

LAMINATE TUBE HAVING ENHANCED RESILIENCY BY A BLOCK COPOLYMER

[0001] The present invention relates broadly to dispensers formed from laminates of polymers and foil, and more specifically to collapsible dispensers particularly suited to contain and dispense pastes, gels and creams.

[0002] Dispenser tubes formed of metallic and plastic materials have long been known in the packaging field. Metal dispenser tubes require a coating to prevent attack and corrosion of the metal by alkaline or acid contents of the tube and contamination of the contents by the reaction products.

[0003] Tubes formed of polyethylene and other plastic materials have enjoyed wide commercial success in the packaging of many products. These are both single-layer and multi-layer tubes. For example, U.S. Pat. App. Pub. No. 2007/0272711 A1 discloses elastically deformable dispensers comprising thermoplastic elastomers, such as styrene-ethylene-butadiene-styrene block copolymers.

[0004] However, certain products after a time have been noted to deteriorate when contained in dispensers made entirely of plastic. Plastics as exemplified by polyethylene are to a degree permeable to organics when employed in the relatively low wall thicknesses used in tubular containers. This results in the flavor oils embodied in most dentifrices being reduced in volume during storage, rendering the dentifrice less palatable.

[0005] One solution has been to provide a relatively thin metallic foil barrier layer between the product and the polyethylene tube body to prevent the mentioned loss of essential oils and the absorption of oxygen. Examples of dispensers based on such laminates are disclosed in, e.g., U.S. Pat. Nos. 3,295,725, 4,526,297, 4,595,612, and 5,407,742.

[0006] However, it has been found that certain laminates do not possess properties suitable for use in relatively large dispensers. For example, the inventors have found that tubes made from a PE/tie/foil/tie/PE laminate with the total thickness of 200 microns, in which the PE layers are single-layer or multi-layer structures of HDPE, LLDPE and/or LDPE are perceived by consumers as feeling soft, crumbly and of low quality.

[0007] In order to overcome these deficiencies, it has been proposed to increase the stiffness of the laminate through the use of a higher percentage of HDPE. However, the resulting laminates showed diminished impact tolerance, as evidenced by a failed drop test, suggesting that there was insufficient LDPE or LLDPE in the laminates to provide acceptable impact tolerance along with the desired increase in stiffness.

[0008] JP2005306415A discloses that the properties of a laminate tube container can be improved through the “arbitrary” use of any of a large variety of different resins, such as LDPE, HDPE, acrylonitrile-styrene copolymers, acrylonitrile-butadiene-styrene copolymers, and many others.

[0009] Accordingly, it is desired to provide laminates that overcome the aforementioned deficiencies of existing laminates. It is further desired to provide laminates of simplified construction, which have good impact tolerance and stiffness. It is still further desired to provide dispensers for pastes, gels and creams, which are durable and are perceived by consumers as feeling durable and being of good overall quality.

BRIEF SUMMARY

[0010] Accordingly, a first aspect of the invention comprises a dispenser for storing and dispensing a substance, the dispenser comprising:

- an inner layer comprising an inner layer polymer;

- an outer layer;

- a barrier layer between the inner layer and the outer layer, and comprising a metal foil;

- a compartment defined by an inner surface of the inner layer, said compartment for storing the substance; and

- a resealable opening for dispensing selected amounts of the substance,

- wherein the outer layer comprises an outer layer polymer and a block copolymer effective to provide the outer layer with an impact resistance at least 5% greater than a reference structure.

[0011] In certain embodiments of the first aspect of the invention, the impact resistance of the outer layer is at least 20% greater than the impact resistance of the reference structure.

[0012] In certain embodiments of the first aspect of the invention, when the outer layer has a thickness of 120 microns, the impact resistance of the outer layer is greater than 180 g.

[0013] In certain embodiments of the first aspect of the invention, the inner layer polymer and the outer layer polymer are polyethylene.

[0014] In certain embodiments of the first aspect of the invention, the inner layer polymer comprises LDPE, the outer layer polymer comprises LDPE and HDPE, and the block copolymer comprises an SBS block copolymer having thermoplastic elastomer properties.

[0015] In certain embodiments of the first aspect of the invention, the metal foil comprises aluminum.

[0016] In certain embodiments of the first aspect of the invention, the dispenser further comprises an inner adhesive layer between the inner layer and the barrier layer, and an outer adhesive layer between the barrier layer and the outer layer. In such embodiments, the inner adhesive layer and the outer adhesive layer preferably comprise ethylene acrylic acid.

[0017] In certain embodiments of the first aspect of the invention, the barrier layer is bonded directly to the inner layer and the outer layer without any adhesive therebetween. In such embodiments, it is preferred that the inner layer and the outer layer are radiation graft modified and/or plasma modified for direct adhesion to the barrier layer.

[0018] In certain embodiments of the first aspect of the invention, the dispenser is sufficiently collapsible such that the substance can be extruded from the opening.

[0019] In certain embodiments of the first aspect of the invention, the substance in the dispenser is a member selected from the group consisting of a paste, a gel and a cream. In such embodiments, the substance is preferably a dentifrice and more preferably a toothpaste.

[0020] A second aspect of the invention comprises a dispenser for storing and dispensing a substance, the dispenser comprising:

- an inner layer comprising LDPE;

- an outer layer;

- an aluminum barrier layer between the inner layer and the outer layer;

- a compartment defined by an inner surface of the inner layer, said compartment for storing the substance; and

- a resealable opening for dispensing selected amounts of the substance,

- wherein the outer layer comprises LDPE, HDPE and an SBS block copolymer having thermoplastic elastomer properties.

[0021] In certain embodiments of the second aspect of the invention, the outer layer has an impact resistance at least 5% greater than a reference structure.

[0022] In certain embodiments of the second aspect of the invention, the outer layer has an impact resistance at least 20% greater than a reference structure.

[0023] In certain embodiments of the second aspect of the invention, when the outer layer has a thickness of 120 microns, the impact resistance of the outer layer is greater than 180 g.

[0024] In certain embodiments of the second aspect of the invention, the dispenser further comprises an inner adhesive layer between the inner layer and the barrier layer, and an outer adhesive layer between the barrier layer and the outer layer, wherein the inner adhesive layer and the outer adhesive layer comprise ethylene acrylic acid.

[0025] In certain embodiments of the second aspect of the invention, the barrier layer is bonded directly to the inner layer and the outer layer without any adhesive therebetween. In such embodiments, it is preferred that the inner layer and the outer layer are radiation graft modified and/or plasma modified for direct adhesion to the barrier layer.

[0026] In certain embodiments of the second aspect of the invention, (a) the outer layer has an impact resistance at least 20% greater than a reference structure; (b) when the outer layer has a thickness of 120 microns, the impact resistance of the outer layer is greater than 180 g; and (c) the substance is toothpaste.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] The invention will be described in conjunction with the following drawings in which like reference numerals designate like elements and wherein:

[0028] FIG. 1 is a side elevational view of a dispenser of a first embodiment of the invention, wherein portions of the body walls are broken away to more fully illustrate the multilayered structure.

[0029] FIG. 2 is a side elevational view of a dispenser of a second embodiment of the invention, wherein portions of the body walls are broken away to more fully illustrate the multilayered structure.

DETAILED DESCRIPTION

[0030] As used throughout, ranges are used as shorthand for describing each and every value that is within the range. Any value within the range can be selected as the terminus of the range. In addition, all references cited herein are hereby incorporated by reference in their entireties. In the event of a conflict in a definition in the present disclosure and that of a cited reference, the present disclosure controls. It is understood that when formulations are described, they may be described in terms of their ingredients as is common in the art, notwithstanding that these ingredients may react with one another in the actual formulation as it is made, stored and used and such products are intended to be covered by the formulations described.

[0031] Unless otherwise specified, all percentages and amounts expressed herein and elsewhere in the specification should be understood to refer to percentages by weight. The amounts given are based on the active weight of the material.

[0032] The invention is largely based on the discovery that laminates comprising polyethylene and block copolymer possess qualities favorable to the production of collapsible dispensers. In particular, laminates of the invention possess enhanced impact resistance as evidenced by improved performance in drop tests and puncture tests.

[0033] Block copolymers preferred for use in the invention are linear ABA block copolymers, including but not limited to styrenic block copolymers (SBC), such as styrene-butadiene-styrene (SBS) block copolymers and styrene-ethylene-butadiene-styrene block copolymers.

[0034] Most preferred among these are SBS block copolymers having the properties of thermoplastic elastomers. Other properties preferably possessed by the copolymers include excellent thermostability, very high elongation at break and/or extreme elastic recovery. STYROFLEX™, an SBS block copolymer available from BASF, is a particularly preferred example of a copolymer suitable for use in the invention. (See, e.g., Huber et al., "Impact modifier boosts toughness of films." *Plastics, Additives and Compounding*. Volume 10, Issue 1, January-February 2008, Pages 30-33.) In one embodiment, the SBS block copolymer is STYROFLEX™ 2G 66. In certain embodiments, the STYROFLEX™ 2G 66 has a styrene content of at least 65% and a rubber fraction of at least 70%. Typical properties of STYROFLEX™ 2G 66 are:

RHEOLOGICAL	ASTM Test Method	Property Value
Melt Volume Rate 200 °C/5 Kg	D-1238	11
PHYSICAL	ASTM Test Method	Property Value
Specific Gravity	D-792	1.00
Water absorption saturated at 23°C, %	D-570	0.07
MECHANICAL	ASTM Test Method	Property Value
Hardness, Shore A	D-2240	91
Hardness, Shore D	D-2240	36
Flexural Stress at 5% deflection, MPa (psi)	D-790	2.7 (392)
Tensile Modulus, MPa (psi) 23°C (73°F)	D-638	128 (18,600)
Tensile Strength, Yield (2in/min), MPa (psi) 23°C (73°F)	D-638	3.1 (450)

Flexural Modulus, MPa (psi) 23°C (73°F)	D-790	83 (12,000)
IMPACT	ASTM Test Method	Property Value
Notched Izod Impact, J/M (ft-lbs/in) 23°C (73°F)	D-256	NB
THERMAL	ASTM Test Method	Property Value
Vicat, B/1 (120 deg. C/h, 10N), °C(°F)	D-1525	48 (118)
ELECTRICAL	ASTM Test Method	Property Value
Volume Resistivity	D-257	>1E13
Surface Resistivity	D-257	>1E13
Dielectric Constant (1000000 Hz, 0,0394 in)	D-150	2.5
OPTICAL	ASTM Test Method	Property Value
Light Transmission, %	D-1003	93
Refractive Index		1.56
BLOWN FILM PROPERTIES	ASTM Test Method	Property Value
Elongation at Break (MD), %	D-882	550
Elongation at Break (TD), %	D-882	540
Tensile Modulus (MD), MPa	D-882	170 (24,600)
Tensile Modulus (TD), MPa	D-882	128 (18,600)
Elmendorf Tear (MD), g (lbs.)	D-1922	530 (1.17)
Elmendorf Tear (TD), g (lbs.)	D-1922	541 (1.19)
Haze, %	D-1003	1
Oxygen Transmission Rate (23°C/0% RH), cc/100in ² /day (cc/m ² /day)	D-3985	360 (5580.0)
Water Vapor Transmission Rate (23°C/100% RH), g/100in ² /day (g/m ² /day)	F-1249	0.63 (9.8)
Puncture, Energy at Peak Force, J(in-lb)	D-3763	2.4 (21.3)
Puncture, Total Energy, J(in-lb)	D-3763	3.4 (30.2)
Water Shrinkage (100°C for 30 sec.), %		0.63

[0035] Non-limiting examples of other suitable block copolymers include: KRATON™ D SBS series, such as D 1101, 1102, 1153, 1155, etc.; KRATON™ D styrene-isoprene-styrene (SIS) series, such as D 1111, 1113, 1117, 1119, etc.; KRATON™ G series, such as styrene-ethylene-butylene-styrene (SEBS): G 1633, 1650, 1651 etc. and styrene-ethylene-propylene-styrene (SEPS): G 1730,

etc. Additional suitable SBS block copolymers can be identified using the foregoing properties as a guide and purchased or prepared in accordance with known techniques, such as those disclosed and/or claimed in U.S. Pat. No. 7,169,848.

[0036] The block copolymer can be provided as discrete layer of the laminate and/or it can be blended with other materials, such as polyethylene, in layer of the laminate.

[0037] A non-limiting example of the blended embodiment of the invention is shown in FIG. 1. As described in Table 1 below, the laminate of dispenser 10 comprises a single outside layer 20, which comprises a blend of high-density polyethylene (HDPE), low-density polyethylene (LDPE) and STYROFLEX™. This embodiment is essentially a three-layer laminate of inner layer 12, barrier layer 16 and outside layer 20, with inner adhesive layer 14 of ethylene acrylic acid (EAA) bonding barrier layer 16 to inner layer 12 and outer adhesive layer 18 of EAA bonding barrier layer 16 to outside layer 20. The laminate (and more specifically an inner surface of inner layer 12) defines a compartment for storing a substance to be dispensed. Selected amounts of the substance are dispensed through a resealable opening, such as a threaded nozzle and cap 22.

[0038] Table 1. Blended block copolymer embodiment of FIG. 1.

Ref. No.	Layer	Material	Wt%	Ingredient Density (g/ml)	Melt Index (MI)	Layer Density (g/ml)	Thickness (microns)
20	Outside	STYROFLEX HDPE LDPE	13.0% 78.2% 8.8%	1.002 0.961 0.925	3 0.7 1.9	0.963	120
18	Outer Adhesive	EAA	100%	0.93	7	0.93	15
16	Barrier	Aluminum Foil	100%	2.71	n/a	2.71	12
14	Inner Adhesive	EAA	100%	0.932	9	0.932	15
12	Inner	LDPE	100%	0.925	1.9	0.925	38

[0039] In embodiments of the invention comprising a single outside layer, the layer preferably comprises a blend of 10 to 95 wt.% polyethylene and 0 to 50 wt.% of an SBS block copolymer, more preferably 70 to 90 wt.% polyethylene and 10 to 30 wt.% of an SBS block copolymer. More preferably, the outside layer comprises 0 to 10 wt.% LDPE, 70 to 85 wt.% HDPE and 10 to 20 wt.% of an SBS block copolymer, such as STYROFLEX™.

[0040] FIG. 2 shows a non-limiting example of the embodiment of the invention wherein the copolymer is provided as a discrete layer of the laminate. As described in Table 2 below, the

laminate comprises first outer layer 24 of LDPE below second outer layer 26 of HDPE below third outer layer 28 of STYROFLEX™. The three layers are preferably coextruded together. This embodiment is essentially a five-layer laminate of inner layer 12, barrier layer 16 and the three outer layers, with inner adhesive layer 14 of ethylene acrylic acid (EAA) bonding barrier layer 16 to inner layer 12 and outer adhesive layer 18 of EAA bonding barrier layer 16 to first outer layer 24.

[0041] Table 2. Block copolymer layer embodiment of FIG. 2.

Ref. No.	Layer	Material	Wt%	Ingredient Density (g/ml)	MI	Layer Density (g/ml)	Thickness (microns)
28	Third Outer	STYROFLEX™	13.0%	1.002	3	0.963	15
26	Second Outer	HDPE	78.2%	0.961	0.7		94
24	First Outer	LDPE	8.8%	0.925	1.9		11
18	Outer Adhesive	EAA	100%	0.93	7	0.93	15
16	Barrier	Aluminum Foil	100%	2.71	n/a	2.71	12
14	Inner Adhesive	EAA	100%	0.932	9	0.932	15
12	Inner	LDPE	100%	0.925	1.9	0.925	38

[0042] In embodiments of the invention wherein the block copolymer is provided as a discrete outermost layer, the block copolymer will provide a soft touch and firm gripping surface.

[0043] The foregoing embodiments of the invention simplify construction of dispensers relative to current constructions, wherein six or more different resins are used to prepare at least three outer layers and at least three inner layers. Preferred laminates of the invention comprise only 2 or (as shown above) only 3 different resins, in addition to the barrier layer and the adhesive layers. The simplification of construction is expected to result in reduced manufacturing costs.

[0044] Further simplification of construction can be achieved through the elimination of tie (adhesive) layers between the foil layer and adjacent polymer layers. For example, inner layer 12 and outer layer 20 can be treated to adhere directly to barrier layer 16 so as to eliminate inner adhesive layer 14 and outer adhesive layer 18, which are present in the embodiment of FIG. 1. Inner layer 12 and outer layer 20 can be made adherent by, e.g., radiation graft modification or plasma modification.

[0045] In certain embodiments, gamma radiation is used to graft a grafting agent to at least one of inner layer 12 and outer layer 20, such that the modified layer(s) adhere(s) directly to barrier layer 16. Suitable grafting agents include but are not limited to acrylic acids, such as ethylene acrylic acid, and the like. Preferably ethylene acrylic acid is radiation grafted to polyethylene layers to render the layers adherent to aluminum. Examples of grafting techniques suitable for use in the present invention are disclosed in, e.g., U.S. Patent Nos. 3,115,418 and 3,270,090 and Guimon, "Radiation grafting of high density polyethylene and polypropylene." *Radiat. Phys. Chem.* 14, pp. 841–846 (1979).

[0046] In certain embodiments, plasma modification is used to make at least one of inner layer 12 and outer layer 20 adhere directly to barrier layer 16. Examples of plasma modification techniques suitable for use in the present invention are disclosed in, e.g., Statutory Invention Reg. No. H1164, which discloses a method of treating the surface of polymer films, such as PE films, with a low temperature gas plasma so as to improve the subsequent bonding of aluminum to the polymer surface without the need for adhesives; Hall et al., "Activated gas plasma surface treatment of polymers for adhesive bonding" *Journal of Applied Polymer Science*, Volume 13 Issue 10, Pages 2085 – 2096 (2003); and Minford, "Handbook of aluminum bonding technology and data" (CRC Press, 1993) at e.g., p.13.

[0047] In preferred embodiments of the invention comprising the use of plasma treated layers, the plasma is atmospheric plasma, such as that produced by an atmospheric plasma system available from Enercon Industries Corp. (Menomonee Falls, WI). Preferred parameters for this treatment step are as follows:

Parameter	Preferred	More Preferred
Power Supply Frequency	50-300K	About 150K
Speed (m/s)	0.0508 – 1 (10-200 ft./min.)	0.5 (100 ft./min.)
Gap (mm)	0.025 – 0.25 (0.01-0.1 inch)	0.114 (0.045 inch)
Power (KW)	2-20	About 6
Watt Density W/m ²	21.7 – 217 (2-20 W/ft ²)	About 130 (12 W/ft ²)

[0048] The treatment is preferably conducted with a gaseous mixture of 80% HYDROSTAR™ H-10 (which is a 90:10 mixture of Ar:H₂ available from Praxair) and 20% Oxygen. It is further preferred to use a ceramic electrode having a width of 1500-1600 mm, more preferably 1524 mm for the treatment.

[0049] Plasma treatment increases the surface tension of polymeric substrates, as evidenced by increased dyne levels (e.g., above 50) and decreased contact angle values (e.g., below 60). The resultant layers are preferably hot pressed to barrier layer 16 at an elevated pressure (preferably 172367 Pa – 689470 Pa (25-100 psi), more preferably 448156 Pa (65 psi)) and temperature (preferably 149-204°C (300-400°F), more preferably 177°C (350°F)) for a time (preferably 30-60 seconds, more preferably 40 seconds) sufficient to achieve satisfactory bonding without adhesives.

[0050] Inner layer 12 is preferably compatible with the contents of dispenser 10, as inner layer 12 contacts the contents. Inner layer 12 is ideally impenetrable and inert with respect to the contents under normal storage and usage conditions. When the contents of the container are intended for consumption and/or administration to living organisms, inner layer 12 preferably comprises only food and/or medical grade polymer(s). Inner layer 12 preferably comprises polyethylene, and particularly LDPE, such as LDPE 2420 F from BASF.

[0051] The contents of dispenser 10 are preferably in the form of a paste, a gel, or a cream, and find application in, e.g., the cosmetic, pharmaceutical, veterinary, construction, maintenance and/or mechanical arts. Examples of the contents (or substance) suitable for storage in and extrusion from dispenser 10 include but are not limited to dentifrices, toothpastes, tooth gels, tooth creams, skin creams, sun blocks, adhesives, paints, lubricants, and cleaning materials.

[0052] Inner layer 12 is preferably inert with respect to the contents. Practically speaking, however, it is also within the scope of the invention for inner layer 12 to absorb some amount of flavorant and/or other ingredients from the contents of dispenser 10. It is also within the scope of the invention for inner layer 12 to be somewhat permeable with respect to the contents of dispenser 10, or select ingredients therein.

[0053] Inner adhesive layer 14 bonds inner layer 12 to barrier layer 16. Suitable adhesives include but are not limited to a copolymer of ethylene and acrylic acid or methacrylic acid, or sodium or zinc salts thereof in a diluent system. Non-limiting examples of preferred adhesives include the ethylene acrylic acids PRIMACOR™ 3340 from Dow Chemical Co. and NUCREL™ 30707 from DuPont.

[0054] In certain embodiments of the invention, inner layer 12 bonds directly to barrier layer 16 without inner adhesive layer 14.

[0055] Barrier layer 16 is provided to prevent the transfer of materials across the multilayered laminate structure of dispenser 10. Preferably, barrier layer 16 comprises a metal foil, such as aluminum foil. A non-limiting example of a preferred aluminum foil is 8011 alloy from North China Aluminum Co. Ltd.

[0056] Outer adhesive layer 18 bonds the outermost side of barrier layer 16 to outer layer 20 (in the embodiment of FIG. 1) or first outer layer 24 (in the embodiment of FIG. 2). The materials of outer adhesive layer 18 are preferably and independently selected from the same materials as inner adhesive layer 14. In certain embodiments of the invention, outer layer 20 or first outer layer 24 bonds directly to barrier layer 16 without outer adhesive layer 18. In some of these embodiments, inner layer 12 also bonds directly to barrier layer 16 without inner adhesive layer 14.

[0057] The thicknesses of the laminate and the layers thereof are largely dictated by desired functionality and costs. The preferred thickness range of each of the layers is as follows:

[0058] Table 3. Thickness of blended block copolymer embodiments.

Layer	Preferred Thickness Range	More Preferred Thickness Range
Inner (12)	10 – 100 microns	30-50 microns
Inner Adhesive (14)	0 – 50 microns	10 – 30 microns
Barrier (16)	5 – 30 microns	9 – 20 microns
Outer Adhesive (18)	0 – 50 microns	10 – 30 microns
Outer Layer (20)	50 – 300 microns	100 – 200 microns

[0059] Table 4. Thickness of block copolymer layer embodiments.

Layer	Preferred Thickness Range	More Preferred Thickness Range
Inner (12)	10 – 100 microns	30-50 microns
Inner Adhesive (14)	0 – 50 microns	10 – 30 microns
Barrier (16)	5 – 30 microns	9 – 20 microns
Outer Adhesive (18)	0 – 50 microns	10 – 30 microns
First Outer (24)	10 – 100 microns	10-30 microns
Second Outer (26)	10 – 200 microns	70 – 120 microns
Third Outer (28)	5 – 30 microns	10 – 20 microns

[0060] The figures show preferred embodiments of the inventive dispenser 10, wherein the dispenser is provided in the form of a collapsible tube. Suitable techniques for forming such tubes are disclosed in U.S. Pat. No. 3,295,725. Other types of dispensers are also within the scope of the invention. The dispensers can be flexible or rigid. The shape of dispensers is not particularly

limited, but is preferably tubular. In addition, laminates of the invention can be used for the components of a pump dispenser inclusive of the barrel, piston, diaphragm, nozzle, spout and the like. However, a preferred use is in dentifrice tubes.

[0061] The invention will be illustrated in more detail with reference to the following Examples, but it should be understood that the present invention is not deemed to be limited thereto.

EXAMPLE 1

[0062] A three-layer film with a total thickness of 120 microns was blown according to the outer film structure (24/26/28) shown in Table 2.

[0063] Impact resistance testing showed that the impact resistance of this film was 376 g. (All impact resistance values referenced herein are measured and defined in accordance with Chinese State Standard GB 9639-88: "Impact Resistance Test of Plastic Film and Sheet", which is equivalent to ISO 7765-85.)

COMPARATIVE EXAMPLE 1

[0064] A control film was prepared, which had the same 120 μm thickness as the film of Example 1, but comprised the following laminate structure:

LLDPE-LDPE (80-20) / HDPE-LLDPE(60-40) / LLDPE-LDPE (80-20)

[0065] The thickness of each layer was respectively 18 μm , 84 μm and 18 μm .

[0066] The impact resistance of this film was only 152 g, less than 50% of the impact resistance of the film of Example 1.

EXAMPLE 2

[0067] A one-layer film with a total thickness of 120 microns was blown according to the outer film structure (20) shown in Table 1. The film had an impact resistance of 182 g, 20% greater than the film of Comparative Example 1.

[0068] Thus, the invention provides films, laminates and dispensers with enhanced impact resistance. In certain embodiments, a laminate (or film) of the invention having a thickness of 120 microns has an impact resistance greater than 152 g or greater than 160 g or greater than 180 g or greater than 200 g or greater than 300 g or greater than 375 g. In certain of these embodiments, the 120 μm laminate (or film) of the invention has an impact resistance less than 1000 g or less than 750 g or less than 500 g, and preferably has an impact resistance of 180-400 g. In certain embodiments, a laminate (or film) of the invention has an impact resistance at least 5% or at least 10% or at least 20% or at least 50% greater than a reference structure. As used herein, the term "reference

structure” means a laminate (or film) of the same thickness as the inventive laminate (or film), which comprises at least one of the same polymer(s) as the inventive laminate (or film) but is free of the block copolymer. More preferably, the reference structure is identical in composition to the inventive laminate (or film) but for the absence of the block copolymer.

[0069] While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

WHAT IS CLAIMED IS:

1. A dispenser for storing and dispensing a substance, the dispenser comprising:
a compartment for storing the substance; and
an opening in the dispenser in communication with the compartment for dispensing the substance,
an inner layer defining an inner surface of the compartment;
an outer layer defining the outer surface of the dispenser;
a barrier layer disposed between the inner layer and the outer layer;
wherein the outer layer comprises a outer coating of a block copolymer, the copolymer coating being effective to provide the outer layer with an impact resistance at least 5% greater than a reference structure.
2. The dispenser of claim 1, wherein the impact resistance of the outer layer is at least 20% greater than the impact resistance of the reference structure.
3. The dispenser of any preceding claim, wherein when the outer layer has a thickness of 120 microns, the impact resistance of the outer layer is greater than 180 g.
4. The dispenser of any preceding claim, wherein the inner layer comprising an inner layer polymer and the outer layer comprises an outer layer polymer.
5. The dispenser of any preceding claim, wherein the inner layer polymer and the outer layer polymer comprise polyethylene.
6. The dispenser of any preceding claim, wherein the inner layer polymer comprises LDPE, the outer layer polymer comprises LDPE and HDPE, and the block copolymer comprises an SBS block copolymer having thermoplastic elastomer properties.
7. The dispenser of any preceding claim, wherein the barrier layer comprises a metal foil.
8. The dispenser of claim 7, wherein the metal foil comprises aluminum.
9. The dispenser of any preceding claim, further comprising an inner adhesive layer between the inner layer and the barrier layer, and an outer adhesive layer between the barrier layer and the outer layer.
10. The dispenser of claim 9, wherein the inner adhesive layer and the outer adhesive layer comprise ethylene acrylic acid.
11. The dispenser of any of claims 1-10, wherein the barrier layer is bonded directly to the inner layer and the outer layer without any adhesive therebetween.

12. The dispenser of any preceding claim, wherein the dispenser is sufficiently collapsible such that the substance can be extruded from the opening.
13. The dispenser of any preceding claim, wherein the substance in the dispenser is a member selected from the group consisting of a paste, a gel and a cream.
14. The dispenser of claim 13, wherein the substance is a dentifrice.
15. The dispenser of claim 14, wherein the substance is toothpaste.
16. A dispenser for storing and dispensing a substance, the dispenser comprising:
 - an inner layer comprising LDPE;
 - an outer layer;
 - an aluminum barrier layer between the inner layer and the outer layer;
 - a compartment defined by an inner surface of the inner layer, said compartment for storing the substance; and
 - a resealable opening for dispensing selected amounts of the substance,wherein the outer layer comprises LDPE, HDPE and an SBS block copolymer having thermoplastic elastomer properties.
17. The dispenser of claim 16, wherein the outer layer has an impact resistance at least 5% greater than a reference structure.
18. The dispenser of claim 16, wherein the outer layer has an impact resistance at least 20% greater than a reference structure.
19. The dispenser of any of claims 16-18, wherein when the outer layer has a thickness of 120 microns, the impact resistance of the outer layer is greater than 180 g.
20. The dispenser of any of claims 16-19, further comprising an inner adhesive layer between the inner layer and the barrier layer, and an outer adhesive layer between the barrier layer and the outer layer, wherein the inner adhesive layer and the outer adhesive layer comprise ethylene acrylic acid.
21. The dispenser of any of claims 16-20, wherein the barrier layer is bonded directly to the inner layer and the outer layer without any adhesive therebetween.
22. The dispenser of claim 21, wherein the inner layer and the outer layer are radiation graft modified and/or plasma modified for direct adhesion to the barrier layer.
23. The dispenser of any of claims 16-22, wherein: (a) the outer layer has an impact resistance at least 20% greater than a reference structure; (b) when the outer layer has a thickness of 120

microns, the impact resistance of the outer layer is greater than 180 g; and (c) the substance is toothpaste.