MICROPOROUS SEPARATOR FOR LITHIUM BATTERY, AND PREPARATION METHOD THEREFOR

TECHNICAL FIELD

[0001] The present disclosure relates to the technical field of lithium-ion batteries, specifically to a microporous separator for a lithium battery and a preparation method thereof.

BACKGROUND

[0002] Polyolefin-based microporous membranes are widely used as separation membranes for separation and selective permeation of various substances, as isolation materials, and the like. For example, polyolefin-based microporous membranes are used as precision filtration membranes, separators for fuel cells, separators for capacitors, base materials for functional membranes filled with functional materials into pores to exhibit new functions, separators for batteries, and the like. Among these applications, polyolefin-based microporous membranes are particularly suitable as separators for lithium-ion batteries that are widely used in notebook computers, mobile phones, digital cameras, and the like. Reasons therefor can include that polyolefin-based microporous membranes have excellent mechanical strength and shutdown characteristics.

[0003] However, existing separators fail to achieve a balance among puncture strength, deformation memory effect duration, and compression set. Therefore, there remains a need for a separator having high puncture strength, a short deformation memory effect duration, and a low compression set.

SUMMARY

[0004] According to the present disclosure, by appropriately controlling the crystallinity of a microporous separator and the quantity proportion of polyolefin chain segments with a specified molecular weight, a lithium-ion battery separator having high puncture strength, a short deformation memory effect duration, and a low compression set can be obtained. In addition, the present disclosure has also found that controlling parameters of an extrusion step in a separator manufacturing process contributes to controlling the compression resistance of the separator.

[0005] A first aspect of the present disclosure provides a microporous separator for a lithium battery. The microporous separator is a porous polyolefin membrane. In the microporous separator, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of 2 million to 5 million is 5 mol%-8 mol%, preferably 5 mol%-7 mol%, and

more preferably 6 mol%-7 mol%. The microporous separator has a crystallinity at a first-time temperature rise and a crystallinity at a second-time temperature rise, where the crystallinity at the first-time temperature rise is ≥ 65%, and a difference between the crystallinity at the first-time temperature rise and the crystallinity at the second-time temperature rise is > 15%.

[0006] In some embodiments, in the microporous separator, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of greater than 5 million and not more than 9 million is 0.5 mol%-2 mol%, preferably 0.5 mol%-1.5 mol%.

[0007] In some embodiments, the crystallinity at the first-time temperature rise is 65%-80%, preferably 68%-75%.

[0008] In some embodiments, the crystallinity at the second-time temperature rise is ≤ 50%, preferably 35%-50%, and more preferably 45%-50%.

[0009] In some embodiments, the difference between the crystallinity at the first-time temperature rise and the crystallinity at the second-time temperature rise is ≥ 16%, preferably 16%-45%, and more preferably 18%-30%.

[0010] In some embodiments, the microporous separator satisfies one or a combination of more of the following:

[0011] a) a puncture strength per unit thickness of the microporous separator is ≥ 85 gf/μm, preferably ≥ 90 gf/μm;

[0012] b) a deformation memory effect duration of the microporous separator in a thickness direction is 0 s-200 s, preferably 0 s-100 s, more preferably 0 s-50 s, more preferably 0 s-20 s, and most preferably 0 s-10 s;

[0013] c) a compression set of the microporous separator is ≤ 2.5%, preferably ≤ 1.5%, more preferably ≤ 1%, and further preferably ≤ 0.7%; and

[0014] d) a thickness of the microporous separator is 1 μm-30 μm, preferably 4 μm-12 μm.

[0015] In some embodiments, the microporous separator is a separator made from a polyolefin resin, where the polyolefin resin has a molecular weight distribution of 3-6, preferably 3.5-5.5, and more preferably 4.5-5.

[0016] In some embodiments, in the polyolefin resin, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of 2 million to 5 million is 5 mol%-9 mol%, preferably 5 mol%-8 mol%, and more preferably 6 mol%-8 mol%.

[0017] In some embodiments, in the polyolefin resin, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of greater than 5 million and not more than 9 million is 0 mol%-2 mol%, preferably 0.2 mol%-1.5 mol%.

[0018] A second aspect of the present disclosure provides a preparation method of a microporous separator for a lithium battery, characterized by including the following steps:

[0019] (a) melt-kneading a mixture containing a polyolefin resin and a plasticizer to form a melt;

[0020] (b) extruding the melt obtained in step (a) and solidifying the extruded melt into a thick sheet;

[0021] (c) stretching the thick sheet obtained in step (b) in a machine direction (MD) and in a transverse direction (TD) perpendicular to the machine direction to obtain a stretched body;

[0022] (d) removing the plasticizer from the stretched body obtained in step (c) to obtain a separator precursor; and

[0023] (e) heat-setting the separator precursor obtained in step (d) to obtain the microporous separator for a lithium battery;

[0024] where the polyolefin resin has a crystallinity of ≤ 50%, preferably 35%-50%, and in the polyolefin resin, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of 2 million to 5 million is 5 mol%-9 mol%, preferably 5 mol%-8 mol%, and more preferably 6 mol%-8 mol%.

[0025] In some embodiments, in step (a), in the polyolefin resin, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of greater than 5 million and not more than 9 million is 0 mol%-2 mol%, preferably 0.2 mol%-1.5 mol%.

[0026] In some embodiments, the polyolefin resin has a molecular weight distribution of 3-6, preferably 3.5-5.5, and more preferably 4.5-5.

[0027] In some embodiments, the polyolefin resin is selected from polyethylene, polypropylene, polybutene, polymethylpentene, copolymers thereof, and blends thereof; and preferably, the polyethylene is selected from low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), and ultrahigh density polyethylene (UHDPE).

[0028] In some embodiments, in step (a), an extruder is used to perform the melt-kneading, where parameters of the extruder include an extruder temperature of 150 °C-260 °C and an extruder screw speed of 60 r/min-125 r/min.

[0029] In some embodiments, a weight ratio of the polyolefin resin to the plasticizer is between 15:85 and 35:65, preferably between 18:82 and 23:77.

[0030] In some embodiments, in step (b), the mixture is extruded through a die lip of a die head and attached onto a casting roll to be cooled and solidified to form a thick sheet, where the

die lip has an opening a, the thick sheet has a thickness h, and a swelling ratio is defined as A = h / a, A being controlled to be greater than or equal to 1.2.

[0031] In some embodiments, a roll speed of the casting roll is 3 m/min-8 m/min, and a temperature of the die head is 160 °C-240 °C.

[0032] In some embodiments, in step (c), stretching in the MD is performed at 80 °C-120 °C with a stretching ratio of 4-7, and stretching in the TD is performed at 90 °C-135 °C with a stretching ratio of 4-15.

[0033] In some embodiments, in step (e), the heat-setting is at least one selected from oven heat treatment and roll heat treatment. Preferably, the oven heat treatment is performed at a temperature of 120 °C-150 °C. Preferably, the roll heat treatment is performed at a temperature of 50 °C-70 °C.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0034] Before further describing the present disclosure, certain terms used in the specification, embodiments, and appended claims are collected in the following paragraphs. The definitions listed herein should be read and understood by those skilled in the art in light of the rest of the present disclosure. Unless otherwise defined, all technical and scientific terms used herein have the same meanings as commonly understood by those ordinarily skilled in the art to which the present disclosure belongs.

[0035] As used herein, the term “about”, when referring to a value, means including variations thereof, such as ±10%, ±5%, ±1% or ±0.1% of a specific value.

[0036] As used herein, the term “substantially the same”, when referring to two values, means that the difference between the two values is less than 10%, 5% or 1% of an average of the two values.

[0037] As used herein, the term “polyolefin” may be a polyolefin homopolymer (i.e., a single type of polyolefin polymer), a polyolefin copolymer, or a polyolefin blend.

[0038] As used herein, the term “blend” refers to a physical mixture of two or more homopolymers, copolymers, or homopolymers and copolymers having different molecular structures. Specifically, the blend may include different polymers, i.e., at least two polymers having different chemical properties (for example, polyethylene, polypropylene, and/or ethylene-propylene copolymer having different chemical properties); and/or polymers that are chemically identical but have different characteristics (for example, two different polyethylenes having different characteristics (such as density, molecular weight, molecular weight distribution, rheology, and additive (composition and/or percentage))).

[0039] As used herein, the term “machine direction”, also referred to as MD, refers to a direction in which the machine is operated.

[0040] As used herein, the term “transverse direction”, also referred to as TD, refers to a direction perpendicular to the direction in which the machine is operated.

[0041] The first aspect of the present disclosure provides a microporous separator for a lithium battery. The microporous separator is a porous polyolefin membrane. In the microporous separator, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of 2 million to 5 million is 5 mol%-8 mol%, preferably 5 mol%-7 mol%, and more preferably 6 mol%-7 mol%. The microporous separator has a crystallinity at a first-time temperature rise and a crystallinity at a second-time temperature rise, where the crystallinity at the first-time temperature rise is ≥ 65%, and a difference between the crystallinity at the first-time temperature rise and the crystallinity at the second-time temperature rise is > 15%.

[0042] In the microporous separator, the quantity proportion of the polyolefin chain segment components with a weight-average molecular weight of 2 million to 5 million can be any one of 5 mol%, 5.1 mol%, 5.2 mol%, 5.3 mol%, 5.4 mol%, 5.5 mol%, 5.6 mol%, 5.7 mol%, 5.8 mol%, 5.9 mol%, 6 mol%, 6.1 mol%, 6.2 mol%, 6.3 mol%, 6.4 mol%, 6.5 mol%, 6.6 mol%, 6.7 mol%, 6.8 mol%, 6.9 mol%, 7 mol%, 7.1 mol%, 7.2 mol%, 7.3 mol%, 7.4 mol%, 7.5 mol%, 7.6 mol%, 7.7 mol%, 7.8 mol%, 7.9 mol%, or 8 mol%, or a range formed by any two thereof.

[0043] In the present disclosure, the porous polyolefin membrane refers to a porous separator prepared using a polyolefin resin. The polyolefin resin can be any polyolefin resin commonly used in the art for preparing microporous separators for lithium batteries, and can be, for example, selected from polyethylene (including, for example, LDPE, LLDPE, HDPE, UHDPE), polypropylene, polybutene, polymethylpentene, copolymers thereof, and blends thereof, among which at least one of polyethylene and polypropylene is preferred.

[0044] In some specific embodiments of the present disclosure, in order to further improve the memory duration and the puncture strength, in the microporous separator, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of greater than 5 million and not more than 9 million is 0.5 mol%-2 mol%, preferably 0.5 mol%-1.5 mol%.

[0045] In the microporous separator, the quantity proportion of the polyolefin chain segment components with a weight-average molecular weight of greater than 5 million and not more than 9 million can be any one of 0.5 mol%, 0.6 mol%, 0.7 mol%, 0.8 mol%, 0.9 mol%, 1 mol%, 1.1 mol%, 1.2 mol%, 1.3 mol%, 1.4 mol%, 1.5 mol%, 1.6 mol%, 1.7 mol%, 1.8 mol%, 1.9 mol%, or 2 mol%, or a range formed by any two thereof.

[0046] In some specific embodiments of the present disclosure, the crystallinity at the first-time temperature rise of the microporous separator is higher than the crystallinity at the second-time temperature rise. In some specific embodiments, the crystallinity at the first-time temperature rise of the microporous separator is 65%-80%, preferably 68%-75%. In some specific embodiments, the crystallinity at the second-time temperature rise of the microporous separator is ≤ 50%, preferably 35%-50%, and more preferably 45%-50%. In some specific embodiments, the difference between the crystallinity at the first-time temperature rise and the crystallinity at the second-time temperature rise is ≥ 16%, preferably 16%-45%, and more preferably 18%-30%.

[0047] In the microporous separator, the crystallinity at the first-time temperature rise can be, for example, any one of 65%, 66%, 67%, 68%, 69%, 70%, 71%, 72%, 73%, 74%, 75%, 76%, 77%, 78%, 79%, or 80%, or a range formed by any two thereof; and the crystallinity at the second-time temperature rise can be, for example, any one of 35%, 36%, 37%, 38%, 39%, 40%, 41%, 42%, 43%, 44%, 45%, 46%, 47%, 48%, 49%, or 50%, or a range formed by any two thereof. The difference between the crystallinity at the first-time temperature rise and the crystallinity at the second-time temperature rise can be, for example, any one of 16%, 17%, 20%, 22%, 25%, 27%, 30%, 32%, 35%, 37%, 40%, 42%, or 45%, or a range formed by any two thereof.

[0048] According to the present disclosure, the polyolefin resin may be used as long as it is capable of producing the microporous separator for a lithium battery required by the present disclosure. In order to provide a microporous separator having more excellent puncture strength, deformation memory effect duration, and compression set, preferably, in the polyolefin resin, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of 2 million to 5 million is 5 mol%-9 mol%, preferably 5 mol%-8 mol%, and more preferably 6 mol%-8 mol%. Preferably, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of greater than 5 million and not more than 9 million is 0 mol%-2 mol%, preferably 0.2 mol%-1.5 mol%.

[0049] In the polyolefin resin, the quantity proportion of the polyolefin chain segment components with a weight-average molecular weight of 2 million to 5 million can be any one of 5 mol%, 5.5 mol%, 6 mol%, 6.5 mol%, 7 mol%, 7.3 mol%, 7.5 mol%, 8 mol%, 8.5 mol%, or 9 mol%, or a range formed by any two thereof.

[0050] In the polyolefin resin, the quantity proportion of the polyolefin chain segment components with a weight-average molecular weight of greater than 5 million and not more than

9 million can be any one of 0 mol%, 0.2 mol%, 0.5 mol%, 1 mol%, 1.3 mol%, 1.5 mol%, 1.8 mol%, or 2 mol%, or a range formed by any two thereof.

[0051] In some specific embodiments of the present disclosure, preferably, the polyolefin resin has a molecular weight distribution of 3-6, preferably 3.5-5.5, and more preferably 4.5-5.

[0052] In some specific embodiments of the present disclosure, the microporous separator satisfies one or a combination of more of the following:

[0053] a) a puncture strength per unit thickness of the microporous separator is ≥ 85 gf/μm, preferably ≥ 90 gf/μm;

[0054] b) a deformation memory effect duration of the microporous separator in a thickness direction is 0 s-200 s, preferably 0 s-100 s, more preferably 0 s-50 s, more preferably 0 s-20 s, and most preferably 0 s-10 s;

[0055] c) a compression set of the microporous separator is ≤ 2.5%, preferably ≤ 1.8%, ≤ 1.5%, ≤ 1% or ≤ 0.7%; and

[0056] d) a thickness of the microporous separator is 1 μm-30 μm, preferably 4 μm-12 μm.

[0057] In order to obtain a microporous separator having more excellent puncture strength, deformation memory effect duration, and compression set, the microporous separator of the present disclosure is preferably a separator prepared by a wet process. That is, the microporous separator has a three-dimensional network structure in which a plurality of fibrils are interlaced and connected, and the plurality of fibrils are interlaced and connected to form pores. Herein, the fibrils in the microporous separator are obtained by stretching and orienting the polymer during film preparation, and the pores are formed after an extraction agent extracts the plasticizer from the film.

[0058] The second aspect of the present disclosure provides a preparation method of a microporous separator for a lithium battery, the preparation method including the following steps:

[0059] (a) melt-kneading a mixture containing a polyolefin resin and a plasticizer to form a melt;

[0060] (b) extruding the melt obtained in step (a) and solidifying the extruded melt into a thick sheet;

[0061] (c) stretching the thick sheet obtained in step (b) in a machine direction (MD) and in a transverse direction (TD) perpendicular to the machine direction to obtain a stretched body;

[0062] (d) removing the plasticizer from the stretched body obtained in step (c) to obtain a separator precursor; and

[0063] (e) heat-setting the separator precursor obtained in step (d) to obtain the microporous separator for a lithium battery;

[0064] where the crystallinity of the polyolefin resin is ≤ 50%, preferably 35%-50%, and more preferably 40%-50%; and in the polyolefin resin, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of 2 million to 5 million is 5 mol%-9 mol%, preferably 5 mol%-8 mol%, and more preferably 6 mol%-8 mol%.

[0065] In the polyolefin resin, a crystallinity of the polyolefin resin can be, for example, any one of 20%, 25%, 30%, 35%, 40%, 41%, 42%, 43%, 44%, 45%, 46%, 47%, 48%, 49%, or 50%, or a range formed by any two thereof.

[0066] In the polyolefin resin, the quantity proportion of the polyolefin chain segment components with a weight-average molecular weight of 2 million to 5 million can be any one of 5 mol%, 5.5 mol%, 6 mol%, 6.5 mol%, 7 mol%, 7.3 mol%, 7.5 mol%, 8 mol%, 8.5 mol%, or 9 mol%, or a range formed by any two thereof.

[0067] According to the present disclosure, by treating the mixture containing appropriate polyolefin resin and plasticizer according to the preparation method of the present disclosure, a microporous separator having excellent puncture strength, deformation memory effect duration, and compression set can be obtained, which is suitable for applications in lithium batteries.

[0068] In the present disclosure, the polyolefin resin can be any polyolefin resin commonly used in the art for preparing microporous separators for lithium batteries, and can be, for example, selected from polyethylene (including, for example, LDPE, LLDPE, HDPE, UHDPE), polypropylene, polybutene, polymethylpentene, copolymers thereof, and blends thereof, among which polyethylene and/or polypropylene is preferred.

[0069] According to the present disclosure, the polyolefin resin as a raw material can be a single type of polyolefin resin or a mixture of multiple types of polyolefin resins. When multiple types of polyolefin resins are used, each polyolefin resin must satisfy the physical properties required by the present disclosure.

[0070] From the viewpoint of better film-forming uniformity and memory duration, regardless of whether a single type of polyolefin or a mixture of multiple types of polyolefins is used, the crystallinity of one or two or more polyolefin resins contained in the polyolefin resin is ≤ 50%.

[0071] In the present disclosure, the plasticizer is preferably a non-volatile solvent capable of forming a homogeneous solution above the melting point of the polyolefin resin when mixed with the polyolefin resin, and can be, for example, paraffin oil, diethyl phthalate, or palm oil, preferably paraffin oil having a kinematic viscosity at 40 °C of 35 mm^2/s-120 mm^2/s, and further preferably paraffin oil having a kinematic viscosity at 40 °C of 40 mm^2/s-55 mm^2/s. The testing method for kinematic viscosity is based on GB/T 265.

[0072] According to the present disclosure, in step (a), a weight ratio of the polyolefin resin to the plasticizer is preferably between 15:85 and 35:65, more preferably between 18:82 and 23:77. The weight ratio of the polyolefin resin to the plasticizer can specifically be any one of 15:85, 16:84, 17:83, 18:82, 19:81, 20:80, 21:79, 22:78, or 23:77, or a range formed by any two thereof. By using the above weight ratio of the polyolefin resin to the plasticizer, the comprehensive performance of the microporous separator can be improved.

[0073] In order to further improve the puncture strength, deformation memory effect duration, and compression set of the microporous separator, preferably, in the polyolefin resin, the quantity proportion of polyolefin chain segment components with a weight-average molecular weight of greater than 5 million and not more than 9 million is 0 mol%-2 mol%, preferably 0.2 mol%-1.5 mol%.

[0074] In some specific embodiments of the present disclosure, preferably, the polyolefin resin has a molecular weight distribution of 3-6, preferably 3.5-5.5, and more preferably 4.5-5.

[0075] According to the present disclosure, in step (a), any existing method capable of forming a melt from the mixture can be used for the treatment, for example, an extruder can be used to perform the melt-kneading. As some preferred embodiments, the parameters of the extruder include an extruder temperature of 150 °C-260 °C, preferably 180 °C-250 °C, and an extruder screw speed of 60 r/min-125 r/min, preferably 70 r/min-90 r/min.

[0076] According to the present disclosure, in step (b), the method of extruding the melt and solidifying the extruded melt into a thick sheet need only be capable of forming a thick sheet having a desired thickness.

[0077] The inventors of the present disclosure have also found through in-depth research that controlling the parameters of the extrusion step in the separator manufacturing process helps to control the compression resistance of the separator. Under the condition of fixed extrusion quantity, the thick sheet in step (b) can be achieved by a combination of a die lip opening and a casting speed. Assuming that a die swell ratio of the polymer melt is k, a flow rate of the melt upon exiting the die is v, a die lip opening is a, a casting speed is b, and a thickness of the thick sheet is h, then $h = a * k * (v / b)$, $kv = (h / a) * b$, and a swelling ratio is defined as $A = h / a$, then the smaller A is, the worse the compression resistance of the separator is. In cases where the mixture is extruded through a die lip of a die head and attached onto a casting roll to be cooled and solidified to form the thick sheet, the die lip opening is a, the thickness of the thick sheet is h, and the swelling ratio is defined as $A = h / a$, where A is preferably controlled to be greater than or equal to 1.2, for example, 1.2-1.5.

[0078] In the present disclosure, the swelling ratio A can be controlled jointly by a roll speed of the casting roll, the flow rate of the melt upon exiting the die, and the die lip opening, and the flow rate of the melt upon exiting the die can be comprehensively adjusted by the extruder screw speed and a temperature of the die head.

[0079] Further, the roll speed of the casting roll can be 3 m/min-8 m/min, preferably 5 m/min-6 m/min; the temperature of the die head can be 160 °C-240 °C, preferably 180 °C-220 °C. Preferably, the temperature of the casting roll can be 20 °C-60 °C.

[0080] Further, the die lip opening can be 0.5-4 mm, preferably 0.8 mm-3 mm.

[0081] Further, the thickness of the thick sheet can be 1-5 mm, preferably 1.2 mm-2 mm.

[0082] According to the present disclosure, in step (c), the thick sheet is stretched to obtain a stretched body. The stretching includes stretching in the MD and stretching in the TD. Specifically, the stretching in the MD can be performed before the stretching in the TD, or the stretching in the TD can be performed before the stretching in the MD, or the stretching in the MD and the stretching in the TD can be performed simultaneously. Preferably, the stretching in the MD is performed before the stretching in the TD. In addition, the stretching in the MD and the stretching in the TD described above can each independently be single-stage stretching or multi-stage stretching of two or more stages. From the viewpoint of stretching uniformity, mechanical strength, and prevention of membrane breakage, multi-stage stretching is preferred.

[0083] In some specific embodiments of the present disclosure, in step (c), the stretching in the MD is performed at 80 °C-120 °C with a stretching ratio of 4-7, and the stretching in the TD is performed at 90 °C-135 °C with a stretching ratio of 4-15. Preferably, the stretching in the MD is performed at 95 °C-110 °C with a stretching ratio of 6-8, and the stretching in the TD is performed at 105 °C-125 °C with a stretching ratio of 6-10.

[0084] According to the present disclosure, in step (d), the plasticizer can be removed from the stretched body by any method, and it is preferred to remove the plasticizer from the stretched body using an extraction agent. As the extraction agent, a reagent that is a poor solvent for the polyolefin resin and a good solvent for the plasticizer is preferred. In addition, the extraction agent preferably has a boiling point lower than the melting point of the porous polyolefin resin membrane. The extraction agent can be an alkane-based extraction agent, preferably a halogenated hydrocarbon-based extraction agent, with dichloromethane being most preferred.

[0085] As a method of removing the plasticizer from the stretched body using an extraction agent, the plasticizer in the stretched body can be removed by means of circulation feed of the extraction agent. Preferably, the circulation feed rate of the extraction agent is 1 m^3/h-5 m^3/h.

After the extraction, the stretched body is heated for drying optionally by one or more of a hot roll, a heating plate, and hot air, and a drying temperature is preferably 20 °C-150 °C.

[0086] In some preferred embodiments of the present disclosure, after step (d) and before the heat-setting treatment in step (e), a further stretching treatment can further be included, preferably a further stretching treatment in the TD (also referred to as TD secondary stretching). Preferably, the TD secondary stretching is performed at 120 °C-140 °C with a stretching ratio of 1-2; and preferably, the TD secondary stretching is performed at 130 °C-140 °C with a stretching ratio of 1.1-1.5. The TD secondary stretching described above can be single-stage stretching or multi-stage stretching of two or more stages. From the viewpoint of stretching uniformity, mechanical strength, and prevention of membrane breakage, multi-stage stretching is preferred.

[0087] According to the present disclosure, the method and conditions of the heat-setting treatment in step (e) are not particularly limited, for example, the heat-setting can be at least one selected from oven heat treatment and roll heat treatment. Preferably, the oven heat treatment is performed at a temperature of 120 °C-150 °C; and preferably, the roll heat treatment is performed at a temperature of 50 °C-70 °C. In addition, the oven heat treatment can last for 2 s-30 s, and the roll heat treatment can last for 5 s-60 s.

[0088] By adopting the above preparation method for the preparation, in the obtained microporous separator, the quantity proportion of the polyolefin chain segment components with a weight-average molecular weight of 2 million to 5 million is 5 mol%-8 mol%, preferably 5 mol%-7 mol%, and more preferably 6 mol%-7 mol%, and the microporous separator has the crystallinity at the first-time temperature rise of ≥ 65% and the crystallinity at the second-time temperature rise of < 50%. Preferably, in the microporous separator, the quantity proportion of the polyolefin chain segment components with a weight-average molecular weight of greater than 5 million and not more than 9 million is 0.5 mol%-2 mol%, preferably 0.5 mol%-1.5 mol%.

[0089] In some specific embodiments of the present disclosure, the microporous separator satisfies one or a combination of more of the following:

[0090] a) the puncture strength per unit thickness of the microporous separator is ≥ 85 gf/μm, preferably ≥ 90 gf/μm, and more preferably ≥ 100 gf/μm;

[0091] b) the deformation memory effect duration of the microporous separator in the thickness direction is 0 s-200 s, preferably 0 s-100 s, more preferably 0 s-50 s, more preferably 0 s-20 s, and most preferably 0 s-10 s;

[0092] c) the compression set of the microporous separator is ≤ 2.5%, preferably ≤ 1.8%, more preferably ≤ 1.5%, and most preferably ≤ 1%; and

[0093] d) the thickness of the microporous separator is 1 μm-30 μm, preferably 4 μm-12 μm.

[0094] A third aspect of the present disclosure provides a microporous separator for a lithium battery obtained by the preparation method of the second aspect of the present disclosure described above.

[0095] In the following Examples and Comparative Examples, the testing methods for relevant parameters are as follows.

[0096] (1) The quantity proportions of the polyolefin chain segments with a weight-average molecular weight of 2 million to 5 million and the polyolefin chain segments with a weight-average molecular weight of greater than 5 million and not more than 9 million were measured in accordance with GB/T 36214.4-2018.

[0097] (2) The compression set was measured using a TMA (Thermomechanical Analyzer, Waters, model Q400).

[0098] (3) The crystallinity at the first-time temperature rise and the crystallinity at the second-time temperature rise of the microporous separator were measured using a differential scanning calorimeter, and the testing method was as follows: the separator was heated for the first time at 10 °C/min to above the melting point of the polyolefin and kept at that temperature for 3 min to obtain the crystallinity at the first-time temperature rise of the polyolefin, then cooled at 10 °C/min to ≤ 40 °C and kept at that temperature for 3 min, and then heated for the second time at 10 °C/min to above the melting point of the polyolefin to obtain the crystallinity at the second-time temperature rise of the polyolefin. Herein, the crystallinity at the first-time temperature rise of the polyolefin separator is obtained by dividing the melting enthalpy of the polyolefin measured during the first heating process by the standard melting enthalpy of the polyolefin; and the crystallinity at the second-time temperature rise of the polyolefin separator is obtained by dividing the melting enthalpy of the polyolefin measured during the second heating process by the standard melting enthalpy of the polyolefin. In the measurement, the heating temperatures were both 200 °C. For polyethylene, the standard melting enthalpy of polyethylene is calculated as 293 J/g, and for polypropylene, the standard melting enthalpy of polypropylene is calculated as 209 J/g.

[0099] In addition, the crystallinity of the raw material was measured using the above testing method for the crystallinity at the second-time temperature rise.

[0100] (4) The puncture strength was measured with reference to GB-T 36363-2018. Puncture strength per unit thickness = puncture strength/membrane thickness.

[0101] (5) The deformation memory effect duration was measured according to the following method: A loading force of 500 mN was applied to the microporous separator in the thickness direction, and after the force was kept constant for 300 s, the force value was decreased at a rate

of 30 mN/min. The time difference between the time point when the compression loading force of the microporous separator is maximum and the time point when the compression deformation of the microporous separator reaches the lowest point is the deformation memory effect duration. The deformation memory effect duration reflects the deformation response speed of the microporous membrane in the thickness direction; especially after the battery is squeezed or undergoes a collision process, a short deformation memory effect duration (rapid recovery) enables timely recovery, maintaining close contact with the positive and negative electrode sheets and avoiding direct contact between the positive and negative electrode sheets to ensure battery safety. A separator having a long deformation memory effect duration still undergoes deformation after the external force is removed, and the positive and negative electrode sheets become loose and displaced to come into contact, resulting in a short circuit, thereby causing safety problems.

[0102] Example 1

[0103] A polyethylene resin (UHDPE, with relevant properties in Table 1, prepared by KOREA PETROCHEMICAL IND. CO., LTD.) and a plasticizer (paraffin oil having a kinematic viscosity at 40 °C of 45 mm^2/s) were mixed at a weight ratio of 20:80, and melt-kneaded by an extruder to form a melt, where an extruder temperature was 220 °C and an extruder screw speed was 80 r/min.

[0104] The above melt was cooled and solidified by a casting roll to form a thick sheet, where a temperature of the casting roll was 25 °C, and other parameters are listed in the process section in Table 1. The obtained thick sheet was stretched in the MD and subjected to primary stretching in the TD, with specific conditions listed in Table 1.

[0105] Dichloromethane was used as an extraction agent to remove the plasticizer (paraffin oil), and then drying was performed under the action of hot air at 55 °C. Thereafter, secondary stretching in the TD was performed, followed by a heat-setting treatment (roll heat treatment) in the MD, with specific conditions listed in Table 1, thereby obtaining a microporous separator for a lithium battery.

[0106] Examples 2 to 18 and Comparative Examples 1 to 4

[0107] Microporous separators were prepared with reference to the method of Example 1. The differences between the preparation methods for the microporous separators specifically adopted in Examples 2 to 18 and Comparative Examples 1 to 4 and that of Example 1 are detailed in Table 1, and the parameters not shown in Table 1 are the same as those of Example 1.

[0108] Table 1

	Microporous separator					Raw material				Process			
	Proportion A/%	Proportion B/%	Crystallinity at first-time temperature rise/%	Crystallinity at second-time temperature rise/ %	Difference between crystallinity at first-time temperature rise and crystallinity at second-time temperature rise	Proportion A/%	Proportion B/%	Crystallinity /%	Molecular weight distribution	Roll speed of casting roll /m/min	Die lip opening (a)/mm	Thickness of thick sheet (h)/mm	Swelling ratio A
Example 1	6.2	1	65	45	20	7	1.3	45	4.5	6	1.2	1.5	1.3
Example 2	6.2	1	68	45	23	7	1.3	45	4.5	6	1.2	1.5	1.3
Example 3	6.2	1	72	45	27	7	1.3	45	4.5	6	1.2	1.5	1.3
Example 4	6.2	1	75	45	30	7	1.3	45	4.5	6	1.2	1.5	1.3
Example 5	6.2	1	80	45	35	7	1.3	45	4.5	6	1.2	1.5	1.3
Example 6	6.2	1	72	35	37	7	1.3	35	4.5	6	1.2	1.5	1.3
Example 7	6.2	1	72	30	42	7	1.3	30	4.5	6	1.2	1.5	1.3
Example 8	6.2	1	80	50	30	7	1.3	50	4.5	6	1.2	1.5	1.3
Example 9	6.2	1	80	30	50	7	1.3	30	4.5	6	1.2	1.5	1.3
Example 10	6.2	1	72	50	22	7	1.3	50	4.5	6	1.2	1.5	1.3
Example 11	6.2	1	72	45	27	7	1.3	45	5	6	1.2	1.5	1.3
Example 12	6.2	1.8	72	45	27	7	2.1	45	4.5	6	1.2	1.5	1.3
Example 13	6.2	1.5	72	45	27	7	1.8	45	4.5	6	1.2	1.5	1.3
Example 14	6.2	0.5	72	45	27	7	0.2	45	4.5	6	1.2	1.5	1.3
Example 15	5.3	1	72	45	27	6	1.3	45	4.5	6	1.2	1.5	1.3
Example 16	7.9	1	72	45	27	9	1.3	45	4.5	6	1.2	1.5	1.3
Example 17	6.2	1	67	50	17	7	1.3	50	4.5	6	1.2	1.5	1.3
Example 18	6.2	1	72	45	27	7 7.3	1.3 1.5	50, 70wt% 40, 30wt%	4.5 4.5	6	1.2	1.5	1.3
Example 19	6.2	1	72	55	17	7	1.3	55	4.5	6	1.2	1.5	1.3
Comparative Example 1	6.2	1	60	45	15	7	1.3	45	4.5	6	1.2	1.5	1.3
Comparative Example 2	6.2	1	70	55	15	7	1.3	55	4.5	6	1.2	1.5	1.3
Comparative Example 3	4.4	1	72	45	27	4.8	1.3	45	4.5	6	1.2	1.5	1.3
Comparative Example 4	9	1	72	45	27	9.5	1.3	45	4.5	6	1.2	1.5	1.3

Table 1 (Continued)

	MD stretching		TD primary stretching		TD secondary stretching		MD heat-setting		Thickness /μm	Puncture strength per unit thickness /gf/um	Deformation memory effect duration /s	Compression deformation rate /%
	Stretching temperature /°C	Stretching ratio	Stretching temperature /°C	Stretching ratio	Stretching temperature /°C	Stretching ratio	Heat-setting temperature /°C	Heat-setting ratio				
Example 1	95	6.5	110	7	133	1.4	135	0.94	11	92	20	1.3
Example 2	95	6.5	110	8	133	1.4	135	0.94	11	95	8	0.98
Example 3	95	7	110	8	133	1.4	135	0.96	11	98	5	0.48
Example 4	95	7	110	9	133	1.4	135	0.97	11	101	3	0.4
Example 5	95	7.5	110	10	133	1.4	135	0.96	11	112	45	0.28
Example 6	95	7	110	8	133	1.4	135	0.96	11	98	48	0.5
Example 7	95	7	110	8	133	1.4	135	0.96	11	86	62	0.56
Example 8	95	7.5	110	10	133	1.4	135	0.97	11	128	17	0.3
Example 9	95	7.5	110	10	133	1.4	135	0.95	11	93	55	0.3
Example 10	95	7	110	8	133	1.4	135	0.96	11	123	4	0.4
Example 11	95	7	110	8	133	1.4	135	0.96	11	98	6	0.51
Example 12	95	7	110	8	133	1.4	135	0.96	11	108	11	0.48
Example 13	95	7	110	8	133	1.4	135	0.96	11	105	5	0.46
Example 14	95	7	110	8	133	1.4	135	0.96	11	98	5	0.54
Example 15	95	7	110	8	133	1.4	135	0.96	11	96	10	0.6
Example 16	95	7	110	8	133	1.4	135	0.96	11	98	16	0.33
Example 17	95	6.2	110	7	133	1.4	135	0.96	11	120	42	0.52
Example 18	95	7	110	8	133	1.4	135	0.96	11	98	5	0.5
Example 19	95	7	110	8	133	1.4	135	0.96	11	110	112	0.63
Comparative Example 1	95	5	110	5	133	1.4	135	0.93	11	72	231	2.8
Comparative Example 2	95	6.8	110	8	133	1.4	135	0.94	11	106	226	0.82
Comparative Example 3	95	7	110	8	133	1.4	135	0.96	11	70	38	0.64
Comparative Example 4	95	7	110	8	133	1.4	135	0.96	11	103	201	0.3

[0109] In the table, “Proportion A” represents the quantity proportion of polyolefin chain segments with a weight-average molecular weight of 2 million to 5 million, and “Proportion B” represents the quantity proportion of polyolefin chain segments with a weight-average molecular weight of greater than 5 million and not more than 9 million. In Example 18, the raw material was obtained by mixing two polyethylenes having crystallinities of 50% and 40% at a weight ratio of 7:3.

[0110] From the comparison between Examples 1-18 and Comparative Examples 1 and 2 in Table 1, it can be seen that by using the method of the present disclosure to control the quantity of polyolefin chain segments with a weight-average molecular weight of 2 million to 5 million as well as the crystallinities at the first-time temperature rise and the second-time temperature rise of the microporous separator, a microporous separator having good puncture strength, deformation memory effect duration, and compression set can be obtained; whereas the crystallinity at the first-time temperature rise of Comparative Example 1 did not satisfy the requirements of the present disclosure, and the obtained microporous separator had poor puncture strength, deformation memory effect duration, and compression set; the difference between the crystallinities at the first-time temperature rise and the second-time temperature rise of Comparative Example 2 did not satisfy the requirements of the present disclosure, and the obtained microporous separator had poor deformation memory effect duration; and the quantity proportions of polyolefin chain segments with a weight-average molecular weight of 2 million to 5 million of Comparative Examples 3 and 4 did not satisfy the requirements of the present disclosure, and the obtained microporous separators had poor puncture strength or deformation memory effect duration.

[0111] From the comparison of Examples 3 and 12-14, it can be seen that when the quantity proportion of polyolefin chain segments with a weight-average molecular weight of greater than 5 million and not more than 9 million in the microporous separator was 0.5 mol%-1.5 mol%, the deformation memory effect duration of the microporous separator could be further reduced.

[0112] From the comparison of Examples 3, 15, and 16, it can be seen that when the quantity proportion of polyolefin chain segments with a weight-average molecular weight of 2 million to 5 million in the microporous separator was 5 mol%-7 mol%, the deformation memory effect duration of the microporous separator could be further reduced.

[0113] From the comparison of Examples 1-5, it can be seen that when the crystallinity at the first-time temperature rise of the microporous separator was 68%-75%, both a good compression set and an excellent deformation memory effect duration could be achieved.

[0114] From the comparison of Examples 3 and 6-9, it can be seen that when the crystallinity at the second-time temperature rise of the microporous separator was 45%-50%, higher puncture strength could be achieved while having both good deformation memory effect duration and compression set.

[0115] Unless otherwise specified in the context, the singular forms “a”, “an”, and “the” in this specification and appended claims include the plural forms. Unless otherwise defined, all technical and scientific terms used herein have the same meanings as those commonly understood by those ordinarily skilled in the art. In addition to the specific order disclosed, the methods described herein can be performed in any logically possible order.

[0116] The representative examples are intended to assist in illustrating the present disclosure, and are not intended for or should not be construed as limiting the scope of the present disclosure. In fact, in addition to those shown and described herein, various modifications of the present disclosure and many other embodiments thereof will become apparent to those skilled in the art, including the embodiments and references to the scientific and patent documents cited herein. The embodiments contain important additional information, examples, and guidance that may be employed in the practice of the present disclosure in its various embodiments and equivalents.

CLAIMS

1. A microporous separator for a lithium battery, wherein the microporous separator is a porous polyolefin membrane, in the microporous separator, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of 2 million to 5 million is 5 mol%-8 mol%, preferably 5 mol%-7 mol%, and more preferably 6 mol%-7 mol%, and the microporous separator has a crystallinity at a first-time temperature rise and a crystallinity at a second-time temperature rise, wherein the crystallinity at the first-time temperature rise is ≥ 65%, and a difference between the crystallinity at the first-time temperature rise and the crystallinity at the second-time temperature rise is > 15%.

2. The microporous separator for a lithium battery according to claim 1, wherein in the microporous separator, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of greater than 5 million and not more than 9 million is 0.5 mol%-2 mol%, preferably 0.5 mol%-1.5 mol%.

3. The microporous separator for a lithium battery according to claim 1 or 2, wherein the crystallinity at the first-time temperature rise is 65%-80%, preferably 68%-75%; and/or

the crystallinity at the second-time temperature rise is ≤ 50%, preferably 35%-50%, and more preferably 45%-50%; and/or

the difference between the crystallinity at the first-time temperature rise and the crystallinity at the second-time temperature rise is ≥ 16%, preferably 16%-45%, and more preferably 18%-30%.

4. The microporous separator for a lithium battery according to any one of claims 1 to 3, wherein the microporous separator satisfies one or a combination of more of the following:

a) a puncture strength per unit thickness of the microporous separator is ≥ 85 gf/μm, preferably ≥ 90 gf/μm;

b) a deformation memory effect duration of the microporous separator in a thickness direction is 0 s- 200 s, preferably 0 s-100 s, more preferably 0 s-50 s, more preferably 0 s-20 s, and most preferably 0 s-10 s;

c) a compression set of the microporous separator is ≤ 2.5%, preferably ≤ 1.5%, more preferably ≤ 1%, and further preferably ≤ 0.7%; and

d) a thickness of the microporous separator is 1 μm-30 μm, preferably 4 μm-12 μm.

5. The microporous separator for a lithium battery according to any one of claims 1 to 4, wherein the microporous separator is a separator made from a polyolefin resin, wherein the polyolefin resin has a molecular weight distribution of 3-6, preferably 3.5-5.5, and more preferably 4.5-5.

6. The microporous separator for a lithium battery according to claim 5, wherein in the polyolefin resin, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of 2 million to 5 million is 5 mol%-9 mol%, preferably 5 mol%-8 mol%, and more preferably 6 mol%-8 mol%; and/or

in the polyolefin resin, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of greater than 5 million and not more than 9 million is 0 mol%-2 mol%, preferably 0.2 mol%-1.5 mol%.

7. A preparation method of a microporous separator for a lithium battery, wherein the preparation method comprises following steps:

(a) melt-kneading a mixture comprising a polyolefin resin and a plasticizer to form a melt;

(b) extruding the melt obtained in step (a) and solidifying the extruded melt into a thick sheet;

(c) stretching the thick sheet obtained in step (b) in a machine direction (MD) and in a transverse direction (TD) perpendicular to the machine direction to obtain a stretched body;

(d) removing the plasticizer from the stretched body obtained in step (c) to obtain a separator precursor; and

(e) heat-setting the separator precursor obtained in step (d) to obtain the microporous separator for a lithium battery;

wherein a crystallinity of the polyolefin resin is ≤ 50%, preferably 35%-50%, and more preferably 40%-50%; and in the polyolefin resin, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of 2 million to 5 million is 5 mol%-9 mol%, preferably 5 mol%-8 mol%, and more preferably 6 mol%-8 mol%.

8. The preparation method according to claim 7, wherein in step (a), in the polyolefin resin, a quantity proportion of polyolefin chain segment components with a weight-average molecular weight of greater than 5 million and not more than 9 million is 0 mol%-2 mol%, preferably 0.2 mol%-1.5 mol%; and/or

the polyolefin resin has a molecular weight distribution of 3-6, preferably 3.5-5.5, and more preferably 4.5-5; and/or

the polyolefin resin is selected from polyethylene, polypropylene, polybutene, polymethylpentene, copolymers thereof, and blends thereof; and preferably, the polyethylene is selected from low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), and ultrahigh density polyethylene (UHDPE).

9. The preparation method according to claim 7 or 8, wherein in step (a), an extruder is used to perform the melt-kneading, wherein parameters of the extruder comprise an extruder temperature of 150 °C-260 °C and an extruder screw speed of 60 r/min -125 r/min; and/or

a weight ratio of the polyolefin resin to the plasticizer is between 15:85 and 35:65, preferably between 18:82 and 23:77.

10. The preparation method according to any one of claims 7 to 9, wherein in step (b), the mixture is extruded through a die lip of a die head and attached onto a casting roll to be cooled and solidified to form the thick sheet, wherein the die lip has an opening a, the thick sheet has a thickness h, and a swelling ratio is defined as A = h / a, A being controlled to be greater than or equal to 1.2; and

further, a roll speed of the casting roll is 3 m/min -8 m/min, and a temperature of the die head is 160 °C-240 °C.

11. The preparation method according to any one of claims 7 to 10, wherein in step (c), the stretching in the MD is performed at 80 °C-120 °C with a stretching ratio of 4-7, and the stretching in the TD is performed at 90 °C-135 °C with a stretching ratio of 4-15.

12. The preparation method according to any one of claims 7 to 11, wherein in step (e), the heat-setting is at least one selected from oven heat treatment and roll heat treatment, wherein preferably the oven heat treatment is performed at a temperature of 120 °C-150 °C, and/or the roll heat treatment is performed at a temperature of 50 °C-70 °C.