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(54) Title: POLYMERIC FILMS AND PACKAGES PRODUCED THEREFROM

(57) Abstract: Polymeric film having linear tear properties produced by blowing or casting include a layer of a blend of a cyclic olefin copolymer and a polyethylene. Such films which consist of a core layer of the blend and two outer layers of different polymers from the core layer can be torn relatively easily along substantially straight lines substantially along the direction of blowing or casting, with or without the presence of a starter cut or nick, but with relative difficulty perpendicular thereto even with a starter cut or nick.



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Polymeric Films and Packages Produced Therefrom

This invention concerns polymeric films and packages produced therefrom and in particular films and packages having linear tear open properties.

The problems associated with tearing open packages formed by heat sealing polymers together have been addressed in US4098406. In particular, US4098406 discloses using blends of 12 to 95wt% of an ionomer resin, for example Surlyn, and from 5 to 88wt% of polyethylene optionally containing units derived from vinyl acetate to produce films having linear tear properties, particularly when used to make heat sealed packages.

Although the films disclosed in US4098406 do have good linear tear properties when they are torn substantially in the machine direction of the films, they generally require a cut or nick in the edge of the films in order to start the tear. Furthermore, their moisture vapor and oxygen barrier properties are low for some end uses.

According to the present invention there is provided a polymeric film having linear tear properties, the film having been produced by blowing or casting and comprising a layer of a blend of a cyclic olefin copolymer and a polyethylene.

It has surprisingly been found that films in accordance with the present invention consisting of a core layer of the blend and two outer layers of different polymers from the core layer can be torn relatively easily along substantially straight lines substantially along the direction of blowing or casting, with or without the presence of a starter cut or nick, but with relative difficulty perpendicular thereto even with a starter cut or nick.

The tear properties of films of the present invention are particularly surprising in the light of US6111019 which describes compression molded films produced from melt blends of LLDPE and ethylene/norbornene copolymers which have high tear strengths which require a modified Elmendorf tear test to measure them.

Furthermore, films of the present invention have exhibited good water vapor and oxygen barrier properties when compared with prior art films having linear tear properties. In addition, the puncture resistance of films of the present invention are in general comparable with those of analogous films which do not contain a cyclic olefin copolymer.

The cyclic olefin copolymer used in the blend will usually have a glass transition temperature T_g of greater than 30°C but less than 220°C. A preferred range of glass transition temperatures for these copolymers is from 50 to 175°C, a particularly preferred range being from 65 to 160°C.

Preferred cyclic olefin copolymers for use in accordance with the present invention are cyclic olefin/ethylene copolymers and more preferably norbornene/ethylene copolymers. The norbornene

content of these polymers is preferably from 20 to 80 weight percent.

A particularly preferred cyclic olefin copolymer for use in the present invention is sold by Hoechst AG as COC8007 (glass transition temperature $T_g = 70^\circ\text{C}$), and it is believed that this is a copolymer containing a minor proportion of units derived from norbornene and a major proportion of units derived from ethylene, with the copolymerisation having been effected in the presence of a metallocene catalyst. However, other cyclic olefin copolymers can be used containing units derived from norbornene or other cyclic olefins.

The polyethylene used in the blend can be selected from a wide variety of polyethylenes, for example those having densities in the range of from 0.915g/cm^3 to 0.935g/cm^3 . Thus the polyethylene can be selected from linear low density polyethylenes, linear medium density polyethylenes, and low density polyethylenes.

The weight ratio of the cyclic olefin copolymer to the polyethylene used in the blends can be varied over a wide range, for example from 10 to 90 wt% of the cyclic olefin copolymer and from 90 to 10 wt% of the polyethylene.

Films in accordance with the present invention preferably include at least one further polymeric layer, and more preferably at least two further polymeric layers with the layer of the blend between two of such layers. The use of at least one polymeric layer on each side of the layer of the blend in general serves to provide physical protection to the layer of the blend.

The further polymeric layers are preferably formed from polyolefins which optionally contain units derived from vinyl acetate, for example low density polyethylene, linear low density polyethylene, linear medium density polyethylene, and ethylene/vinyl acetate copolymers.

Films in accordance with the present invention can be produced by blowing or casting using known methods for producing polymeric films, for example by extruding melts of the polymers required for the respective layer or layers, and then either cooling them to form a cast film or blowing them in a so-called bubble process.

Cast films will usually be produced using a linear slot die and blown films will usually be produced using an annular die.

When the films are produced by casting as opposed to blowing, they are generally not stretched during or after extrusion, but in general they will be oriented to a greater or lesser degree in the direction of extrusion.

When the films are produced by blowing, the blown bubble is preferably subjected to expansion ratios in the machine and cross directions of at least 1.1:1, but they can be up to 2:1. The expansion ratio in the machine direction is preferably greater than that in the transverse direction.

Films in accordance with the present invention in general exhibit particularly good linear tear properties along the machine direction used to produce them, that is whether they are merely cast or are blown. Tearing of the films in other directions will in general be less satisfactory due to relatively high tear strengths in these directions.

Films in accordance with the present invention can be produced to a variety of thicknesses, the particular thickness generally being determined by the end use to which the films are to be put. However, they will usually be at least 50 μ m thick, but they can be 150 μ m thick or more. Blown films of the present invention are preferably from 50 to 80 μ m thick, and cast films of the present invention are preferably from 100 to 150 μ m thick.

The blend of a cyclic olefin copolymer and a polyethylene preferably forms a core layer from 15 to 60 μ m thick, the films preferably having two outer layers which can be of the same or different thicknesses, for example one can be from 20 to 25 μ m thick with the other being from 25 to 60 μ m thick. It has been surprisingly found that films having core layers formed from a blend of a cyclic olefin copolymer and a polyethylene, where the core layer represent less than 40% of the total thickness of the films, have good linear tear properties in the direction of blowing or casting combined with good water vapor barrier properties.

Packages in accordance with the present invention are preferably in the form of bags, in particular with top and bottom faces made of the same material. If desired, the packages can include breathable patches sealed thereto, for example to allow the ingress of a sterilant gas and/or for the balancing the pressure within the packages with the outside air. The oxygen transmission rate and the water vapor properties of the film used to form breathable packages is then relatively unimportant.

The following Examples are given by way of illustration only. In the Examples, Elmendorf tear strengths were determined according to ASTM F1249, water vapor transmission rates were determined according to ASTM F1249, and puncture resistance was determined according to ASTM D3763-99.

Example 1 (Comparison)

A mono-layered film was produced by extruding a linear low density polyethylene through a slot die, the resulting film being 126 μ m thick.

The mean Elmendorf tear strengths of this film in both the machine (MD) and cross (CD) directions, the mean moisture vapor transmission rate, and the force require to puncture this film were measured and the results are shown in Table 1.

Example 2

A three layered film was produced by coextruding through a slot die a melt of a blend of 80wt% of the linear low density polyethylene used in Example 1 and 20wt% of the cyclic olefin copolymer sold by Hoechst AG as COC8007 to form a core layer of the film, the two outer layers of the film being formed from the same linear low density polyethylene.

The total thickness of the resulting film was 126µm, the core layer being 48µm thick, with one outer layer being 18µm thick and the other being 60µm thick.

The physical properties tested for the film of Example 1 were measured and the results are shown in Table 1.

Example 3

A three layered film was produced in a similar manner to that of Example 2 except that the core layer was formed from 70wt% of the same linear low density polyethylene and 30wt% of the same cyclic olefin copolymer. The total film thickness was 126µm, the core and outer layers being of the same thickness as in Example 2.

Example 4 (comparison)

A mono-layered film was produced by extruding a linear medium density polyethylene through a slot die, the resulting film being 126µm thick.

The mean Elmendorf Tear Strengths of this film in both the machine and cross directions, the mean moisture vapor transmission rate, and the force require to puncture this film were measured and the results are shown in Table 1.

Example 5

A three layered film was produced by coextruding through a slot die a melt of a blend of 80wt% of the linear medium density polyethylene used in Example 4 and 20wt% of the cyclic olefin copolymer sold by Hoechst AG as COC8007 to form a core layer of the film, the two outer layers of the film being formed from the same linear low density polyethylene.

The total thickness of the resulting film was 126µm, the core layer being 48µm thick, with one outer layer being 18µm thick and the other being 60µm thick.

The physical properties tested for the film of Example 1 were measured and the results are shown in Table 1.

Example 6

A three layered film was produced in a similar manner to that of Example 5 except that the core layer was formed from 70wt% of the same linear medium density polyethylene and 30wt% of the same cyclic olefin copolymer. The total film thickness was 126µm, the core and outer layers being of the same thickness as in Example 2.

Table 1

Example	Mean Elmendorf Tear Strength (mN)		Water Vapor Transmission (g/m ² /d)	Puncture Force (N)
	MD	CD		
1 (comp)	14100	15000	8.0	>100
2	850	3010	4.0	46
3	1730	3600	3.5	58
4 (comp)	3100	3500	7.8	43
5	1000	3170	3.9	46
6	800	3360	3.6	46

Table 1 shows that the films in accordance with the present invention had considerably lower tear strengths in the machine direction (MD) compared with the cross direction (CD), both tear strengths being less than for mono-layer films produced from the respective linear polyethylenes alone. The films of the present invention also had lower water vapor transmission rates than those of the comparison films.

Example 7 (comparison)

A mono-layer film was produced by extruding a melt of Surlyn 1652 (Trade Mark) through a ring die and blowing it to produce a film

70µm thick, the blow up ratio in the machine and cross directions being 1.45:1.

The mean Elmendorf tear strength of this film in both the machine (MD) and cross (CD) directions, the mean moisture vapor transmission rate, and the force require to puncture this film were measured and the results are shown in Table 2.

Example 8 (comparison)

A three layer film was produced by coextruding through a ring die a core layer consisting of 90wt% of Surlyn 1652 and 10wt% of an ethylene/vinyl acetate copolymer (4.5wt% vinyl acetate), with one outer layer formed from linear low density polyethylene and the other being formed from the ethylene/vinyl acetate copolymer of the core layer and blowing up the resultant bubble at a blow up ratio in the machine and cross directions of 1.45:1.

The core layer of the resulting film was 23µm thick, the outer layer formed from linear low density polyethylene was 23µm thick, and the other outer layer was 24µm thick, the total thickness of the film being 70µm.

The Elmendorf tear tests strengths of this film in the machine and transverse directions, the water vapor transmission rate and the puncture resistance of this film are shown in Table 2.

Example 9 (comparison)

A mono-layer film was produced by extruding a melt of the linear low density polyethylene used in Example 1-6 through a ring die and blowing it to produce a film 70µm thick, the blow up ratio in the machine and cross directions being 1.45:1.

The mean Elmendorf tear strength of this film in both the machine (MD) and cross (CD) directions, the mean moisture vapor

transmission rate, and the force require to puncture this film were measured and the results are shown in Table 2.

Example 10

A three layer film was produced by coextruding through a ring die a core layer of a blend of 72wt% of the linear low density polyethylene used in Examples 1-6 with 28wt% of the cyclic olefin copolymer used in Examples 2, 3, 5 and 6, and two outer layers of the linear low density polyethylene, the extrudate being blown up a blow up ratio of 1.45 in both the machine and cross directions.

The resulting film had a core layer 23 μ m thick, with one outer layer being 23 μ m thick and the other being 24 μ m thick.

The mean Elmendorf tear strength of this film in both the machine (MD) and cross (CD) directions, the mean moisture vapor transmission rate, and the force require to puncture this film were measured and the results are shown in Table 2.

Examples 11-12

Examples 7 and 9 were repeated except that the films produced had a thickness of 58 μ m.

The mean Elmendorf tear strength of this film in both the machine (MD) and cross (CD) directions, the mean moisture vapor transmission rate, and the force require to puncture this film were measured and the results are shown in Table 2.

Example 13

Example 8 was repeated, except that the film produced had a core layer 19 μ m thick and the two outer layers were respectively 19 and 20 μ m thick, the total thickness of the film being 58 μ m thick.

The mean Elmendorf tear strength of this film in both the machine (MD) and cross (CD) directions, and the force required to puncture this film were measured and the results are shown in Table 2.

Table 2

Example	Mean Elmendorf Tear Strength (mN)		Puncture Force (N)
	MD	CD	
7 (comp)	3400	6500	48
8 (comp)	1300	5200	29
9 (comp)	3030	6600	73
10	1700	1000	34
11 (comp)	2300	5800	57
12 (comp)	2480	5400	60
13	1400	800	48

As can be seen from Table 2, the films of the present invention (Examples 10 and 13) had particularly low Elmendorf tear strengths in the machine direction compared with the comparison films of the same thickness.

Claims

1. A polymeric film having linear tear properties, the film having been produced by blowing or casting and comprising a layer of a blend of a cyclic olefin copolymer and a polyethylene.
2. A film according to claim 1, wherein the cyclic olefin copolymer has a glass transition temperature T_g of greater than 30°C .
3. A film according to claim 1 or claim 2, wherein the cyclic olefin copolymer has a glass transition temperature T_g of less than 220°C .
4. A film according to any of the preceding claims, wherein the cyclic olefin copolymer has a glass transition temperature of from 50 to 175°C .
5. A film according to any of the preceding claims, wherein the cyclic olefin copolymer comprises a norbornene/ethylene copolymer.
6. A film according to claim 5, wherein the norbornene/ethylene copolymer contains from 20 to 80 weight percent of units derived from norbornene.
7. A film according to any of the preceding claims, wherein the polyethylene comprises a linear low density polyethylene, a linear medium density polyethylene, or a low density polyethylene.
8. A film according to any of the preceding claims, wherein the polyethylene has a density in the range of from 0.915g/cm^3 to 0.935g/cm^3 .

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9. A film according to any of the preceding claims, wherein the blend comprises from 10 to 90 wt% of a cyclic olefin copolymer and from 90 to 10 wt% of a polyethylene.
10. A film according to any of the preceding claims, including at least one further polymeric layer.
11. A film according to claim 10, including at least two further polymeric layers with the layer of the blend between two of such layers.
12. A film according to claim 10 or claim 11, wherein the further polymeric layer or layers comprise a polyolefin optionally containing units derived from vinyl acetate.
13. A film according to claim 12, wherein the polyolefin of the further polymeric layer or layers comprises low density polyethylene, linear low density polyethylene, linear medium density polyethylene, or an ethylene/vinyl acetate copolymer.
14. A film according to any of the preceding claims, which has been produced by blowing and has expansion ratios in both the machine and transverse directions of up to 2:1.
15. A film according to any of claims 1 to 13, which has been produced by casting.
16. A film according to claim 1, substantially as herein described.
17. A package comprising a film according to any of the preceding claims sealed around an article.
18. A package according to claim 17, which includes a breathable patch sealed thereto.

19. A package according to claim 17 or claim 18, wherein the article comprises medical equipment.

20. A package according to claim 17, substantially as herein described.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L23/04 C08L23/08 B32B27/32 C08J5/18

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/66639 A (REXAM MED PACKAGING LTD ; CHRISTOPHERSON ROY (GB); STELL DAVID THOMAS) 13 September 2001 (2001-09-13) the whole document	1-10, 12-20
X	WO 98/44043 A (EXXON CHEMICAL PATENTS INC) 8 October 1998 (1998-10-08) cited in the application abstract; claims 1-13 page 1, lines 15-22 page 8, line 4 page 10, lines 3-6 page 16, lines 18-30 page 17, lines 1-5 ----- -/--	1-16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 14, 31 December 1998 (1998-12-31) & JP 10 237234 A (TAMAPORI KK), 8 September 1998 (1998-09-08) abstract	1,7-17
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