

9

PATENT SPECIFICATION

(11) 1 526 722

1 526 722

- (21) Application No. 29807/74 (22) Filed 5 July 1974
(21) Application No. 53644/74 (22) Filed 11 Dec. 1974
(21) Application Nos. 5971/75 and 5972/75 (22) Filed 12 Feb. 1975
(23) Complete Specification filed 27 Aug. 1975
(44) Complete Specification published 27 Sept. 1978
(51) INT CL² B32B 27/06, 31/30
(52) Index at acceptance

B5N 2706 3130

B5A 1G1 1G2 1G3X 1G7AX 1G7B 1R314C1A 1R314C1C
1R314C1F 1R322



(54) A METHOD FOR PRODUCING A LAMINATED HIGH STRENGTH SHEET

(71) I, OLE-BENDT RASMUSSEN, a Danish subject, of 7, Topstykket, DK-3460 Birkerød, Denmark, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of manufacturing a laminated sheet having high strength, and to such sheets themselves.

Cross-laminates of uniaxially oriented films of crystalline polymers are known to exhibit a generally highly advantageous combination of different strength properties of which the most surprising has been the tear propagation strength (cf. U.S. Patent No. 3,322,613) especially when the bonding between the layers is sufficiently weak that during tearing from an incision the layers will delaminate around the notch. As a result they split or flow in different directions and the notch effect is smoothed out, this being termed a "forking effect". Sheets of this kind are particularly useful for various heavy duty applications such as tarpaulin substitutes, cover sheets, heavy duty bags, and heavy duty wrapping film.

The most expedient method of producing a sheet of the above kind is described in British Patent Specification No. 816,607, and consists in strongly orienting the molecules of a tubular film in its longitudinal direction, helically cutting and unfolding it to a flat film with the orientation at bias (e.g. 45°C), and subsequently continuously laminating this film with a similarly produced flat film, while the respective directions of orientation are arranged in criss-crossing relationship.

It is known that, for a given thickness, the tear propagation resistance is pronouncedly increased by use of 3 layers with 3 different directions of orientation, e.g. obtained by laminating 1 longitudinally

oriented film with 2 films which are oriented at bias as described above.

One drawback of the process described above (and the resultant product) is that it is practically impossible to produce really thin film, so that the economic advantage of producing a high strength but low weight film is not fully attained. In practice the lowest weight for each layer that can be achieved when spiral-cutting and laminating is about 30 g/M². Thus for a 2-layer laminate, the lower limit is about 60 g/M² while for a 3-layer laminate (which is mentioned above is necessary for proper utilization of the tear-stopping effects) it is about 90 g/M².

A second draw-back is the practical limitation in width caused by the rotation of heavy machine-parts and bobbins in connection with the spiral cutting. Generally the width is limited to about 1.5—2 M.

A third draw-back relates to certain energy-absorption values for the cross-laminates. Relatively low energy-absorption has been found with regard to high-speed tearing (Elmendorf tear test) and for low and high speed tensile testing (TEA strength and Elmendorf impact strength). It appears that the very anisotropic character of the layers is disadvantageous. If for instance a 2-ply cross-laminate of this kind is drawn parallel to the direction of orientation in one of the layers, then the yield point and the elongation at break are in essence determined by that layer.

Earlier attempts to overcome the above-mentioned drawbacks, and to provide for a cheaper production process for a product with similar or analogous properties, is described in my British Patent Specification No. 1,261,397. In that specification a process is disclosed which produces a criss-crossing structure through a die with rotating parts, while forming in the same die a soft and weaker middle zone by

50
55
60
65
70
75
80
85
90

18

coextrusion. The method comprises co-extruding several concentric or almost concentric layers of crystalline polymer alternating with layers of a softer polymer, and dividing the layers inside the die by means of teeth arranged in rows and fixed to the cylindrical die walls pointing from the concave wall surface inwardly, and from the convex wall surface outwardly. The die-parts are rotated in opposite directions and thereby the layers are divided according to lefthand helices near one and righthand helices near the other sheet surface. The combing can either be carried through to the middle of the film or be limited to portions near the surfaces. The coextrusion of polymers before the combing zone is adapted to provide for a soft and weak middle-zone.

The film extruded by this method can be considered to be or unoriented material. However, the alternating stiff layers of a "first polymer" and soft layers of a "second polymer" divided to filaments in a linear pattern by the teeth imparts to each half-part of the sheet a tendency to split or flow in one direction, and since the linear patterns at the two surfaces criss-cross each other and a tendency to delaminate is provided, there is obtained a tear-stopping effect which is analogous to the "forking" effect in a true cross-laminate.

The above specification further proposes to biaxially stretch the laminate under such conditions that instead of yielding biaxially oriented layers the molecular orientation is generally uniaxial in each layer, with the direction of orientation in different layer criss-crossing each other. In order to obtain such uniaxial orientation, the second material must be very prone to yield, e.g. because it is still molten or semi-molten while the first material is solid, and the filaments of the first material must be kept straightened out by biaxial strain.

Although the above method would in principle solve the problems of obtaining a lower thickness and higher width in cross laminates there were found some essential difficulties during the later technical developments. It was confirmed that the extrusion method was commercially feasible for manufacture of unoriented film with high tear propagation strength, but with a low impact strength due to the lack of orientation. However, essential drawbacks were found in connection with a subsequent biaxial stretching. As also indicated in the above specification, one must use a relatively great number of rows of the teeth in the extrusion die in order to obtain the fibre finess which is necessary for the stretching system.

This, however, made the maintenance of the die difficult and caused frequent "hang-

up" of polymer lumps between the teeth. Further, the interaction between the teeth in one half-part of the die and those in the other half-part made it necessary either to use excessive amounts of soft middle layer material, or to limit the combing to two relatively thin surface zones of the sheet. Further, it was very difficult to establish and maintain the biaxial stretching conditions necessary for obtaining a generally uniaxial molecular orientation as described.

I have now discovered that a high strength laminate can be made by a method comprising extruding at least two layers of molten polymeric blend, each comprising a blend of polymers that are incompatible such that on solidification the blend comprises a dispersion of one polymer in a polymeric matrix, attenuating each layer while molten before, during or after extrusion to distort the particles in each layer into a fibrillar grain structure having a predominant direction of splittability after solidification into a film, bonding the layers with the said predominant directions transverse to each other, solidifying the layers if they are not already solidified, and biaxially orienting the resulting laminate by orienting it in substantially uniaxial steps, the biaxial orientation being conducted at a temperature sufficiently low to maintain the predominant direction of splittability of each film and the bonding being sufficiently weak to permit local delamination of the films upon tearing of the laminate.

This method is based partly upon the discovery that a strongly biaxially oriented film, in which the directions of orientation are preferably perpendicular to each other and each degree of orientation is preferably approximately the same, will exhibit a pronounced direction of splittability provided the film is made by solidification of a molten layer made by extruding a dispersion of polymer particles and melt attenuating the layer to form the fibrillar grain structure as described above so that if a laminate of two such films, formed by lamination either before or after solidification of the molten layer into a film, is formed with the appropriate degree of bonding between the films then a high strength low weight laminate can be produced.

In the following description I use the term "melt attenuation" to describe the concept of distorting the polymer in each layer while molten into the desired fibrillar grain structure. It is achieved by drawing the melt, e.g. as a sheet after extrusion but before solidification or by forcing the melt to flow through an appropriate slit constriction in an extrusion head. This grain structure must be such that if a film was formed of the molten layer by itself that film

70

75

80

85

90

95

100

105

110

115

120

125

130

(11)

would have a predominant direction of splittability. As explained below the layer can be solidified into a film before bonding the layer to another molten layer or film that is to be part of the laminate or the bonding may be conducted while the layer is still molten, the laminate being subsequently solidified. Also as explained below each layer may consist of a single layer of polymeric blend but more usually will comprise a layer of polymeric blend and one or more other layers of polymeric material, for example each of the said at least two layers may comprise a layer of molten polymeric blend and a layer of adhesive polymeric material on either or both faces of it.

A product according to the invention is a laminate comprising at least two biaxially oriented films bonded to one another, each film comprising particles of polymeric material that have a fibrillar grain structure that imparts a predominant direction of splittability to that film but that follows a zig-zag course through the film, and in this laminate the films are bonded to one another with the said orientations transverse to each other and with bonding between the films that is sufficiently weak that local delamination of the films can occur upon tearing of the laminate.

Thus products of the invention and products made by the method of the invention comprise cross-bonded films each having a distinct fibrous morphology on two scales. On a macro-scale each film has a predominant direction of splittability, this predominant direction being provided by the fibrillar particles of the film extending predominantly along that direction. However on a micro-scale parts of the fibrils are strongly deflected from this predominant direction and the fibrillar grain in the film follows a zig-zag course.

The predominant direction of splittability must be transverse to each other. They can be at any angle whereby they are transverse. There may be more than two films in the laminate in which event for instance one film may have its predominant direction of splittability at 45° to the longitudinal direction, a central film may have its predominant direction of splittability along the longitudinal direction, and a third film may have its predominant direction of splittability perpendicular to the first film.

Apparatus according to the invention suitable for use in the described method comprises means for extruding at least two layers of molten polymeric material, means for attenuating each layer while molten before, during or after extrusion to give a predominant direction of splittability to a film formed from that layer by solidification, means for bringing the layers together

and bonding them with the said predominant orientations transverse to each other, and means for biaxially orienting the resultant laminate by orienting it in substantially uniaxial steps.

Provided a molten polymeric blend is used in which the dispersed polymers are sufficiently incompatible that they remain dispersed but sufficiently compatible that a useful film is made, as described below, melt attenuation as described results in the production of a unidirectional fibrous morphology which can be observed in an ordinary microscope. Some uniaxial orientation may also be produced during the melt attenuation, but this orientation is generally very weak. When the film (which can for instance consist of equal weights of polypropylene and polyethylene) is drawn at an angle to the grain direction, e.g. perpendicularly, then the fibre portions, as seen on a micro-scale, will deflect and branch out, but it is still possible to follow the zig-zagging path of the grain from branch-point to branch-point, and when following different paths in this manner it will be found that, on a macro-scale there is still a predominant unidirectional grain, and in particular the film retains its predominant direction of splittability. This macro-structure is very different from the filament structure described in British Patent Specification No. 1,261,397.

After some elongation perpendicular to the grain direction, e.g. about 40% elongation, examination of the film in polarized light (or preferably by x-ray diffraction) shows that the molecular orientation is equal in all directions. After further drawing in the same direction, there is still a pronounced splittability along the grain direction, till at a certain point, e.g. about 80% total elongation, there is no longer a predominant direction of splittability but instead splittability is equal in all directions. On further drawing, the main direction of splittability will coincide with the main direction of molecular orientation. The film can be elongated for instance 100% in this direction, and then drawn in the original grain direction until it no longer has a predominant molecular orientation but instead has equal molecular orientation in all directions. At this point there is again a marked splittability in the original grain direction, and by microscopical examination it will be possible, although difficult, to follow the zig-zagging course of the grain and see that on a macro-scale, the original grain direction still in essence coincides with the direction of splittability.

The products of and made by the invention are particularly suitable for almost any high-strength application where

70

75

80

85

90

95

100

105

110

115

120

125

130

(2)

energy absorption is essential, no matter whether this is energy absorption during tear propagation, puncturing, or impact. The splittability of the layers in connection with the weak bonding between the layers produces a forking effect similar to that in cross-laminates of uniaxially oriented film, but the energy absorption during fast tearing (Elmendorff tear test) is essentially higher. Further, most impact properties, in particular Elmendorff impact strength, are improved, and so will usually be the energy-absorption during fast puncturing (Beach-strength). These improvements are considered to be a result partly of the biaxial character of the orientation in each layer, and partly of the distinct fibrous morphology within each of the films. The biaxial orientation further has the advantage that the laminates of uniaxially oriented films do not have.

It has been mentioned above that the process for producing cross-lamination of uniaxially oriented films, under practical conditions gives a rather high sheet thickness (about 90 gr per sq.m for a 3-ply) and a rather low sheet width. In both respects the present method is greatly advantageous due to the fact that the sheet is strongly stretched in two or more directions after the lamination. Thus, it is technically and economically feasible to obtain about 10 g/M² weight for each of the films in the laminate, i.e. about 30 g/M² for a 3-ply laminate. This greatly widens the field of uses.

If the polymers in each layer are too compatible, e.g. different polyamides, they will not form a dispersion of particles of one polymer in a matrix of another such as to form a grain as described. Blends of semi-compatible or incompatible coextrudable thermoplastic polymers should be used and preferably the content of one polymer is not too predominant. To be on the safe side, there should not be more than 85% of any polymer in the blend. If the chosen polymers are highly incompatible, they are preferably made more compatible by modification with an alloying agent.

The best properties will be obtained if the grain is formed of crystal threads cemented together by small amounts of a surrounding elastomer. By small amounts is meant about 5-20% of the total.

In order to keep the contents of elastomer low and still obtain a distinct fibrous morphology with the elastomer tending to surround the other material, the elastomer is preferably used as alloying agent for two other polymers. Thus a preferred blend is two crystalline incompatible polyolefins—e.g. iso- or syndiotactic polypropylene and high- or low density polyethylene—with addition of a sticky polymer

which bonds to both—e.g. atactic polypropylene, ethylene-propylene-rubber (preferably a sticky type with a high content of propylene), and polyisobutylene of a mol-weight as commonly used for pressure sensitive adhesives.

The melt attenuation, by which the fibrillar grain structure is formed, can be carried out in different ways. For instance it can be by gradual reduction of the spacing of the exit chamber in the extrusion die, or by passage of the molten material between a row of closely spaced partitions in the die, or by stretching in molten state after the exit of the die, or by combinations of such steps.

The direction of splittability and the splittability in the films is determined by measuring the tear propagation resistance by the tongue tear method in different directions. The direction of splittability is understood as the direction which exhibits the lowest tear propagation strength, while the splittability is understood as the ratio between the highest tear propagation resistance and the lowest tear propagation resistance. The splittability in the films after the biaxial orientation should preferably be greater than 2:1. However 1.5:1 can be tolerated.

In order to allow a local delamination during tearing, and thereby make the tear fork, it is essential to bond the layers sufficiently weakly. If the bond formed is an even bond, and the thickness of each layer is 20 g/M², a peel strength between about 5 g/cm and 500 g/cm is generally suitable. Since there is competition between rupturing forces and delaminating forces during tearing, the upper limit depends on the layer thickness and is generally proportional to the latter.

There are various ways of establishing and controlling the strength of the bonding. The most practical involve at some step a coextrusion of a special layer of adhesive component (to increase adhesion) or a "release component" (to reduce or eliminate adhesion).

It is essential for the biaxial orientation to be conducted in at least two, and preferably several, steps each of which are substantially uniaxial. It was found that simultaneous stretching in two directions destroyed the grain so that no forking effect was achieved. There is also a tendency to destroy the grain by stretching near the melting point of the major components of the sheet and so the temperature should be held sufficiently low to avoid substantial reduction in splittability. I believe that recrystallization and other physical phase rearrangement phenomena play a role in this connection. In any case the best properties have been found by stretching below the recrystallization temperature

70

75

80

85

90

95

100

105

110

115

120

125

130

which e.g. for polypropylene is about 70—80°C, and even lower temperatures are preferable. For stretching at such low temperatures special stretching methods are necessary which are described below.

Preferably the biaxial orientation produced by the stretching below the melting point should in any direction have a component at least equal to the orientation produced by the melt-attenuation and generally it is preferable to make the said biaxial orientation much stronger. Degree of orientation should in this connection be measured by x-ray defraction, but for quick and approximate examination of relative values, observations of interference colours between crossed "Polaroid" filters are also suitable: "Polaroid" is a trade mark.

The overall bond between the films should be weak, in order to enable a local delamination to take place during tear propagation. This, however, does not necessarily mean that the bonding must be uniformly weak all over the surface. Preferably there is strong adhesive bonding in spots or lines and no or weak adhesive bonding over the remaining portions, the adjacent surfaces of the films. This gives good tear strength. The necessary local delamination is easily started, but is thereafter stopped or will proceed under great resistance. At the same time the strongly bonded portions prevent delamination of the laminate in or adjacent to a glued or welded seam under tension, which otherwise can easily occur.

By a suitable choice of the bonding pattern, the different bonding strengths, and the type of rupture to be obtained in the weak-bond or no-bond areas (whether brittle or more fluid) the tearing properties can be controlled to suit different purposes.

The provision of strong bond and weak or no bond areas as described is particularly useful when relatively thin layers are being bonded. It has already been mentioned that there is a competition between rupturing and delaminating forces during tear propagation, which means that easier start of delamination is required the thinner the layers are. Generally the described variable bonding will always be used if the layers are thinner than about 40 or 50 g/M².

The use of strong-bond/weak-bond or strong-bond/no-bond patterns are in fact well-known in connection with cross-laminates of films which are uniaxially oriented or are biaxially oriented in a very unbalanced manner, cf. the specifications of U.S. Patents Nos. 3,496,056 and 3,342,657, British Patent No. 1,316,640 and Danish Patent No. 1,197,733. However, the layers of such known laminates, when tested individually, exhibit extremely low impact and puncture resistance (except in case of

special and expensive polymers such as e.g. nylon 6), whereas it has been found that the individual films in the present invention exhibit pronouncedly and surprisingly higher impact and puncture resistance. Therefore, a weaker adhesion (or no adhesion) in the relevant areas and/or a larger extension of these areas is allowable without any significant loss of impact or puncture strength.

Preferably the variable bonding is provided by having on one or both faces of at least two layers of stripes or spots of an adhesive substance or a release substance. The latter should be a substance, preferably a polymer material, with either a low cohesive strength in itself or with a low adhesion to the adjacent polymer layer.

Whether a release or an adhesive substance is to be chosen depends on whether and to what extent the polymer blends are compatible with each other and of the uniting method, e.g. the temperature used during lamination.

In any case, by the described method it is possible to control closely the magnitude of the bonding force.

Preferably the stripes or dots of release substance are staggered (offset from one another) on the two sides of a central layer. This gives the advantage that during tearing, the free or weakly bonded parts of the midlayer will elongate because of the stretching forces applied, and will absorb some energy thus further stopping the notch effect.

Although in some methods it is advantageous to attenuate and bond while the streams are fluid and before extrusion it is often preferred to bond after extrusion, attenuation being conducted before, during or after extrusion and solidification being conducted at any convenient time after extrusion, for example after either or both of the streams is in the form of a solid film. Thus a preferred method according to the invention comprises extruding and attenuating the layers mutually independently before bonding them. This method is advantageous since it permits the production of the most uniaxial direction of splittability, or grain, in each film.

One way of carrying out this method comprises extruding at least one layer from a rotating circular extrusion exit slot and so attenuating this layer while still fluid that its predominant direction of splittability is at an angle with the machine direction, and applying this layer to and carrying it forward by one or more solid preformed films or tubes having a different direction of splittability. Thus a solid preformed film may be passed along a mandrel that extends through the centre of the rotating extrusion dye. This film will thus catch and carry

70

75

80

85

90

95

100

105

110

115

120

125

130

(1A)

forward the rotating fluid stream which will thus be wound around the solid film as an outer film having a helical direction of splittability.

5 As already mentioned, the tear propagation strength for a given total thickness is significantly better in a 3-layered laminate than in a 2-layered laminate. Therefore it is also preferable to
10 extrude two or more films successively out of two or more mutually contra-rotating extrusion slots onto the same solid film in the manner mentioned above.

15 A further advantage of the method using a preformed film is the possibility of allowing the use of polymers that could not be used by themselves (e.g. polymers of very high molecular weight) but which can be used because of the supporting and conveying effect of the film on the mandrel, which can be very close to the circular exit slot.

20 In the above description, the rotating fluid tubular layer is drawn inwardly from the rotating extrusion die to the solid conveying film. This feature will generally be advantageous because the elastic tensions produced by the rotation tend to reduce the diameter of the tubular fluid film, thus promoting the catching of the
25 fluid film of, and its sticking to the forewarded, solid film. However, this method can be operated with the preformed film of a generally tubular shape having a diameter greater than that of the rotating exit slot, and by blowing or by other means extrude the fluid, rotating, tubular film outwardly unto the solid film. Instead of
30 rotating the extrusion die a mandrel may rotate and the die may be fixed.

40 It should be noted, that be machine direction is here meant the forewarding direction of the solid preproduced film.

45 A particularly preferred method of the invention comprises rotating at least two concentric tubular streams molten polymer blends relative to one another during and immediately after passage of the streams through the exit part of an extrusion die while attenuating the streams and thereby
50 forming in each resultant layer a direction of splittability transverse that of an adjacent layer, and subsequently bonding the tubular layers after they have left the exit part of the extrusion die and while they are still fluid.

55 An advantage of this process is that the different process steps, viz. extrusion, attenuating, uniting with the grain of adjacent layers in criss-crossing relationship and biaxial stretching, can be carried
60 out in line. Preferably the sheet consists of three layers with the grain of the midlayer extending longitudinally as will be further described later in connection with the description of the drawings. Compared to
65

the previously described process it has the advantage that all layers are extruded from the same die, but this is achieved at the expense of the conveying effect.

70 In another method of the invention the layers are solidified before being bonded. This permits the use of simpler and more conventional equipment. A preferred method, that can be conducted using particularly cheap and simple machinery but at
75 the expense of the advantages connected with an inline operation, is one in which each of the films is made by extruding a tubular layer, attenuating it by drawing it longitudinally whilst still fluid, solidifying it and cutting it helically, unfolding it to a flat film with an oblique direction of splitting and then the films are bonded to one another.

85 Another method of operating in which the bonding is conducted after solidification is one in which the film is made by extruding a layer, attenuating it predominantly in the transverse direction while still fluid by lateral tentering and solidifying
90 the film, and then bonding the films to one another. This method is suitable for the production of rather wide layers. The lateral tentering can be carried out by means of a tenter frame preferably in an oven with circulating air which is kept at a temperature slightly above the melting point.

100 In order to simplify the lamination of separately extruded and solidified films, and thereby also make lamination of thinner film possible at least the first phase of the uniting process may be combined with at least the first phase of the lateral stretching process involved in the biaxial orientation.
105 This essentially helps preventing the formation of pleats during lamination. If the desirable stretching temperature is lower than the temperature necessary for sticking the films together, the first e.g. 10—20% of the stretching can take place at a higher temperature without any noticeable harm.

115 In order to facilitate bonding after extrusion an adhesive polymer, that is lower melting than the blend may be coextruded on at least one surface of at least one of the layers. Preferably the adhesive polymer is such that bonding can be achieved without application of heat but during the simultaneous stretching of two films while
120 they are pressed together. Thus I have found that under such conditions, particularly as described in more detail below, there is a high tendency to cold weld adjacent films together. This discovery is the subject also of my divisional application No. 16900/78 (Serial No. 1,526,724). Thus only a small degree of stickiness is required, e.g. surface layers of a polymer of ethylene with 16% vinyl acetate have been found to
130

7
weld at room temperature in this manner, yielding a peel strength of 10 g/cm. The bonding strength can subsequently be increased by passage over or between heated rollers.

5 The adhesive polymer may be coextruded in stripes. It is thus possible to obtain the strong-bond/weak-bond or strong-bond/no-bond pattern as explained above.

10 Another method of obtaining such a bonding pattern comprises coextruding on one of adjacent surfaces of two layers a continuous ply of an adhesive polymer, and further to provide stripwise or spotwise the other of said surfaces with a release layer.

15 Still another method of obtaining this kind of bonding pattern comprises coextruding the adhesive polymer in stripes on two adjacent surfaces of two layers with the stripes on one layer lying in criss-crossing relationship with those of the other layer. By this method one can obtain zones of no bond having a dotted configuration.

20 The biaxial stretching necessarily involves applying lateral stretching forces and preferably these forces are distributed substantially evenly over the plane of the sheet.

25 As previously mentioned, the stretching process is preferably carried out at a relatively low temperature, e.g. room temperature, and use as normally of a tenter frame under those circumstances will almost inevitably give an uneven necking-down with a laterally varied tear-propagation strength.

30 It is known to produce lateral stretching under even application of the stretching forces, see French Patent No. 1,331,095 and British Patent No. 1,078,732. Both make use of 2 rubber conveyor belts which are expanded laterally at the same time as they are firmly pressed together, thereby gripping and drawing the film.

35 A more convenient method of achieving the effect comprises carrying out the lateral stretching in several steps each comprising stretching the sheet to a configuration of temporary evenly distributed substantially longitudinal pleats by applying pressure along lines extending substantially in the longitudinal direction of the sheet, and carrying out the longitudinally stretching in one or several steps. This deflection is achieved by making a linear impression on the sheet. A convenient method of causing this linear impression, and thus deflecting the sheet into the pleated configuration, comprises passing the laminate through the nips of several pairs of intermeshing grooved rollers in which the grooves extend substantially in the longitudinal direction of the sheet (i.e. transverse to the axis of the rollers). Preferably the longitudinal stretching is thereafter conducted continuously preferably within a short

stretching zone. It should be noted that a strictly even distribution of the stretching forces are not necessary but — on the contrary — a certain unevenness on a fine scale will be advantageous as far as tear propagation strength is concerned. It has in particular been found advantageous for the tear propagation strength to vary the state of orientation in a pattern of striations (see Figs. 8 and 9) in such manner that in one set of striations the biaxial orientation is unbalanced and is strongest parallel or nearly parallel to the striations, while in the intervening striations it is preferably also unbalanced but is strongest perpendicularly or nearly perpendicularly to the striations.

Thus preferably the striations from two sets A and B interspersed with one another each striation comprising portions of each of the oriented films, and in which the striations A are relatively thick and have been uniaxially cold stretched in a pronouncedly unbalanced manner with the main axis of cold stretching generally substantially parallel to the direction of striations and with the tear propagation direction forming a small angle to the direction of orientation, while the striations B are relatively thin, have been biaxially cold stretched in a balanced or unbalanced manner with their main axis of cold stretching criss-crossing with the direction of the striations.

Preferably, substantial lateral contraction of the sheet is allowed during the longitudinal stretching and, preferably, lateral stretching is essentially finished before the longitudinal stretching is started. The use of the described method is of particular value when especially high tear propagation and puncture resistances is desirable, and relatively low yield point is allowable. This method gives higher elongation at break. In order to allow the contraction at the same time as the longitudinal stretching is carried out in a narrow zone, the laminate is preferably supplied with very fine, longitudinal pleats—in analogy to what is disclosed in U.S. Patent No. 3,233,029. In this connection, a suitable result is usually obtained when the fine pleats formed by the last step of the lateral stretching method using intermeshing rollers are maintained in the sheet when the latter is fed into the longitudinal stretching zone.

Although it is stated above that there are advantages in producing a striated pattern of orientation and thickness variations, especially with a view to the tear propagation resistance, this effect should normally not be exaggerated since this would have an adverse effect as well on printability as on the puncture resistance against sharp items.

(16)

The object of the use of intermeshing rollers as described therefore is to avoid an exaggerated tendency to sharp formation of the lineary stretching zones, which usually would occur if the sheet were longitudinally oriented in any significant degree.

Instead of bonding the layers after extrusion, as described above, they may be bonded before extrusion. A preferred method of this type comprising rotating at least two concentric tubular streams of molten polymer blends relative to one another during passage through an annular extrusion die while conducting the attenuation of each stream, thereby forming predominant directions of splitability in each stream that are transverse to one another, and bonding the fluid streams into a tubular laminate and then extruding the tubular laminate while fluid and then solidifying it. This method does not have some of the advantages of methods in which bonding is conducted after extrusion, since it is impossible to obtain truly uniaxial directions of splitability, but does have the advantage of reducing the size of the apparatus required and length of path, since the laminate already exists by the time it is extruded from the extrusion die. The die can easily be constructed to extrude three or more layers. Preferably a polymer for increasing or reducing the strength of bonding between the layers is coextruded on the face of at least one adjacent layer.

This general method wherein two concentric tubular streams are bonded before leaving the extrusion die as described above, and apparatus suitable for use in this method, are the subject of my Divisional Patent Application No. 16899/78 (Serial No. 1,526,723).

Due to the fibrous morphology of the films formed by described process there will often be internal voids within each film. These voids generally do not merge with one another. This effect is particularly significant when the stretching takes place at a relatively low temperature, and the resultant laminate will thus be opaque to a greater or lesser extent. This effect can be utilized to produce a white laminate without using pigment, but can be abolished by subsequent pressure rolling. Naturally the films can contain white pigment if desired.

The invention will now be described in more detail with reference to the drawings, of which

Figure 1 shows a section through an extrusion-die for manufacturing of a sheet material according to the invention;

Figure 2 shows in perspective view with displaced sections the principle of an extrusion die with two counter-rotating exit slots and means to extrude two layers through each slot;

Figure 3 shows in a view similar to Figure 2, the principle of an extrusion die with two counterrotating and one fixed slot and with interjacent exit slots for air streams;

Figure 4 in perspective view and partly in section shows the principle of a rotating-ring-formed extrusion die with a mandrel extending through its centre;

Figure 5 is a flow-sheet of a preferred embodiment of the method according to the invention;

Figure 6 is a process-line of a preferred cold stretching method;

Figure 7 is a detail of the "grooved rollers" which perform the lateral stretching in uneven zones, called "striations";

Figure 8 is a schematic sketch, on an enlarged scale, of the pattern of the striations and the orientation therein, of a film cross-stretched according to the process-line of Figure 6;

Figure 9 is an enlarged cross-section of the film of Figure 8 as actually observed by microscopy. However for the sake of clarity, the thickness is shown on a scale twice that of the width.

The extrusion die shown in Figure 1 is an example of one that may be used, in which two polymer-in-polymer dispersions are extruded into a common collecting chamber through two rows of partitions, which are rotating in opposite directions. The two dispersion streams 1 and 2 are fed through inlet channels in the lower part of the die to annular channels 4 and 5 respectively in the two walls in the annular track 6, in which the two rings 7 and 8 are moved in opposite directions by driving means, e.g. by teeth and toothed wheels (not shown). The two rings 7 and 8 are supplied with rows of partitions 9 and 10 respectively, by which two rows of openings 11 and 12 are formed, through which the two dispersions are extruded into the collecting chamber 15, formed by the two parts 13 and 14, and terminating in the exit slot 16. For the sake of simplicity the partitions 9 and 10 are shown as radially extending, but in real fact they are placed at an angle to the radial direction to prevent the formation of die-lines in the extruded sheet. By the extrusion through the two rotating rings 7 and 8 the two dispersions each become attenuated and thereby acquire a fibrillar morphology and thus a direction of splitability, as discussed above. The two arrays of attenuated streams thereafter unite in the collecting chamber 15 to form a laminate with criss crossing fibrous morphology. The thickness of this laminate is reduced by the passage through the exit slot 16 and further by a normal draw-down and blow process. Hereafter the film is stretched both in the longitudinal and the transverse direction at a relatively low temperature. Due to the two

different fibre directions the two half-parts of the film exhibit tendencies to split in different directions during tearing. The materials, from which the two half-parts are formed, are so selected that they adhere poorly to each other. The material thereby delaminates in a small area around the incision, from which tearing takes place, and this will smooth out the notch effect.

The die shown in Figure 2 consists of four main parts, viz. a fixed inlet part (17) for circular distribution of the polymers as explained below, a fixed bearing part (18), and supported here by the two rotating parts (19) and (20) which form one exit orifice (21). The polymer blend (A) and the polymer (B) are fed to the inlet part (17) where they are distributed in concentric circular streams. (A) is extruded through the annular conduits (22) and (23), for which either one or two extruders may be used. (B) is extruded through the annular conduit (24). For even distribution, (22), (23) and (24) are supplied with distribution baffles or other distribution means (not shown).

For the sake of clarity, the bearings and sealings between the bearing part (18), the rotating part (19), and the rotating part (20), are not shown, neither are the drives for (19) and (20).

From the three annular conduits (22), (23) and (24) the polymer streams pass the bearing part (18) through three circular arrays of channels (25), (26) and (27), each communicating with an annular chamber (28), (29) and (30) respectively.

The two rotating parts (19) and (20) are preferably rotated at almost equal velocity, but in different directions, as indicated by the arrows (31) and (32). Each rotary part in itself is a coextrusion die for two layers, one consisting of (A) and one of (B). For the sake of clarity, reference figures for explanation of the flow are shown only on part (20), but the flow through part (19) is similar. From the chamber (29) polymer blend (A) passes into the rotating part through channels (33), while polymer (B) from chamber (30) passes into the rotating part through channels (34). Inside the rotating part are two annular conduits (35) and (36) in communication with, respectively, the channels (33) and (34), and separated from each other by a thin circular wall (37).

Having passed the edge of the wall (37) (A) and (B) merge together in an annular collecting chamber (38), which terminates in the exit orifice (21). By the passage through the annular conduit (35) and the collecting chamber (38), the thickness of the fluid sheet is strongly reduced whereby the material is attenuated.

The partitions between adjacent channels (33) and (34) respectively ought to be

streamlined, as shown. For the sake of clarity they extend radially in the drawing, but in real fact they should be forming an angle with this direction to reduce the tendency of the forming of die-lines.

"Polymer blend A" is a blend of two incompatible or semi-compatible polymers, while "Polymer B" is adapted to give the sheet a suitable tendency to delaminate. It may therefore, e.g. consist of an elastomer which is a poor adhesive for the two layers of A, and may be extruded in stripes. However, if the channels 22 and 23 are fed with two different polymer blends, that are mutually incompatible, the polymer blend B may be an adhesive with a relative strong bond to the two polymer blends, and it must in that case be extruded in stripes or otherwise interrupted.

The device shown in Figure 3 consists of essentially similar main parts (39), (40), (41) and (42), but there is one exit slot (53) and (54) respectively in each of the rotating parts (41) and (42), and there is further a fixed exit slot (43) which is formed by the bearing part (40). From the three sets of annular conduits (44), (45) and (46) the polymer streams (C) and (D) pass the bearing part (40) through channels (47) and (48), respectively, and into the three annular chambers (49) and (50), of which the latter continues in the fixed exit slot (43). Each of the chambers (49) is formed of a fixed part (40) and a rotating part (41) or (42). Through channels (51) in (41) and (42) each of the chambers (49) communicate with the corresponding one of the two annular chambers (52) in the rotating parts, and each chamber (52) terminates in an exit slot (53) and (54), respectively.

Arrows (55) and (56) show the direction of rotations.

Having left the die, the three tubular films are fused together at the same time as the two films formed of (C) are subjected to torsion due to the rotations of (41) and (42).

From the outside and inside of the part (40), air is led through channels (55) ending in orifices (56). For the sake of clarity, the channels (55) from the outside of the part (40) are not shown. Through other channels (57) in the parts (41) and (42), the air is led through exit slots (58) and (59) between the fixed part (40) and the rotating parts (41) and (42) respectively. The channels in the part (42) are not shown, for the sake of clarity. The ring-shaped pockets of air thus created between adjacent layers, prevent the rotating outer and inner polymer films pleating against the midlayer immediately outside the exit slots.

Preferably the extruded film is blown, and both internal and external air-cooling is applied.

The arrangement shown in Figure 2 is

(H)

18

usually simpler to operate than that shown in Figure 3, while the latter offers some special possibilities. One is to use expanded polymer for the middle layer, and another is to achieve a longitudinal grain (i.e. a longitudinal direction of splittability) in this layer, so that there will be 3 grains in the sheet. The presence of 3 instead of 2 directions in connection with the preferable tendency to delaminate, will significantly increase the tear propagation strength. Besides the attenuation process is more definitely finished before the lamination, which as previously mentioned is advantageous.

In Figure 4, (60) is a rotating ring formed extrusion die. Through a fixed part of the extruder-die (not shown), which is in sealed connection with the rotating part (60), a polymer blend is fed into a circular groove (61) and led to the exit slot (62) through channels (63), that are separated by thin, plateformed partitions (64). For the sake of clarity the partitions (64) are shown radially extending, but they are in real fact forming an angle with radial plans to avoid die-lines in the resultant sheet. (65) is a mandrel that is fixed by means, not shown, and (66) is a preformed flat sheet that has a longitudinal direction of splittability and that is folded to a tubular shape around the mandrel (65). For the sake of clarity a space is shown between the mandrel (65) and the folded sheet (66), but naturally the sheet is lying tight against the mandrel. The sheet (66) is pulled through the extrusion die over the mandrel as indicated by the arrow (67). When the polymer film (70) still fluid leaves the rotating exit slot (62) it is caught by the folded sheet (66) because of the elastic retention in the attenuated polymer blend, and thus wound around said folded sheet and forwarded along with it, obtaining a helically running direction of splittability indicated by the arrows (68).

The direction of splittability in the preformed, folded sheet (66) is indicated by the arrows (69).

The bonding strength may be controlled e.g. by coextruding an adhesive layer with the film (66). With a sufficiently high temperature of the mandrel (65), the lamination of the sheet may be achieved solely by this. However, often the film (70) is shock-cooled on the mandrel, in which case the temperature of the mandrel may be insufficient for the welding of the two films (66) and (70) together. The lamination may therefore be completed by hot- or cold-welding after the films have left the mandrel (65).

With the words machine direction, is meant the forwarding direction of the sheet (66).

The flow-sheet of Figure 5 schematically

shows different steps of a preferred method in which the use of rotating die-parts is avoided. The last two steps can be carried out by the cold-stretching method indicated by the process-line of Figure 6, in which section "Q" is the cross-stretching line and section "R" is the longitudinal stretching line. The system of rollers in section "Q" consists of driven nip-rollers (71), driven grooved rollers (72), idle rollers (73) and rollers (74) having a longitudinal section resembling a banana. The banana rollers (74) after each step serve to draw out the pleats produced by the lateral stretching. Over the idle-roller (75), the film (79) enters section "R", the longitudinal stretching line, where it is drawn through a water bath (76) serving to remove heat generated by the stretching and maintain a suitable stretching temperature e.g. at 20°—40°C. Finally it is wound onto a bobbin (77).

The arrow (78) indicates the machine direction.

In Figure 7 a pair of driven grooved rollers (72) are shown in detail with the film (79) pressed and stretched between the teeth (80) of the rollers (72).

In Figure 8 the relative lengths of the arrows in the striations I and II of the film (79) indicate the relative amounts of orientation achieved by the biaxial stretching method shown in Figure 6 and Figure 7.

In Figure 8 as well as in Figure 9 the numbers I and II indicates the striations, A and B respectively, discussed above, which generally have varying width and uneven character. Furthermore it should be noted, that the outer layers (81) and (82) of the film (79) are not always symmetrical with respect to the thin mid-layer (83). This asymmetry further serves to make a tear fork.

For economical reasons, the present invention is particularly useful with blends which mainly contain crystalline polyolefins. Best are for the most the most common application blends of polypropylene and high- or low-density-polyethylene. What blending ratio should be applied, and whether high- and low-density polyethylene should be used depends on the desired stiffness, low temperature strength, and in general on which strength properties are particularly wanted. In order to obtain a sufficient cohesive strength in each layer, the polypropylene should either be a copolymer semi-compatible with polyethylene, e.g. polypropylene with 2—5% by weight contents of ethylene, or there should be used a suitable alloying agent. In this connection it is sufficient to maintain high contents of the atactic modification in the iso(syndio)tactic polypropylene during manufacture of this polymer instead of removing this "impurity", as normally done.

It is a special object of the invention that polypropylene with high contents of the atactic material can be made highly useful. Other alloying agents have been mentioned earlier in the specification.

Economically interesting are also blends of polypropylene and an elastomer — e.g. ethylene-propylene-rubber, ethylene-vinylacetate copolymer, polyisobutylene or a thermoplastic rubber based on butadiene/styrene.

When particularly high low-temperature resistance and/or high flexibility is desired, blends of low-density polyethylene and a semi-compatible rubber is preferable. It will be understood that the blend needs not be formed by mechanical blending, but can be formed in the polymerization process. Thus, polypropylene with extreme high contents of the atactic component can be useful without any further admixture, and the known polymerization processes which aim at making blends of polypropylene, polyethylene, and block polymers formed of ethylene and propylene can also be adapted.

Considering polymers outside the polyolefin groups, the following combinations for example are useful for special purposes: a) Polyester/polyamide or polyurethane, b) polyester or polyamide/polycarbonate, c) vinylidene-copolymers in different combinations.

In addition to the layers with the special morphology as described, there may also be layers with special properties. Thus, it is almost always advantageous to co-extrude thin surface layers of a suitable adhesive component in order to enable sealing of the laminate without running the orientation. As another example it will also often be necessary or advantageous, especially for food packaging, to add one or more special layers to improve barrier properties.

The high-strength laminate according to the invention of particular value for sacks and bags and is believed to be advantageous for use within the following fields:

1) Food packaging: Heavy duty food bags in general, by itself or combined with paper. Frozen food packaging.

2) Non-food packaging: Fertilizer bags, cement bags, bags for valuable chemicals, e.g. plastics granules, bags for coarse chemicals (e.g. rock salt, rock pieces) and for other sharp items, wrapping of steel plates, packaging of carpets, baling-wrap, e.g. of cotton, wool, lumber wrap, grocery bags, individual packaging of machine-parts, weapons, etc., sterilization-bags for heavy or sharp objects, miscellaneous, e.g. for textile, apparel, paper, drugs, soaps, toiletries, tobacco.

3) Packaging, such as containers, in which at least part is a laminate: Shrink wrap and stretch wrap for pallets, trash bags, in

particular compactor bags, industrial shipping packs.

4) Non-packaging: Fumigating film, earth converting for erosion control, lining of ponds, water reservoirs and channel construction, road underlay, wind screens, green house film, plant-protection film (agricultural and horticultural), covers over dumps of agricultural and horticultural products such as silage, or materials such as salt; weathering protection of animals, raincoats, tents, inflatable architectural structures, water inflated structures, lighter-than-air-buoyant structures, rib-constructions (architectural, cheap vessels), cushion-pillows as fillers in cargos, railroad car liners, truck covers, weathering protection over buildings under construction, water barriers over cement constructions to retard drying, insulation of roof under shingles, insulation of refrigeration rooms, or as films in house construction, ceiling tiles, general building papers (in lamination with paper) cheap swimming-pool constructions, and industrial tapes.

In the Examples all percentages are by weight.

Example 1

A three layer tubular film is extruded having the following composition: Middle layer (70% of total). Blend of 85% isotactic polypropylene of gas-phase type ("Novolen") with high atactic content with 15% ethylene-vinylacetate copolymer (16% vinylacetate). Both surface layers (one 10% of total, the other one 20% of total): Ethylene-vinylacetate copolymer (16% vinylacetate) to serve as adhesive layers. The polypropylene has a melt index 0.3—0.6 according to ASTM D 12 38 condition L, while the ethylene-vinylacetate copolymer has a melt index 2.5 according to the same ASTM but condition E. The tubular film is extruded from a 1 mm wide slot at 180°C—230°C and drawn to 0.130 mm in molten state. The blow ratio is kept very low, viz. 1.2:1. Thereafter it is cut helically to a flat film with 45° angle of grain. Two such helically cut films, with their grain perpendicular to each other, and the thinner surface layers facing each other, are fed together at 20°C through 7 sets of "grooved rollers" — see Figures 6 and 7. The width of each groove is 1 mm and the width of each ridge is 0.5 mm. The intermeshing of the ridges with each other (difference of level between the tops) is 2 mm. Between each passage through a set of grooved rollers the pleats formed in the laminate are straightened out. By the mechanical work between the grooved rollers, and due to the copolymer layers which act as adhesive, the two films are hereby cold-welded together with relatively low bonding strength — peel

19

20

12

1,526,722

12

strength measured to 10 gr per cm — and is at the same time cross-drawn. After the 7 passages at 20°C the film is passed once through a similar set of grooved rollers with the same dimensions and intermeshing, but heated to 120°C, whereby there is formed lines of strong bonding.

Finally the laminate is longitudinally oriented by drawing in three steps with about 1 cm stretching-gab (so as to minimize the cross-contraction). The last stretching is so adjusted that the total lateral cold-stretch-ratio and the total longitudinal cold-stretch-ratio are equal, whereby the product hereof i.e. the area-stretch-ratio is 2.4:1.

Test results on the product compared to a heavy duty bag quality low-density polyethylene film of 85% higher sq.m weight and melt index 0.3 according to name ASTM condition E. Gauge 100 gr per sq.m for the laminate and 185 gr per sq.m for the polyethylene film.

Impact strength (measured by falling-ball of diameter: 61 mm, weight 320 gr): For the laminated film of 100 gr per sq.m: 5.5 m.

For the polyethylene film of 180 gr per sq.m: 2.0 m Tongue tear resistance: (Tearing at velocity 100 mm per min, total specimen width 5 cm, incision length 10 cm).

For the laminated film of 100 gr per sq.m: 5.9 kg in the machine direction and 6.8 kg in the transverse direction.

For the polyethylene film of 180 gr per sq.m: 1.3 gr.

Elmendorf tear resistance (shock-tearing): (This test is a modification of standards aiming at a more symmetrical tearing) Results:

For the laminated film of 100 gr per sq.m: in longitudinal direction 441 kg cm per sq.cm, in cross-direction 344 kg cm per sq.cm.

For the polypropylene film of 180 gr per sq.m: in longitudinal direction 167 kg cm

per sq.cm in cross-direction 172 kg cm per sq.cm.

When a piece of the sheet is delaminated by peeling and the structure is examined by microscope, the main layers are seen to have a pronounced fibrous morphology with zig-zagging grain-directions.

Example 2

The procedure of example 1 is repeated with the following modifications:

The three-layer coextruded film had the following compositions: Middle layer (70% in total): Blend of 85% isotactic polypropylene (same type as in ex. 1) with 15% ethylene-propylene-rubber (ab. same melt index as the polypropylene).

Both surface layers (each 15% of total) ethylene-vinylacetate copolymer (same type as in ex. 1). The film was more strongly melt-attenuated after the exit from the die, namely by drawing from 1 mm thickness to 0.065 mm (60 gr per sq.m).

Examinations in polarized light showed that the melt-orientation produced corresponded to about 35% uniaxial cold-drawing. After the spiral-cutting, of this film two were bonded with a third film to produce a 3-ply laminate. The third layer, which was placed in the middle, was with longitudinal grain direction obtained by longitudinal cutting of the same film. The lamination and drawing took place on the machinery of ex. 1, but all steps were carried out at 20°C, and the apparatus was adjusted to produce a total area-stretch ratio of 2.5:1 by which the final laminate thickness became 72 gr per sq.m. The peel strength of the bonding between the layers was measured to 10 gr per cm. Examinations by microscope showed a similar structure as in ex. 1. The following test results were obtained:

		Present film 3 layers 72 gr/sq.m	Comparison unoriented LDPE-film 184 gr/sq.m
Impact strength	gr	1000 grxm	530 grxm
Tear propagation strength	MD(*)	848 grxm	307 grxm
(slow tear)	TD(**)	1120 grxm	620 grxm
Load at break	MD	11.1 kg	10.6 kg
(1" wide samples)	TD	8.3 kg	10.7 kg
Stretch at break	MD	286%	467%
	TD	347%	620%
Shrinkage 1 min. 130°C	MD	28%	—
	TD	14%	—
1 min. 155°C	MD	58%	—
	TD	41%	—

(*) Machine Direction

(**) Transverse Direction

Example 3

A series of sheets all based on polyolefin blends was produced by the extrusion die shown in Figure 2. The diameter of the exit slot (21) of the die was 130 mm and the width of the latter 1 mm. The greatest width of the collecting chamber (38) was 4 mm, which means that the amount of attenuation during the passage through the collecting chamber toward the exit slot was smaller than preferable. The extrusion temperature was about 240°C.

After the longitudinal cutting of the tubular film, the stretching was first carried out laterally using from 4 to 8 steps and thereafter longitudinally using from 2 and 4 steps using the same machinery as used in examples 1 and 2. The composition, flat tube width (measure of blow ratio), stretching temperature, stretch ratio, and results appear from the table below. "Nov" stands for Novolene, a gas-phase polymerized

polypropylene with relatively high contents of the atactic modification, "PE" stands for low density polyethylene, "EPR" stands for ethylene-propylene rubber, "SA 872" "7823" and "8623" are different types of polypropylene with minor contents of polymerized ethylene. EPR/PE stands for a 50:50 blend of ethylene-propylene rubber and low density polyethylene.

The fact that even the best samples of this example generally are inferior to those of example 1 and 2 are explained by a less uniaxial total melt attenuation. A certain biaxial melt-attenuation is inevitable in this embodiment, since the streams are first united inside the die in criss-crossing relationship, and thereafter further melt-attenuated during the passage through the exit and immediately thereafter. On the other hand, this method is particularly simple to operate.

25

30

35

40

Run	Outer Layer Composition	Middle Layer Composition	Orientation Temp. %	(cm) Tube Width	Tongue Tear MD TD	Dart Impact (ft-lbs)
1	70% 7823, 20% PE, 10% EPR	PE-10%	Cold 100%	30	3.3 1.8	2.5
2	80% 7823, 20% EPR	PE-10%	Cold 100%	30	1.7 1.6	2.5
3	80% 7823, 20% EPR	PE-20%	Cold 100%	30	2.7 2.3	2.5
4	70% SA872, 30% PE	PE-10%	Cold 50%	30	7.1 4.6	2.0
5	"	PE-10%	Cold 100%	30	5.7 2.1	2.5
6	"	PE-10%	Hot 50%	30	9.0 4.5	2.0
7	"	PE-10%	Hot 100%	30	7.5 3.0	1.5
8	"	PE-10%	Cold 50%	45	6.6 1.4	2.0
9	"	PE-10%	Cold 100%	45	2.6 1.4	2.0
10	"	PE-10%	Hot 50%	45	5.8 2.4	2.0
11	"	PE-10%	Hot 100%	45	6.4 2.3	2.2
12	100% SA 872	PE-10%	Cold 100%	30	1.2 3.3	2.5
13	"	PE-10%	Cold 100%	30	2.0 1.1	1.5
14	"	EPR/PE-10%	Cold 100%	30	2.1 1.5	2.5
15	"	EPR/PE-10%	Hot 50%	30	3.1 2.1	1.5
16	"	EPR/PE-10%	Hot 100%	30	1.4 1.4	1.5
17	"	EPR-10%	Cold 100%	30	5.6 2.8	2.0
18	80% 7823, 20% EPR	EPR-10%	Cold 100%	30	4.4 1.9	4.0
19	70% 7823, 20% PE, 10% EPR	EPR-10%	Cold 100%	30	4.5 2.9	3.0
20	70% SA872, 30% PE	EPR-10%	Cold 50%	30	6.4 3.0	1.5
21	"	EPR-10%	Cold 100%	30	3.9 2.1	3.0
22	"	EPR-10%	Hot 50%	30	4.9 3.9	1.5

22

TABLE (Continued)

Run	Outer Layer Composition	Middle Layer Composition	Orientation Temp. %	(cm) Tube Width	Tongue Tear MD	Tongue Tear TD	Dart Impact (ft-lbs)
23	70% SA872, 30% PE	EPR-10%	Hot 100%	30	5.3	3.4	2.0
24	"	EPR-10%	Cold 50%	45	6.0	5.0	1.5
25	"	EPR-10%	Cold 100%	45	5.0	3.2	3.0
26	"	EPR-10%	Hot 50%	45	5.6	3.9	1.5
27	"	EPR-10%	Hot 100%	45	5.0	5.4	2.0
28	85% 8623, 10% PE, 5% EPR	EPR-10%	Cold 100%	30	0.63	0.32	2.0
29	90% 8623, 10% EPR	EPR-10%	Cold 100%	30	0.45	0.26	2.0
30	100% SA 872	EPR/PE-20%	Cold 100%	30	4.4	4.3	3.0
31	100% SA 872	EPR/PE-5%	Cold 100%	30	4.5	3.5	2.0
32	80% SA 872, 10% PE, 10% EPR	EPR/PE-10%	Cold 100%	30	3.4	6.3	3.0
33	70% NOV, 30% PE	EPR/PE-10%	Cold 100%	30	4.8	2.4	2.5
34	70% PE, 30% NOV	EPR-10%	Cold 100%	30	4.9	4.2	4.0

24

TABLE (Continued)

Run	Mullen Burst (psi)	Beach Puncture MD TD	Trapezoidal Tear MD TD	Elmendorf Tear MD TD	Basis Weight (g/m ²)
1	20	129 136	6.5 7.1	500-1400 500-1300	73.5
2	30	242 228	8.9 6.8	800- 500-2500	69
3	26	295 241	7.8 6.4	300-1100 300-1000	62
4	37	86 105	11.6 9.5	1200-2400 400-2000	114
5	27	103 118	11.9 7.7	400-2000 1400-3200	73.3
6	35	66 98	10.2 11.4	100-1900 1500-3200	103.7
7	30	67 98	13.6 12.7	500-1500 2400-3000	86.5
8	20	71 105	8.7 8.8	100- 800 1100-2600	77
9	19	69 120	7.8 5.0	200-2900 2200-3200	63.4
10	25	44 52	7.7 8.2	300-1100 1100-3200	77.8
11	20	86 88	9.9 8.7	400-1900 900-3200	61.1
12	21	113 103	6.3 5.4	200-1800 600-2200	54.6
13	22	70 68	7.9 5.8	310 800-2100	79
14	22	126 140	5.3 7.4	200-3000 1500-3200	70.4
15	26	56 44	9.5 8.1	300-3200 100- 300	83.7
16	29	72 64	10.7 7.8	150-2500 200-3200	71.5
17	29	83 105	9.8 8.9	700-3200 800-2000	84.5
18	23	327 278	12.5 8.4	700-3000 1400	88.4
19	20	212 187	10.4 9.0	1000-3200 900-1300	71.4
20	23	93 105	10.3 8.9	300-3200 1100-3200	74.8
21	21	400 115	8.2 7.6	300-3200 700-2100	70
22	26	55 71	11.5 9.4	600-2400 1200-2500	86.9

TABLE (Continued)

Run	Mullen Burst (psi)	Beach Puncture MD TD	Trapezoidal Tear MD TD	Elmendorf Tear MD TD	Basis Weight (g/m ²)
23	20	110 116	8.6 10.2	200-2200 700-1600	64.8
24	26	67 149	13.2 10.1	1400-3000 800-2000	88.7
25	23	124 145	11.5 7.9	1100-2500 1000-2300	82.9
26	23	120 101	9.6 9.3	320-3200 1200-3200	83
27	21	116 113	5.7 8.9	640-3200 600-2700	76
28	20	105 50	2.4 1.8	350- 96	66.3
29	15	66 73	1.8 1.5	240 96	74
30	24	99 94	9.0 7.7	800-2000 2600-3200	73.8
31	23	74 107	8.6 8.4	1400-3000 700-2700	81.7
32	25	110 117	8.4 9.4	700-2000 2400	70.4
33	23	228 194	7.0 7.9		68
34	23	336 343	8.6 6.9		71.2

WHAT I CLAIM IS:—

1. A method of making a laminate comprising extruding at least two layers of molten polymeric blend, each comprising a blend of polymers that are incompatible such that on solidification the blend comprises a dispersion of one polymer in a polymeric matrix, attenuating each layer while molten before, during or after extrusion to distort the particles in each layer into a fibrillar grain structure having a predominant direction of splittability after solidification into a film, bonding the layers with the said predominant directions transverse to each

other, solidifying the layers if they are not already solidified, and biaxially orienting the resulting laminate by orienting it in substantially uniaxial steps, the biaxial orientation being conducted at a temperature sufficiently low to maintain the predominant direction of splittability of each film and the bonding being sufficiently weak to permit local delamination of the film upon tearing of the laminate.

2. A method according to claim 1 in which the bonding is provided by strong adhesive bonding in spots or lines and no or weak adhesive bonding between the

25

TABLE (Continued)

Run	Mullen Burst (psi)	Beach Puncture MD TD	Trapezoidal Tear MD TD	Elmendorf Tear MD TD	Basis Weight (g/m ²)
23	20	110 116	8.6 10.2	200-2200 700-1600	64.8
24	26	67 149	13.2 10.1	1400-3000 800-2000	88.7
25	23	124 145	11.5 7.9	1100-2500 1000-2300	82.9
26	23	120 101	9.6 9.3	320-3200 1200-3200	83
27	21	116 113	5.7 8.9	640-3200 600-2700	76
28	20	105 50	2.4 1.8	350- 96	66.3
29	15	66 73	1.8 1.5	240 96	74
30	24	99 94	9.0 7.7	800-2000 2600-3200	73.8
31	23	74 107	8.6 8.4	1400-3000 700-2700	81.7
32	25	110 117	8.4 9.4	700-2000 2400	70.4
33	23	228 194	7.0 7.9		68
34	23	336 343	8.6 6.9		71.2

WHAT I CLAIM IS:-

1. A method of making a laminate comprising extruding at least two layers of molten polymeric blend, each comprising a blend of polymers that are incompatible such that on solidification the blend comprises a dispersion of one polymer in a polymeric matrix, attenuating each layer while molten before, during or after extrusion to distort the particles in each layer into a fibrillar grain structure having a predominant direction of splittability after solidification into a film, bonding the layers with the said predominant directions transverse to each

other, solidifying the layers if they are not already solidified, and biaxially orienting the resulting laminate by orienting it in substantially uniaxial steps, the biaxial orientation being conducted at a temperature sufficiently low to maintain the predominant direction of splittability of each film and the bonding being sufficiently weak to permit local delamination of the film upon tearing of the laminate.

2. A method according to claim 1 in which the bonding is provided by strong adhesive bonding in spots or lines and no or weak adhesive bonding between the



25
28

remaining portions of adjacent surfaces of the films.

3. A method according to claim 1 or claim 2 in which the bonding is provided by having on one or both adjacent faces of at least two films a release or adhesive substance in spots or stripes.

4. A method according to claim 3 in which the laminate comprises at least three films and in which there are strips or dots of release or adhesive substance staggered on two faces of a central film.

5. A method according to any preceding claim comprising extruding and attenuating the layers mutually independently before bonding them.

6. A method according to claim 5 in which at least one layer is extruded from a rotating circular extrusion slot and so attenuated while still fluid that its predominant orientation of splittability is at an angle with the machine direction, and this layer is applied to and carried forward by one or more solid preformed films or tubes having a different direction of splittability.

7. A method according to claim 5 comprising rotating at least two concentric tubular streams of molten polymer blends relative to one another during and immediately after passage through the exit part of an extrusion die while attenuating the streams and thereby forming in each resultant layer a direction of splittability transverse that of an adjacent layer, and subsequently bonding the tubular layers after they have left the exit part of the extrusion die and while still fluid.

8. A method according to claim 5 in which the layers are solidified before the bonding.

9. A method according to claim 8 in which each of the films of the laminate is made by extruding a tubular layer, attenuating it longitudinally while still fluid, solidifying it and cutting it helically and unfolding it to a flat film having an oblique direction of splittability, and the films are then bonded to one another.

10. A method according to claim 8 in which each of the films is made by extruding a layer, attenuating it predominantly in the transverse direction while still fluid by lateral tenting and solidifying it, and the resultant films are then bonded to one another.

11. A method according to claim 8 in which part at least of the bonding is conducted while at least starting the lateral stretching during the biaxial orientation.

12. A method according to claim 5 in which the bonding of the layers is provided by co-extruding an adhesive polymer on at least one surface of at least one layer, the adhesive polymer being lower melting than the polymer blend.

13. A method according to claim 12 in which the adhesive polymer is coextruded in stripes.

14. A method according to claim 12 in which the adhesive polymer is coextruded on one of the adjacent surfaces of two adjacent layers and release component is deposited on the other in stripes or spots.

15. A method according to claim 12 in which the adhesive polymer is coextruded in stripes on two adjacent surfaces of two layers with the stripes on one layer lying in criss-crossing relationship with those of the other layer.

16. A method according to claim 1 in which the biaxial stretching comprises applying lateral stretching forces substantially evenly distributed over the plane of the sheet.

17. A method according to claim 16 in which the lateral stretching is conducted in several steps each comprising stretching the sheet to a configuration of temporary evenly distributed substantially longitudinal pleats, by applying pressure along lines extending substantially in the longitudinal direction of the sheet, and is followed by one or several steps of longitudinal stretching.

18. A method according to claim 17 in which a temporary pleated configuration is formed by passing the laminate successively through the nips of several pairs of intermeshing grooved rollers in which the grooves extend substantially in the longitudinal direction of the sheet, and the sheet is thereafter continuously longitudinally stretched.

19. A method according to claim 18 in which the bonding of the layers is provided by coextruding an adhesive polymer on at least one surface of at least one layer, the adhesive polymer being lower melting than the polymer blend and being such that bonding occurs during the passage through the nips of the grooved rollers without application of heat.

20. A method according to claim 18 or claim 19 in which substantial lateral contraction of the sheet is permitted to occur during the longitudinal stretching.

21. A method according to any of claims 18 to 20 in which the lateral stretching steps are completed before the longitudinal stretching steps are conducted.

22. A method according to claim 1 comprising rotating at least two concentric tubular streams of molten polymer blends relative to one another during passage through an annular extrusion die while conducting the attenuation of each stream and thereby forming directions of splittability in each stream that are transverse to one another, and bonding the fluid streams into a laminate, and extruding the fluid tubular laminate and then solidifying it.



23. A method according to claim 22 in which a polymer for increasing or reducing the strength of bonding is coextruded on at least one face of adjacent layers.
- 5 24. A method according to claim 1 comprising the additional step of pressure rolling the sheet after the biaxial stretching so as to collapse voids formed in it during the stretching.
- 10 25. A method according to claim 1 substantially as herein described.
26. A laminate made by a method according to any preceding claim.
- 15 27. A laminate comprising at least two biaxially oriented films bonded to one another, each film comprising polymeric material having a fibrillar grain structure that imparts a predominant orientation of splittability to that film but that follows a zig-zag course through the film, and in which the films are bonded to one another with the said orientations transverse to each other and the bonding between the films is sufficiently weak that local delamination of the films can occur upon tearing of the laminate.
- 25 28. A laminate according to claim 27 with at least three layers of biaxially oriented films.
- 30 29. A laminate according to either of the claims 27 and 28 in which the bond between at least two layers is strong in spots or lines and weak or absent in the remaining portions of the adjacent surfaces.
- 35 30. A laminate according to claim 29 and with at least three layers in which the stripes or dots of strong bond or weak bond are staggered on the two sides of a midlayer.
- 40 31. A laminate according to claim 27 comprising two films having an oblique predominant direction of splittability with these directions crossing each other.
- 45 32. A laminate according to claim 31 also comprising a film between the said two films having its direction of splittability longitudinal.
33. A laminate according to claim 27 with at least one film with its direction of splittability in a lateral direction.
- 50 34. A laminate according to claim 27 in which each film has molecular orientation and thickness that varies according to a pattern of generally parallel narrow striations.
- 55 35. A laminate according to claim 34 in which the striations form two sets (A) and (B) interspersed with one another, each striation comprising portions of each of the oriented film, of which the striations (A) are relatively thick, and have been uniaxially cold stretched in a pronouncedly unbalanced manner, with the main axis of cold stretching generally substantially parallel to the direction of the striations, and with the tear propagation direction
- forming a small angle to the direction of orientation. While the striations (B) are relatively thin, have been biaxially cold stretched with their main axis of cold stretching criss-crossing with the direction of the striations.
- 70 36. A laminate according to claim 27 in which the blend forming at least one of said films consists predominantly of a crystalline polyolefin.
- 75 37. A laminate according to claim 36 in which the blend forming at least one of the films comprises a blend of polypropylene and high- and/or low-density polyethylene.
- 80 38. A laminate according to claim 36 in which the said blend contains atactic polypropylene or ethylene-propylene rubber as alloying agent.
- 85 39. A laminate according to claim 27 where the blend forming at least one of the films contains not more than 85% by weight of any polymer.
- 90 40. A laminate according to claim 36 where the polyolefin is a polypropylene copolymer with a 2—5% by weight content of ethylene.
41. A laminate according to claim 36 in which the said blend is of polypropylene and an elastomer.
- 95 42. A laminate according to claim 41 in which the elastomer is atactic polypropylene.
43. A laminate according to claim 41 in which the elastomer is an ethylene-propylene rubber.
- 100 44. A laminate according to claim 41 in which the elastomer is an ethylene-vinylacetate copolymer.
45. A laminate according to claim 41 in which the elastomer is a polyisobutylene.
- 105 46. A laminate according to claim 39 in which the elastomer is a thermoplastic rubber based on butadiene/styrene.
47. A laminate according to claim 27 in which the blend forming at least one film is of a polyester and a polyamide.
- 110 48. A laminate according to claim 27 in which the blend forming at least one film is of a polyester and a polyurethane.
49. A laminate according to claim 27 in which the blend forming at least one film is of a polyester and a polycarbonate.
- 115 50. A laminate according to claim 27 in which the blend forming at least one film is of a polyamide and a polycarbonate.
- 120 51. A laminate according to claim 27 in which the blend forming at least one film is based on a vinylidene copolymer.
52. A laminate according to claim 27 substantially as herein described.
- 125 53. A sack or bag formed of a laminate according to any of claims 26 to 52.
54. A package in which part at least of the packaging is a laminate according to any of claims 26 to 52.
- 130



28

20

1,526,722

20

55. Apparatus suitable for use in the method of claim 1 comprising means for extruding at least two layers of molten polymeric material, means for attenuating each layer while molten before during or after extrusion to give a predominant orientation of splittability in each layer, means for bringing the layers together and bonding them with the said predominant orientations transverse to each other, and

means for biaxially orienting the resulting laminate by orienting it substantially in uniaxial steps.

For the Applicant:
GILL JENNINGS & EVERY,
Chartered Patent Agents,
53 and 64 Chancery Lane,
London WC2A 1HN.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



* C L M S *