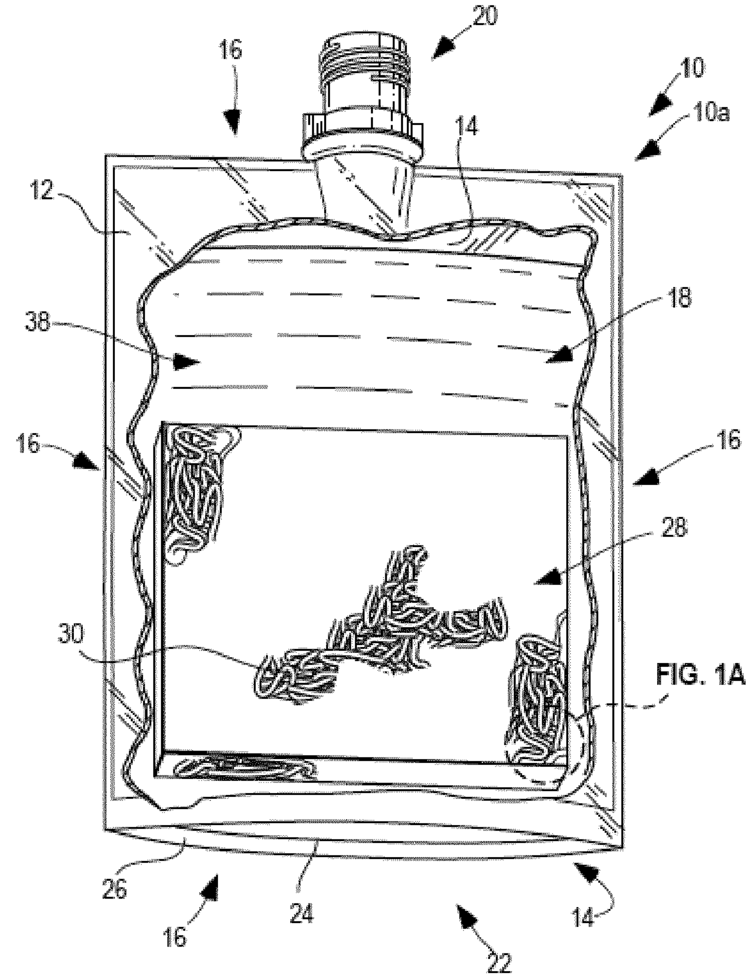

20
16
10
10a
14
12
38
18
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FIG. 1A
26
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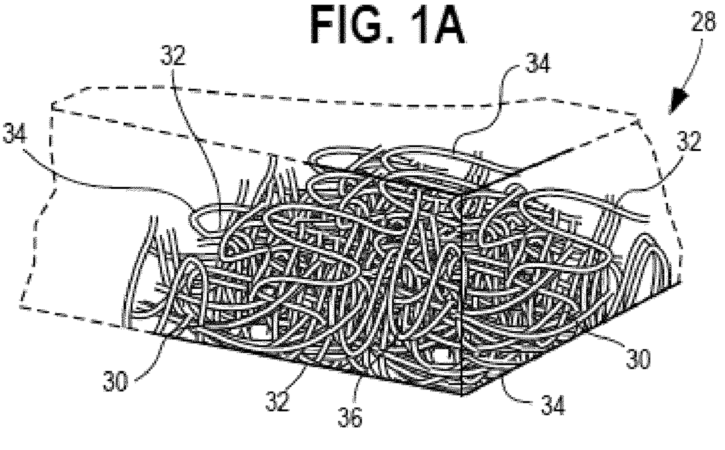
22

FIG. 1A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34

FIG. 2

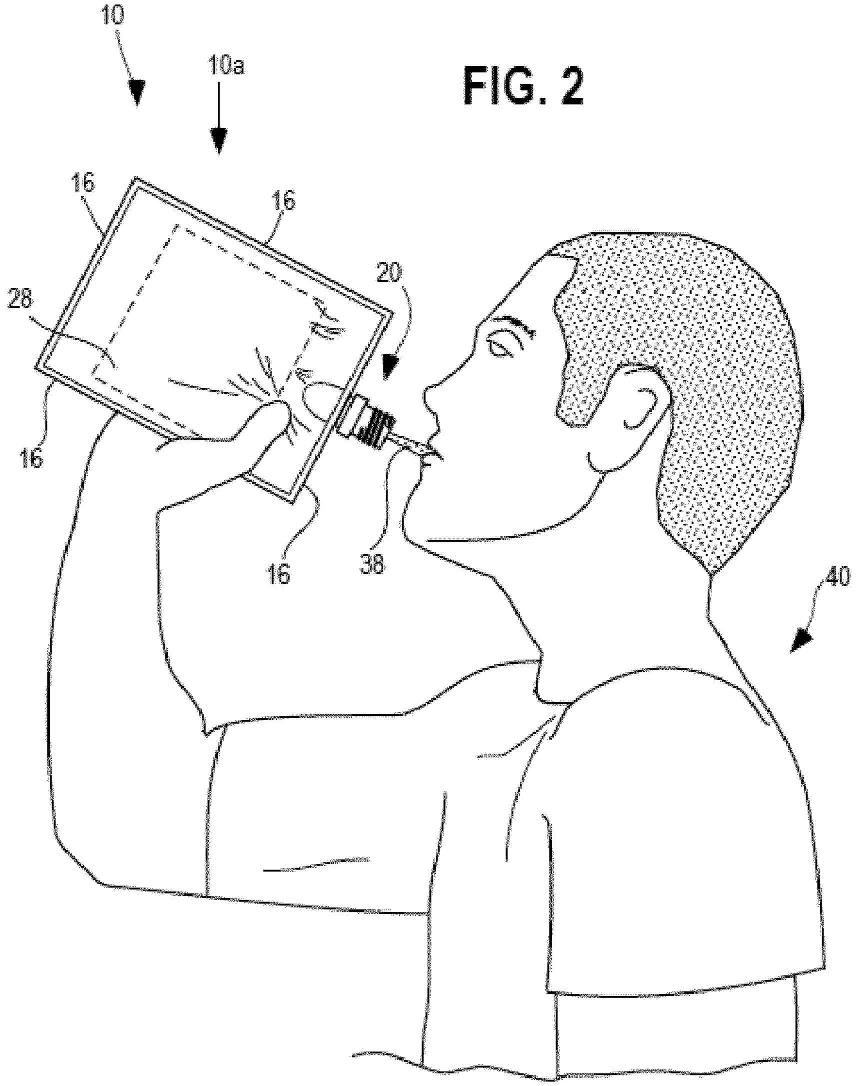


FIG. 3

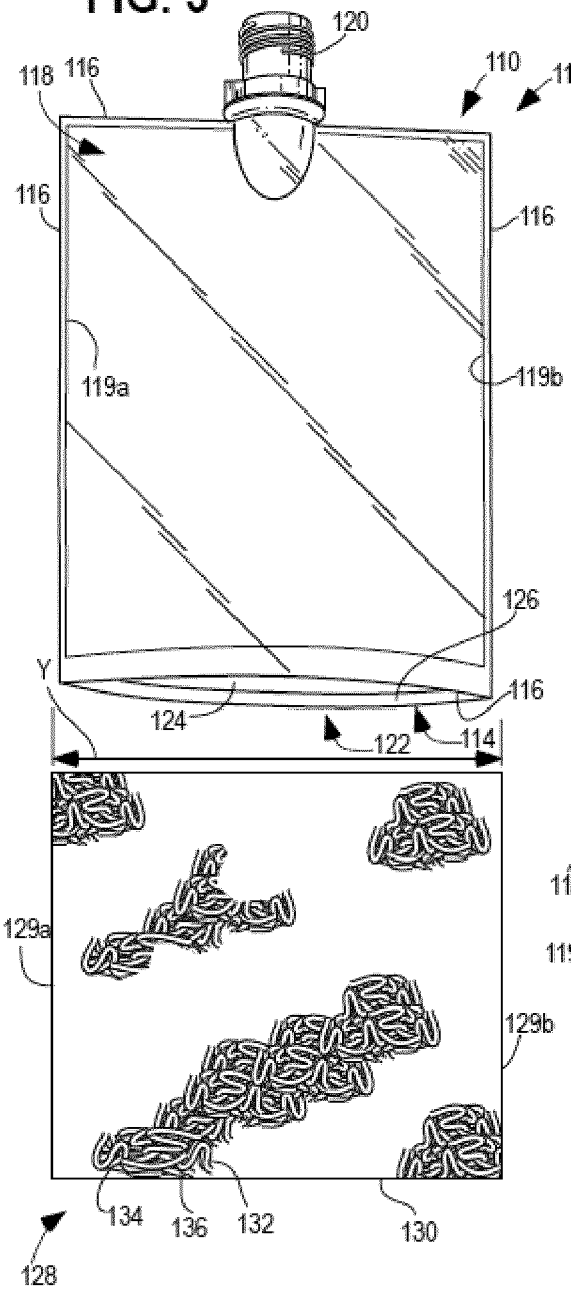
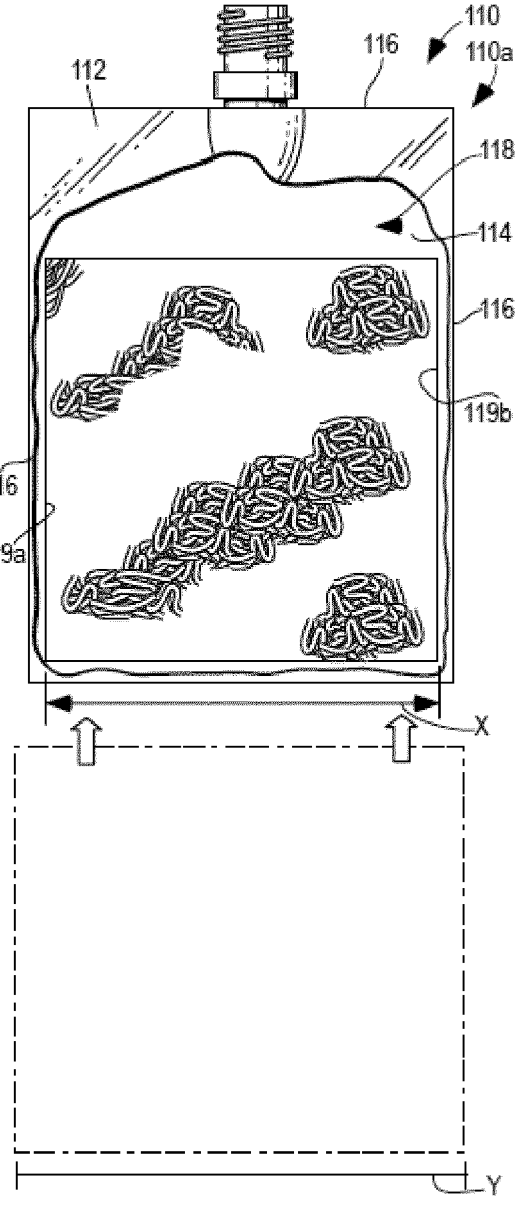

120
118
116
110
110a
116
116
119a
119b
126
Y
116
124
122
114
129a
129b
134
136
132
130
128

FIG. 4


110
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110a
112
118
114
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119b
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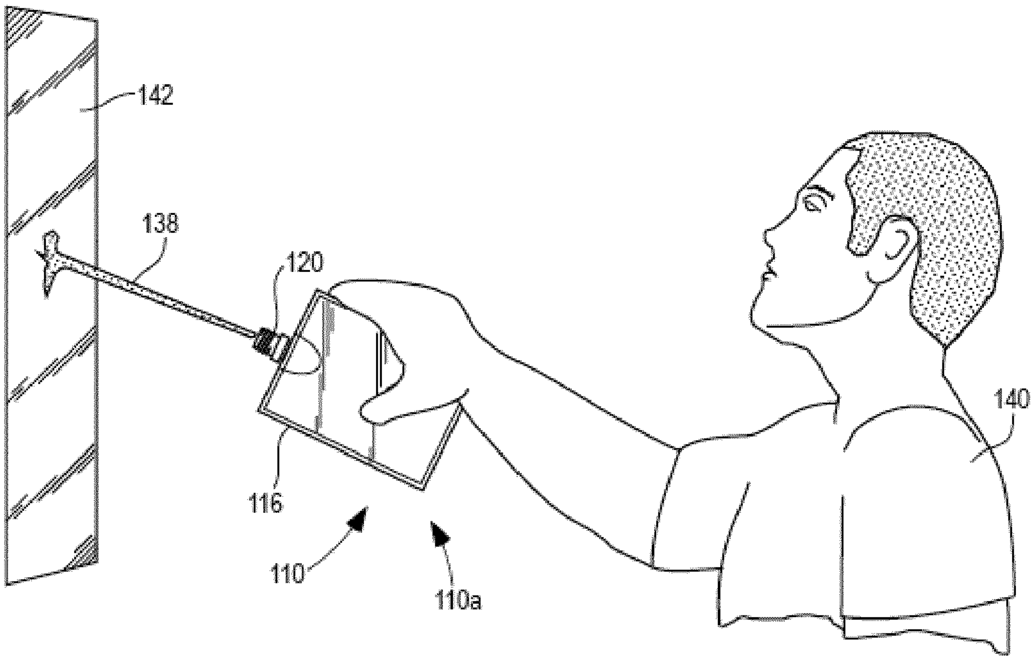
119a
X
128
Y

FIG. 5



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EUROPEAN SEARCH REPORT

Application Number
EP 17 38 2316

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Y	US 4 381 846 A (HECK SAMUEL C) 3 May 1983 (1983-05-03) * column 3, line 26 - column 4, line 4; figure 2 * -----	1-4	INV. B65D75/00 B65D75/54
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			B65D

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	16 November 2017	Balz, Oliver

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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16-11-2017

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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