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(54) **Heat-sealable oriented polymer film**

(57) A process for preparing oriented film in which a film comprising a substrate layer of a propylene homopolymer or copolymer and on at least one surface of said film a layer comprising a blend of 10 to 40% wt of a propylene homopolymer having a M.I. of 5.0 to 10.0 g/10 min and a degree of crystallinity of at least 45% and 60 to 90%wt of a butene-1/ethylene copolymer, the ethylene content in thereof being from 0.2 to 9% mol, this copolymer having a M.I. of 0.4 to 5.0 g/10 min and a degree of crystallinity of at least 35%, is stretched at a temperature above the melting point of the butene-1/ethylene copolymer and the stretched film is subjected to a temperature treatment for a time sufficient to ensure the conversion of the butene-1/ethylene copolymer from the molten state into the I' crystalline state.

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SPECIFICATION

Heat-sealable oriented polymer film

- 5 The present invention is concerned with a process for preparing oriented polymer film, particularly biaxially oriented polypropylene film. 5
- For packaging applications oriented polymer film should have good heat-sealing properties. These can be realized by providing the film on at least one of its surfaces with a special coating comprising a polymer having a lower melting point than the polymer of the substrate film. Examples of such low melting polymers
- 10 are butene-1/propylene copolymers (UKP 1,452,424), butene-1/ethylene copolymers (EP 0,001,490), and 10 butene-1/octene or butene-1/hexene copolymers (UKP 1,582,186). Polymeric blends have also been proposed, cf. UKP 1,495,577, which is i.a. concerned with heat-sealing coatings comprising a blend of a propylene/ethylene copolymer with an ethylene content of 0.25 to 5%wt and a butene-1/propylene copolymer, with a propylene content above 80%wt. Although these prior art references suggest that
- 15 heat-sealing would be possible at temperatures from 100°C upwards, none of these references provide 15 adequate data to show that one can achieve satisfactory heat-seal strength at heat-sealing temperatures in the range of 100 to 115°C when employing modern high-speed packaging equipment.
- Butene-1/ethylene copolymers with an ethylene content of less than 10% mol have a crystalline melting point in the fairly narrow range of 123 to 128°C. In the solid, crystalline state four different crystalline
- 20 modifications can be distinguished, viz. the III modification, the I', II and I modification. The transition 20 temperatures at which upon heating one modification passes into the other are respectively about 90°C, 104°C and 117°C, upon further increasing the temperature the I-modification reaches eventually the crystalline melting point. The ease at which the formation of the various modifications and the transitions thereof take place is increased by incorporating a minor amount of a crystalline polypropylene into the
- 25 butene-1/ethylene copolymer. 25
- The orientation of heat-sealable polypropylene films by stretching is normally effected at temperatures in the range of 145 to 160°C, i.e. at temperatures above the crystalline melting point of the butene-1 ethylene copolymer. In commercial practice, the stretched film, upon leaving the stretching equipment, is exposed to ambient temperature which effects a slow cooling of the film. Upon such slow cooling, the copolymer
- 30 crystallizes to form the II modification. Whilst it would in principle be possible to achieve good heat sealing 30 of the film so produced at temperatures in the order of 105 to 110°C, the instability of II modification unfortunately results in the disadvantage that the good heat-sealing properties are completely lost when, in accordance with customary practice, the stretched film is wound-up on reels for storage and further handling at a later stage.
- 35 The present invention aims at the heat-seal temperature of oriented polypropylene film to be effectively 35 reduced to temperatures in the order of 85 to 95°C. Thereto, the invention provides a process for preparing an oriented film comprising a substrate layer of a homopolymer or copolymer of propylene and on at least one of the surfaces of said film a layer comprising a blend of 10 to 40%wt of a propylene homopolymer havng a M.I. of 5.0 to 10.0 g/10 min and a degree of crystallinity of at least 45% and 60 to 90%wt of a
- 40 copolymer of butene-1 and ethylene having an ethylene content of from 0.2 to 9% mol, a M.I. of 0.4 to 5.0 40 g/10 min and a degree of crystallinity of at least 35%, is stretched at a temperature above the melting point of the butene-1/ethylene copolymer and the stretched film is subjected to a temperature treatment for a time sufficient to ensure the conversion of the butene-1/ethylene copolymer from the molten state into the I' crystalline state.
- 45 Suitable polymers forming the substrate film are propylene homopolymers and propylene copolymers 45 comprising less than 30%wt, preferably less than 10%wt, of another alpha-olefin, e.g. butene-1 or butene-2, but more preferably ethylene. The copolymers may be random or block copolymers and the polymer forming the substrate film may comprise the usual additives, e.g. colouring agents, nucleating agents, thermo-stabilizers, antioxidants, fillers and U.V. absorbers.
- 50 The specified degree of crystallinity is determined in accordance with Differential Scanning Calorimetric 50 Analysis, employing extruded polymer nibs which are directly obtained from the (co)polymerization plant. The Melt Index of the polymer is determined in accordance with ASTM-1238 at 230°C for the propylene polymer and 190°C for the butene-1/ethylene copolymer.
- Whilst the process of this invention is of particular interest for the production of co-extruded heat-sealable
- 55 film, other techniques for producing multi-layered film may be employed as well, such as lamination of two 55 or three extruded films, extrusion coating, and emulsion coating. The film may be oriented by stretching in the machine direction or in the transverse direction, or, more preferably, in both directions which is the case for biaxially oriented film. In the latter process the transverse stretching will normally be applied next to stretching in the machine direction, which is of particular interest as to the required obtaining of stretched
- 60 film wherein the butene-1/ethylene copolymer is present in the molten state. Therefore, the first (lengthwise) 60 stretching will normally be carried out at temperatures of from 120 to 135°C and the second (transverse) stretching at higher temperatures, preferably from 150 to 165°C.
- In between extrusion and stretching the film may be subjected to chill-roll cooling or water-bath quenching but this is not of critical importance for obtaining the benefits of this invention. However, since in
- 65 the majority of the commercial film stretching lines chill-roll cooling is common practice, this will therefore 65

be the preferred mode of operation.

Normally the stretched substrate film will have a thickness of from 10 to 80 microns, that of the copolymer coating will usually be from 1 to 6 microns. Corona treatment may be employed to improve the printability and other properties of the oriented film.

5 Particularly suitable butene-1/ethylene copolymers for the coating layer are those having an ethylene 5
content of from 0.5 to 5% mol. The butene-1/ethylene copolymers are random copolymers and their degree
of crystallinity is determined as set out hereinabove. The preferred blending ratio for producing the coating
layer is 70 to 85%wt of butene-1/ethylene copolymer and 15 to 30%wt of propylene homopolymer. The
10 coating layer is applied to at least that surface of the film which is subjected to sealing. The other surface of 10
the film may be non-coated, coated with the same composition as employed in this invention or with another
copolymer composition, e.g. a random ethylene-propylene copolymer comprising from 1 to 6% ethylene. In
the latter case one obtains heat-sealed films with outstanding haze properties.

Propylene homopolymers and butene-1/ethylene copolymers having the required degree of crystallinity
are commercially available. They can be prepared by conventional (co)polymerization methods employing
15 Ziegler/Natta coordination catalysts. 15

When the film leaves the stretching equipment it is of essential importance that the butene-1/ethylene
copolymer is still in the molten state and not in the I or II crystalline modification, otherwise the advantage of
a stable, low heat-sealing temperature is not obtained. The film is then subjected to a temperature treatment
for a time which is short enough to ensure formation of the butene-1/ethylene copolymer in the I' crystalline
20 modification. To this end the film may be passed through an annealing chamber which is kept at 20
temperature of 60 to 105°C, provided the circulation of gaseous medium, e.g. air, in this chamber is such as
to ensure that the temperature of the film is lowered fast enough to achieve the desired formation of the I'
modification. This annealing may improve the heat-set properties of the film. It is however preferred to
separate the heat-setting operation from the operation in which the I' modification is formed. To this end the
25 film is subjected to a forced cooling operation upon leaving the stretching equipment, e.g. by blowing cooled 25
air with a temperature of -10 to +12°C onto the film, or, which is more convenient, by contacting the film
with a chill-roll which is kept at an internal temperature of at most 60°C. Instead of chill-roll quenching, it is
also possible to employ quenching in a water-bath or to spray cold cooling liquid, e.g. water, onto the film.
Heat-setting of the film may then be carried out either before or after the quenching operation. When
30 effecting a preceding heat-setting operation it is important to keep the butene-1/ethylene copolymer in the 30
molten state during heat-setting and when effecting a subsequent heat-setting operation it is important to
maintain the I' modification of the butene-1/ethylene copolymer. This sets certain temperature restrictions
for the possible heat-setting operations: for a preceding operation the temperature should not be reduced to
a value below 135°C and for a subsequent heat-setting operation the temperature of the film should not be
35 increased to a value above 125°C. 35

Example I

Oriented polypropylene film was manufactured employing a commercial coextrusion/stretching produc-
tion line having a final linear film transport speed of 100 m/min. Upon leaving the extrusion orifice the flat
40 film was cast on a chill-roll which was operated on an internal cooling temperature of 20°C. The film had a 40
core-thickness of 1.4 mm and was provided on each side with a coating with a thickness of 0.05 mm.
Stretching in the longitudinal direction was effected at a ratio of 5:1 and a temperature of 125°C, the
subsequent stretching in the transverse direction was effected at a ratio of 10:1 and a temperature of 155°C.
The core of the film was prepared from a commercial polypropylene grade with a Melt-Index (M.I.) of 3
45 dg/min. For the coating layers a number of different compositions was investigated. 45

For film A₁, a blend was employed comprising 25%wt of a polypropylene grade having a crystallinity of
50% and a M.I. of 8 dg/min and 75%wt of a commercial butene-1/ethylene copolymer with an ethylene
content of 2.8% mol, a M.I. of 1 dg/min and a crystallinity of 40%. Film A₂, was made using a coating
composition comprising 25%wt of the same propylene homopolymer as employed for film A₁, and 75%wt of
50 a commercial butene-1/ethylene copolymer having an ethylene content of 1.4% mol, a crystallinity of 45% 50
and a M.I. of 4 dg/min.

For comparison films B to F were produced: Film B, using a coating composition comprising 75%wt of the
butene-1 copolymer of film A₁, and 25%wt of a commercial ethylene-propylene block copolymer, with an
ethylene content of 7%wt, a crystallinity of 41% and a M.I. of 3 dg/min; Film C using a coating composition
55 comprising 75%wt of the same butene-1 copolymer employed in film A₁ and 25%wt of a random 55
ethylene-propylene copolymer with an ethylene content of 3.8%wt, a crystallinity of 35% and a M.I. of 7
dg/min; Film D using a coating composition of 75%wt of the same butene-1/ethylene copolymer employed
in Film A₁ and 25%wt of a commercial propylene homopolymer having a crystallinity of 50% and a M.I. of 3.5
dg/min; Film E using a coating composition of 75%wt of the same butene-1/ethylene copolymer employed in
60 Film A₁ and 25%wt of a commercial propylene homopolymer having a crystallinity of 50% and a M.I. of 2 60
dg/min; Film F using a coating comprising 100%wt of a butene-1 homopolymer having a crystallinity of 50%
and M.I. of 8 dg/min.

At a distance of 0.5 m from the exit of the transverse stenter a chill-roll was placed which was operated at
an internal cooling temperature of 20°C and which could be raised and lowered to vary the contact-angle of
65 the film. In the lower position the contact-angle was 0°, hence there was no contact and thus no quenching of 65

the film, in the higher position the contact angle was 120°. The chill-roll had an external diameter of 0.3 m. The film was wound-up on a reel which was placed at a distance of 2 m from the exit of the transverse stenter.

Heat-seal threshold temperatures were determined using the method disclosed in U.K. P 1,452,424 taking as the threshold value the lowest heat-seal temperature yielding a heat-seal strength of 300 g/25 mm.

The results are presented in Table I wherein HSTT' stands for the heat-seal threshold temperature of non-quenched film.

TABLE I

Film	HSTT, °C	HSTT', °C
A ₁	85	105
A ₂	87	110
B	95	115
C	110	118
D	99	115
E	110	118
F	115	121

Example II

Flat uncoated film was cast on a quench roll using the polymeric blend of 25%wt propylene homopolymer and 75%wt butene-1/ethylene copolymer described in Example I for producing film A₁.

This film was subjected to differential scanning calorimetry (DSC). The resulting diagram showed one peak at 90°C, marking the presence of the I' crystalline modification, one lower peak at 114°C for the II modification and one peak at 159°C. When the molten film was slowly cooled to room temperature at a rate of 20°C/min. DSC analysis of the cooled film showed a diagram with only two peaks at 114° and 159°C, thus marking the complete disappearance of the I' modification.

From the quenched and non-quenched films A₁, B, C and E the coating layers were peeled-off from the substrate film and subjected to DSC analysis. In each quenched sample the DSC diagram showed larger peaks at 90°C than at 104°C thus marking the presence of the I' modification in a significantly larger proportion than the II modification.

Samples of non-quenched film A₁, which were stored for 100 hours at room temperature showed upon DSC analysis the complete disappearance of the II modification and the presence of the I modification having a peak at 117°C. This disappearance corresponds with a significant increase in HSTT; the latter was found to be 114°C for non-quenched film stored for 100 hours at room temperature.

Example III

Heat-setting experiments were carried out by employing 10% relaxation at 115°C, respectively 138°C. The film employed was film A₁ described in Example I. The heat-setting at both temperatures was effected before quenching of the film and after transverse stretching ("preceding heat-setting"), respectively subsequent to quenching of the film ("following heat-setting"). The HSTT data of the heat-set films are included in Table II.

TABLE II

Operation	Temp. °C	HSTT, °C
Preceding heat-setting	115	105
Preceding heat-setting	138	85
Following heat-setting	115	85
Following heat-setting	138	105

55 CLAIMS

1. A process for preparing oriented polymer film in which a film comprising a substrate layer of a propylene homopolymer or copolymer and on at least one of the surfaces of said film a layer comprising a blend of 10 to 40%wt of a propylene homopolymer having a M.I. of 5.0 to 10.0 g/10 min and a degree of crystallinity of at least 45% and 60 to 90%wt of a copolymer of butene-1 and ethylene, the ethylene content in this copolymer being from 0.2 to 9% mol, this copolymer having a M.I. of 0.4 to 5.0 g/10 min and a degree of crystallinity of at least 35%, is stretched at a temperature above the melting point of the butene-1/ethylene copolymer and the stretched film is subjected to a temperature treatment for a time sufficient to ensure the conversion of the butene-1/ethylene copolymer from the molten state into the I' crystalline state.

2. A process as claimed in claim 1, wherein biaxially oriented film is produced.

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3. A process as claimed in claim 1 or 2, wherein the butene-1/ethylene copolymer comprises from 0.5% to 5% mol ethylene.
4. A process as claimed in claims 1 to 3, wherein the temperature treatment comprises a forced cooling operation.
- 5 5. A process as claimed in claim 4, wherein the cooling operation comprises contacting the stretched film with a chill roll which is kept at an internal temperature of at most 60°C. 5
6. A process as claimed in claims 1 to 5, wherein the stretched film is heat-set at a temperature above 135°C before subjecting the film to the aforesaid temperature treatment.
- 10 7. A process as claimed in claims 1 to 5, wherein the stretched film is heat-set at a temperature of less than 125°C next to subjecting the film to the aforesaid temperature treatment. 10