

STRETCHED STYRENE-BASED RESIN MOLDINGS AND A PROCESS FOR PRODUCTION THEREOF

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to stretched styrene-based resin moldings and a process for the production thereof. More particularly, it is concerned with stretched styrene-based resin moldings which are excellent in heat resistance, solvent resistance, chemical resistance, electric insulating properties, mechanical strength, modulus of elasticity, dimensional stability and transparency, and consequently can be used in various applications; and a process for efficiently producing these stretched styrene-based resin moldings.

2. Description of the Related Art

The styrene polymers which have been hitherto used are those having atactic configuration as obtained by radical polymerization. However, improvement in physical properties by stretching such atactic styrene polymers cannot be expected.

Styrene polymers having isotactic configuration are also known, and an attempt to stretch them has been made (Kobunshi Kagaku (Polymer Chemistry), 21, 206 (1964)). However, a satisfactory stretching effect in such isotactic styrene polymers cannot be obtained because the rate of crystallization is slow and the main chain composed of carbon-carbon bonds in the styrene polymers has spiral

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structure.

The present inventors' research has found that stretched moldings having excellent physical properties can be obtained if styrene-based resins of high syndiotacticity as developed by the present inventors' group (Japanese Patent Application Laid-Open No. 104818/1987) are stretched.

SUMMARY OF THE INVENTION

An object of the present invention is to provide stretched styrene-based resin moldings which are excellent in heat resistance, solvent resistance, chemical resistance, mechanical strength, modulus of elasticity, dimensional stability and transparency.

Another object of the present invention is to provide stretched styrene-based resin moldings which are excellent in electric insulating properties, for instance, a breakdown voltage at 25°C of at least 30 kV/mm.

Still another object of the present invention is to provide a process for efficiently producing these stretched styrene-based resin moldings.

The present invention relates to a stretched styrene-based resin molding as obtained by subjecting a styrene-based resin having mainly syndiotactic configuration and a weight average molecular weight of at least 50,000 to uniaxial stretching to at least two times the original length, or alternatively to biaxial stretching to at least 1.2 times the original length and width.

The present invention also relates to a process for

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producing a stretched styrene-based resin molding which comprises stretching the above styrene-based resin to the above draw ratios. More concretely, the process of the present invention comprises heat melting the above styrene-based resin and stretching it in a specified range of temperature immediately after the heat melting, or alternatively comprises quenching the styrene-based resin molten by heat melting and then stretching it to the above draw ratios.

The present invention also relates to a stretched styrene-based resin molding as obtained by heating the above stretched styrene-based resin molding at from a temperature of 10°C higher than the glass transition temperature to a temperature of 5°C lower than the melting point, for example, at a temperature of 120 to 250°C.

BRIEF DESCRIPTION OF THE DRAWING

The figure is a graph showing the temperature dependency of the dielectric constant and dielectric loss tangent of the film obtained in Example 10.

DESCRIPTION OF PREFERRED EMBODIMENTS

The material for producing the stretched moldings of the present invention is a styrene-based resin having mainly syndiotactic configuration and a weight average molecular weight of at least 50,000. The syndiotactic configuration means a stereostructure in which phenyl groups or substituted phenyl groups as side chains are located alternately in opposite directions relative to the main chain composed of



carbon-carbon bonds. The tacticity is quantitatively determined by the nuclear magnetic resonance method using a carbon isotope (^{13}C -NMR method). The tacticity as determined by the ^{13}C -NMR method is indicated in terms of proportions of structural units continuously connected to each other, i.e., a diad in which two structural units are connected to each other, a triad in which three structural units are connected to each other, and a pentad in which five structural units are connected to each other. The styrene-based resin having mainly the syndiotactic configuration of the present invention includes polystyrene, poly(alkylstyrene), poly(halogenated styrene), poly(alkoxystyrene), polyvinyl benzoate and mixtures thereof, and copolymers containing the above polymer units as the main component and each having syndiotacticity such that the proportion of a diad is at least 75% and preferably at least 85%, or the proportion of a pentad (racemi pentad) is at least 30% and preferably at least 50%.

In the case of styrene-based resins with low syndiotacticity, satisfactory stretching effect can not be expected even if they are subjected to the stretching treatment.

The above poly(alkylstyrene) includes polymethylstyrene, polyethylstyrene, polyisopropylstyrene, poly(tert-butylstyrene) and the like. The poly(halogenated styrene) includes polychlorostyrene, polybromostyrene, polyfluorostyrene and the like. The poly(alkoxystyrene)

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includes polymethoxystyrene, polyethoxystyrene and the like. Of these styrene-based resins, polystyrene, poly(p-methylstyrene), poly(m-methylstyrene), poly(p-tert-butylstyrene), poly(p-chlorostyrene), poly(m-chlorostyrene), poly(p-fluorostyrene), and a copolymer of styrene and p-methylstyrene are most preferable.

The styrene-based resin to be used in the present invention needs to have a weight average molecular weight of at least 50,000, preferably at least 100,000, most preferably at least 300,000. The molecular weight distribution is not critical. If the weight average molecular weight is less than 50,000, difficulties such as breakage in stretching operation hinders a sufficient stretching, or a stretched molding having high mechanical strength and heat resistance cannot be obtained.

The styrene-based resin having mainly syndiotactic configuration can be obtained, for example, by polymerizing a styrene-based monomer (corresponding to the desired styrene-based resin) by the use of a catalyst comprising a titanium compound and a condensate of water and trialkylaluminum in the presence or absence of an inert hydrocarbon solvent (Japanese Patent Application Laid-Open No. 187708/1987).

In the present invention, the aforementioned styrene-based resin having mainly syndiotactic configuration is used as the material for the stretched molding. In addition, materials as prepared by adding other polymers (e.g., styrene-based resins having atactic configuration, styrene-



based resin having isotactic configuration, low molecular weight styrene-based resins having syndiotactic configuration, and polymers other than the styrene-based resins), inorganic powders such as metal powder, talc and mica, inorganic fibers such as glass fiber, an antistatic agent, a lubricant, an anti-clouding agent, a heat stabilizer, a dye, a pigment and the like to the above styrene-based resin having mainly syndiotactic configuration can be used. The amount of the other polymer, inorganic powder, inorganic fiber or additive to be used is 0.0005 to 10 parts by weight and preferably 0.001 to 5 parts by weight and most preferably 0.01 to 3 parts by weight per 100 parts by weight of the styrene-based resin having mainly syndiotactic configuration.

In the present invention, the styrene-based resin having mainly syndiotactic configuration or material obtained by compounding other components thereto is used as a raw material and is molded by extrusion molding, calender molding, blow molding or injection molding and so forth to produce a sheet (film or preliminary molding) and tube for stretching. In this case, the raw material is usually melted by heating and molded in the desired form by the use of various molding machines, but the raw material may be molded in a softened state without heat melting. The melting temperature of the raw material is usually preferably not lower than the melting point to not higher than the decomposition point of the styrene-based polymer used or

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compounds thereof. For instance, when the styrene-based polymer is polystyrene, the melting temperature is 260 to 350°C and preferably 280 to 330°C. If the temperature is too high, undesirable problems occur, such as decomposition of the raw material. Thickness of the sheet is not critical and is usually chosen from the range of not more than 5 mm, preferably 3 mm to 20 μ m. If the thickness is in excess of 5 mm, the sheet sometimes becomes difficult to stretch by internal crystallization. The crystallinity of the sheet (film) is not more than 25%, preferably not more than 15% and most preferably not more than 10%.

An effective way to produce a sheet having the lowest crystallinity as possible, particularly a sheet having a large thickness, is that the raw material which has been heat melted be quenched at the time of molding. The temperature of the coolant in this quenching is desirably adjusted to a temperature of 10°C or more, preferably 20°C or more and further preferably 30°C or more lower than the glass transition temperature of the styrene-based polymer or compounds thereof. For instance, when the styrene-based polymer is polystyrene, the temperature is not higher than 80°C, preferably not higher than 70°C, and most preferably not more than 60°C. The quenching rate is from 200 to 3°C/sec., preferably from 200 to 5°C/sec. and most preferably from 200 to 10°C/sec. If the temperature of the coolant is too high and quenching rate is too low, cooling becomes slow and the material becomes turbid as a result of partial



crystallization.

The thickness of the sheet for stretching as obtained above is not critical. It is preferred, however, that the unevenness in thickness be minimized. More specifically, it should be controlled to be not more than 15% and particularly preferably not more than 5%. Surface irregularities are preferably controlled to be not more than 1 μm (measured according to JIS B0601).

The sheet is generally stretched uniaxially or biaxially while heating at a temperature of from glass transition temperature of the raw material to a temperature 10°C lower than the melting point thereof. A temperature of the glass transition temperature to the cold crystallization temperature of it is preferred. Therein stretching rate is preferably 100%/min. to 500,000%/min. In the case of uniaxial stretching, the sheet should be stretched at a draw ratio of at least 2, preferably 3 to 10. In the case of biaxial stretching, the sheet should be stretched at a draw ratio of at least 1.2, preferably at least 1.5, more preferably 2.5 to 8.5, most preferably 3 to 5 in each direction. If the draw ratio is too small, physical properties of sheet, film or tape of the stretched molding are not satisfactorily improved. In the case of biaxial stretching, the sheet may be stretched simultaneously in the machine direction (MD) and transverse direction (TD), or may be stretched successively in the desired order.

In the present invention, particularly in the case of

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biaxial stretching, the raw material can be subjected to inflation molding or stretching blow molding directly without formation of a sheet or preliminary molding to produce a biaxially stretched molding (e.g., a biaxially stretched film). In this inflation molding or stretching blow molding, it is effective so as to prevent melt fracture, roughness of surface and the like that the resin be maintained at a temperature of at least 20°C higher than its melting point. If, however, the melt temperature is too high, the decomposition of the resin proceeds in molding. Therefore, the melt temperature is preferably lower than the decomposition point. When the styrene-based polymer is polystyrene, for instance, the melt temperature is usually adjusted to the range of 270 to 330°C, preferably 280°C to 300°C. In the inflation molding, where stretching is effected immediately after molten extrusion, the stretching temperature is preferably 5 to 150°C lower and more preferably 10 to 100°C lower than the melting point. In the case of stretching blow molding, the preform before stretching may be either a hot parison or a cold parison. In inflation molding or stretching blow molding, if the blow-up ratio is decreased, uniaxial stretching is realized.

Uniaxial stretching or biaxial stretching according to the present invention provides a stretched molding having excellent heat resistance, solvent resistance, chemical resistance, mechanical properties and electric insulating properties. It is also effective that the stretched molding



is further annealed (heated) at a temperature of 10°C or more higher than the glass transition temperature to a temperature of 5°C or more lower than the melting point, for example, at a temperature of 120 to 250°C. Improvement in heat resistance and so forth cannot be expected if the annealing temperature is lower than a temperature of 10°C higher than the glass transition temperature. On the other hand, problems such as melting of a part or the whole if it is in excess of a temperature of 5°C lower than the melting point. The annealing time is usually 1 second to 100 hours, preferably 5 seconds to 100 hours and most preferably 20 seconds to 10 hours. The annealing is usually carried out in the air atmosphere or in an atmosphere of inert gas such as argon and nitrogen. It is more effective during the annealing the stretched molding in a state of tension. This annealing further increases heat resistance, dimensional stability and so forth of the stretched molding.

When the styrene-based resin is stretched and molded into a wrapping material or container according to the present invention, a transparent stretched molding can be obtained, the contents of which can be seen and maintains heat resistance and solvent resistance of the raw material; because the styrene-based resin used as the raw material has high syndiotacticity and transparency such that the haze is not more than 30%.

Moreover, a stretched molding can be obtained which is excellent in electric properties such as electric insulating



properties (e.g., a breakdown voltage (BDV) at 25°C of at least 30 kV/mm) and dielectric properties.

Accordingly, the molding of the present invention can be used as a food wrapping material (e.g., sheet, film or bottle), a housing material for electric or electronic parts, a wrapping material, and further as an electric insulator, e.g., condenser, cable and transverter and other industrial films.

The present invention is described in greater detail with reference to the following examples.

REFERENCE EXAMPLE 1

(1) (Preparation of Methylauminoxane)

200 ml of toluene was placed in a reactor, and 47.4 ml (492 millimoles) of trimethylaluminum and 35.5 g (142 millimoles) of copper sulfate pentahydrate were added thereto and reacted with each other at 20°C for 24 hours.

Then the solid portion was removed from the reaction mixture to obtain a toluene solution containing 12.4 g of methylaluminoxane.

(2) (Production of Polystyrene having Syndiotactic Configuration)

2 L (L=liter) of toluene as a solvent, and 5 mmol of tetraethoxytitanium and 500 mmol (as aluminum atom) of methylaluminoxane obtained in abovedescribed (1) as catalyst components were placed in a reactor, and then 15 L of styrene was added at 50°C and polymerized for 4 hours.

After polymerization, the reaction product was washed

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with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 2.5 kg of a styrene-based resin (polystyrene). The polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 95% by weight of an extraction residue. The weight average molecular weight of the residue was 800,000. A ^{13}C -NMR analysis (solvent: 1,2-dichlorobenzene) showed a peak at 145.35 ppm, ascribable to the syndiotactic structure, and the syndiotacticity in terms of the racemi pentad as calculated from the peak area was 96%. The melt viscosity of the styrene polymer as determined with a capillary rheometer using Autograph 1125 (manufactured by Instron Copy.) was 7×10^4 poises under conditions of temperature 300°C and rate of shear 10/sec.

(3) (Production of Polystyrene having Syndiotactic Configuration)

2 L of toluene as a solvent, and 5 mmol of tetraethoxytitanium and 300 mmol (as aluminum atom) of methylaluminoxane obtained in abovedescribed (1) as catalyst components were placed in a reactor, and then 15 L of styrene was added at 55°C and polymerized for 4 hours.

After polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 2.5 kg of a styrene-based resin (polystyrene). The polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 97% by weight of the extraction



residus. The weight average molecular weight of the residue was 400,000. A ^{13}C -NMR analysis showed a peak at 145.35 ppm, ascribable to the syndiotactic structure, and the syndiotacticity in terms of the racemi pentad as calculated from the peak area was 98%.

The melt viscosity of the styrene polymer as determined under the same conditions as above (2) was 2×10^4 poises.

(4)(Production of Polystyrene having Syndiotactic Configuration)

2 L of toluene as a solvent, and 1 mmol of cyclopentadienyltitanium trichloride and 500 mmol (as aluminum atom) of methylaluminoxane obtained in abovedescribed (1) as catalyst components were placed in a reactor, and then 3.6 L of styrene was added at 20°C and polymerized for 1 hour.

After polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 330 g of a styrene-based resin(polystyrene). The polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 95% by weight of an extraction residue. The weight average molecular weight of the residue was 290,000, the number average molecular weight thereof was 158,000 and the melting point was 270°C. A ^{13}C -NMR analysis showed a peak at syndiotacticity in terms of the racemi pentad as calculated from the peak area was 96%. The melt viscosity of the styrene polymer as determined under the same conditions as above (2) was 4×10^3 poises.

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(5)(production of Polystyrene having Syndiotactic Configuration)

50 ml of toluene as a solvent, and 0.075 mmol of tetraethoxytitanium and 7.5 mmol (as aluminum atom) of methylaluminoxane obtained in abovedescribed (1) as catalyst components were placed in a reactor, and then 225 ml of styrene was added at 40°C and subsequently hydrogen was introduced therein until the hydrogen pressure reached 5 kg/cm². Polymerization was performed for 1.5 hours.

After polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 15.0 g of a styrene-based resin(polystyrene). The polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 95% by weight of an extraction residue. The weight average molecular weight of the residue was 16,000 and the number average molecular weight thereof was 3,000. A ¹³C-NMR analysis showed a peak at 145.35 ppm, ascribable to the syndiotactic structure, and the syndiotacticity in terms of the racemi pentad as calculated from the peak area was 98%.

EXAMPLE 1

To the polystyrene obtained in Reference Example 1(2) were added 0.7 part by weight of bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite and 0.1 part by weight of tetraquis(methylene(3,5-di-tert-butyl-4-hydroxy-hydrocinnamate))methane as antioxidants, and the resulting

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mixture was extruded and pelletized by the use of a twin-screw extruder having a diameter of 40 mm.

The pellets thus obtained were introduced in a single-screw extruder having a diameter of 40 mm and equipped with a T die at the top thereof, and extruded under conditions of cylinder temperature 290°C, T die temperature 300°C, through put 4.2 kg/hr. while quenching to 30°C at average quenching rate of 50°C/sec. to produce a sheet having a thickness of 600 μm .

The sheet for stretching as obtained above was transparent and had a density of 1.04 g/cm³, a glass transition temperature of 90°C and a crystallinity of 2%. The sheet was subjected to simultaneous biaxial stretching (draw ratio: 2x2) at 125°C to obtain a stretched film. This stretched film was subjected to annealing in a state of tension at 160°C for 20 seconds. The physical properties of the film are shown in Table 1.

The sheet was uniaxially stretched in MD at a draw ratio of 4.5 at a stretching temperature of 120°C to obtain a stretched film. The physical properties of the film are shown in Table 1.

EXAMPLE 2

The film obtained in Example 1 was subjected to heat treatment in a state of tension at 210°C for 20 seconds. The physical properties of the film thus treated are shown in Table 1.

EXAMPLE 3

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The sheet for stretching as obtained in Example 1 was subjected to simultaneous biaxial stretching (draw ratio: 2x2) at 125°C to obtain a stretched film. The physical properties of the film are shown in Table 1.

EXAMPLE 4

The film as obtained in Example 3 was subjected to annealing in a state of tension at 160°C for 20 seconds. The physical properties of the film are shown in Table 1.

EXAMPLE 5

The sheet for stretching as obtained in Example 1 was subjected to simultaneous biaxial stretching (draw ratio: 4x4) at 120°C to obtain a stretched film. The physical properties of the film are shown in Table 1.

EXAMPLE 6

The sheet for stretching as obtained in Example 1 was first stretched to a draw ratio of 3.5 times in MD and then to a draw ratio of 3 times in TD to obtain a stretched film. The physical properties of the film are shown in Table 1.

EXAMPLE 7

A styrene-based polymer (polystyrene), having a weight average molecular weight of 1,500,000 and a syndiotacticity in a racemi pentad of 96%, was produced in the same manner as in Reference Example 1 except that the polymerization temperature was changed from 50°C to 35°C. 2 parts by weight of talc powder as a lubricant was added to the polystyrene, and the resulting mixture was molded into a sheet at 280°C by the use of a calender roll. The surface temperature of the

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roll for cooling the sheet was 10°C.

The sheet was then subjected to simultaneous biaxial stretching (draw ratio: 2.5 x 2.5) at 120°C to obtain a stretched film. The physical properties of the film are shown in Table 1.

EXAMPLE 8

To a mixture of 90 parts by weight of the polystyrene obtained in Reference Example 1 and 10 parts by weight of atactic polystyrene (trade name: NF20; weight average molecular weight: 300,000; produced by Idemitsu Petrochemical Co., Ltd.) were added 0.1 part by weight of bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite and 0.1 part by weight of tetraquis(methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)) methane, and the resulting mixture was extruded and pelletized by the use of a twin-screw extruder having a diameter of 40 mm.

The pellets thus obtained were introduced into a single screw extruder having a diameter of 40 mm and equipped with a T die at the top thereof, and extruded under conditions of cylinder temperature 290°C, T die temperature 300°C and through put 4.2 kg/hr. while quenching to 20°C at average quenching rate of 50°C/sec. to obtain a sheet having a thickness of 600 μ m.

The sheet thus obtained had a density of 1.04 g/cm³, a glass transition temperature of 100°C and a crystallinity of 2%.

The sheet was subjected to simultaneous biaxial

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stretching (draw ratio: 3.5 x 3.5) at 125°C to obtain a stretched film. The physical properties of the film are shown in Table 1.

EXAMPLE 9

The pellets obtained in Example 1 were molded by the use of an injection molding machine to produce a preliminary molding (outer diameter: 28 mm; total length: 150 mm; thickness: 2.0 mm; weight: 35 g). This preliminary molding (crystallinity: 5%) was subjected to biaxial stretching blow molding by heating it at 130°C for 50 seconds with an infrared ray heater and blowing nitrogen gas at a pressure of 25 kg/cm² in a stretching blow molding machine to obtain a hollow container having a volume of 1 L. The physical properties of the container are shown in Table 1.

EXAMPLE 10

An original film was produced in the same manner as in Example 4, using the styrene polymer obtained in Reference Example 1 (3). The average quenching rate was 40°C/sec. and the cooling temperature was 30°C. The original film thus obtained (thickness: 0.4 mm; crystallinity: 4%) was subjected to simultaneous biaxial stretching in both MD and TD each to 4 times the original length (draw ratio: 4 x 4), and then annealed at 260°C for 15 seconds. The results are shown in Table 1.

EXAMPLE 11

An original film was produced in the same manner as in Example 4, using the styrene polymer obtained in Reference

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Example 1 (4). The quenching rate was 30°C/sec. and the cooling temperature was 30°C. The original film thus obtained (thickness: 0.5 mm; crystallinity: 4%) was subjected to simultaneous biaxial stretching in both MD and TD each to 4.5 times the original length (draw ratio: 4.5 x 4.5), and then annealed at 250°C for 10 seconds. The results are shown in Table 1.

COMPARATIVE EXAMPLE 1

The physical properties of the sheet (not-stretched sheet) as obtained in Example 1 are shown in Table 1.

COMPARATIVE EXAMPLE 2

An original sheet for stretching as obtained in Example 1 was subjected to annealing in a state of tension at 150°C for 600 seconds. The physical properties of the sheet are shown in Table 1.

COMPARATIVE EXAMPLE 3

To the styrene polymer obtained in Reference Example 1 (5) was added the same antioxidant as used in Example 1, and the resulting mixture was press molded to obtain an amorphous original film. On heating the amorphous original film to 120°C, the film was deformed by the weight thereof and could not be stretched.

EXAMPLE 12

The sheet of 0.1 mm thickness obtained in the same manner as in Example 1 was subjected to simultaneous biaxial stretching (draw ratio: 2.0 x 2.0) at 125°C to obtain a stretched film having a thickness of 50 µm. This film was



further subjected to annealing at 210°C.

The physical properties of the sheet are shown in Table 2. The sheet was measured for changes with temperature of dielectric constant and dielectric loss tangent by the use of an apparatus for measuring a dielectric constant (produced by Toyo Seiki Co., Ltd.) at a frequency of 976 Hz. The results are shown in Fig. 1

It can be seen from Fig. 1 that the temperature dependency of dielectric constant and dielectric loss is small.

EXAMPLES 13 TO 16

Stretched films of 25 μ m thickness were produced in the same manner as in Example 12 except that the thickness of original sheet, the stretching temperature, draw ratio, annealing temperature and annealing time were changed as shown in Table 2.

The physical properties of the films are shown in Table 2.

COMPARATIVE EXAMPLE 4

A stretched film was produced in the same manner as in Example 10 except that atactic polystyrene (NF 20) was used in place of the polystyrene obtained in Reference Example 1, and the stretching temperature and the draw ratio were changed to 120°C and 3.0 x 3.0, respectively.

The stretched film melted upon application of heat treatment at 170°C.

COMPARATIVE EXAMPLE 5

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The pellets obtained in Example 1 were heat pressed and then quenched to obtain a sheet (crystallinity: 6%) having a thickness of 3 mm. This sheet was subjected to annealing at 170°C for 600 seconds. The results are shown in Table 2.

REFERENCE EXAMPLE 2

(Production of Styrene Copolymer having Mainly Syndiotactic Configuration)

6 L of toluene as a solvent, and 5 mmol of tetraethoxytitanium and 500 mmol (as aluminum atom) of methylaluminoxane as catalyst components were placed in a reactor, and then 48.75 mol of styrene and 1.25 mol of p-methylstyrene were added thereto at 50°C and polymerized for 2 hours.

After of polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 640 g of a copolymer. This copolymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 80% by weight of an extraction residue. The copolymer, the residue, had a weight average molecular weight of 440,000, a number average molecular weight of 240,000 and a melting point of 255°C. The p-methylstyrene unit content of the copolymer was 5 mol%.

A ^{13}C -NMR analysis of the copolymer showed peaks at 145.11 ppm, 145.22 ppm and 142.09 ppm.

EXAMPLE 17

A stretched film was produced in the same manner as in

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Example 12 except that the styrene copolymer obtained in Reference Example 2 was used and the draw ratio was changed to 3.5 x 3.5.

The physical properties of the film are shown in Table 2.

EXAMPLE 18

To a mixture of 95 parts by weight of the polystyrene obtained in Reference Example 1 and 5 parts by weight of glass fiber having an average fiber length of 3 mm (produced by Asahi Fiber Glass Co., Ltd.; fiber diameter: 10-15 μ m; in the chopped strand form) were added 0.1 part by weight of bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite and 0.1 part by weight of tetraakis(methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate))methane as antioxidants, and the resulting mixture was extruded and pelletized by the use of a twin-screw extruder having diameter of 40 mm.

The pellets thus obtained were introduced into a single screw extruder having a diameter of 40 mm and equipped with a T die at the top thereof, and extruded under conditions of cylinder temperature 290°C, T die temperature 300°C and through put 4.2 kg/hr. while quenching to 30°C at average quenching rate of 75°C/sec. to obtain a sheet having a thickness of 200 μ m.

The sheet was subjected to simultaneous biaxial stretching (draw ratio: 2 x 2) at 125°C to obtain a stretched film. The physical properties of the film are shown in Table 2.

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Table 1

No.	Resin ^{*1}	Weight ^{*2} Average Molecular Weight	Cooling Rate °C/sec.	Cooling Temp. °C	Stretch- ing Temp. °C	Mode of Stretch- ing	Draw Ratio		Original Sheet or Film	
							MD	TD	Thick- ness mm	Crystal- linity %
Example 1	SPS	800,000	50	30	120	Uniaxial	4.5	1.0	0.6	2
Example 2	SPS	800,000	50	30	120	Uniaxial	4.5	1.0	0.6	2
Example 3	SPS	800,000	50	30	125	Simultaneous Biaxial	2.0	2.0	0.6	2
Example 4	SPS	800,000	50	30	125	Simultaneous Biaxial	2.0	2.0	0.6	2
Example 5	SPS	800,000	50	30	120	Simultaneous Biaxial	4.0	4.0	0.6	2
Example 6	SPS	800,000	50	30	125	Sequential Biaxial	3.5	3.0	0.6	2
Example 7	SPS	1,500,000	75	10	120	Simultaneous Biaxial	2.5	2.5	0.6	2
Example 8	SPS	800,000	20	30	125	Simultaneous Biaxial	3.5	3.5	0.6	2
Example 9	SPS	800,000	100	5	130	Simultaneous Biaxial	3.3	3.3	2.0	5

Table 1 (continued-1)

No.	Annealing		Stretched Molding		Tensile Strength (kg/cm ²)		Tensile Modulus (kg/cm ²)		Haze %	Temp. of 2% Deformation °C
	Temp. °C	Time sec.	Thick- ness μm	Crystal- linity %	MD	TD	MD	TD		
Example 1	-	-	130	51	12	5	101	30	2	110
Example 2	210	20	130	55	13	5.5	110	41	3	209
Example 3	-	-	150	28	10.5	10	39	38	2	115
Example 4	160	20	150	50	10.6	10.2	39	39	5	158
Example 5	-	-	40	46	12	11.8	42	41	2	120
Example 6	-	-	55	44	11	10.4	39	38	2	121
Example 7	213	20	100	51	14	13	43	42	25	210
Example 8	-	-	50	45	11.5	10	39	38	2	121
Example 9	-	-	200	49	11.2	11	39	39	5	120



Table 1 (continued-2)

No.	Resin *1	Weight Average Molecular Weight *2	Cooling Rate °C/sec.	Cooling Temp. °C	Stretch- ing Temp. °C	Mode of Stretch- ing	Draw Ratio		Original Sheet or Film	
							MD	TD	Thick- ness mm	Crystal- linity %
Example 10	SPS	400,000	40	30	115	Simultaneous Biaxial	4.0	4.0	0.4	4
Example 11	SPS	250,000	30	30	115	Simultaneous Biaxial	4.5	4.5	0.5	4
Comparative Example 1	SPS	800,000	50	30	-	-	1.0	1.0	0.6	2
Comparative Example 2	SPS	800,000	50	30	-	-	1.0	1.0	0.6	2
Comparative Example 3	SPS	16,000	100	10	120	Simultaneous Biaxial	Unable to Stretch		0.6	2

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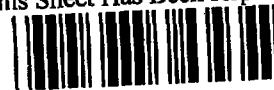


Table 1 (continued-3)

No.	Annealing		Stretched Molding		Tensile Strength (kg/cm ²)		Tensile Modulus (kg/cm ²)		Haze %	Temp. of 2% Deformation °C
	Temp. °C	Time sec.	Thick- ness μm	Crystal- linity %	MD	TD	MD	TD		
Example 10	260	15	25	55	12	12	50	45	1.5	259
Example 11	250	10	25	54	12	12	52	47	1.5	254
Comparative Example 1	-	-	-	-	6.6	4.5	28	29	2	90
Comparative Example 2	150	600	-	41	5.8	4.3	30	30	45	143
Comparative Example 3	-	-	-	-	-	-	-	-	-	-

*1 SPS: syndiotactic polystyrene, COMe: syndiotactic poly(styrene-p-methyl styrene)

*2 measured by Gel Permeation Chromatography (GPC) using 1,2,4-trichlorobenzene as solvent

*3 measured by Differential Scanning Calorimeter (DSC)

*4 Temperature of 2% deformation measured by Thermal Mechanical Analysis (TMA)

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Table 2

No.	Resin ^{*1}	Weight ^{*2} Average Molecular Weight	Cooling Rate °C/sec.	Cooling Temp. °C	Stretch- ing Temp. °C	Mode of Stretch- ing	Draw Ratio	
							MD	TD
Example 12	SPS	800,000	50	30	125	Simultaneous Biaxial	2.0	2.0
Example 13	SPS	800,000	50	30	125	Simultaneous Biaxial	4.0	4.0
Example 14	SPS	800,000	50	30	125	Simultaneous Biaxial	4.0	4.0
Example 15	SPS	800,000	50	30	125	Sequential Biaxial	3.5	3.0
Example 16	SPS	800,000	50	30	170	Sequential Biaxial	3.0	3.0
Example 17	COME	440,000	25	30	125	Simultaneous Biaxial	3.5	3.5
Example 18	SPS	800,000	75	10	125	Simultaneous Biaxial	2.0	2.0
Comparative Example 4	(SPS)	800,000	100	10	-	-	1.0	1.0

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Table 2 (continued)

No.	Original Sheet or Film		Annealing		Stretched Molding		*4 Temp. of 2% Deformation °C	*5 BDV kV/mm
	Thick- ness mm	Crystal- linity %	Temp. °C	Time sec.	Thick- ness μm	Crystal- linity %		
Example 12	0.1	2	210	30	25	51	215	200
Example 13	0.4	3	240	30	25	53	240	270
Example 14	0.4	3	190	600	25	52	200	270
Example 15 ¹	0.25	3	240	20	25	50	242	270
Example 16	0.2	2	240	30	25	49	241	280
Example 17	0.25	3	170	100	25	48	219	260
Example 18	0.1	2	220	30	25	53	240	205
Comparative Example 4	3	6	170	600	-	49	151	22

*1 to *4 same as in Table 1

*5 Breakdown Voltage (BVD) measured according to JIS C-2110 at 25°C

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WHAT IS CLAIMED IS:

1. A stretched styrene-based resin molding as obtained by subjecting a styrene-based polymer having mainly syndiotactic configuration and a weight average molecular weight of at least 50,000 to uniaxial stretching of at least two times or to biaxial stretching of at least 1.2 times in each direction.
2. The molding as claimed in Claim 1, having heat resistance and such transparency that the haze is not more than 30%.
3. The molding as claimed in Claim 1, having such electric insulating properties that the breakdown voltage at 25 °C is at least 30 kV/mm.
4. A process for producing a stretched styrene-based resin molding which comprises subjecting a styrene-based resin having mainly syndiotactic configuration and a weight average molecular weight of at least 50,000 to uniaxial stretching of at least two times or biaxial stretching of at least 1.2 times in each direction.
5. A process for producing a stretched styrene-based resin molding which comprises heat melting a styrene-based resin having mainly syndiotactic configuration and a weight average molecular weight of at least 50,000, quenching the molten resin, and then subjecting the quenched resin to uniaxial stretching at a draw ratio of at least two times or biaxial stretching at a draw ratio of at least 1.2 times in each direction.

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6. The process as claimed in Claim 5, wherein quenching rate is from 200 to 3°C/sec.

7. A stretched styrene-based resin molding as obtained by subjecting the stretched styrene-based resin molding of Claim 1 to annealing at a temperature of 10°C higher than the glass transition temperature to a temperature of 5°C lower than melting point.

8. The stretched styrene-based resin molding as claimed in Claim 7 wherein the temperature of annealing is 120°C to 250°C.

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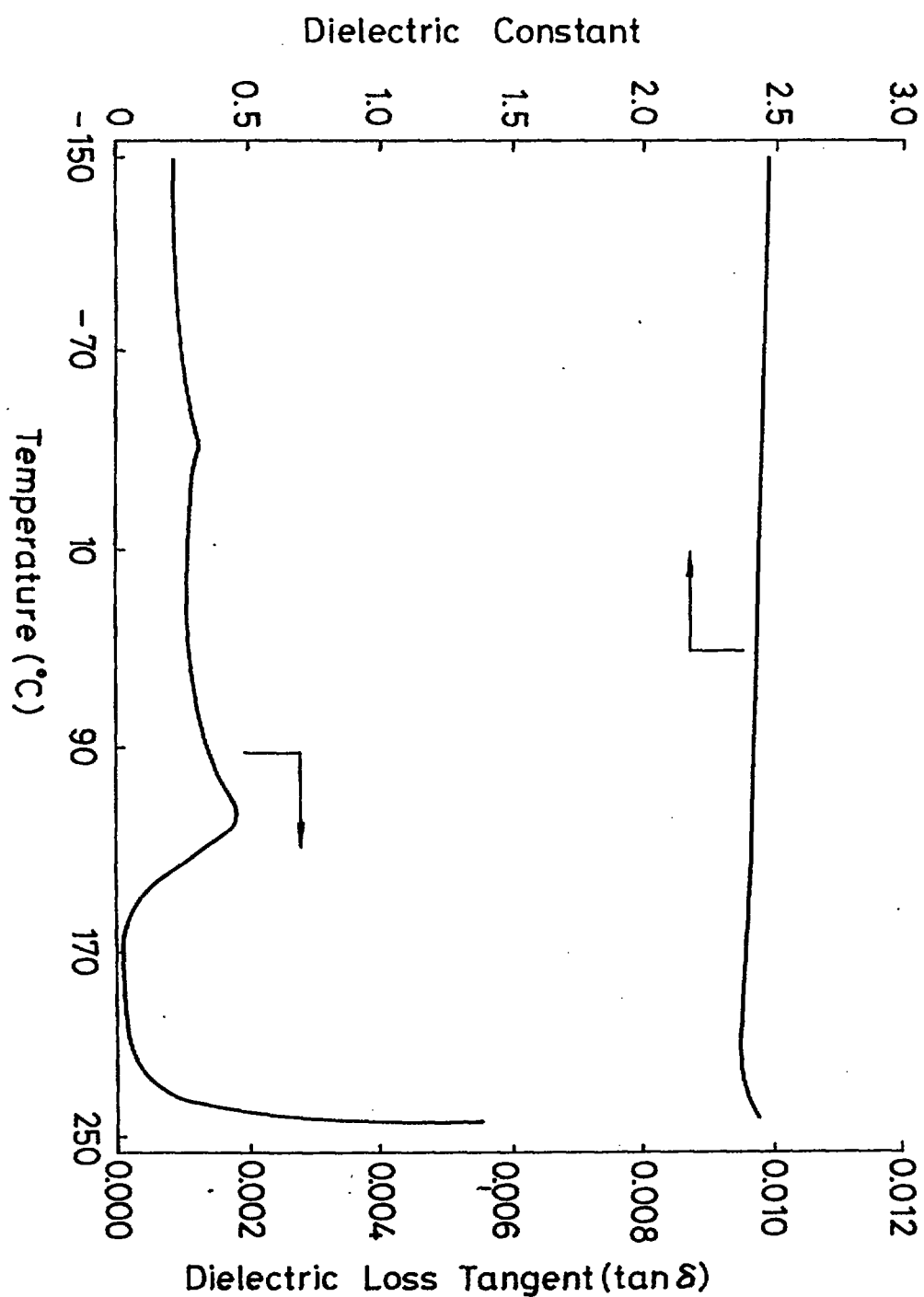
ABSTRACT OF THE DISCLOSURE

Stretched moldings (e.g., stretched films, sheets or bottles) of styrene-based resins (e.g., polystyrene) having mainly syndiotactic configuration and a weight average molecular weight of at least 50,000, and a process for the production thereof are disclosed. The stretched moldings are obtained by uniaxially stretching the styrene-based resins at a draw ratio of at least 2 times, or biaxially stretching at a draw ratio of at least 1.2 times in each direction. The stretched moldings are excellent in heat resistance, chemical resistance, solvent resistance, electric insulating properties, mechanical strength and so forth, and thus can be used as food wrapping materials, housing materials for electric or electronic parts, and so forth.

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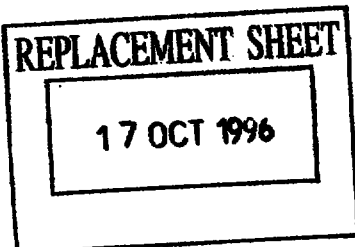


Fig. 1



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REPLACEMENT SHEETS		SG
☒ Description :	paged .1. to paged .26.	
☒ Claim(s) :	paged .27. to paged .28.	
☒ Drawing(s) :	paged .29. to paged .30.	
☒ Abstract :	paged .31. to paged .32.	
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STRETCHED STYRENE-BASED RESIN MOLDINGS AND A PROCESS FOR
PRODUCTION THEREOF

BACKGROUND OF THE INVENTION

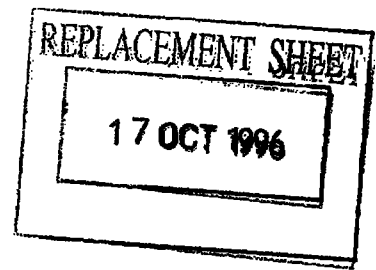
1. Field of the Invention

The present invention relates to stretched styrene-based resin moldings and a process for the production thereof. More particularly, it is concerned with stretched styrene-based resin moldings which are excellent in heat resistance, solvent resistance, chemical resistance, electric insulating properties, mechanical strength, modulus of elasticity, dimensional stability and transparency, and consequently can be used in various applications; and a process for efficiently producing these stretched styrene-based resin moldings.

2. Description of the Related Art

The styrene polymers which have been hitherto used are those having atactic configuration as obtained by radical polymerization. However, improvement in physical properties by stretching such atactic styrene polymers cannot be expected.

Styrene polymers having isotactic configuration are also known, and an attempt to stretch them has been made (Kobunshi Kagaku (Polymer Chemistry), 21, 206 (1964)). However, a satisfactory stretching effect in such isotactic styrene polymers cannot be obtained because the rate of crystallization is slow and the main chain composed of carbon-carbon bonds in the styrene polymers has spiral



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structure.

The present inventors' research has found that stretched moldings having excellent physical properties can be obtained if styrene-based resins of high syndiotacticity as developed by the present inventors' group (Japanese Patent Application Laid-Open No. 104818/1987) are stretched.

SUMMARY OF THE INVENTION

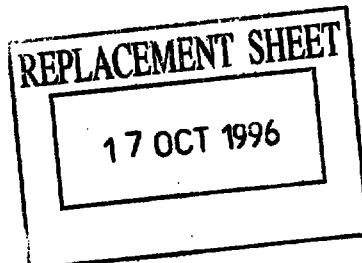
An object of the present invention is to provide stretched styrene-based resin moldings which are excellent in heat resistance, solvent resistance, chemical resistance, mechanical strength, modulus of elasticity, dimensional stability and transparency.

Another object of the present invention is to provide stretched styrene-based resin moldings which are excellent in electric insulating properties, for instance, a breakdown voltage at 25°C of at least 30 kV/mm.

Still another object of the present invention is to provide a process for efficiently producing these stretched styrene-based resin moldings.

The present invention relates to a stretched styrene-based resin molding as obtained by subjecting a styrene-based resin having mainly syndiotactic configuration and a weight average molecular weight of at least 50,000 to uniaxial stretching to at least two times the original length, or alternatively to biaxial stretching to at least 1.2 times the original length and width.

The present invention also relates to a process for



producing a stretched styrene-based resin molding which comprises stretching the above styrene-based resin to the above draw ratios. More concretely, the process of the present invention comprises heat melting the above styrene-based resin and stretching it in a specified range of temperature immediately after the heat melting, or alternatively comprises quenching the styrene-based resin molten by heat melting and then stretching it to the above draw ratios.

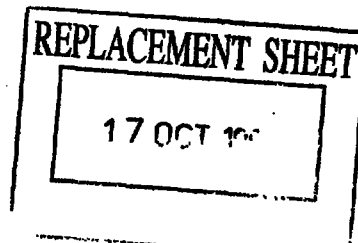
The present invention also relates to a stretched styrene-based resin molding as obtained by heating the above stretched styrene-based resin molding at from a temperature of 10°C higher than the glass transition temperature to a temperature of 5°C lower than the melting point, for example, at a temperature of 120 to 250°C.

BRIEF DESCRIPTION OF THE DRAWING

The figure is a graph showing the temperature dependency of the dielectric constant and dielectric loss tangent of the film obtained in Example 10.

DESCRIPTION OF PREFERRED EMBODIMENTS

The material for producing the stretched moldings of the present invention is a styrene-based resin having mainly syndiotactic configuration and a weight average molecular weight of at least 50,000. The syndiotactic configuration means a stereostructure in which phenyl groups or substituted phenyl groups as side chains are located alternately in opposite directions relative to the main chain composed of

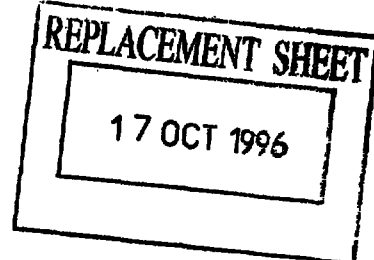


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carbon-carbon bonds. The tacticity is quantitatively determined by the nuclear magnetic resonance method using a carbon isotope (^{13}C -NMR method). The tacticity as determined by the ^{13}C -NMR method is indicated in terms of proportions of structural units continuously connected to each other, i.e., a diad in which two structural units are connected to each other, a triad in which three structural units are connected to each other, and a pentad in which five structural units are connected to each other. The styrene-based resin having mainly the syndiotactic configuration of the present invention includes polystyrene, poly(alkylstyrene), poly(halogenated styrene), poly(alkoxystyrene), polyvinyl benzoate and mixtures thereof, and copolymers containing the above polymer units as the main component and each having syndiotacticity such that the proportion of a diad is at least 75% and preferably at least 85%, or the proportion of a pentad (racemi pentad) is at least 30% and preferably at least 50%.

In the case of styrene-based resins with low syndiotacticity, satisfactory stretching effect can not be expected even if they are subjected to the stretching treatment.

The above poly(alkylstyrene) includes polymethylstyrene, polyethylstyrene, polyisopropylstyrene, poly(tert-butylstyrene) and the like. The poly(halogenated styrene) includes polychlorostyrene, polybromostyrene, polyfluorostyrene and the like. The poly(alkoxystyrene)

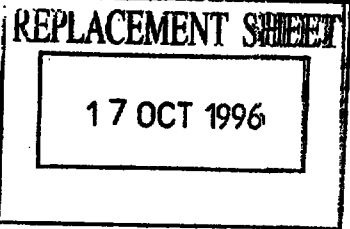


includes polymethoxystyrene, polyethoxystyrene and the like. Of these styrene-based resins, polystyrene, poly(p-methylstyrene), poly(m-methylstyrene), poly(p-tert-butylstyrene), poly(p-chlorostyrene), poly(m-chlorostyrene), poly(p-fluorostyrene), and a copolymer of styrene and p-methylstyrene are most preferable.

The styrene-based resin to be used in the present invention needs to have a weight average molecular weight of at least 50,000, preferably at least 100,000, most preferably at least 300,000. The molecular weight distribution is not critical. If the weight average molecular weight is less than 50,000, difficulties such as breakage in stretching operation hinders a sufficient stretching, or a stretched molding having high mechanical strength and heat resistance cannot be obtained.

The styrene-based resin having mainly syndiotactic configuration can be obtained, for example, by polymerizing a styrene-based monomer (corresponding to the desired styrene-based resin) by the use of a catalyst comprising a titanium compound and a condensate of water and trialkylaluminum in the presence or absence of an inert hydrocarbon solvent (Japanese Patent Application Laid-Open No. 187708/1987).

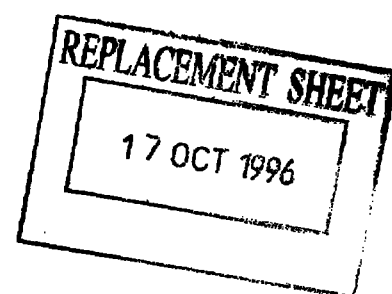
In the present invention, the aforementioned styrene-based resin having mainly syndiotactic configuration is used as the material for the stretched molding. In addition, materials as prepared by adding other polymers (e.g., styrene-based resins having atactic configuration, styrene-



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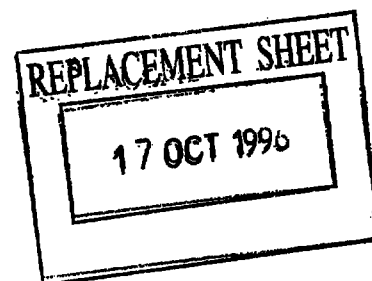
based resin having isotactic configuration, low molecular weight styrene-based resins having syndiotactic configuration, and polymers other than the styrene-based resins), inorganic powders such as metal powder, talc and mica, inorganic fibers such as glass fiber, an antistatic agent, a lubricant, an anti-clouding agent, a heat stabilizer, a dye, a pigment and the like to the above styrene-based resin having mainly syndiotactic configuration can be used. The amount of the other polymer, inorganic powder, inorganic fiber or additive to be used is 0.0005 to 10 parts by weight and preferably 0.001 to 5 parts by weight and most preferably 0.01 to 3 parts by weight per 100 parts by weight of the styrene-based resin having mainly syndiotactic configuration.

In the present invention, the styrene-based resin having mainly syndiotactic configuration or material obtained by compounding other components thereto is used as a raw material and is molded by extrusion molding, calender molding, blow molding or injection molding and so forth to produce a sheet (film or preliminary molding) and tube for stretching. In this case, the raw material is usually melted by heating and molded in the desired form by the use of various molding machines, but the raw material may be molded in a softened state without heat melting. The melting temperature of the raw material is usually preferably not lower than the melting point to not higher than the decomposition point of the styrene-based polymer used or



compounds thereof. For instance, when the styrene-based polymer is polystyrene, the melting temperature is 260 to 350°C and preferably 280 to 330°C. If the temperature is too high, undesirable problems occur, such as decomposition of the raw material. Thickness of the sheet is not critical and is usually chosen from the range of not more than 5 mm, preferably 3 mm to 20 μ m. If the thickness is in excess of 5 mm, the sheet sometimes becomes difficult to stretch by internal crystallization. The crystallinity of the sheet (film) is not more than 25%, preferably not more than 15% and most preferably not more than 10%.

An effective way to produce a sheet having the lowest crystallinity as possible, particularly a sheet having a large thickness, is that the raw material which has been heat melted be quenched at the time of molding. The temperature of the coolant in this quenching is desirably adjusted to a temperature of 10°C or more, preferably 20°C or more and further preferably 30°C or more lower than the glass transition temperature of the styrene-based polymer or compounds thereof. For instance, when the styrene-based polymer is polystyrene, the temperature is not higher than 80°C, preferably not higher than 70°C, and most preferably not more than 60°C. The quenching rate is from 200 to 3°C/sec., preferably from 200 to 5°C/sec. and most preferably from 200 to 10°C/sec. If the temperature of the coolant is too high and quenching rate is too low, cooling becomes slow and the material becomes turbid as a result of partial



crystallization.

The thickness of the sheet for stretching as obtained above is not critical. It is preferred, however, that the unevenness in thickness be minimized. More specifically, it should be controlled to be not more than 15% and particularly preferably not more than 5%. Surface irregularities are preferably controlled to be not more than 1 μm (measured according to JIS B0601).

The sheet is generally stretched uniaxially or biaxially while heating at a temperature of from glass transition temperature of the raw material to a temperature 10°C lower than the melting point thereof. A temperature of the glass transition temperature to the cold crystallization temperature of it is preferred. Therein stretching rate is preferably 100%/min. to 500,000%/min. In the case of uniaxial stretching, the sheet should be stretched at a draw ratio of at least 2, preferably 3 to 10. In the case of biaxial stretching, the sheet should be stretched at a draw ratio of at least 1.2, preferably at least 1.5, more preferably 2.5 to 8.5, most preferably 3 to 5 in each direction. If the draw ratio is too small, physical properties of sheet, film or tape of the stretched molding are not satisfactorily improved. In the case of biaxial stretching, the sheet may be stretched simultaneously in the machine direction (MD) and transverse direction (TD), or may be stretched successively in the desired order.

In the present invention, particularly in the case of

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biaxial stretching, the raw material can be subjected to inflation molding or stretching blow molding directly without formation of a sheet or preliminary molding to produce a biaxially stretched molding (e.g., a biaxially stretched film). In this inflation molding or stretching blow molding, it is effective so as to prevent melt fracture, roughness of surface and the like that the resin be maintained at a temperature of at least 20°C higher than its melting point. If, however, the melt temperature is too high, the decomposition of the resin proceeds in molding. Therefore, the melt temperature is preferably lower than the decomposition point. When the styrene-based polymer is polystyrene, for instance, the melt temperature is usually adjusted to the range of 270 to 330°C, preferably 280°C to 300°C. In the inflation molding, where stretching is effected immediately after molten extrusion, the stretching temperature is preferably 5 to 150°C lower and more preferably 10 to 100°C lower than the melting point. In the case of stretching blow molding, the preform before stretching may be either a hot parison or a cold parison. In inflation molding or stretching blow molding, if the blow-up ratio is decreased, uniaxial stretching is realized.

Uniaxial stretching or biaxial stretching according to the present invention provides a stretched molding having excellent heat resistance, solvent resistance, chemical resistance, mechanical properties and electric insulating properties. It is also effective that the stretched molding

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is further annealed (heated) at a temperature of 10°C or more higher than the glass transition temperature to a temperature of 5°C or more lower than the melting point, for example, at a temperature of 120 to 250°C. Improvement in heat resistance and so forth cannot be expected if the annealing temperature is lower than a temperature of 10°C higher than the glass transition temperature. On the other hand, problems such as melting of a part or the whole if it is in excess of a temperature of 5°C lower than the melting point. The annealing time is usually 1 second to 100 hours, preferably 5 seconds to 100 hours and most preferably 20 seconds to 10 hours. The annealing is usually carried out in the air atmosphere or in an atmosphere of inert gas such as argon and nitrogen. It is more effective during the annealing the stretched molding in a state of tension. This annealing further increases heat resistance, dimensional stability and so forth of the stretched molding.

When the styrene-based resin is stretched and molded into a wrapping material or container according to the present invention, a transparent stretched molding can be obtained, the contents of which can be seen and maintains heat resistance and solvent resistance of the raw material; because the styrene-based resin used as the raw material has high syndiotacticity and transparency such that the haze is not more than 30%.

Moreover, a stretched molding can be obtained which is excellent in electric properties such as electric insulating

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properties (e.g., a breakdown voltage (BDV) at 25°C of at least 30 kV/mm) and dielectric properties.

Accordingly, the molding of the present invention can be used as a food wrapping material (e.g., sheet, film or bottle), a housing material for electric or electronic parts, a wrapping material, and further as an electric insulator, e.g., condenser, cable and transverter and other industrial films.

The present invention is described in greater detail with reference to the following examples.

REFERENCE EXAMPLE 1

(1) (Preparation of Methylaluminoxane)

200 ml of toluene was placed in a reactor, and 47.4 ml (492 millimoles) of trimethylaluminum and 35.5 g (142 millimoles) of copper sulfate pentahydrate were added thereto and reacted with each other at 20°C for 24 hours.

Then the solid portion was removed from the reaction mixture to obtain a toluene solution containing 12.4 g of methylaluminoxane.

(2) (Production of Polystyrene having Syndiotactic Configuration)

2 L (L=liter) of toluene as a solvent, and 5 mmol of tetraethoxytitanium and 500 mmol (as aluminum atom) of methylaluminoxane obtained in abovedescribed (1) as catalyst components were placed in a reactor, and then 15 L of styrene was added at 50°C and polymerized for 4 hours.

After polymerization, the reaction product was washed

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with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 2.5 kg of a styrene-based resin (polystyrene). The polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 95% by weight of an extraction residue. The weight average molecular weight of the residue was 800,000. A ^{13}C -NMR analysis (solvent: 1,2-dichlorobenzene) showed a peak at 145.35 ppm, ascribable to the syndiotactic structure, and the syndiotacticity in terms of the racemi pentad as calculated from the peak area was 96%. The melt viscosity of the styrene polymer as determined with a capillary rheometer using Autograph 1125 (manufactured by Instron Copy.) was 7×10^4 poises under conditions of temperature 300°C and rate of shear 10/sec.

(3) (Production of Polystyrene having Syndiotactic Configuration)

2 L of toluene as a solvent, and 5 mmol of tetraethoxytitanium and 300 mmol (as aluminum atom) of methylaluminoxane obtained in abovedescribed (1) as catalyst components were placed in a reactor, and then 15 L of styrene was added at 55°C and polymerized for 4 hours.

After polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 2.5 kg of a styrene-based resin (polystyrene). The polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 97% by weight of the extraction

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residus. The weight average molecular weight of the residue was 400,000. A ^{13}C -NMR analysis showed a peak at 145.35 ppm, ascribable to the syndiotactic structure, and the syndiotacticity in terms of the racemi pentad as calculated from the peak area was 98%.

The melt viscosity of the styrene polymer as determined under the same conditions as above (2) was 2×10^4 poises.

(4)(Production of Polystyrene having Syndiotactic Configuration)

2 L of toluene as a solvent, and 1 mmol of cyclopentadienyltitanium trichloride and 500 mmol (as aluminum atom) of methylaluminoxane obtained in abovedescribed (1) as catalyst components were placed in a reactor, and then 3.6 L of styrene was added at 20°C and polymerized for 1 hour.

After polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 330 g of a styrene-based resin(polystyrene). The polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 95% by weight of an extraction residue. The weight average molecular weight of the residue was 290,000, the number average molecular weight thereof was 158,000 and the melting point was 270°C. A ^{13}C -NMR analysis showed a peak at syndiotacticity in terms of the racemi pentad as calculated from the peak area was 96%. The melt viscosity of the styrene polymer as determined under the same conditions as above (2) was 4×10^3 poises.

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The sheet for stretching as obtained in Example 1 was subjected to simultaneous biaxial stretching (draw ratio: 2x2) at 125°C to obtain a stretched film. The physical properties of the film are shown in Table 1.

EXAMPLE 4

The film as obtained in Example 3 was subjected to annealing in a state of tension at 160°C for 20 seconds. The physical properties of the film are shown in Table 1.

EXAMPLE 5

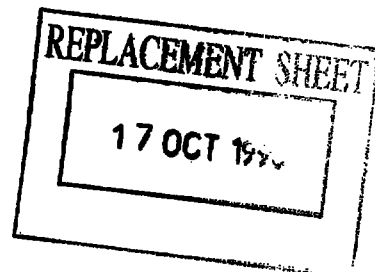
The sheet for stretching as obtained in Example 1 was subjected to simultaneous biaxial stretching (draw ratio: 4x4) at 120°C to obtain a stretched film. The physical properties of the film are shown in Table 1.

EXAMPLE 6

The sheet for stretching as obtained in Example 1 was first stretched to a draw ratio of 3.5 times in MD and then to a draw ratio of 3 times in TD to obtain a stretched film. The physical properties of the film are shown in Table 1.

EXAMPLE 7

A styrene-based polymer (polystyrene), having a weight average molecular weight of 1,500,000 and a syndiotacticity in a racemi pentad of 96%, was produced in the same manner as in Reference Example 1 except that the polymerization temperature was changed from 50°C to 35°C. 2 parts by weight of talc powder as a lubricant was added to the polystyrene, and the resulting mixture was molded into a sheet at 280°C by the use of a calender roll. The surface temperature of the



roll for cooling the sheet was 10°C.

The sheet was then subjected to simultaneous biaxial stretching (draw ratio: 2.5 x 2.5) at 120°C to obtain a stretched film. The physical properties of the film are shown in Table 1.

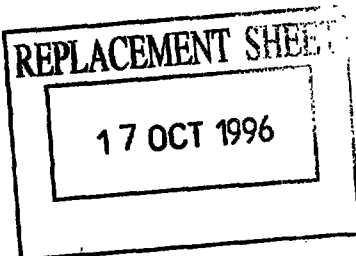
EXAMPLE 8

To a mixture of 90 parts by weight of the polystyrene obtained in Reference Example 1 and 10 parts by weight of atactic polystyrene (trade name: NF20; weight average molecular weight: 300,000; produced by Idemitsu Petrochemical Co., Ltd.) were added 0.1 part by weight of bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite and 0.1 part by weight of tetraquis(methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)) methane, and the resulting mixture was extruded and pelletized by the use of a twin-screw extruder having a diameter of 40 mm.

The pellets thus obtained were introduced into a single screw extruder having a diameter of 40 mm and equipped with a T die at the top thereof, and extruded under conditions of cylinder temperature 290°C, T die temperature 300°C and through put 4.2 kg/hr. while quenching to 20°C at average quenching rate of 50°C/sec. to obtain a sheet having a thickness of 600 μm .

The sheet thus obtained had a density of 1.04 g/cm³, a glass transition temperature of 100°C and a crystallinity of 2%.

The sheet was subjected to simultaneous biaxial



stretching (draw ratio: 3.5 x 3.5) at 125°C to obtain a stretched film. The physical properties of the film are shown in Table 1.

EXAMPLE 9

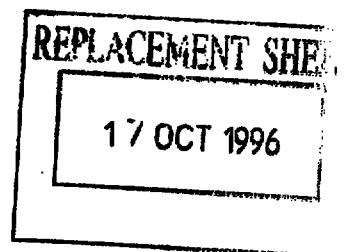
The pellets obtained in Example 1 were molded by the use of an injection molding machine to produce a preliminary molding (outer diameter: 28 mm; total length: 150 mm; thickness: 2.0 mm; weight: 35 g). This preliminary molding (crystallinity: 5%) was subjected to biaxial stretching blow molding by heating it at 130°C for 50 seconds with an infrared ray heater and blowing nitrogen gas at a pressure of 25 kg/cm² in a stretching blow molding machine to obtain a hollow container having a volume of 1 L. The physical properties of the container are shown in Table 1.

EXAMPLE 10

An original film was produced in the same manner as in Example 4, using the styrene polymer obtained in Reference Example 1 (3). The average quenching rate was 40°C/sec. and the cooling temperature was 30°C. The original film thus obtained (thickness: 0.4 mm; crystallinity: 4%) was subjected to simultaneous biaxial stretching in both MD and TD each to 4 times the original length (draw ratio: 4 x 4), and then annealed at 260°C for 15 seconds. The results are shown in Table 1.

EXAMPLE 11

An original film was produced in the same manner as in Example 4, using the styrene polymer obtained in Reference



Example 1 (4). The quenching rate was 30°C/sec. and the cooling temperature was 30°C. The original film thus obtained (thickness: 0.5 mm; crystallinity: 4%) was subjected to simultaneous biaxial stretching in both MD and TD each to 4.5 times the original length (draw ratio: 4.5 x 4.5), and then annealed at 250°C for 10 seconds. The results are shown in Table 1.

COMPARATIVE EXAMPLE 1

The physical properties of the sheet (not-stretched sheet) as obtained in Example 1 are shown in Table 1.

COMPARATIVE EXAMPLE 2

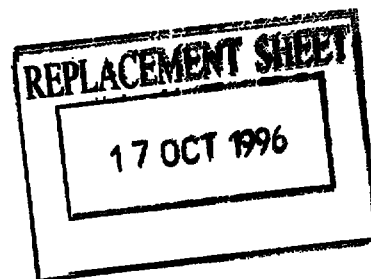
An original sheet for stretching as obtained in Example 1 was subjected to annealing in a state of tension at 150°C for 600 seconds. The physical properties of the sheet are shown in Table 1.

COMPARATIVE EXAMPLE 3

To the styrene polymer obtained in Reference Example 1 (5) was added the same antioxidant as used in Example 1, and the resulting mixture was press molded to obtain an amorphous original film. On heating the amorphous original film to 120°C, the film was deformed by the weight thereof and could not be stretched.

EXAMPLE 12

The sheet of 0.1 mm thickness obtained in the same manner as in Example 1 was subjected to simultaneous biaxial stretching (draw ratio: 2.0 x 2.0) at 125°C to obtain a stretched film having a thickness of 50 µm. This film was



further subjected to annealing at 210°C.

The physical properties of the sheet are shown in Table 2. The sheet was measured for changes with temperature of dielectric constant and dielectric loss tangent by the use of an apparatus for measuring a dielectric constant (produced by Toyo Seiki Co., Ltd.) at a frequency of 976 Hz. The results are shown in Fig. 1

It can be seen from Fig. 1 that the temperature dependency of dielectric constant and dielectric loss is small.

EXAMPLES 13 TO 16

Stretched films of 25 μ m thickness were produced in the same manner as in Example 12 except that the thickness of original sheet, the stretching temperature, draw ratio, annealing temperature and annealing time were changed as shown in Table 2.

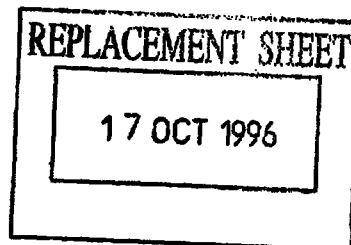
The physical properties of the films are shown in Table 2.

COMPARATIVE EXAMPLE 4

A stretched film was produced in the same manner as in Example 10 except that atactic polystyrene (NF 20) was used in place of the polystyrene obtained in Reference Example 1, and the stretching temperature and the draw ratio were changed to 120°C and 3.0 x 3.0, respectively.

The stretched film melted upon application of heat treatment at 170°C.

COMPARATIVE EXAMPLE 5



The pellets obtained in Example 1 were heat pressed and then quenched to obtain a sheet (crystallinity: 6%) having a thickness of 3 mm. This sheet was subjected to annealing at 170°C for 600 seconds. The results are shown in Table 2.

REFERENCE EXAMPLE 2

(Production of Styrene Copolymer having Mainly Syndiotactic Configuration)

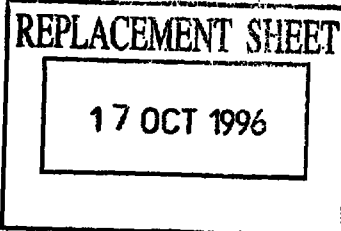
6 L of toluene as a solvent, and 5 mmol of tetraethoxytitanium and 500 mmol (as aluminum atom) of methylaluminoxane as catalyst components were placed in a reactor, and then 48.75 mol of styrene and 1.25 mol of p-methylstyrene were added thereto at 50°C and polymerized for 2 hours.

After of polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 640 g of a copolymer. This copolymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 80% by weight of an extraction residue. The copolymer, the residue, had a weight average molecular weight of 440,000, a number average molecular weight of 240,000 and a melting point of 255°C. The p-methylstyrene unit content of the copolymer was 5 mol%.

A ¹³C-NMR analysis of the copolymer showed peaks at 145.11 ppm, 145.22 ppm and 142.09 ppm.

EXAMPLE 17

A stretched film was produced in the same manner as in



Example 12 except that the styrene copolymer obtained in Reference Example 2 was used and the draw ratio was changed to 3.5 x 3.5.

The physical properties of the film are shown in Table 2.

EXAMPLE 18

To a mixture of 95 parts by weight of the polystyrene obtained in Reference Example 1 and 5 parts by weight of glass fiber having an average fiber length of 3 mm (produced by Asahi Fiber Glass Co., Ltd.; fiber diameter: 10-15 μ m; in the chopped strand form) were added 0.1 part by weight of bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite and 0.1 part by weight of tetraquis(methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate))methane as antioxidants, and the resulting mixture was extruded and pelletized by the use of a twin-screw extruder having diameter of 40 mm.

The pellets thus obtained were introduced into a single screw extruder having a diameter of 40 mm and equipped with a T die at the top thereof, and extruded under conditions of cylinder temperature 290°C, T die temperature 300°C and through put 4.2 kg/hr. while quenching to 30°C at average quenching rate of 75°C/sec. to obtain a sheet having a thickness of 200 μ m.

The sheet was subjected to simultaneous biaxial stretching (draw ratio: 2 x 2) at 125°C to obtain a stretched film. The physical properties of the film are shown in Table 2.

Table 1

No.	Resin ^{*1}	Weight ^{*2} Average Molecular Weight	Cooling Rate °C/sec.	Cooling Temp. °C	Stretch- ing Temp. °C	Mode of Stretch- ing	Draw Ratio		Original Sheet or Film.	
							MD	TD	Thick- ness mm	Crystal- linity %
Example 1	SPS	800,000	50	30	120	Uniaxial	4.5	1.0	0.6	2
Example 2	SPS	800,000	50	30	120	Uniaxial	4.5	1.0	0.6	2
Example 3	SPS	800,000	50	30	125	Simultaneous Biaxial	2.0	2.0	0.6	2
Example 4	SPS	800,000	50	30	125	Simultaneous Biaxial	2.0	2.0	0.6	2
Example 5	SPS	800,000	50	30	120	Simultaneous Biaxial	4.0	4.0	0.6	2
Example 6	SPS	800,000	50	30	125	Sequential Biaxial	3.5	3.0	0.6	2
Example 7	SPS	1,500,000	75	10	120	Simultaneous Biaxial	2.5	2.5	0.6	2
Example 8	SPS	800,000	20	30	125	Simultaneous Biaxial	3.5	3.5	0.6	2
Example 9	SPS	800,000	100	5	130	Simultaneous Biaxial	3.3	3.3	2.0	5

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Table 1 (continued-1)

No.	Annealing		Stretched Molding		Tensile Strength (kg/cm ²)		Tensile Modulus (kg/cm ²)		Haze %	Temp. *4 of 2% Deformation °C
	Temp. °C	Time sec.	Thick- ness μm	Crystall- linity %	MD	TD	MD	TD		
Example 1	-	-	130	51	12	5	101	30	2	110
Example 2	210	20	130	55	13	5.5	110	41	3	209
Example 3	-	-	150	28	10.5	10	39	38	2	115
Example 4	160	20	150	50	10.6	10.2	39	39	5	158
Example 5	-	-	40	46	12	11.8	42	41	2	120
Example 6	-	-	55	44	11	10.4	39	38	2	121
Example 7	213	20	100	51	14	13	43	42	25	210
Example 8	-	-	50	45	11.5	10	39	38	2	121
Example 9	-	-	200	49	11.2	11	39	39	5	120

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Table 1 (continued-2)

No.	Resin #1	Weight #2 Average Molecular Weight	Cooling Rate °C/sec.	Cooling Temp. °C	Stretch- ing Temp. °C	Mode of Stretch- ing	Draw Ratio		Original Sheet or Film	
							MD	TD	Thick- ness mm	Crystal- linity %
Example 10	SPS	400,000	40	30	115	Simultaneous Biaxial	4.0	4.0	0.4	4
Example 11	SPS	250,000	30	30	115	Simultaneous Biaxial	4.5	4.5	0.5	4
Comparative Example 1	SPS	800,000	50	30	-	-	1.0	1.0	0.6	2
Comparative Example 2	SPS	800,000	50	30	-	-	1.0	1.0	0.6	2
Comparative Example 3	SPS	16,000	100	10	120	Simultaneous Biaxial	Unable to Stretch		0.6	2

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Table 1 (continued-3)

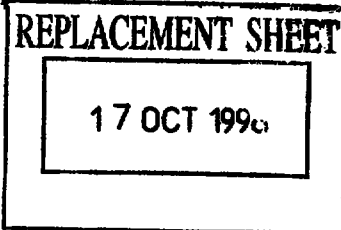
No.	Annealing		Stretched Molding		Tensile Strength (kg/cm ²)		Tensile Modulus (kg/cm ²)		Haze %	Temp. of 2% Deformation °C
	Temp. °C	Time sec.	Thick- ness μm	Crystal- linity %	MD	TD	MD	TD		
Example 10	260	15	25	55	12	12	50	45	1.5	259
Example 11	250	10	25	54	12	12	52	47	1.5	254
Comparative Example 1	-	-	-	-	6.6	4.5	28	29	2	90
Comparative Example 2	150	600	-	41	5.8	4.3	30	30	45	143
Comparative Example 3	-	-	-	-	-	-	-	-	-	-

*1 SPS: syndiotactic polystyrene, COMe: syndiotactic poly(styrene-p-methyl styrene)

*2 measured by Gel Permeation Chromatography (GPC) using 1,2,4-trichlorobenzene as solvent

*3 measured by Differential Scanning Calorimeter (DSC)

*4 Temperature of 2% deformation measured by Thermal Mechanical Analysis (TMA)



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Table 2

No.	Resin ^{*1}	Weight ^{*2} Average Molecular Weight	Cooling Rate °C/sec.	Cooling Temp. °C	Stretch- ing Temp. °C	Mode of Stretch- ing	Draw Ratio	
							MD	TD
Example 12	SPS	800,000	50	30	125	Simultaneous Biaxial	2.0	2.0
Example 13	SPS	800,000	50	30	125	Simultaneous Biaxial	4.0	4.0
Example 14	SPS	800,000	50	30	125	Simultaneous Biaxial	4.0	4.0
Example 15	SPS	800,000	50	30	125	Sequential Biaxial	3.5	3.0
Example 16	SPS	800,000	50	30	170	Sequential Biaxial	3.0	3.0
Example 17	COME	440,000	25	30	125	Simultaneous Biaxial	3.5	3.5
Example 18	SPS	800,000	75	10	125	Simultaneous Biaxial	2.0	2.0
Comparative Example 4	(SPS)	800,000	100	10	-	-	1.0	1.0

Table 2 (continued)

No.	Original Sheet or Film		Annealing		Stretched Molding		Temp. of 2% Deformation °C	BDV ^{*5} kV/mm
	Thick- ness mm	Crystal- linity %	Temp. °C	Time sec.	Thick- ness μm	Crystal- linity %		
Example 12	0.1	2	210	30	25	51	215	200
Example 13	0.4	3	240	30	25	53	240	270
Example 14	0.4	3	190	600	25	52	200	270
Example 15	0.25	3	240	20	25	50	242	270
Example 16	0.2	2	240	30	25	49	241	280
Example 17	0.25	3	170	100	25	48	219	260
Example 18	0.1	2	220	30	25	53	240	205
Comparative Example 4	3	6	170	600	-	49	151	22

*1 to *4 same as in Table 1

*5 Breakdown Voltage (BVD) measured according to JIS C-2110 at 25°C

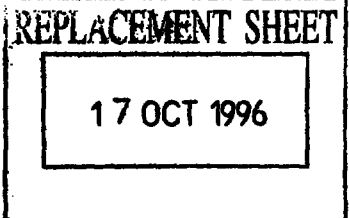
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WHAT IS CLAIMED IS:

1. A stretched styrene-based resin molding as obtained by subjecting a styrene-based polymer having mainly syndiotactic configuration and a weight average molecular weight of at least 50,000 to uniaxial stretching of at least two times or to biaxial stretching of at least 1.2 times in each direction.
2. The molding as claimed in Claim 1, having heat resistance and such transparency that the haze is not more than 30%.
3. The molding as claimed in Claim 1, having such electric insulating properties that the breakdown voltage at 25 °C is at least 30 kV/mm.
4. A process for producing a stretched styrene-based resin molding which comprises subjecting a styrene-based resin having mainly syndiotactic configuration and a weight average molecular weight of at least 50,000 to uniaxial stretching of at least two times or biaxial stretching of at least 1.2 times in each direction.
5. A process for producing a stretched styrene-based resin molding which comprises heat melting a styrene-based resin having mainly syndiotactic configuration and a weight average molecular weight of at least 50,000, quenching the molten resin, and then subjecting the quenched resin to uniaxial stretching at a draw ratio of at least two times or biaxial stretching at a draw ratio of at least 1.2 times in each direction.

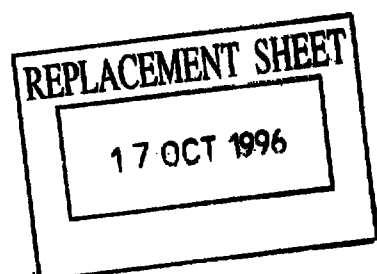




6. The process as claimed in Claim 5, wherein quenching rate is from 200 to 3°C/sec.

7. A stretched styrene-based resin molding as obtained by subjecting the stretched styrene-based resin molding of Claim 1 to annealing at a temperature of 10°C higher than the glass transition temperature to a temperature of 5°C lower than melting point.

8. The stretched styrene-based resin molding as claimed in Claim 7 wherein the temperature of annealing is 120°C to 250°C.

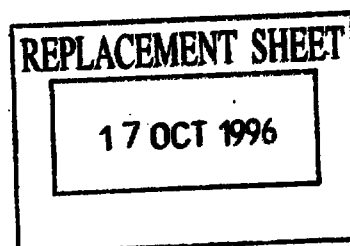


STRETCHED STYRENE-BASED RESIN MOLDINGS AND A PROCESS FOR PRODUCTION THEREOF

ABSTRACT OF THE DISCLOSURE

Stretched moldings (e.g., stretched films, sheets or bottles) of styrene-based resins (e.g., polystyrene) having mainly syndiotactic configuration and a weight average molecular weight of at least 50,000, and a process for the production thereof are disclosed. The stretched moldings are obtained by uniaxially stretching the styrene-based resins at a draw ratio of at least 2 times, or biaxially stretching at a draw ratio of at least 1.2 times in each direction. The stretched moldings are excellent in heat resistance, chemical resistance, solvent resistance, electric insulating properties, mechanical strength and so forth, and thus can be used as food wrapping materials, housing materials for electric or electronic parts, and so forth.

FIGURE 1



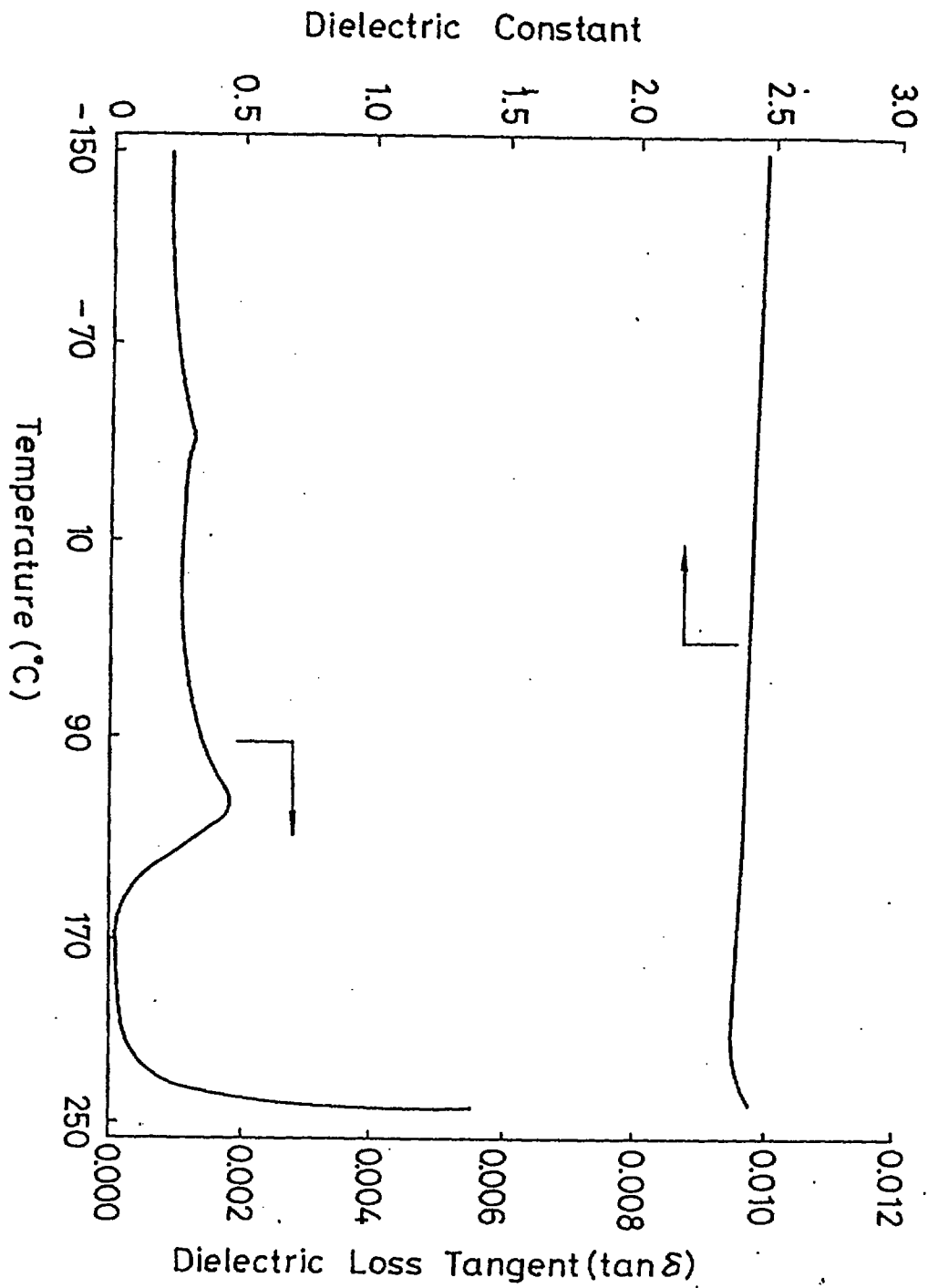


Fig. 1

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