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(54) Title: ANISOTROPIC THIN FOAMED POLYETHYLENE SHEET AND APPLICATIONS THEREOF

(57) Abstract: This invention relates to an anisotropic multilayer film comprising one or more foam layers, wherein at least one layer comprises 10 to 100 percent by weight LLDPE with a melt index of 0.2 to 2 g/10 min. The film in this invention can have a surface with an average Sheffield smoothness, according to TAPPI T 538, of less than 100. The film in this invention can have a puncture propagation tear resistance, in accordance with ASTM D2582, greater than 650 g/mil.

Anisotropic Thin Foamed Polyethylene Sheet and Applications Thereof

Field

This invention relates to a multilayer foam film which may be used for packaging application. In some embodiments, the present invention relates to an anisotropic foamed polyethylene film comprising at least one layer of linear low-density polyethylene (LLDPE) wherein an inert gas such as carbon dioxide, nitrogen or a mixture of carbon dioxide and nitrogen is introduced into the polymer melt to enhance processability. The fabrication of monolayer or multilayer films, with or without foamed layers, is within the scope of this invention and technique. The films can be used in a wide range of applications such as trash bags, grocery bags, food wrap, sous vide packaging, standup pouches, pet food bags, surface protection, and liquid packaging.

Background

Due to the commercial significance of polymer films, it is imperative to improve the properties of the film products. More specifically the mechanical property can be improved by various methods such as manipulating the structure of the resin or taking advantage of particular additives. In a blown film process, typically the tear strength in the machine direction (MD) deteriorates due to the alignment of polymer chains. The cells in the foamed film are also very prone to be elongated in the machine direction which may increase the amount of cell coalescence and hence the mechanical properties can be further deteriorated.

To improve the mechanical properties and more specifically the tear strength of the film, crosslinking is an option, however, it adds to the cost and complexity of the process and results in a non-recyclable product. Traditionally, high melt index (high-MI) linear low-density polyethylene (LLDPE) is blended with LDPE, which is widely used in a blown film line, to improve the tear strength in the machine direction, tensile strength, and elongation at break. On the other hand, high-MI LLDPE shows relatively poor melt strength which is a crucial factor to stabilize the blown bubble. For this reason, the use of high-MI LLDPE resin is limited to a small fraction in a blend with LDPE. The use of the fractional melt index LLDPE or low-MI LLDPE in blown film process is not conventionally of interest due to the difficulties in processing and achieving a good surface quality.

The surface quality and smoothness of the thin film, and the blown bubble depends on a few factors including die geometry, molecular weight and molecular weight distribution of the resin, flow rate, and the structure of the polymer. Extrusion instability manifests first as the presence of any nonuniformity on the extrudate's surface or in the cross section along the machine direction, defined as the melt fracture, which results in a film with a poor appearance. Sharkskin melt fracture is observed for many linear polymers such as HDPE and LLDPE. Most commercially available branched polymers including LDPE, however, shows gross melt fracture which happens at much higher wall shear stress compared to the shear stress at which sharkskin melt fracture starts to happen. In extrusion foam processing, the inclusion of a blowing agent which results in a different viscosity behavior of a melt during processing have a significant effect on the melt fracture of the polymers, hence the improvement of the surface quality of the film. The printing quality on the film is determined by a few important parameters based on the printing method, all of which are mutually dependent on the surface smoothness of the film to result in a uniform ink coverage on the surface of the film.

Martinez et al. disclosed, in their patent US8512837B2, a foamed film produced by using a chemical and physical blowing agent together, using a blend of LDPE and LLDPE with a specific fabrication condition. Their blend comprised a high-MI LLDPE and low-MI branched LDPE which provided a balance of mechanical strength from the LLDPE fraction and an adequate amount of melt strength from highly branched LDPE fraction to help inflating the bubble. Martinez et al. assert that the use of LLDPE in non-cross-linked foaming applications has been limited to a small amount where the major component is high melt strength LDPE. This is mainly because LLDPE possesses a poor melt strength which further becomes worse for the grades with a higher melt index. Accordingly, Martinez et. al. stated that the traditional methods of increasing the MD tear strength such as the use of low MI LLDPE or the use of pure or rich blends of LLDPE resin, in general, are not necessarily viable for foamed applications and thus no foam film having a thickness of 1 to 10 mils are known to have a sufficient and satisfactory MD tear strength. So, Martinez et al. employed a particular blend of LLDPE and LDPE together with specific fabrication condition to make a foamed film of a thin gauge with MD tear properties similar to an equivalent gauge non-foamed sheet of the same composition.

In their patent US10011697B2, Van der Ven et al. disclosed a polyethylene foamed film comprising a blend of LDPE, LLDPE, and HDPE, wherein 0.5 to 4.5 percent by weight of HPDE is added into the blend. Those skilled in the art will recognize that a small amount of HDPE is often added to a blend of LDPE and

LLDPE which can improve the miscibility. For example, De Vos et al., in EP2164893B1, disclose the use of HDPE in the formulation of a polyethylene foam.

In a conventional blown film line, the production of film from LLDPE is mostly avoided because of the extensive amount of difficulties in processing. The most important of which is forming a stable bubble using a high MI LLDPE that exhibits a poor melt strength. In the current invention, we are using LLDPE with a very low melt index, or fractional melt index, which can offer an enhanced MD tear strength, improved gas and moisture permeation properties compared to that of LDPE, far better environmental stress cracking resistance, and an enhanced tensile strength at yield.

Processing of either a rich blend or pure LLDPE with a fractional or a very low melt index in a blown film line with a very narrow gap and producing a film with a smooth surface has been very challenging. The rationale behind using such a polymer blend is to take advantage of the good properties of an inexpensive and commercially available LLDPE and mLLDPE, more specifically the grades with a very low melt index, which is of our most interest, and one of the objectives of this invention.

We benefited from the introduction of inert gas into the polymer melt. The plasticization effects of the dissolved blowing agents, which alters the viscosity of the resin, makes us capable of processing the low melt index resin through a very narrow gap. In foaming applications, operating through a narrow gap results in a high extrusion pressure favorable for foaming. That is, not only it increases the solubility and keeps the gas dissolved in the polymer until the die exit, but also causes a high pressure drop rate. This abrupt and significant drop in pressure causes large numbers of nuclei to be formed and suppresses the growth of the bubbles, resulting in smaller cells in the foam structure. The viscosity modification caused by a small amount of dissolved gas, e.g. less than 0.5 wt%, may hinder or delay the occurrence of shark skin melt fracture and results in a very smooth surface quality to the film.

Summary

This invention relates to a multilayer thermoplastic film comprising one or more foam layers. In some embodiments, at least one layer comprises 10 to 100 percent by weight LLDPE with a melt index of 0.2 to 2 g/10 min.

The film in this invention can have a surface with an average Sheffield smoothness, according to TAPPI T 538, of less than 100, specifically less than 50, more specifically less than 20, and the most specifically less than 10.

The film in this invention can have a puncture propagation tear resistance, in accordance with ASTM D2582, greater than 650 g/mil, preferably greater than 750 g/mil, and most preferably greater than 900 g/mil.

In some aspects, an anisotropic multilayer foamed film comprising one or more foam layers is provided. At least one layer comprises 10 to 100 percent by weight LLDPE with a melt index of 0.2 to 2 g/10 min, and the resulting film has a surface with an average Sheffield smoothness of less than 100.

In some aspects, an anisotropic multilayer foamed film comprising one or more foam layers, is provided. At least one layer comprises 10 to 100 percent by weight LLDPE with a melt index of 0.2 to 2 g/10 min, and the resulting film has a puncture propagation tear resistance greater than 500 g/mil.

In some aspects, a process of making a multilayer foam film is provided. The method comprises processing a first fluid stream of polymeric material comprising polyethylene in an extruder and processing a second fluid stream of a second polymeric material in an extruder. The method further comprises co-extruding the first fluid stream and the second fluid stream through an annular die to form a multilayer film. The multilayer film comprises a polyethylene layer and a layer comprising the second polymeric material. A supercritical physical blowing agent may be introduced into the first fluid stream and/or the second fluid stream in the extruder. The resulting multilayer film comprises at least one foam layer, and the multilayer film has an average Sheffield smoothness of less than 100 according to TAPPI T 538.

For example, an inert gas such as nitrogen, or carbon dioxide, or a mixture of carbon dioxide and nitrogen, in the supercritical state, can be introduced into the extruder at a very high injection pressure to form a single-phase polymer/gas mixture which improves the processing ability of the polymer.

In some embodiment, the resin used can be a rich blend of LLDPE with a fractional or very low melt index in the range of 0.2 to 2 gr/10 min as determined in accordance with ASTM D1238, and a density in the range of 0.915 to 0.935 gr/cm^3.

The film of this invention can be used in a wide range of applications in packaging such as collation shrink, pouches, lamination, pet food bags, surface protection, trash bag, grocery bags, food wrap, pallet wrap, shrink film, labels, and pouches for FFS packaging. The fabrication of a monolayer foam film is within the scope of this invention.

Detailed description

The singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise.

As used in the specification and in the claims, the term "comprising" may include the embodiment "consisting of" and "consisting essentially of."

All ranges disclosed herein are inclusive of the recited endpoint and independently combinable (for example, the range of from 2 grams to 10 grams" is inclusive of the end points, 2 grams and 10 grams, and all the intermediate values)

As used herein, approximating language may be applied to modify any quantitative representation that may vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as "about" and "substantially," may not be limited to the precise value specified. The modifier "about" should also be considered as disclosing the range defined by the absolute value of the two endpoints. For example, the expression "from about 2 to about 4" also discloses the range "from 2 to 4".

The present disclosure relates to multilayer or monolayer polyethylene foam film suitable to be used in a wide range of applications such as collation shrink, pouches, lamination, pet food bags, surface protection, agricultural films, geomembrane, packaging, trash bag, grocery bags, food wrap, pallet wrap, shrink film, labels, and pouches for FFS packaging. The fabrication of either a monolayer or a multilayer film is within the scope of this invention and technique and one or more layers of the film may be foamed.

The term "anisotropic" refers to the fact that certain properties of the foamed film differs depending on the direction along which the property is measured. For the purpose of this disclosure, properties were measured against two direction (in-flow or machine direction (MD), and cross-flow or transverse direction(TD)) which are perpendicular to each other.

The term "foam" in this invention refers to a cellular structure formed when a gas is blown into the molten polymer, and bubbles nucleate when the gas diffuses out of the polymer, right after the application of a thermodynamic instability, as the polymer solidifies.

Generally, the desired application of a thin film determines the essential physical and mechanical properties of the film which subsequently concludes the best resin or a blend of a few resins and additives for processing. Furthermore, the processing properties is a crucial factor in material selection. More

specifically, in the blown film process of this invention where the head pressure is high because of a very narrow gap, the melt fracture should be avoided, and the resin should have a good thermal stability and high enough melt strength. Various thermoplastics can be used in the blown film process of this invention such as polyethylene (PE), polypropylene (PP), polystyrene (PS), ethylene vinyl acetate (EVA), ethylene vinyl alcohol (EVOH), polyvinyl chloride (PVC), Polyvinylidene chloride (PVDC), polyamide (PA), polyurethane (PU), or any of the resins known as TPE family such as, but not limited to, propylene-ethylene copolymer, Thermoplastic Olefin (TPO), Thermoplastic Polyurethane (TPU). The LLDPE copolymer in this invention can include an α-olefin co-monomer such as butene, hexane, or octene.

In some embodiments, the process of making the multilayer foam film described herein comprising the processing a first fluid stream of polymeric material comprising polyethylene in an extruder; processing a second fluid stream of a second polymeric material in an extruder; and co-extruding the first fluid stream and the second fluid stream through an annular die to form a multilayer foam film comprising a polyethylene layer and a layer comprising the second polymeric material, wherein a supercritical physical blowing agent is introduced into the first fluid stream and/or the second fluid stream in the extruder; and in some embodiments the process may make a multilayer film comprising more than 2 layers, e.g., three, five, six, seven, eight, or nine layers. In some embodiments, the process of making the multilayer product described herein can make a multilayer film comprising any combination of layers from 3 to 14 layers.

In some embodiments, the process of making the multilayer film described herein comprising the processing of multiple fluid streams, e.g., 2 to 9 streams, of polymeric materials in multiple extruders, e.g., 2 to 9 extruders, and co-extruding the fluid streams through an annular die to form a multilayer film, e.g., 3 to 14 layers, wherein a supercritical blowing agent is introduced in at least one of the fluid streams inside the extruder.

The choice of material in this invention could be determined in separate ways based on processing requirements, product properties, and material specification. The processing requirement in a blown film process dictates the use of a high melt strength resin to get a stable bubble. Low-density polyethylene (LDPE) is relatively easy to process resin at a lower processing temperature compared to HDPE. Because of the existence of long chain branching, all LDPE grades show a rather high processing melt strength. Therefore, an entirely stable bubble with a relatively low frost line height can be examined with a PE blend the majority of which is LDPE. Moreover, LDPE shows an elongational thickening behavior which can

further increase the melt strength and can cause strain hardening. On the other hand, generally LDPE presents a rather low tear strength along the machine direction (MD).

Typically, film manufacturers capitalize on a blend of LDPE and high-MI LLDPE, while the blend is an immiscible blend in many cases, wherein LDPE improves the processing ability and ductility while the LLDPE enhances the modulus and strength. In a conventional blown film line, the production of the film from LLDPE is mostly avoided because of the extensive amount of difficulties in processing. The most important of which is forming a stable bubble using a high MI LLDPE that exhibits a poor melt strength. In this invention, we are using LLDPE with a very low melt index, or fractional melt index, which can offer an enhanced MD tear strength, improved gas and moisture permeation properties compared to that of LDPE, far better environmental stress cracking resistance, and an enhanced tensile strength at yield.

In blown film extrusion, typically sharkskin melt fracture occurs when LLDPE is processed through a narrow die gap. Furthermore, LLDPE with low melt index, which offers an improved toughness, shows a higher tendency to melt fracture than a high-MI LLDPE, as do metallocene catalyzed resins (mLLDPE) which have a narrow molecular weight distribution than conventional LLDPEs. In this invention, a very small and precise amount of supercritical gas, as a processing aid and blowing agent, is injected into the molten polymer at a high pressure, for example greater than 34 bar, inside an efficient and effectual mixer, e.g., cavity transfer mixer, as an extension to the extruder's barrel. For example, the supercritical blowing agent used in this invention can be either nitrogen, carbon dioxide or a mixture of nitrogen and carbon dioxide. The temperature of the mixer could be accurately controlled within ±1°C. The inclusion of a very small amount of gas could offer a few important advantages in blown film extrusion. First, it could reduce the back pressure which allows processing at a higher throughput and delayed any bubble instability. Therefore, melt fracture could be reduced significantly. Second, the possibility of using a very low melt index LLDPE with narrow molecular weight distribution, to include metallocene α-olefin copolymers, became viable for processing to improve the film properties.

In some embodiments, The LLDPE component of the resin has a melt index in the range 0.1 to 1.2 g/10min as is determined by ASTM D1238. In some embodiment the LLDPE has a melt index of 0.5 to 1 g/10 min. The LLDPE component of the resin can have a density of 0.915 to 0.935 g/cm^3. The polyethylene resin may be comprised of 70 to 90 percent by weight copolymer and from 30 to 10 percent by weight homopolymer, corresponding to 100 percent by weight. The LLDPE component of the resin may be a copolymer containing one or more of the α-olefins; 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. In another case, the polyethylene resin can be a blend of 51 to 99 percent by weight LLDPE with

a very low MI in the range of 0.2 to 1 g/10min, as determined by ASTM D1238, and 1 to 49 percent by weight LDPE. In some cases, the polyethylene blend may contain up to 10 percent by weight HDPE that might improve the miscibility of the blend. Also, for example, the LLDPE component of the resin may be a blend of mLLDPE and LLDPE.

In some embodiment, the resin used can be a rich blend of LLDPE with a fractional or very low melt index in the range of 0.2 to 2 gr/10 min as determined in accordance with ASTM D1238, and a density in the range of 0.915 to 0.935 gr/cm^3.

In some cases, at least one layer of the film has 0.05 to 15 percent by weight of an inorganic additive, an organic additive or a mixture of an inorganic and an organic additive. In some other cases, the polymer composition of each layer may comprise some apt amounts of other additives to include pigments, antistatic agents, UV stabilizers, and antioxidant. In another embodiment, at least one layer includes a clarifying agent at less than 1 percent by weight, preferably less than 0.5 percent by weight, more preferably less than 0.1 percent by weight, and mostly preferably less than 0.05 percent by weight.

A multilayer film, comprising at least one foam layer, fabricated using this invention in a blown film process has sets of significantly improved physiomechanical properties compared to the film articles of the prior art, to the best of applicant's knowledge, as in particular puncture propagation tear (PPT) resistance, acc. to ASTM D2582, can be greater than 650 g/mil, more specifically can be greater than 750 g/mil, and most specifically can be greater than 900 g/mil. In some cases, the MD tear resistance, acc. to ASTM D9929, can be greater than 100 g.mil, more specifically can be greater than 200g/mil, and most specifically can be greater than 300 g/mil. In some embodiments, the foam film resulting from the present invention has a far better cellular morphology compared to the existing prior arts, as it can have uniformly distributed cells with an average cell size of 10 – 1000 µm, an average cell density of 10^2 – 10^9 cells/cm^3, and an expansion ratio of the foamed layer from 1 to 9 . in one other case, the expansion ratio of any foamed layer is less than 1.1 compared to the non-foamed layer of the same composition.

In some embodiments, the multilayer foam film described herein has an average Sheffield smoothness, according to TAPPI T 538, of less than 70, in some embodiments, less than 50, in some embodiments, less than 30, and in some embodiments less than 10.

In some embodiments, the foam film described herein has a thickness of about 0.4 to 100 mils. In some other embodiments, the film has the mass per unit area of 5 to 950 gsm (gr/cm^2).

All the equipment used in this invention are very well-known to the skilled persons in the art and well labeled and extensively described in the literature. In some cases, the film can be produced by the blown film process using an annular die with a die gap from 0.45 to 1.3 mm and a blow-up ratio ranging from 2:1 to 3.5:1. Higher blow-up ratios can result in a more balanced MD/TD orientation which improved overall film toughness. The die geometry and specification may be manufactured according to the patent with the application number of US 2012/0228793 A1.

As it was explained earlier, a very small amount of a physical blowing agent in a super critical condition can be injected into the molten resin, at a very precisely controlled rate, inside a mixer with a very effectual distributive and dispersive element before entering the annular die. This unit is controlled as a separate temperature zone with an accuracy of ±1 °C and a gas injection pressure variation below 1%. The plasticization effect of the gas results in a viscosity change of the molten resin, specifically the aforementioned low-MI PE resin, which enhances the processibility of the resin at a lower temperature compared to the processing temperature which is used conventionally. This also may benefit and assist ones to manipulate the crystallization kinetics of the resin to improve a few properties.

In the blown film process of this invention, because of the overall high specific heat capacity of polyethylene, the transverse stretch of the bubble could be delayed until the film became cooler, which enhanced the bubble stability and the frost line height. This caused the bubble expansion in transverse direction to occur at a lower temperature and shorter period of time which is very effective to increase the molecular orientation in the transverse direction, therefore, to improve the MD tear strength.

In some other embodiments the film in this invention can be produced by the blown film process, cast film process, or any method known in the art.

The following examples demonstrate the process of the present disclosure. The examples are only demonstrative and are intended to put no limit on the disclosure with regards to the materials, conditions, or the processing parameters set forth herein.

Examples

Samples of multilayer film (three layers) were produced on a blown film line comprising one 80mm main extruder and two 70mm co-extruders. The core extruder was equipped with a supercritical gas injection unit, capable of injecting nitrogen or carbon dioxide, and a 90mm MuCell Transfer Mixer, both from MuCell Extrusion LLC.

All samples were produced with a polyethylene blend comprising LLDPE copolymer with an α-olefin co-monomer comprises 1-octene with MFI=1 and the density of 0.935. The foamed core layer of all samples contains talc as the cell nucleating agent which was added in the form of a 67% talc filled LDPE masterbatch. The solid layers comprised from 53.5 wt% to 86 wt% the aforementioned LLDPE of the total composition.

Supercritical nitrogen was used as a physical blowing agent and was injected into the MuCell Transfer Mixer (MTM) at the concentration from 0.0662% to 0.0737%, very accurately, into the molten polymer. To characterize the tear and impact resistance of the foam films a Spencer Impact tester from Thwing-Albert, capable of performing the Elmendorf tear resistance test and Spencer impact test, was used. The smoothness of the products (Sheffield unit) was evaluated using a Gurley™ 4340 Automatic Densometer & Smoothness Tester.

Sample	Sample E			Sample F			Sample G		
Density (gr/cm^3)	0.78			0.76			0.81		
Thickness (um)	102			94			92		
Throughput (kg/hr)	422.4			421.7			422.5		
PBA %	0.0662			0.0737			0.0727		
Basic weight (gr/m^2)	79.6			71.4			74.5		
Line speed (m/min)	17.8			19			18.2		
Die Gap (mm)	0.6			0.6			0.6		
Layers	Skin A	Core	Skin B	Skin A	Core	Skin B	Skin A	Core	Skin B
LLDPE wt%, MFI 1	76	63.5	55	76	53.5	55	86	53.5	55
67% talc filled LDPE	0	15	0	0	15	0	0	15	0
Layer Thickness (um)	25.5	50.3	26.3	23.2	47.7	23.2	24.1	43.8	24.1
Layer Density (gr/cm^3)	0.97	0.59	0.95	0.97	0.56	0.95	0.97	0.64	0.95
Layer Throughput (kg/hr)	131	158.7	132.7	132.5	158.8	130.4	132.5	159.6	130.4
Layer Volume Ratio (%)	25	49.3	25.7	24.6	50.7	24.7	26.2	47.6	26.2
Tear Strength MD (grf)	1137.1			1055.5			866.1		
Tear Strength TD (grf)	1574.4			1715			1518.9		
Tensile Strength at Break MD (MPa)	19.4			18.2			19.3		
Tensile Strength at Break TD (MPa)	17.3			17.5			16.8		
Yield Stress MD (MPa)	11.1			10.1			10.5		
Yield Stress TD (MPa)	10.3			10.25			9.7		
Elongation at Break MD (%)	942			892			918		
Elongation at Break TD (%)	970			928			928		
1% Sec. Modulus MD (MPa)	325			285			294		
1% Sec. Modulus TD (MPa)	299			317			287		
Toughness MD (in. Ibf/in^3)	15988			14509			15731		
Toughness TD (in. Ibf/in^3)	15432			14343			13549		
PPT MD (grf)	2604.3			2989.8			2603.3		
PPT TD (grf)	5072.4			4390.3			4309.8		
PPT MD (gr/mil)	667.1			902.4			783.7		
PPT TD (gr/mil)	1299.2			1325.2			1297.4		
Tear length in PPT MD (cm)	2.9			3.2			3.4		
Tear length in PPT TD (cm)	1.6			1.8			1.4		
Smoothness (Sheffield Unit)	9.8			6.9			10.7		

All the samples listed in the table above were made with the same processing condition and the same throughput. Sample F was made based on the sample E but with a lower weight per unit area and the same resin composition by the inclusion of a higher amount of supercritical gas up to 0.0737%. The Sheffield smoothness of the film in sample F improved, e.g. down to 6.9 Sheffield unit, as well as the puncture propagation tear resistance of the film, e.g. up to about 900 gr/mil. Sample G was made based on sample F, but with the inclusion of higher amount of LLDPE in the Skin A which resulted in a little higher

PPT. The tensile properties, including the yield strength, as well as the tear strength in the machine direction for all the samples were comparable to, or in some case surpasses, that of the similar foam films or equivalent solid counterparts in existing prior art.

Claims

1. An anisotropic multilayer foamed film comprising one or more foam layers, wherein at least one layer comprises 10 to 100 percent by weight LLDPE with a melt index of 0.2 to 2 g/10 min, and the resulting film has a surface with an average Sheffield smoothness of less than 100.

2. An anisotropic multilayer foamed film comprising one or more foam layers, wherein at least one layer comprises 10 to 100 percent by weight LLDPE with a melt index of 0.2 to 2 g/10 min, and the resulting film has a puncture propagation tear resistance greater than 500 g/mil.

3. The film of any preceding claims which is produced by the blown film process, cast film process, or any method known in the art.

4. The film of any preceding claims wherein a supercritical physical blowing agent is intoduced to the foam layer.

5. The film of any preceding claims wherein a supercritical physical blowing agent is introduced into the molten resin inside the mixing section of the extruder during the process.

6. The film of any preceding claims wherein the supercritical blowing agent used is either nitrogen, carbon dioxide or a mixture of nitrogen and carbon dioxide.

7. The film in claim 1 which is produced using an extrusion die with a die gap of 0.45 to 1.3 mm.

8. The film in claim 1 wherein the film is produced by the blown film process using an annular extrusion die and a blow-up ratio of 2:1 to 3.5:1.

9. The film of claim 1 wherein a nucleating agent is used to produce a foamed layer with an average cell size of 10 to 1000 μm.

10. The film of any preceding claims wherein the foam layer comprises nucleating agent with a concentration of about 0.05 to 15 percent by weight of an inorganic additive, an organic additive or a mixture of an inorganic and an organic additive.

11. The film of any preceding claims wherein the cell density in the foam layer is 10^2 to 10^9 cells/cm^3 and the film density is 0.1 to 0.9 g/cm^3.

12. The film of any preceding claims wherein at least one layer contains some apt amounts of other additives to include pigments, antistatic agents, UV stabilizers, and antioxidant.

13. The film of any preceding claim wherein at least one layer is a solid layer.

14. The film of any preceding claim wherein the film has an average Sheffield smoothness of less than 70, preferably less than 50, more preferably less than 30, and most preferably less than 10.

15. The film of any preceding claims wherein the film has a puncture propagation tear resistance greater than 650 g/mil, preferably greater than 750 g/mil, and most preferably greater than 900 g/mil.

16. The film of any preceding claims wherein the thickness of the film is 0.4 to 100 mils.

17. The film of any preceding claims wherein the mass per unit area is 5 to 950 gsm.

18. The film of any preceding claims wherein the MD tear resistance is greater than 100 g/mil, preferably greater than 200 g/mil, and most preferably greater than 300 g/mil.

19. The film of any preceding claims wherein the LLDPE has a solid density of 0.915 to 0.935 g/cm^3.

20. The film of any preceding claims wherein the LLDPE has a melt index of 0.5 to 1 g/10 min

21. The film of any preceding claims wherein the LLDPE is a copolymer of ethylene and one or more alpha-olefins: 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene..

22. The film of any preceding claims wherein at least one layer comprises a blend of 70 to 90 percent by weight of a copolymer and 10 to 30 percent by weight of a homopolymer, corresponding to 100 percent by weight.

23. The film of any preceding claims wherein at least one layer comprises a blend of less than 10 percent by weight HDPE, corresponding to 100 percent by weight.

24. A multilayer film of any preceding claims wherein at least one layer comprises HDPE, LDPE, PP, PET, PA, PVC, EVOH, TPU, PVDC, PVOH, ethylene-octene copolymer, an olefinic copolymer or interpolymer, ionomer, maleic anhydride or any of the resins known as TPE family such as, but not limited to, propylene-ethylene copolymer, Thermoplastic Olefin (TPO), Thermoplastic Polyurethane (TPU).

25. A multilayer film of any preceding claims wherein at least one layer includes a clarifying agent at less than 1 percent by weight, preferably less than 0.5 percent by weight, more preferably less than 0.1 percent by weight, and mostly preferably less than 0.05 percent by weight.

26. A co-extruded and/or laminated multilayer film comprises at least one layer film of any preceding claims.

27. The film of any preceding claims wherein the expansion ratio of any foamed layer is less than 1.1 compared to the non-foamed layer of the same composition.

28. The film of any preceding claims where the film is a monolayer film.

29. The film of any preceding claims wherein the film has a solid skin on at least one surface.

30. An article prepared using the film of any preceding claims.

31. The article of any of any preceding claims wherein the article is used as a trash bag, grocery bags, food wrap, pallet wrap, shrink film, labels, pouches for FFS packaging, collation shrink, standup pouches, lamination, pet food bags, geomembrane, agricultural film, surface protection film, and packaging.

32. A process of making a multilayer foam film comprising:
processing a first fluid stream of polymeric material comprising polyethylene in an extruder;
processing a second fluid stream of a second polymeric material in an extruder;
and co-extruding the first fluid stream and the second fluid stream through an annular die to form a multilayer film comprising a polyethylene layer and a layer comprising the second polymeric material,
wherein a supercritical physical blowing agent is introduced into the first fluid stream and/or the second fluid stream in the extruder, and the resulting multilayer film comprising at least one foam layer, and the multilayer film has an average Sheffield smoothness of less than 100 according to TAPPI T 538.

33. The process of claim 32 which is blown film process, cast film process, or any method known in the art.

34. The process of any of claims 32-33 which is using an extrusion die with a die gap of 0.45 to 1.3 mm.

35. The process of any of claims 32-34 wherein the film is produced by the blown film process using an annular extrusion die and a blow-up ratio of 2:1 to 3.5:1.

36. The process of any of claims 32-35 wherein a supercritical physical blowing agent is introduced into the molten resin inside the mixing section of the extruder during the process.

37. The process any of of claims 32-36 wherein the supercritical blowing agent used is either nitrogen, carbon dioxide or a mixture of nitrogen and carbon dioxide.

38. The process of any of claims 32-37 wherein the supercritical blowing agent is introduced inside the mixing section of the extruder at the injection pressure greater than 34 bar, preferably greater than 70 bar, more preferably greater than 240 bar, and most preferably greater than 380 bar.

39. The process of any of claims 32-38 wherein a nucleating agent is used to produce a layer with cellular structure with an average cell size of 10 to 1000 μm.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 19/61870

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B32B 27/06; B32B 27/32; B32B 5/18 (2020.01)

CPC - B32B 27/065; B32B 27/32; B32B 5/18; B32B 7/02; C08J 5/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6,723,793 B2 (Oswald et al.) 20 April 2004 (20.04.2004) Entire document, especially col 9, ln 55-57; and col 17, ln 62-67	1-3 and 7-9
A	US 5,925,450 A (Karabedian et al.) 20 July 1999 (20.07.1999) Entire document, especially abstract; col 10, ln 66 Table 12 and column col 11, ln 16-17	1-3 and 7-9
A	US 2016/0059514 A1 (Mondi Consumer Packaging Technologies GmbH) 3 March 2016 (03.03.2016) Entire document, especially para [0010], [0030] and [0056]	1-3 and 7-9
A	US 6,506,866 B2 (Jacobsen et al.) 14 January 2003 (14.01.2003) Entire docment, especially col 7, ln 24-25 and col 50, ln 58 2	1-3 and 7-9
A	US 20170101518 A1 (Berry Plastics Corporation) 13 April 2017 (13.04.2017) Entire document, especially abstract, para [0039], [0042], [0052], [0202], [0214], [0219]	1-3 and 7-9

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 March 2020	20 APR 2020
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Lee Young Telephone No. PCT Helpdesk: 571-272-4300

Form PCT/ISA/210 (second sheet) (July 2019)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 19/61870

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.: 4-6, 10-31, 35-39
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: claims 1-3 and 7-9 directed to an anisotropic multilayer foamed film.
Group II: claims 15-20 directed to a process of making a multilayer foam film.

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special technical features:

Continue on the first page

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-3 and 7-9

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

International application No.
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Continued from Box III

Group I requires an anisotropic material comprising one or more foam layers, wherein at least one layer comprises 10 to 100 percent by weight LLD PE with a melt index of 0.2 to 2 g/10 min, a puncture propagation tear resistance greater than 500 g/mil which is not required by Group II

Group II requires a process of making comprising: processing a first fluid stream of polymeric material comprising polyethylene in an extruder; processing a second fluid stream of a second polymeric material in an extruder; and co-extruding the first fluid stream and the second fluid stream through an annular die to form a multilayer film comprising a polyethylene layer and a layer comprising the second polymeric material, wherein a supercritical physical blowing agent is introduced into the first fluid stream and/or the second fluid stream in the extruder, and the resulting multilayer film comprising at least one foam layer, and the multilayer according to TAPPI T 538, which is not required by Group I.

Shared technical features:

Groups I-II share the technical feature multilayer foamed film comprising polyethylene the film has a surface with an average Sheffield smoothness of less than 100.

However, this shared technical feature does not provide a contribution over the prior art because these shared technical feature is anticipated by US 5,925,450 A to Karabedian et al. (hereinafter 'Karabedian') teaches multilayer foamed film (abstract 'The foam may be coextruded with one or more layers of thermoplastic film') comprising polyethylene (col 11, ln 16-17 'to make foam polypropylene and polyethylene foam sheet material') the film has a surface with an average Sheffield smoothness of less than 100 (col 10, ln 57 and 66 Table 12 Heading 'Sheffield Smoothness - Foam/Mandrel Side' and column Smoothness 'N (94%) ... 4.84').

Groups I-II therefore, lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature providing a contribution over the prior art.

Note:
claims 4-6, 10-31, 35-39 determined unsearchable because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).