The invention relates to a coextrusion die for producing a multilayer film or sheet of thermoplastic materials. The coextrusion die includes a die outlet, a first die section for producing a core layer, a second die section for producing a first skin layer, the second die section having a cross flow manifold, the cross flow manifold having a flow path wherein a portion of a melt stream of the thermoplastic material traverses the second die section's length more than once, and a third die section for producing a second skin layer, the third die section having a cross flow manifold, the cross flow manifold having a flow path wherein a portion of a melt stream of the thermoplastic material traverses the third die section's length more than once.
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FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL,
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DESCRIPTION

COEXTRUSION DIE AND MANIFOLD SYSTEM THEREFOR

FIELD OF THE INVENTION

[0001] This disclosure relates generally to an extrusion apparatus for producing a film or sheet of thermoplastic material.

BACKGROUND OF THE INVENTION

[0002] Coextrusion dies are used in manufacturing processes to make a variety of goods. Some dies, for example, are used to form thin films, sheets or other elongated shapes of plastic material. Many advantages are achieved by the production of multiple layer constructions of thin films as this construction enables a combination of properties not available in a mono-layer structure. Originally, such products were prepared principally by laminating separately formed films or sheets together by adhesives, heat or pressure.

[0003] Techniques have been developed for melt laminating which involves joining two or more diverse materials (e.g., thermoplastic materials) from separate molten layers under pressure within a die to emerge as a single laminated material. Such processes make use of the laminar flow principle which enables two or more molten layers under proper operating conditions to join in a common flow channel without intermixing at the contacting interfaces. These multiple layer extrusion systems have come into use as a convenient way to provide for the formation of multiple layers of similar or dissimilar materials.

[0004] Various extrusion dies have been produced to extrude multiple layer films. One general configuration of device utilized a first die section which combined the various layers of materials. The combined materials were then flattened and extruded through a second die section. An example of this type of device is illustrated by U.S. Patent No. 5,316,703, incorporated by reference herein in its entirety. This type of device was limited in effectiveness because of the requirement in thin film production that the multi-layer
sheet or web have uniform thickness across the width or transverse direction (TD) of the extruded sheet. As may be appreciated, if there are great differences in viscosity, temperature and flow rate between the melted resins that form the resin layers, it can be difficult to obtain multi-layer sheets of uniform thickness.

[0005] Multiple manifold die systems are designed with an individual flow channel or manifold for each layer and normally the layers are brought into contact just before the exit of the die. Because the layers are joined only near the final exit slot, materials with somewhat diverse rheological properties can be processed. The individual layers can be formed at the desired thickness before combining with the remaining layers and adjustments of the flow speed for each individual layer can be effected to maintain uniformity of flow between the various layers. This is necessary, since any tendency towards differences between flows at the junction point between layers can cause non-uniformity in the product.

[0006] A die assembly can be modular and is typically assembled from a plurality of parts and then set in a die station as an integral device. For example, a die assembly can comprise a first die part and a second die part, which together form the components that allow a fluid to enter the assembly and be properly emitted therefrom. The first die part includes a first lip and the second die part includes a second lip, these lips defining a feed gap therebetween that determines the thickness of the fluid film emitted therefrom.

[0007] Center feed extrusion dies are commonly used in today's plastics industry. A flow stream entering the manifold undergoes flow divergence, as a result of which there occurs a division of the stream into substreams that flow in generally opposite directions to both ends of the manifold. Pressure drop occurs as each substream flows from the centerline of the manifold to its respective manifold end.

[0008] Typically, center feed extrusion dies have a tear drop-shaped, flat manifold, which may in a form known as a coat hanger manifold, a fish tail manifold, or a T-type manifold. To overcome the pressure drop and produce a substantially equal flow volume
of a stream across the stream width, this type of die may further include a flow pressure-
compensating preland channel. Also known is a center feed extrusion die having a two
stage, flow pressure-compensating, preland channel. This type of apparatus is exemplified

[0009] A die assembly can have a fixed feed gap or a flexible feed gap. With a fixed
feed gap, the lips are not movable relative to each other, so that the thickness of the feed
gap will always be the same dimension. With a flexible feed gap, one lip is movable
relative to the other lip so as to enable adjustment of the feed gap along the width of the
assembly. A flexible feed gap is typically accomplished by assembling the first die part so
that it contains a flexible web between its rear portion and its front portion (to which the
first lip is attached), as well as means for moving the front portion in localized areas.
Movement of the front portion results in the adjustment of the position of the Hp relative to
the other lip and, thus, the thickness of the feed gap in the relevant localized area.

[0010] In flexible feed gap operations, localized adjustments of the feed gap can
usually be accomplished with conventional die assembly designs in order to accommodate
a particular run. However, once initial adjustments are made (i.e., once the movable lip is
moved from its original adjustment), returning the lip to a known position is not so easily
done, if it is even possible. Also, without a clean die and specialized equipment, it is
impossible to adjust a feed gap on an industry standard flex die to a known precision gap
opening.

[0011] The production of certain specialty films, such as microporous polyolefin
membranes have presented additional requirements in the design of coextrusion dies for
their production. Microporous polyolefin membranes are useful as separators for primary
batteries and secondary batteries such as lithium ion secondary batteries, lithium-polymer
secondary batteries, nickel-hydrogen secondary batteries, nickel-cadmium secondary
batteries, nickel-zinc secondary batteries, silver-zinc secondary batteries, etc. When the
microporous polyolefin membrane is used as a battery separator, particularly as a lithium
ion battery separator, the membrane's performance significantly affects the properties, productivity and safety of the battery. Accordingly, the microporous polyolefin membrane should have suitably well-balanced permeability, mechanical properties, dimensional stability, shutdown properties, meltdown properties, etc. The term "well-balanced" means that the optimization of one of these characteristics does not result in a significant degradation in another.

[0012] As is known, it is desirable for the batteries to have a relatively low shutdown temperature and a relatively high meltdown temperature for improved battery safety, particularly for batteries exposed to high temperatures under operating conditions. Consistent dimensional properties, such as film thickness, are essential to high performing films. A separator with high mechanical strength is desirable for improved battery assembly and fabrication, and for improved durability. The optimization of material compositions, casting and stretching conditions, heat treatment conditions, etc. have been proposed to improve the properties of microporous polyolefin membranes.

[0013] In general, microporous polyolefin membranes consisting essentially of polyethylene (i.e., they contain polyethylene only with no significant presence of other species) have relatively low meltdown temperatures. Accordingly, proposals have been made to provide microporous polyolefin membranes made from mixed resins of polyethylene and polypropylene, and multi-layer, microporous polyolefin membranes having polyethylene layers and polypropylene layers in order to increase meltdown temperature. The use of these mixed resins and the production of multilayer films having layers of differing polyolefins can make the productions of films having consistent dimensional properties, such as film thickness, all the more difficult.

[0014] WO 2005/113657 discloses a microporous polyolefin membrane having conventional shutdown properties, meltdown properties, dimensional stability and high-temperature strength. The membrane is made using a polyolefin composition comprising (a) a polyethylene resin composition comprising lower molecular weight polyethylene and
higher molecular weight polyethylene, and (b) polypropylene. This microporous polyolefin membrane is produced by the so-called "wet process".

[0015] WO 2004/089627 discloses a microporous polyolefin membrane made of polyethylene and polypropylene comprising two or more layers, the polypropylene content being more than 50% and 95% or less by mass in at least one surface layer, and the polyethylene content being 50 to 95% by mass in the entire membrane.

[0016] JP7-216118A discloses a battery separator formed from a porous film comprising polyethylene and polypropylene as indispensable components and having at least two microporous layers each with different polyethylene content. The polyethylene content is 0 to 20% by weight in one microporous layer, 21 to 60% by weight in the other microporous layer, and 2 to 40% by weight in the overall film. The battery separator has relatively high shutdown-starting temperature and mechanical strength.

[0017] JP U3048972 discloses an extrusion die design said to eliminate flow divergence of the molten polymer within the extrusion manifold. The proposed die design is provided with two manifolds to form two slit currents. The molten polymer is fed into a first inlet at an end of a first manifold and a second inlet at the end of a second manifold on the opposite side of the first inlet. Two slit currents flow together inside the die. It is theorized that due to the absence of flow divergence of the melt inside the manifold, it may be possible to achieve uniform flow distribution within the die. This is said to result in improved thickness uniformity in the transverse direction the film or the sheet.

[0018] Despite these advances in the art, there remains a need for coextrusion dies and manifold systems capable of producing microporous polyolefin membranes and other high quality multilayer films.

**SUMMARY OF THE INVENTION**

[0019] Provided is a coextrusion die for producing a multilayer film or sheet comprising thermoplastic materials. The coextrusion die includes a die outlet through
which a layered mixture of polymer and diluent is extruded as a multilayer film or sheet, a
first die section for producing a core layer, the first die section having a flat manifold, the
flat manifold having a feed entrance and a pressure manifold in communication with the
slotted die outlet, a second die section for producing a first skin layer, the second die
section having a cross flow manifold, the cross flow manifold having a flow path wherein a
portion of the polymer-diluent mixture traverses the second die section's length more than
once, the cross flow manifold having a feed entrance and a pressure manifold in
communication with the slotted die outlet, and a third die section for producing a second
skin layer, the third die section having a cross flow manifold, the cross flow manifold
having a flow path wherein a portion of the polymer-diluent mixture traverses the third die
section's length more than once, the cross flow manifold having a feed entrance and a
pressure manifold in communication with the slotted die outlet.

[0020] In another aspect, a process for producing a multilayer film or sheet of
thermoplastic materials is also provided. The process includes the steps of combining at
least a first polyolefin composition and at least a first solvent to prepare a first polyolefin
solution, combining at least a second polyolefin composition and at least a second solvent
to prepare a second polyolefin solution, coextruding the first and second polyolefin
solutions through a coextrusion die, the coextrusion die comprising (i) a die outlet through
which the polyolefin solutions are extruded to form a multilayer extrudate, (ii) a first die
section for producing a core layer of the extrudate, the first die section having a flat
manifold, the flat manifold having a feed entrance for the second polyolefin solution and a
pressure manifold in communication with the slotted die outlet, (iii) a second die section
for producing a first skin layer of the extrudate, the second die section having a cross flow
manifold, the cross flow manifold having a flow path wherein a portion of the first
polyolefin solution traverses the second die section's length more than once, the cross flow
manifold having a feed entrance and a pressure manifold in communication with the
slotted die outlet, (iv) and a third die section for producing a second skin layer of the
extrudate, the third die section having a cross flow manifold, the cross flow manifold having a flow path wherein a portion of the first polyolefins solution traverses the third die section's length more than once, the cross flow manifold having a feed entrance and a pressure manifold in communication with the slotted die outlet, to form an extrudate.

[0021] It has been found that the shape memory characteristics of a polyolefin can be a factor in maintaining uniform transverse direction film and sheet thickness as the film or sheet exits a coextrusion die. Shape memory effects have been observed in conventional extrusion and coextrusion of sheets and films, i.e., those extrudates from polymer melts containing at most a small amount of solvent. It was expected that shape-memory effects would not be observed in extruding mixtures of polyolefin and diluent because the presence of the diluent should reduce the number of polymer chain entanglements. It was, therefore, surprising to observe a shape memory effect in polymer extrudates containing a significant amount of solvent, e.g., in the range of at least 10 wt.%, or at least 25 wt.%, or at least 50 wt.%, or at least 75 wt.%, based on the weight of the extrudate.

[0022] It has also been found that coextrusion die manifold design can influence the shape memory phenomena. As such, in an exemplary form disclosed herein, the cross flow manifold is provided with a flow path of a length sufficient to substantially eliminate the shape memory characteristics of the thermoplastic material.

[0023] In a still further exemplary form disclosed herein, the die outlet is a slotted die outlet which includes a first die lip and a second die lip, the first die lip including a flexible lip bar having actuatable means located along a length thereof.

[0024] In yet a further exemplary form disclosed herein, the actuatable means of the first die lip includes a plurality of individual lip bolts effective for varying the width of the slotted die outlet in a region adjacent a point of adjustment.

[0025] In yet a further exemplary form disclosed herein, a skin layer feedblock is provided for dividing a flow of skin layer polyolefin solution (the first polyolefin solution) into a first flow and a second flow, the first flow feeding a feed entrance of the second die
section for producing a first skin layer and the second flow feeding a feed entrance of the third die section for producing a second skin layer.

[0026] These and other advantages, features and attributes of the disclosed coextrusion dies and manifold systems and their advantageous applications and/or uses will be apparent from the detailed description that follows, particularly when read in conjunction with the figures appended hereto.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] FIG. 1 is an end view of a coextrusion die for producing a multilayer film or sheet of thermoplastic materials, in accordance herewith;

[0028] FIG. 2 is a side view of a first die section taken along line 2—2 of FIG. 1, showing a coat hanger manifold for producing a core layer of a multilayer film or sheet of thermoplastic materials, in accordance herewith;

[0029] FIG. 3 is a perspective view of a first portion of a second die section taken along line 3—3 of FIG. 1, showing a cross flow manifold for producing a skin layer of a multilayer film or sheet of thermoplastic materials, in accordance herewith;

[0030] FIG. 4 is a perspective view of a second portion of a second die section taken along line 3—3 of FIG. 1, showing a cross flow manifold for producing a skin layer of a multilayer film or sheet of thermoplastic materials, in accordance herewith;

[0031] FIG. 5 is a side view of a coextrusion die for producing a multilayer film or sheet of thermoplastic materials showing a flexible lip bar having externally actutable means, in accordance herewith; and

[0032] FIG. 6 is a schematic view of a coextrusion die for producing a multilayer film or sheet of thermoplastic materials showing the respective flow paths of the thermoplastic materials (e.g., the combined polymer and diluent), in accordance herewith;

[0033] FIG. 7 is a perspective view of a coat hanger extrusion die showing the flow path of the thermoplastic material;
FIG. 8 is a perspective view of a cross flow extrusion die showing the flow path of the thermoplastic material;

FIG. 9 is a cross sectional representation of a two layer film;

FIG. 10 is a cross sectional representation of a three layer film; and

FIG. 11 is a cross sectional representation of a three layer film.

DETAILED DESCRIPTION OF THE INVENTION

Reference is now made to FIGS. 1-11, wherein like numerals are used to designate like parts throughout.

Referring now to FIGS. 1-5, a coextrusion die 10 for producing a multilayer film or sheet of thermoplastic materials, in accordance herewith, is shown. Coextrusion die 10 includes a die outlet 12, which may be a slotted die outlet, as shown, through which a mixture of polymer and diluent may be extruded as a multilayer film or sheet (extrudate). Coextrusion die 10 also includes a first die section 14 for producing a core or intermediate layer. First die section 14 is provided with a flat manifold, which may be in the form of a coat hanger manifold 16, as shown, or a fish tail manifold, or a T-type manifold. As shown in detail by reference to FIG. 2, coat hanger manifold 16 has a feed entrance 18 at apex 20 and a pressure manifold 22 in communication with slotted die outlet 12.

Coextrusion die 10 also includes a second die section 24 for producing a first skin layer. As shown in detail by reference to FIGS. 3 and 4, second die section 24 is provided with a cross flow manifold 26 (a). As may be seen, cross flow manifold may be provided with a flow path 28 wherein a portion of the polymer-diluent mixture traverses the length of second die section 24 more than once. Cross flow manifold 26 (a) also is provided with a feed entrance 30 and a pressure manifold 32 in communication with said slotted die outlet 12.

When three-layer films or sheets are desired, a third die section 34 for producing a second skin layer may be provided. Third die section 34 can also be provided
with a cross flow manifold 26. As with second die section 24, the cross flow manifold 26
(b) of third die section 34 may have a flow path 28 wherein a portion of the polymer-
diluent mixture traverses the length of third die section 34 more than once. The cross flow
manifold 26 of third die section 34 is provided with a feed entrance 30 and a pressure
manifold 32 in communication with said slotted die outlet 12.

[0042] When forming multilayer microporous polyolefin membrane films and sheets
from mixtures of the polyolefins and diluents described hereinbelow, a characteristic of
these materials is their inherent propensity for shape memory. As is known to those skilled
in the art, shape-memory plastics have a thermoplastic phase and a "frozen" phase. The
initial shape is "memorized" in the frozen phase, with the shape-memory effect permitting
its recovery from whatever temporary shape the plastic has been formed into. As may be
appreciated, a polymer chain has an ideal spatial configuration (Gaussian coil) in a melt
state or in a solution without perturbation. When the polymer is deformed by an external
force, e.g., shear flow, the polymer relaxes its shape returns to the ideal Gaussian coil by
allowing itself to diffuse in the polymer axis direction. The relaxation time strongly
depends on the number of entanglements, therefore, the higher the molecular weight of the
polymer and the higher the polymer concentration of the solution is, the longer the
relaxation time required.

[0043] The shape memory characteristics of a polyolefin-diluent mixture can be a
factor in maintaining uniform transverse direction film and sheet thickness as the film or
sheet exits the coextrusion die. It has been found that manifold design can influence and
correct for this phenomenon. As such, in one form, cross flow manifold 26 of second die
section 24 and cross flow manifold 26 of third die section 34 each have a flow path of a
length sufficient to substantially eliminate the shape memory characteristics of the
extrudate. In another form, where a bi-layer film or sheet is to be produced, cross flow
manifold 26 of second die section 24 has a flow path of a length sufficient to substantially
eliminate the shape memory characteristics of the extrudate.
In another form, cross flow manifold 26 of second die section 24 and cross flow manifold 26 of third die section 34 each have a flow path wherein at least a portion of the polymer-diluent traverses the length of second die section 24 and the length of third die section 34, respectively, at least twice. In yet another form, where a bi-layer film or sheet is to be produced, cross flow manifold 26 of second die section 24 has a flow path wherein a portion of the polymer-diluent mixture traverses said second die section's length at least twice.

As shown with particular reference to FIGS. 1, 4 and 5, slotted die outlet 12 of coextrusion die 10 may be provided with a first die lip 36 and a second die lip 38, first die lip 36 including a flexible lip bar 40 having externally actuatable means 42 located along a length thereof. As shown, externally actuatable means 42 includes a plurality of individual lip bolts 44, each Hp bolt 44 effective for varying the width of slotted die outlet 12 in a region adjacent to a point of adjustment.

As shown with particular reference to FIG. 6, coextrusion die 10 can be provided with a skin layer feedblock 46 for dividing a flow of skin layer material into a first flow S1 and a second flow S2, the first flow S1 feeding feed entrance 30 of said second die section 24 for producing a first skin layer and the second flow S2 feeding feed entrance 30 of third die section 34 for producing a second skin layer.

In another form, wherein a bi-layer film or sheet is produced, coextrusion die 10 is provided with a skin layer feedblock (not shown) for feeding feed entrance 30 of second die section 24 for producing a first skin layer.

In one form, as shown with particular reference to FIG. 6, coextrusion die 10 can be provided with a core layer feed inlet 48 in fluid communication with feed entrance 18 at apex 20 of coat hanger manifold 16.

The coextrusion dies and manifold systems disclosed herein overcome a difficulty when coextruding a mixture of polyolefm and diluent, e.g., polyolefm solution, through a die in a variety of processes, including a "wet" microporous polyolefm
membrane film or sheet process. Wet processes for producing multi-layer microporous membranes are disclosed, e.g., in PCT Publication WO2008/016174 and in published U.S. Patent Applications US2008/0057388 and US2008/0057389, all of which are incorporated by reference herein in their entirety. As may be seen by reference to FIG. 7, this difficulty stems from the fact that when a coat hanger manifold (CH) die 100 is used for the extrusion of a monolayer microporous polyolefin membrane film or sheet 102, shape-memory effects in the extrudate cause a thickness non-uniformity along the transverse direction of the extrudate. As may be appreciated, shape-memory effects in the extrudate tend to act in a direction perpendicular to the flow of the polyolefin-diluent mixture "S" in the die manifold 104. Since, in coat hanger manifold die 100, the primary direction of flow in the manifold is toward the die lip 106, the shape-memory effect tends to occur in the transverse direction of the extrudate. This causes a redistribution of material in the extrudate toward the extrudate's center along the transverse direction.

[0050] Referring now to FIG. 8, in the case of monolayer extrusion dies, it has been discovered that this issue can be overcome through the use of a cross flow manifold (CF) die 200, where the mixture S is made to traverse the width of the die manifold 204 at least two times before mixture S approaches the die lip 206. As may be appreciated, this results in a significant amount of mixture S in the die manifold flowing in a direction parallel to die lip 206. Consequently, shape memory effects will occur primarily in the machine direction, resulting in a more uniform distribution of the extrudate in the transverse direction.

[0051] Experience suggests that the relative lack of transverse direction shape memory in a film or sheet made using a cross flow die would make it practical to produce a two layer coextruded film or sheet having one layer extruded through a cross flow manifold die and the second layer coextruded through a coat hanger manifold die. However, this has been found not to be the case, as may be seen from the cross-sectional representation of such an extrudate 300, depicted in FIG. 9. As shown, the intimate planar contact of the
two layers 302 and 304 is not sufficient to overcome the shape memory effect in layer 302, the layer extruded from the coat hanger manifold die. Consequently, one interested in making a two layer coextruded film or sheet would be led to use a combination of cross flow manifold dies. However, the use of three cross flow manifold dies to make a coextruded three layer film or sheet from mixtures of polyolefin and diluent would be very expensive and the dies difficult to manufacture due to their complexity.

[0052] Referring now to FIG. 10, the coextrusion dies and manifold systems disclosed herein are based on the discovery that a three layer extrudate 400, produced using cross flow dies for the skin layers 402 is believed to fix the position of the material within core layer 404 produced using a coat hanger manifold die, as a result of the large planar interfaces. This prevents much of the transverse direction thickness variation that would otherwise occur in layer 404 as a result of shape memory effects. This is unexpected since the results obtained in the case of the two layer film 300 of FIG. 9 would lead one skilled in the art to use a cross flow/cross flow/cross flow coextrusion die, rather than a cross flow/coat hanger/cross flow coextrusion die.

[0053] As depicted by FIG. 10, a small amount of core layer 404 thickness non-uniformity may still occur when a coat hanger manifold die is used for core layer 404 and cross flow manifold dies used for skin layers 402. Referring also to FIG. 7, it is believed that this is not the result of shape memory effects in the core layer 404, but rather the result of an increase in the apparent viscosity of the polyolefin-diluent mixture S under shear conditions in die manifold 104, preventing sufficient polyolefin-diluent mixture S from reaching the ends of the die channels 108 near the outside edges of the die 100. Since the apparent viscosity of the mixture S in the die channel is higher, the amount of mixture S made available near the transverse edges of the die lip 106 is less than that which would be predicted based on the viscosity measured during rheological testing. The insufficiency of core-layer material available near the ends of the die lip 106 is believed to result in the core layer thickness non-uniformity illustrated in FIG. 10.
[0054] To address this issue, in one form, the pressure manifold of the core layer coat hanger manifold die 100 may be enlarged near its transverse ends 108 from the cross sectional area that exists at its midpoint. Sufficient core layer polyolefin solution S can then be made available near the transverse ends of the die lip 106 to significantly reduce the amount of transverse thickness variation in the core layer of a three layer coextruded film or sheet. As shown in FIG. 11, a three-layer coextruded microporous polyolefin membrane film or sheet 500, produced using a die having this modified coat hanger manifold structure, with an enlarged cross section near the transverse ends of the pressure manifold, can produce a film or sheet 500 having a pair of skin layers 502 and a core layer 504 of uniform cross section. As indicated above, this coextrusion die is less complicated and less expensive than a coextrusion die having a cross flow/cross flow/cross flow structure and is compatible with a wider range of polyolefin-diluent mixtures than a conventional cross flow/coat hanger/cross flow structure, resulting in greater thickness uniformity in the transverse direction for polyolefin-diluent mixtures exhibiting a relatively large difference in viscosity under test conditions compared to their viscosities in the die under process conditions.

[0055] As indicated, the coextrusion dies and manifold systems disclosed herein are useful in forming multilayer microporous polyolefin membrane films and sheets. These films and sheets find particular utility in the critical field of battery separators. In one form, the multi-layer, microporous polyolefin membrane comprises two layers. The first layer (e.g., the skin, top or upper layer of the membrane) comprises a first microporous layer material, and the second layer (e.g., the bottom or lower or core layer of the membrane) comprises a second microporous layer material. For example, the membrane can have a planar top layer when viewed from above on an axis approximately perpendicular to the transverse and longitudinal (machine) directions of the membrane, with the bottom planar layer hidden from view by the top layer.
In another form, the multi-layer, microporous polyolefin membrane comprises three or more layers, wherein the outer layers (also called the "surface" or "skin" layers) comprise the first microporous layer material and at least one core or intermediate layer comprises the second microporous layer material. In a related form, where the multi-layer, microporous polyolefin membrane comprises two layers, the first layer consists essentially of the first microporous layer material and the second layer consists essentially of the second microporous layer material. In a related form where the multi-layer, microporous polyolefin membrane comprises three or more layers, the outer layers consist essentially of the first microporous layer material and at least one intermediate layer consists essentially of (or consists of) the second microporous layer material.

Starting materials having utility in the production of the afore-mentioned films and sheets will now be described. As will be appreciated by those skilled in the art, the selection of a starting material is not critical as long as an extrusion die and manifold system employing cross flow manifold principles can be applied. Suitable polymers, diluents, and amounts thereof for producing microporous film using dies described herein are disclosed in WO2008/016174, US2008/0057388, and US2008/0057389, for example. In one form, the first and second microporous layer materials are produced from polyethylene. In one form, the first microporous layer material is produced from a first polyethylene ("PE-I") having an Mw value of less than about 1 x 10^6 or a second polyethylene ("UHMWPE-I") having an Mw value of at least about 1 x 10^6. In one form, the first microporous layer material can contain a first polypropylene ("PP-I"). In one form, the first microporous layer material comprises one of (i) a polyethylene (PE), (ii) an ultra high molecular weight polyethylene (UHMWPE), (iii) PE-I and PP-I, or (iv) PE-I, UHMWPE-I, and PP-I.

In one form of the above (ii) and (iv), UHMWPE-I can preferably have an Mw in the range of from about 1 x 10^6 to about 15 x 10^5 or from about 1 x 10^6 to about 5 x 10^6 or from about 1 x 10^6 to about 3 x 10^6, and preferably contain no more than about 7 wt.\%.
on the basis of total amount of PE-I and UHMWPE-I in order to obtain a microporous layer having a hybrid structure as described in WO2008/016174, and can be at least one of homopolymer or copolymer. In one form of the above (iii) and (iv), PP-I can be at least one of a homopolymer or copolymer, or can preferably contain no more than about 25 wt.%, more preferably about 2 wt.% to about 15 wt.%, most preferably about 3 wt.% to about 10 wt.%, on the basis of total amount of the first layer microporous material. In one form, the Mw of polyolefin in the first microporous layer material can have about 1 x 10^6 or less, or in the range of from about 1 x 10^5 to about 1 x 10^6 or from about 2 x 10^5 to about 1 x 10^6 in order to obtain a microporous layer having a hybrid structure defined in the later section. In one form, PE-I can preferably have an Mw ranging from about 1 x 10^4 to about 5 x 10^5, or from about 2 x 10^5 to about 4 x 10^5, and can be one or more of a high-density polyethylene, a medium-density polyethylene, a branched low-density polyethylene, or a linear low-density polyethylene, and can be at least one of a homopolymer or copolymer.

[0059] In one form, the second microporous layer material comprises one of: (i) a fourth polyethylene having an Mw of at least about 1 x 10^6, (UHMWPE-2), (ii) a third polyethylene having an Mw that is less than 1 x 10^6 and UHMWPE-2 and the fourth polyethylene, wherein the fourth polyethylene is present in an amount of at least about 8% by mass based on the combined mass of the third and fourth polyethylene; (iii) UHMWPE-2 and PP-2, or (iv) PE-2, UHMWPE-2, and PP-2. In one form of the above (ii), (iii) and (iv), UHMWPE-2 can contain at least about 8 wt.%, or at least about 20 wt.%, or at least about 25 wt.%, based on the total amount of UHMWPE-2, PE-2 and PP-2 in order to produce a relatively strong multi-layer, microporous polyolefin membrane. In one form of the above (iii) and (iv), PP-2 can be at least one of a homopolymer or copolymer, and can contain 25 wt.% or less, or in the range of from about 2% to about 15%, or in the range of from about 3% to about 10%, based on the total amount of the second microporous layer material. In one form, preferable PE-2 can be the same as PE-I, but can be selected
independently. In one form, preferable UHMWPE-2 can be the same as UHMWPE-I, but can be selected independently.

[0060] In addition to the first, second, third, and fourth polyethylenes and the first and second polypropylenes, each of the first and second layer materials can optionally contain one or more additional polyolefins and/or a polyethylene wax, e.g., one having an Mw in the range of about 1 x 10³ to about 1 x 10⁴, as described in US2008/0057388.

[0061] In one form, a process for producing a two-layer microporous polyolefin membrane is provided wherein a coextrusion die and manifold system of the type disclosed herein is employed. In another form, the microporous polyolefin membrane has at least three layers and is produced through the use of a coextrusion die and manifold system of the type shown in FIGS. 1-6. The production of the microporous polyolefin membrane will be mainly described in terms of two-layer and three-layer membrane.

[0062] In one form, a three-layer microporous polyolefin membrane comprises first and third microporous layers constituting the outer layers of the microporous polyolefin membrane and a second (core) layer situated between (and optionally in planar contact with) the first and third layers. In another form, the first and third layers are produced from a first mixture of polyolefin and diluent, e.g., a first polyolefin solution, and the second (core) layer is produced from a second mixture of polyolefin and diluent, e.g., a second polyolefin solution.

[0063] In one form, a method for producing the multi-layer, microporous polyolefin membrane is provided. The method comprises the steps of (1) combining (e.g., by melt-blending) a first polyolefin composition and a at least one first diluent (e.g., solvent) to prepare a first polyolefin solution, (2) combining a second polyolefin composition and at least one second diluent (e.g., solvent) to prepare a second polyolefin solution (the first and second diluents can be referred to as "membrane-forming" solvents), (3) coextruding the first and second polyolefin solutions through a die of the type disclosed herein to form an extrudate, (4) optionally cooling the extrudate to form a multi-layer, cooled extrudate, (5)
removing at least a portion of the membrane-forming solvents from the multi-layer extrudate or cooled extrudate to form the multi-layer membrane, and (6) optionally removing from the membrane at least a portion of any remaining volatile species. An optional stretching step (7), and an optional hot solvent treatment step (8), etc. can be conducted between steps (4) and (5), if desired. After step (6), an optional step (9) of stretching a multi-layer, microporous membrane, an optional heat treatment step (10), an optional cross-linking step with ionizing radiations (11), and an optional hydrophilic treatment step (12), etc., can be conducted if desired. The order of the optional steps is not critical.

[0064] The first polyolefin composition comprises polyolefin resins as described above that can be combined, e.g., by dry mixing or melt blending with an appropriate membrane-forming solvent to produce the first polyolefin solution. Optionally, the first polyolefin solution can contain various additives such as one or more antioxidant, fine silicate powder (pore-forming material), etc., as described in WO2008/016174.

[0065] The first and second diluents, e.g., the membrane-forming solvents can be solvents that are liquid at room temperature. Suitable diluents include those described in WO200/016174, US2008/0057388 and US2008/005789.

[0066] In one form, the resins, etc., used to produce to the first polyolefin composition are melt-blended in, e.g., a double screw extruder or mixer. For example, a conventional extruder (or mixer or mixer-extruder) such as a double-screw extruder can be used to combine the resins, etc., to form the first polyolefin composition. The membrane-forming solvent can be added to the polyolefin composition (or alternatively to the resins used to produce the polyolefin composition) at any convenient point in the process. For example, in one form where the first polyolefin composition and the first membrane-forming solvent are melt-blended, the solvent can be added to the polyolefin composition (or its components) at any of (i) before starting melt-blending, (ii) during melt blending of the first polyolefin composition, or (iii) after melt-blending, e.g., by supplying the first
membrane-forming solvent to the melt-blended or partially melt-blended polyolefin composition in a second extruder or extruder zone located downstream of the extruder zone used to melt-blend the polyolefin composition.

[0067] Suitable process conditions for combining the polyolefin and diluent are described in WO2008/0161174, US2008/0057388, and US2008/0057389, for example.

[0068] The amount of the first polyolefin composition in the first polyolefin solution is not critical. In one form, the amount of first polyolefin composition in the first polyolefin solution can range from about 1 wt.% to about 75 wt.%, based on the weight of the polyolefin solution, for example from about 20 wt.% to about 70 wt.% The balance of the first polyolefin solution can be solvent. The second polyolefin solution can be prepared by the same methods used to prepare the first polyolefin solution.

[0069] The amount of the second polyolefin composition in the second polyolefin solution is not critical. In one form, the amount of second polyolefin composition in the second polyolefin solution can range from about 1 wt.% to about 75 wt.%, based on the weight of the second polyolefin solution, for example from about 20 wt.% to about 70 wt.% The balance of the second polyolefin solution can be solvent.

[0070] The first and second polyolefin solutions are co-extruded using a coextrusion die of the type disclosed herein, wherein a planar surface of a first extrudate layer formed from the first polyolefin solution is in contact with a planar surface of a second extrudate layer formed from the second polyolefin solution. A planar surface of the extrudate can be defined by a first vector in the machine direction (MD) of the extrudate and a second vector in the transverse direction (TD) of the extrudate.

[0071] In another form, the first extruder containing the first polyolefin solution is connected to a second die section for producing a first skin layer and a third die section for producing a second skin layer, and a second extruder containing the second polyolefin solution is connected to a first die section for producing a core layer. The first and second polyolefin solutions can be co-extruded or laminated to form a three-layer extrudate.
comprising a first and a third layer constituting skin or surface layers produced from the first polyolefin solution; and a second layer constituting a core or intermediate layer of the extrudate situated between and in planar contact with both surface layers, where the second layer is produced from the second polyolefin solution.

[0072] The die gap is generally not critical. For example, the multi-layer-sheet-forming die of the type disclosed herein can have a die gap of about 0.1 mm to about 5 mm. Die temperature and extruding speed are also non-critical parameters. For example, the die can be heated to a die temperature ranging from about 140°C to about 250°C during extrusion. The extruding speed can range, for example, from about 0.2 m/minute to about 15 m/minute. The thickness of the layers of the layered extrudate can be independently selected. For example, the gel-like sheet can have relatively thick skin or surface layers compared to the thickness of an intermediate layer of the layered extrudate.

[0073] While the extrusion has been described in terms of producing two and three-layer extrudates, the extrusion step is not limited thereto. For example, a plurality of dies and/or die assemblies can be used to produce multi-layer extrudates having four or more layers using the principles of the coextrusion dies and methods disclosed herein.

[0074] The multi-layer extrudate can be formed into a multi-layer, gel-like sheet by cooling, for example. Cooling rate and cooling temperature are not particularly critical. For example, the multi-layer, gel-like sheet can be cooled at a cooling rate of at least about 50°C/minute until the temperature of the multi-layer, gel-like sheet (the cooling temperature) is approximately equal to the multi-layer, gel-like sheet's gelatin temperature (or lower). In one form, the extrudate is cooled to a temperature of about 25°C or lower in order to form the multi-layer gel-like sheet.

[0075] In one form, at least a portion of the first and second membrane-forming solvents are removed (or displaced) from the multi-layer extrudate or cooled extrudate in order to form the multi-layer membrane. Suitable methods for removing the solvents are described in WO2008/016174, US2008/0057388, and US2008/0057389, for example.
In one form, the membrane obtained by removing the membrane-forming solvent is dried in order to remove at least a portion of any volatile species in the membrane.

Prior to the step for removing the membrane-forming solvents, the multi-layer extrudate or cooled extrudate can be stretched in order to at least partially orient the extrudate.


Although it is not required, the multi-layer extrudate or cooled extrudate can be treated with a hot solvent. When used, it is believed that the hot solvent treatment provides the fibrils (such as those formed by stretching the multi-layer gel-like sheet) with a relatively thick leaf-vein-like structure. Suitable methods are described in WO 2000/20493.

In one form, multi-layer, microporous membrane can be stretched, at least monoaxially. The stretching method selected is not critical, and conventional stretching methods can be used such as by a tenter method, etc. While it is not critical, the membrane can be heated during stretching. When the multi-layer gel-like sheet has been stretched as described above the stretching of the dry multi-layer, microporous polyolefin membrane can be called dry-stretching, re-stretching, or dry-orientation.

In one form, the multi-layer, microporous membrane can be heat-treated. In one form, the heat treatment comprises heat-setting and/or annealing. When heat-setting is used, it can be conducted using conventional methods such as tenter methods and/or roller methods.

Annealing differs from heat-setting in that it is a heat treatment with no load applied to the multi-layer, microporous polyolefin membrane. The choice of annealing method is not critical, and it can be conducted, for example, by using a heating chamber with a belt conveyer or an air-floating-type heating chamber. Alternatively, the annealing can be conducted after the heat-setting with the tenter clips slackened. The temperature of
the multi-layer, microporous polyolefin membrane during annealing can range from about
the melting point $T_m$ or lower, or in a range from about 60°C to $(T_m - 10°C)$, or from
about 60°C to $(T_m - 5°C)$.

[0083] In one form, the multi-layer, microporous polyolefin membrane can be cross-
linked (e.g., by ionizing radiation rays such as a-rays, (3-rays, 7-rays, electron beams, etc.))
or can be subjected to a hydrophilic treatment (i.e., a treatment which makes the multi-
layer, microporous polyolefin membrane more hydrophilic (e.g., a monomer-grafting
treatment, a surfactant treatment, a corona-discharging treatment, etc.)). Suitable methods
for membrane stretching, heat treatment, annealing, and hydrophilizing are described in

[0084] All patents, test procedures, and other documents cited herein, including
priority documents, are fully incorporated by reference to the extent such disclosure is not
inconsistent and for all jurisdictions in which such incorporation is permitted.

[0085] While the illustrative forms disclosed herein have been described with
particularity, it will be understood that various other modifications will be apparent to and
can be readily made by those skilled in the art without departing from the spirit and scope
of the disclosure. Accordingly, it is not intended that the scope of the claims appended
hereo be limited to the examples and descriptions set forth herein but rather that the claims
be construed as encompassing all the features of patentable novelty which reside herein,
including all features which would be treated as equivalents thereof by those skilled in the
art to which this disclosure pertains.

[0086] When numerical lower limits and numerical upper limits are listed herein,
ranges from any lower limit to any upper limit are contemplated.
1. A coextrusion die for producing a multilayer film or sheet of thermoplastic materials, comprising:

   (a) a die outlet through which a layered extrudate is extruded as a multilayer film or sheet,

   (b) a first die section for producing a core layer, said first die section having a flat manifold, said flat manifold having a feed entrance and a pressure manifold in communication with said slotted die outlet;

   (c) a second die section for producing a first skin layer, said second die section having a cross flow manifold, said cross flow manifold having a flow path wherein a portion of a polymer-diluent mixture traverses said second die section's length more than once, said cross flow manifold having a feed entrance and a pressure manifold in communication with said slotted die outlet; and

   (d) a third die section for producing a second skin layer, said third die section having a cross flow manifold, said cross flow manifold having a flow path wherein a portion of the polymer-diluent mixture traverses said third die section's length more than once, said cross flow manifold having a feed entrance and a pressure manifold in communication with said slotted die outlet.

2. The coextrusion die of claim 1, wherein said flat manifold of said first die section is a coat hanger manifold, a fish tail manifold, or a T-type manifold.

3. The coextrusion die of any preceding claim, wherein said flat manifold is a coat hanger manifold, wherein said feed entrance is positioned at an apex thereof.

4. The coextrusion die of any preceding claim, wherein said pressure manifold of said first die section has a midpoint having a first cross sectional area and transverse ends
having a second cross sectional area, said second cross sectional area greater than said first cross sectional area of said pressure manifold.

5. The coextrusion die of any preceding claim, wherein said die outlet is a slotted die outlet which comprises a first die lip and a second die lip, said first die lip comprising a flexible lip bar having actuable means located along a length thereof.

6. The coextrusion die of claim 5, wherein said actuable means comprises a plurality of individual H-bolts, each of said lip bolts effective for varying the width of said slotted die outlet.

7. The coextrusion die of any preceding claim, further comprising a skin layer feedblock for dividing a flow of skin layer polymer-diluent mixture into a first flow and a second flow, the first flow feeding said feed entrance of said second die section for producing a first skin layer and the second flow feeding said feed entrance of said third die section for producing a second skin layer.

8. The coextrusion die of any preceding claim, wherein said cross flow manifold of said second die section and said cross flow manifold of said third die section each have a flow path wherein a portion of the polymer-diluent mixture traverses said second die section's length and said third die section's length, respectively, at least twice.

9. The coextrusion die of any preceding claim, wherein said cross flow manifold of said second die section and said cross flow manifold of said third die section each have a flow path wherein a portion of the polymer-diluent mixture traverses said second die section's length and said third die section's length, respectively, at least 2.5 times.

10. The coextrusion die of any preceding claim, wherein said cross flow manifold of said second die section and said cross flow manifold of said third die section each have a flow path of a length sufficient to substantially eliminate the shape memory characteristics of the extrudate.

11. A process for making a multilayer extrudate, comprising the following steps:
(a) combining at least a first polyolefin and at least a first diluent to prepare a first mixture,

(b) combining at least a second polyolefin and at least a second diluent to prepare a second mixture,

(c) coextruding the first and second mixtures through a coextrusion die, the coextrusion die comprising (i) a die outlet through which the extrudate is extruded, (ii) a first die section for producing a core layer of the extrudate, the first die section having a flat manifold, the flat manifold having a feed entrance for the second mixture and a pressure manifold in communication with the die outlet; (iii) a second die section for producing a first skin layer of the extrudate, the second die section having a cross flow manifold, the cross flow manifold having a flow path wherein a portion of the first mixture traverses the second die section's length more than once, the cross flow manifold having a feed entrance and a pressure manifold in communication with the slotted die outlet; and (iv) a third die section for producing a second skin layer of the extrudate, the third die section having a cross flow manifold, the cross flow manifold having a flow path wherein a portion of the first mixture traverses the third die section's length at least twice, the cross flow manifold having a feed entrance and a pressure manifold in communication with the slotted die outlet, to form an extrudate.

12. The process of claim 11, wherein the flat manifold of the first die section is a coat hanger manifold, a fish tail manifold, or a T-type manifold.

13. The process of claims 11 or 12, wherein the flat manifold is a coat hanger manifold, wherein the feed entrance is positioned at an apex thereof.

14. The process of any of claims 11 through 13, wherein the pressure manifold of the first die section has a midpoint having a first cross sectional area and transverse ends having a second cross sectional area, said second cross sectional area greater than said first cross sectional area of said pressure manifold.
15. The process of any of claims 11 through 14, wherein the die outlet of the coextrusion die is a slotted die outlet which includes a first die lip and a second die lip, the first die lip comprising a flexible lip bar having actuatatable means located along a length thereof.

16. The process of claim 15, wherein the actuatatable means of the slotted die outlet of the coextrusion die include a plurality of individual lip bolts, each of the lip bolts effective for varying the width of the slotted die outlet.

17. The process of any of claims 11 through 16, wherein the coextrusion die further includes a skin layer feedblock for dividing a flow of the first mixture into a first flow and a second flow, the first flow feeding the feed entrance of the second die section for producing a first skin layer and the second flow feeding the feed entrance of the third die section for producing a second skin layer.

18. The process of any of claims 11 through 17, wherein the cross flow manifold of the second die section and the cross flow manifold of the third die section each have a flow path wherein a portion of the first mixture traverses the second die section's length and the third die section's length, respectively, at least twice.

19. The process any of claims 11 through 18, wherein the cross flow manifold of the second die section and the cross flow manifold of the third die section each have a flow path wherein a portion of the first mixture traverses the second die section's length and the third die section's length, respectively, at least 2.5 times.

20. The process of any of claims 11 through 19, wherein the cross flow manifold of the second die section and the cross flow manifold of the third die section each have a flow path of a length sufficient to substantially eliminate the shape memory characteristics of the extrudate.