

Method of Manufacturing Molded Article and Method of
Suppressing Blister Generation

TECHNICAL FIELD

The present invention relates to a method of producing a molded article made by injection molding a liquid crystalline resin composition, and a method of suppressing blister generation when injection molding a liquid crystalline resin composition.

BACKGROUND ART

A group of plastics called engineering plastics exhibit high strength, and can be used in place of metal components. Among these, a group of plastics termed liquid crystalline resins maintains a crystalline structure when molten, and therefore exhibit advantages such as high strength due to the crystalline structure, low volumetric change between molten and solidifying states due to low change to the crystalline structure when solidifying, and low mold shrinkage.

These types of liquid crystalline resins have superior heat resistance properties and molding properties, and are preferably used as a constituent material of small electronic components. Among them, it has been known that a liquid crystalline resin composition with enhanced heat resistance is acquired if the liquid crystalline resin and an inorganic filler material are suitably melted and kneaded. For example, a liquid crystalline resin composition in which a fibrous

reinforcing material typified by glass fiber and carbon fiber, or inorganic powder and granular material such as silica, mica, clay and glass beads are filled in a liquid crystalline resin is a material suited to electrical and electronic components having thin parts or complex shapes, due to the balance between fluidity and mechanical strength being desirable. The above such liquid crystalline resin composition is used, for example, in the encapsulant of relay components, coil bobbins, connectors, volume components, motor components such as commutators and separators, or elements and the like such as coils, crystal oscillators, and IC chips.

The liquid crystalline resin composition is an extremely superior material in the above-mentioned ways, and is usable in various applications. However, there is a problem in that an improvement should be made to liquid crystalline resin compositions for the case of molding. The problematic point during molding of this liquid crystalline resin composition is that bubbles are contained inside of the molding product due to the liquid crystalline resin composition that is in a molten state during molding taking in air and the generated gas from the materials. When bubbles are included inside of the molding product, the air and gas in the bubbles expand, and the surface of the molding product bulges due to the molding product being exposed to high temperature in heat treatment and the like. This bulging of the surface of the molding product is called blistering.

Sufficiently degassing from a vent hole during melt

extrusion of the resin composition, and not allowing to the resin composition to stagnate for long in the molding machine during molding, for example, can be exemplified as countermeasures for suppressing the generation of the above such blistering. However, the generation of blistering cannot be adequately suppressed by only a change such as in the conditions during such molding.

Therefore, in order to suppress the abovementioned blister generation, improvements in the liquid crystalline resin composition as well as improvements in molding conditions have been made, for example. Patent Document 1 discloses, for example, a method of manufacturing a liquid crystalline polyester composition with a deflection temperature under loading of at least 230°C, a liquid crystalline resin composition obtained by melt kneading a predetermined liquid crystalline resin composition containing a predetermined amount of inorganic filler material with a kneading machine having an clear aperture for removing volatile component from the kneaded material and a pair of double-threaded screws, in which a screw contact ratio of the kneading machine is adjusted to at least 1.60. According to this technology described in Patent Document 1, it is allegedly possible to provide a liquid crystalline resin composition that excels in blistering resistance, while maintaining the basic heat resistance such as the melting point and the deflection temperature under loading of the liquid crystalline resin composition.

Patent Document 1: Japanese Unexamined Patent Application
Publication No. 2003-211443

SUMMARY

Problems to be Solved

As mentioned above, consideration into suppressing the generation of blisters has been actively conducted. With the above-mentioned methods of improving liquid crystalline resin compositions, it becomes necessary to consider whether or not the properties are suited to the application. In other words, in a case of suppressing blister generation of a liquid crystalline resin composition that is preferable in a particular application, since the above-mentioned liquid crystalline resin composition is changed in the method of improving the conventional materials, it is necessary to reconsider whether or not the liquid crystalline resin composition has the desired properties. Therefore, technology for suppressing the generation of blisters irrespective of the type of liquid crystalline resin composition to be used has been demanded so that it is not necessary to make the above-mentioned property considerations.

In addition, it is possible to suppress the generation of blisters if lowering the injection rate when injection molding a liquid crystalline resin material. However, it is strongly demanded to raise the injection rate from the viewpoint of a productivity improvement in the molding product.

The present disclosure has been made in order to solve the

above-mentioned issues, and an object thereof is to provide a method of manufacturing a molded article that can curb the generation of blisters irrespective of the type of liquid crystalline resin composition to be used, as well as can raise the productivity of the molded article to close to the limit, and a method of suppressing the generation of blisters.

Means for Solving the Problems

The present inventors focused on the matter of liquid crystalline resin compositions holding air in the molten state during molding, and carried out diligent research in order to solve the above such problems. As a result, it was found that the holding of air mainly causing blister generation occurs due to the sprue, and further, found the that above-mentioned problems could be solved by deriving the relationship between the maximum injection volume ($V_{c_{max}}$) for which blisters do not generate and the ratio (ϕ_s/ϕ_n) between the exit diameter of the sprue and the exit diameter of the nozzle by a function of a predetermined form ($V_{c_{max}}=f(\phi_s/\phi_n)$), and injection molding a liquid crystalline resin composition under conditions satisfying $V_{c_{max}} < (\phi_s/\phi_n)$, thereby arriving at completion of the present disclosure. More specifically, the present disclosure provides the following.

According to a first embodiment of the present disclosure, a method manufacturing a molded article includes: a step of measuring a maximum injection volume $(V_{c_{max}})_1$ which does not generate a blister on a surface of the molded article when a liquid crystalline resin composition is injection molded under a

predetermined molding condition; a step of measuring a maximum injection volume $(Vc_{\max})_2$ which does not generate a blister on the surface of the molded article when the liquid crystalline resin composition is injection-molded changing a ratio (Φ_s/Φ_n) of an exit diameter (Φ_s) of a sprue and an exit diameter (Φ_n) of a nozzle; and a step of deriving the relation between a maximum injection volume $(Vc_{\max})$ which does not generate a blister and the ratio (Φ_s/Φ_n) of the sprue exit diameter and the nozzle exit diameter by a function $(Vc_{\max} = f(\Phi_s/\Phi_n))$ of a predetermined form, wherein the liquid crystalline resin composition is injection molded under conditions satisfying $Vc_{\max} \text{ (cm}^3\text{/sec)} < f(\Phi_s/\Phi_n)$.

According to an aspect of the present disclosure, there is provided a method of manufacturing a molded article characterized in comprising:

a step of measuring a maximum injection volume $(Vc_{\max})_1$ which does not generate a blister on a surface of the molded article when a liquid crystalline resin composition is injection molded under a predetermined molding condition,

a step of measuring a maximum injection volume $(Vc_{\max})_2$ which does not generate a blister on the surface of the molded article when the liquid crystalline resin composition is injection-molded changing a ratio (Φ_s/Φ_n) of an exit diameter (Φ_s) of a sprue and an exit diameter (Φ_n) of a nozzle, and

a step of deriving the relation between a maximum injection volume ($V_{c_{max}}$) which does not generate a blister and the ratio (Φ_s/Φ_n) of the sprue exit diameter and the nozzle exit diameter by a function ($V_{c_{max}} = f(\Phi_s/\Phi_n)$) of a predetermined form; wherein

the liquid crystalline resin composition is injection molded under conditions satisfying $V_{c_{max}} \text{ (cm}^3\text{/sec)} < f(\Phi_s/\Phi_n)$, and wherein the exit diameter (Φ_n) of said nozzle is no more than 3 mm.

According to a second embodiment of the present disclosure, in the method of manufacturing a molded article as described above, the function of predetermined form is represented by the following Equation (I), and the liquid crystalline resin composition is injection molded under molding conditions satisfying the following Equation (II):

$$V_{c_{max}} \text{ (cm}^3\text{/sec)} < -45(\Phi_s/\Phi_n) + 240 \cdots \text{(I)}$$

$$\Phi_n < 3 \text{ mm} \cdots \text{(II)}$$

According to a third embodiment of the present disclosure, in the method of manufacturing a molded article as described above, the nozzle exit diameter (Φ_n) is no more than 2 mm.

According to a fourth embodiment of the present disclosure, in the method of manufacturing a molded article as described above, the liquid crystalline

resin composition contains a glass fiber.

According to a fifth embodiment of the present disclosure, in the method of manufacturing a molded article as described above, the ratio (Φ_s/Φ_n) of the exit diameter of the sprue and the exit diameter of the nozzle is no more than 4.5.

According to another aspect of the present disclosure, there is provided a method of suppressing blister generation when injection molding a liquid crystalline resin composition by making a ratio of an exit diameter (mm) of a sprue and an exit diameter (mm) of a nozzle (Φ_s/Φ_n) no more than a predetermined value.

According to a further embodiment of the present disclosure, in the method of suppressing blister generation as described in the above aspect, the predetermined value is no more than 4.5 and the exit diameter (Φ_n) of the abovementioned nozzle is no more than 3 mm.

Effects of the Present Disclosure

According to the present disclosure, it is possible to easily derive the conditions with the largest injection volume possible. The productivity of a molding product obtained is higher with a larger injection volume. As a result, it is possible to raise the productivity of a molding product to near the limit when molding a liquid crystalline resin composition. In addition, the present disclosure has no restrictions in the liquid crystalline resin composition to be used therewith. Therefore, reconsideration of the properties due to material changes also become unnecessary, and it is

possible to easily raise the productivity of a molding product made by molding a liquid crystalline resin composition.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an illustration showing a state in which a runner, a sprue and a nozzle are connected;

FIG. 2 is a graph showing a relationship between the ratio (Φ_s/Φ_n) and injection volume $(V_{C_{max}})$; and

FIG. 3 is a graph showing a relationship between the ratio (Φ_s/Φ_n) and injection volume $(V_{C_{max}})$ according to an example.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

Although an embodiment of the present invention will be explained in detail hereinafter, the present invention is not to be at all limited to the following embodiment, and can be implemented by including suitable modifications within the scope of the object of the present invention.

The method of manufacturing a molded article of the present invention includes: a step of measuring a maximum injection volume $(V_{C_{max}})_1$ which does not generate a blister on a surface of the molded article when a liquid crystalline resin composition is injection molded under a predetermined molding condition (hereinafter may be referred to as "first injection volume measurement step"); a step of measuring a maximum injection volume $(V_{C_{max}})_2$ which does not generate a blister on the surface of the molded article when the liquid crystalline resin composition is injection-molded changing a ratio (Φ_s/Φ_n)

of an exit diameter (ϕ_s) of a sprue and an exit diameter (ϕ_n) of a nozzle (hereinafter may be referred to as "second injection volume measurement step"); a step of deriving the relation between a maximum injection volume (VC_{max}) which does not generate a blister and the ratio (ϕ_s/ϕ_n) of the sprue exit diameter and the nozzle exit diameter by a function ($VC_{max} = f(\phi_s/\phi_n)$) of a predetermined form (hereinafter may be referred to as "relational expression derivation step"); and a step of injection molding the liquid crystalline resin composition under conditions satisfying $VC_{max} < f(\phi_s/\phi_n)$ (hereinafter may be referred to as "injection molding step").

First Injection Volume Measurement Step

The first injection volume measurement step is a step of measuring a maximum injection volume (VC_{max})₁ which does not generate blisters on the surface of a molded article, in a case of injection molding a liquid crystalline resin composition under predetermined molding conditions. The method of measuring the maximum injection volume which does not generate blisters is not particularly limited and, for example, the ratio (ϕ_s/ϕ_n) between the exit diameter of the sprue and the exit diameter of the nozzle is fixed to a predetermined value, the condition of injection volume is raised step-wise until blisters generate, and the condition of the injection volume at one step lower than the condition of the injection volume for which blisters generated can be set as the "maximum injection capacity (VC_{max}) for which blisters do not generate". By how much of an interval the injection volume is raised when

increasing the condition of injection volume step-wise to measure the maximum injection volume is changed as appropriate according to the liquid crystalline resin composition to be used. In the present invention, there is a characteristic in obtaining the relationship between the maximum injection volume ($V_{c_{max}}$) which does not generate blisters and the ratio (ϕ_s/ϕ_n) of the sprue exit diameter and the nozzle exit diameter, as described later. In the present step, the maximum injection volume ($V_{c_{max}}$) is obtained at a predetermined ratio (ϕ_s/ϕ_n) required in order to acquire the above-mentioned relationship. The above-mentioned ratio and injection volume obtained in the present step are set as $(\phi_s/\phi_n)_1$ and $(V_{c_{max}})_1$, respectively.

A state in which a runner, sprue and nozzle are connected is shown in FIG. 1. As shown in FIG. 1, the sprue exit diameter is the sprue diameter of the connection portion between the sprue and the runner. In addition, as shown in FIG. 1, the nozzle exit diameter is the nozzle inside diameter at a nozzle tip exit.

Regarding "blister generate on the surface of the molded article", how to determine whether or not blisters generate is not particularly limited. In the present invention, a determination method of molding at least five molded articles by way of injection molding under predetermined molding conditions, conducting reflow processing with a peak temperature of 280°C (reflow processing performed under the conditions described in the Examples, for example) on all of

the molded articles, and evaluating as "blisters generate" if blisters generate even in one according to visual observation, for example, is preferred. By performing blister evaluation of at least five molded articles from injection molding under the same predetermined molding conditions, it is possible to represent the relationship between the maximum injection volume ($V_{C_{max}}$) which does not generate blisters, and the ratio (Φ_s/Φ_n) of the sprue exit diameter and the nozzle exit diameter with a more accurate relational expression.

Predetermined Molding Conditions

The predetermined molding conditions are the conditions during injection molding such as the type of molding machine, mold temperature, injection rate, and screw rotation speed. These conditions are changed to the preferred conditions as appropriate depending on the type of liquid crystalline resin composition to be used. In the present step, the maximum injection volume for which blisters do not generate in the surface of the molded article is measured by changing only the condition of injection volume and repeating injection molding.

As described above, in the present invention, the relationship between the maximum injection volume ($V_{C_{max}}$) which does not generate blisters and the ratio (Φ_s/Φ_n) of the sprue exit diameter and nozzle exit diameter is obtained, as described above. The maximum injection volume which does not generate blisters on the surface of a molded article is thereby measured in the present invention. So long as being a method that measures not the injection rate or the like, but

rather the injection volume and obtains the above-mentioned relationship, there will be the advantage of applicability to molding machines with various screw diameters.

The ratio (Φ_s/Φ_n) between the sprue exit diameter and the nozzle exit diameter is preferably no more than 4.5, as described later.

The present invention can derive conditions at which blisters do not generate in the surface of a molded article when injection molding a liquid crystalline resin composition. The above-mentioned blisters on the surface of a molded article tend to easily generate in a case of the exit diameter of the nozzle being less than 3 mm. Therefore, in a case of predetermined molding conditions in which the exit diameter of the nozzle is less than 3 mm, there is a benefit to using the method of manufacturing a molding article of the present invention. It should be noted that problems arise such as "drooling", when set to conditions in which the exit diameter of the nozzle is 3 mm or more. As a result, it is necessary to set the nozzle diameter to less than 3 mm for most liquid crystalline resin compositions. Therefore, the present invention is beneficial for a very large number of liquid crystalline resin compositions. Herein, "drooling" is a phenomenon in which molten resin discharges from the nozzle. In particular, according to the method of manufacturing a molded article of the present invention, problems other than blisters, drooling and the like do not arise even under conditions with an exit diameter of the nozzle of 2 mm or less,

and thus a molded article made by molding a liquid crystalline resin composition can be obtained with high productivity. In addition, the exit diameter of the nozzle is preferably at least 1 mm from the viewpoint of ensuring liquidity (causing the resin to be completely filled inside of the mold cavity).

Liquid Crystalline Resin Composition

Liquid crystalline resin used in the present invention indicates a melt processable polymer having a property of being able to form an optically anisotropic molten phase. The property of the anisotropic molten phase can be confirmed by a common method employing an orthogonal polarizer. More specifically, confirmation of the anisotropic molten phase can be performed using a Leitz polarizing microscope by observing a molten sample placed on a Leitz hot stage at a magnification of 40 times under a nitrogen atmosphere. When a liquid crystalline resin that can be employed in the present invention is examined between an orthogonal polarizer, polarized light normally penetrates even if in a molten stationary state, for example, and thus exhibits anisotropy optically.

Although the above such liquid crystalline resin is not particularly limited, it is preferably an aromatic polyester or aromatic polyester amide, and a polyester partly containing aromatic polyester or aromatic polyester amide in the same molecular chain is also in the scope thereof. When these are melted at 0.1% by weight concentration in pentafluorophenol at 60°C, it is preferable to use a polyester having a inherent

viscosity (I.V.) of at least about 2.0 dl/g, and more preferably 2.0 to 10.0 dl/g.

Particularly preferable as the aromatic polyester or aromatic polyester amide for liquid crystalline resins that can be employed in the present invention are an aromatic polyester, or aromatic polyester amide having at least one compound selected from the group of aromatic hydroxycarboxylic acid, aromatic hydroxylamine and aromatic diamine as a constituent component.

More specifically,

(1) polyesters mainly composed of at least one of aromatic hydroxycarboxylic acid and derivatives thereof;

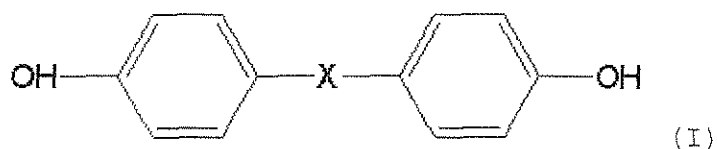
(2) polyesters mainly composed of (a) at least one of aromatic hydroxycarboxylic acid and derivatives thereof, (b) at least one of aromatic dicarboxylic acid, alicyclic dicarboxylic acid and derivatives thereof; and (c) at least one of aliphatic diol, alicyclic diol, aliphatic diol and derivatives thereof;

(3) polyester amides mainly composed of (a) at least one of aromatic hydroxycarboxylic acid and derivatives thereof, (b) at least one of aromatic hydroxylamine, aromatic diamine and derivatives thereof, and (c) at least one of aromatic dicarboxylic acid, alicyclic dicarboxylic acid and derivatives thereof;

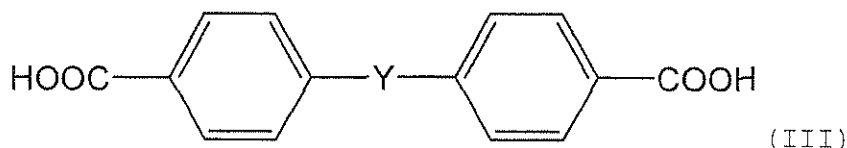
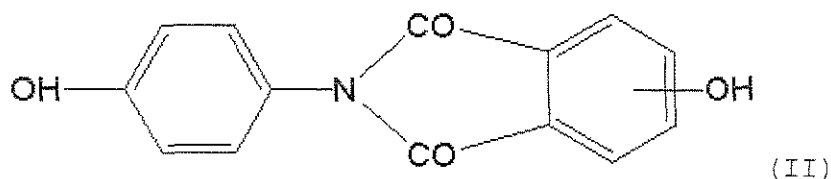
(4) polyester amides mainly composed of (a) at least one of aromatic hydroxycarboxylic acid and derivatives thereof, (b) at least one of aromatic hydroxylamine, aromatic diamine

and derivatives thereof, (c) at least one of aromatic dicarboxylic acid, alicyclic dicarboxylic acid and derivatives thereof, and (d) at least one aromatic diol, alicyclic diol, aliphatic diol and derivatives thereof; etc. can be exemplified, and a molecular weight modifier may be further used together with the above-mentioned constituent components as necessary.

As preferred examples of specific compounds configuring the liquid crystalline resins that can be employed in the present invention, aromatic hydroxycarboxylic acids such as p-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, aromatic diols such as 2,6-naphthalenediol, 1,4-dihydroxynaphthalene, 4,4'-dihydroxybiphenyl, hydroquinone, resorcin, and compounds represented by the following general formula (I) and the following general formula (II); aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, 4,4'-diphenyldicarboxylic acid, 2,6-naphthalenedicarboxylic acid, and compounds represented by the following general formula (III); and aromatic amines such as p-aminophenol and p-phenylenediamine can be exemplified.



(X: is a group selected from an alkylene (C_1 to C_4), alkydene, -O-, -SO-, -SO₂-, -S- and -CO-.)



(Y: is a group selected from $-(CH_2)_n-$ ($n=1$ to 4) and $-O(CH_2)_nO-$ ($n=1$ to 4).)

Among the liquid crystalline resin compositions to be used in the present invention, it may contain at least two types of liquid crystalline resins, and it may contain a resin other than a liquid crystalline resin. In addition, a composition imparted with a desired property may also be contained by adding a nucleating agent, pigment such as carbon black and an inorganic firing pigment, or an added agent such as an antioxidant, a stabilizer, a plasticizer, a lubricant, a mold release agent, a fire retardant, or the like.

In particular, the method of manufacturing a molded article of the present invention is suited for a case of using a liquid crystalline resin composition containing an inorganic filler. The usable inorganic fillers are not particularly limited, and a conventional, well-known one can be used. For the conventional, well-known inorganic fillers, for example, inorganic fibrous materials such as asbestos fiber, silica fiber, silica-alumina fiber, alumina fiber, zirconia fiber, boron nitride fiber, silicon nitride fiber, boron fiber and potassium titanate fiber, and further, the fibrous form of

metals such as stainless steel, aluminum, titanium, copper and brass can be exemplified as fibrous fillers. As powder and granular fillers, carbon black, graphite, silica, quartz powder, glass beads, milled glass fiber, glass balloons, glass powder, silicates like calcium silicate, aluminum silicate, kaolin, talc, clay, diatom earth and wollastonite, oxides of metals like iron oxide, titanium oxide, zinc oxide, antimony trioxide and alumina, carbonates of metals like calcium carbonate and magnesium carbonate, sulfates of metals like calcium sulfate and barium sulfate, other ferrites, silicon carbide, silicon nitride, boron nitride, various metal powders, and the like can be exemplified. Compositions containing a plurality of types of these inorganic fillers are also included among the liquid crystalline resin compositions that are usable in the present invention. In addition, mica, glass flakes, various metallic foils, and the like can be exemplified as plate-like fillers. Among these inorganic fillers, it is preferable to use glass fiber and talc, as described later.

Second Injection Volume Measurement Step

A second injection volume measurement step is a step of changing the ratio (Φ_s/Φ_n) of the exit diameter (Φ_s) of the sprue and the exit diameter (Φ_n) of the nozzle in the predetermined molding conditions of the above-mentioned first injection volume measurement step, and measuring the maximum injection volume ($V_{c_{max}}$) which does not generate blisters on the surface of a molded article, in a case of injection

molding the above-mentioned liquid crystalline resin composition. The above-mentioned ratio (Φ_s/Φ_n) set in the present step and the above-mentioned injection volume $(V_{C_{max}})$ obtained in the present step are defined as $(\Phi_s/\Phi_n)_2$ and $(V_{C_{max}})_2$, respectively. The present invention obtains the relationship between the maximum injection volume $(V_{C_{max}})$ for which blisters do not generate, and the ratio (Φ_s/Φ_n) of the exit diameter of the sprue and the exit diameter of the nozzle, as described later. It is possible to obtain the relationship between the ratio (Φ_s/Φ_n) and injection volume $(V_{C_{max}})$ by obtaining $(\Phi_s/\Phi_n)_2$ and $(V_{C_{max}})_2$ obtained in the present step, in addition to $(\Phi_s/\Phi_n)_1$ and $(V_{C_{max}})_1$ obtained in the above-mentioned first injection volume measurement step. The measurement method for the maximum injection volume for which blisters do not generate is not particularly limited, similarly to the case of the first injection volume measurement step.

It is preferable for the injection volume $(V_{C_{max}})$ to be at least 30 (cm³/s). From the viewpoint of productivity, the case of the injection volume being lower than 30 (cm³/s) is a region in which molding usually is not done when dealing with a liquid crystalline resin.

After the second injection volume measurement step, it is preferable to change the ratio (Φ_s/Φ_n) and perform a third injection volume measurement step to measure a maximum injection volume $(V_{C_{max}})_3$ for which blisters do not generate in the surface of a molded article. This is because the

relationship between the ratio (Φ_s/Φ_n) and the injection volume $(V_{C_{max}})$ can be more accurately obtained by using lots of data. In addition, it is preferable for the injection volume $(V_{C_{max}})$ in the measurement performed after the above-mentioned second injection volume measurement step to be at least 30 (cm^3/s) . This is because the relational expression described later is obtained more accurately.

Relational Expression Derivation Step

A relational expression derivation step is a step of deriving a relationship between the maximum injection volume which does not generate blisters $(V_{C_{max}})$ and the ratio (Φ_s/Φ_n) of the exit diameter of the sprue and the exit diameter of the nozzle with a function of a predetermined form $(V_{C_{max}}=f(\Phi_s/\Phi_n))$. One of the characteristics of the present invention is in having discovered that there is a correlation between the above-mentioned ratio (Φ_s/Φ_n) and the maximum injection volume $(V_{C_{max}})$ for which blisters do not generate, and furthermore, in finding that this relational expression can be applied for many liquid crystalline resin compositions.

The derivation method of the specific relational expression acquires an approximation function $(V_{C_{max}}=f(\Phi_s/\Phi_n))$ as shown in FIG. 2A, from $(\Phi_s/\Phi_n)_1$ and $(V_{C_{max}})_1$ obtained in the first injection volume measurement step and $(\Phi_s/\Phi_n)_2$ and $(V_{C_{max}})_2$ obtained in the second injection volume measurement step. Although the form of the approximation formula is not particularly limited, power approximation, logarithmic approximation, linear approximation, polynomial approximation,

exponential approximation, and the like can be exemplified. It should be noted that the approximation function can be obtained by a conventional, well-known method. For example, it can be obtained with a method using Microsoft Excel spreadsheet software.

In particular, as shown in FIG. 2(b), when the injection volume is lower than a certain fixed value, the relationship between the ratio (Φ_s/Φ_n) and the injection volume ($V_{C_{max}}$) enters a state not generating blisters, regardless of the ratio (Φ_s/Φ_n). Usually, the "certain fixed value" is 30 (cm^3/s). As a result, the important portion for the consideration of molding conditions is the portion of 30 (cm^3/s) or more. This is due to being an invention for raising the productivity of a molded article by manufacturing the molded article under conditions in which the injection volume is as large as possible, and because there is concern over blister generation under conditions of a high injection volume of 30 (cm^3/s) or more. Therefore, the above-mentioned relational expression is preferably obtained from the data of at least the injection volume for which blisters do not generate irrespective of the ratio (Φ_s/Φ_n) (normally 30 (cm^3/s)). In particular, an accurate relational expression can be easily acquired by deriving the relationship between the ratio (Φ_s/Φ_n) and the injection volume ($V_{C_{max}}$) using a linear approximation from only the data before the injection volume ($V_{C_{max}}$) becomes constant (a and b in FIG. 2(b) are constants), as shown in FIG. 2(b).

An inorganic filler as described above can be contained in the liquid crystalline resin composition. The mixing of glass fibers is often performed for an improvement in properties; however, the present invention can be preferably applied also to a liquid crystalline resin composition containing glass fibers. Then, in a case of a liquid crystalline resin composition containing glass fibers, there is a tendency of the relationship between the ratio (Φ_s/Φ_n) and the injection volume ($V_{C_{max}}$) to be $V_{C_{max}}(\text{cm}^3/\text{sec}) = -45 (\Phi_s/\Phi_n) + 240$. In particular, this relational expression can be applied to many liquid crystalline resin compositions containing glass fibers.

As described above, when acquiring the approximation function, a more accurate relational expression can be obtained by acquiring an approximation function from more data of the above-mentioned ratio (Φ_s/Φ_n) and the injection volume ($V_{C_{max}}$). In particular, the relational expression can be obtained more accurately by using at least three data points. Furthermore, the data of the ratio (Φ_s/Φ_n) and the injection volume ($V_{C_{max}}$) are preferably data of at least the injection volume for which blisters do not generate irrespective of the ratio (Φ_s/Φ_n) (normally $30 (\text{cm}^3/\text{s})$).

In addition, for a lower limit of the ratio (Φ_s/Φ_n) of the sprue diameter and nozzle diameter, it is preferable for the ratio (Φ_s/Φ_n) to be at least 1.2 for the reason of fluidity preservation.

Injection Molding Step

An injection molding step is a step of injection molding a

liquid crystalline resin compositions under conditions satisfying $V_{c_{max}} \text{ (cm}^3\text{/sec)} < f \text{ } (\Phi_s/\Phi_n)$. It is a step of performing the manufacturing of a molded article by adjusting the exit diameter of the sprue, exit diameter of the nozzle, and injection volume such that $V_{c_{max}} \text{ (cm}^3\text{/sec)} < f \text{ } (\Phi_s/\Phi_n)$ is satisfied, in addition to the desired molding conditions. In other words, the conditions of the exit diameter of the sprue, exit diameter of the nozzle, and injection volume are set from the region of the forward-slashed portion in FIGS. 2A and 2B. It should be noted that the desired molding conditions are the mold temperature, screw rotation speed, etc., similarly to those explained in the above-mentioned "Predetermined Molding Conditions", and the desired molding conditions are predetermined molding conditions decided based on the liquid crystalline resin composition to be used and the like, set in the first injection volume measurement step, normally.

Although the conditions of the exit diameter of the sprue, exit diameter of the nozzle and injection volume are set from the region of the forward-slashed portions in FIGS. 2A and 2B, as described above, when setting, the above-mentioned conditions are set in a range in which a superior molding product is obtained without other problems such as drooling arising.

In particular, by selecting conditions in which the ratio (Φ_s/Φ_n) of the exit diameter of the sprue and the exit diameter of the nozzle is no more than 4.5, there will be a tendency for blisters not to generate even for a high

injection volume. Therefore, it is preferable to perform injection molding at the condition of the ratio (ϕ_s/ϕ_n) of no more than 4.5. It is thereby possible to suppress blister generation when injection molding a liquid crystalline resin composition, under the condition of the highest injection volume possible, by setting the ratio (ϕ_s/ϕ_n) of the exit diameter (mm) of the sprue and the exit diameter (mm) of the nozzle to no more than a predetermined value. Blisters tend to easily generate in a case of the exit diameter of the nozzle being less than 3 mm. Therefore, the method of suppressing blister generation of the present invention is particularly beneficial in a case of the exit diameter of the nozzle being less than 3 mm. In addition, it is preferable to perform molding in the range of the above-mentioned ratio (ϕ_s/ϕ_n) of at least 1.2 for the reason of fluidity preservation.

In addition, in a case of injection molding a liquid crystalline resin composition as described above, it is preferable for the exit diameter of the nozzle to be set to at least 1.0 mm and less than 3 mm. More preferably, the range of the nozzle diameter is from 1.2 mm to 1.5 mm. In addition, it is preferable for the ratio (ϕ_s/ϕ_n) of the exit diameter of the sprue and the exit diameter of the nozzle to be from 1.2 to 4.5. Herein, in a case of the exit diameter of the nozzle being 1.2 mm, it becomes preferable for the exit diameter of the sprue to be from 1.44 mm to 5.4 mm. Then, in a case of the exit diameter of the nozzle being 1.5 mm, it becomes preferable for the exit diameter of the sprue to be from 1.8

mm to 6.75 mm. As a result, the exit diameter of the sprue is preferably from 1.44 mm to 6.75 mm. Usually, the exit diameter of the sprue used when molding a liquid crystalline resin composition is on the order of 7.0 mm. A liquid crystalline resin composition that is in the molten state has high fluidity. As a result, it is possible to set the exit diameter of the sprue to be small. However, if the exit diameter of the sprue is set too small, the molten resin will not flow easily, and the productivity of the molding product will decrease, even if a liquid crystalline resin with high fluidity in the molten state. As a result, conventionally, the exit diameter of the sprue has been set with sufficient margin so as not to obstruct the flow of molten resin. With the present invention, it is possible to perform molding under conditions in which the injection volume is as high as possible in a range in which the flow of molten resin is not obstructed and problems such as blisters do not occur. As a result, it is possible to acquire a high quality molding product with high productivity. In addition, the liquid crystalline resin composition remaining in a portion of the sprue after molding and having solidified in this portion is re-used. If the method of manufacturing molded articles of the present invention, the volume of resin remaining in the sprue portion will be less since the exit diameter of the sprue can be made smaller than conventionally, and thus the amount of liquid crystalline resin composition that must be re-used can be curbed. As a result, the labor for reusing is reduced, and the productivity

of a high-quality molded article rises.

Such effects being obtained is considered to be due to adjusting the ratio (Φ_s/Φ_n) of the exit diameter of the sprue and the exit diameter of the nozzle so that the molten resin discharged from the nozzle attaches to an inner wall surface of the sprue in the vicinity of the inlet of the sprue, and the molten resin progresses until the exit of the sprue so as to follow this inner wall surface, whereby it difficult for air to be held inside the sprue and bubbles are prevented from mixing into the molding product.

EXAMPLES

Although the present invention will be explained in further detail by providing Examples, the present invention is not to be limited by these Examples.

Materials

Liquid Crystalline Resin Composition 1: liquid crystalline resin composition in which glass fibers have been filled at 30% by mass into a liquid crystalline resin (made by Polyplastics Co., Ltd., "VECTRA E950i") with a melting point of 336°C and melt viscosity of 30 Pa·s (measured at 350°C, 1000/s shear velocity)

Liquid Crystalline Resin Composition 2: liquid crystalline resin composition in which glass fibers and talc have been filled at 20% by mass and 15% by mass, respectively, into a liquid crystalline resin (made by Polyplastics Co., Ltd., "VECTRA E950i") with a melting point of 336°C and melt

viscosity of 30 Pa·s (measured at 350°C, 1000/s shear velocity)

Example 1

First Injection Volume Measurement Step

Using the liquid crystalline resin compositions 1 and 2, injection molding was performed using an injection molding machine ("α-50-C" made by Fanuc Corp.) under molding conditions fixing the exit diameter of the nozzle to 1.5 mm, the ratio (Φ_s/Φ_n) of 2, and the other molding conditions shown below. In addition, after performing molding of 5 shots for the condition of each injection volume in sequence from lowest for the injection volumes of 26.5 (cm³/sec), 39.8 (cm³/sec), 53.1 (cm³/sec), 66.3 (cm³/sec), 79.6 (cm³/sec), 92.9 (cm³/sec), 106.1 (cm³/sec), 119.4 (cm³/sec), 132.7 (cm³/sec) and 145.9 (cm³/sec) and 159.2 (cm³/sec), reflow processing (detailed conditions described later) with a peak temperature of 280°C was conducted, and if a shot in which blisters generated was not confirmed in visual observation, molding of 5 shots was performed under a higher injection volume condition, the same reflow processing was conducted, and evaluation was performed visually until blisters generated, whereby the maximum injection volume ($V_{C_{max}}$) for which blisters do not generate (none observed visually) was obtained. The results of the first injection volume measurement step are shown in Table 1.

(Molding Conditions)

Screw diameter: ϕ 26 mm

Screw rotation speed: 100 rpm

Backpressure: 3 MPa

Hold pressure: 50 MPa

Holding time: 1 sec

Cooling time: 5 sec

Suck back: 3 mm

Cycle time: 15 sec

Cylinder temperature: 340°C-340°C-330°C-320°C

Mold temperature: 80°C

(Reflow Conditions)

Apparatus: infrared reflow furnace ("RE-300", made by Japan Pulse Laboratories, Inc.)

Preheat zone temperature setting: 150°C × 3 min

Heat zone temperature setting: 218°C × 2 min

Heating furnace transit time: 5 min

Molding product surface peak temperature: 280°C

(Molding product surface peak temperature is the highest temperature measured by holding a thermocouple to the molding product surface under reflow heating conditions.)

Second Injection Volume Measurement Step

Except for changing the ratio (Φ_s/Φ_n) from 2 to 3.3, the maximum injection volume for which blisters do not generate was obtained by the same method as in the first injection volume measurement step. The results of the second injection volume measurement step are shown in Table 1.

Furthermore, the maximum injection volume for which blisters do not generate was obtained at a value of the ratio (Φ_s/Φ_n) such as those shown below. The ratio (Φ_s/Φ_n) was

changed to 4.7, and the maximum injection volume for which blisters do not generate was obtained by the same method as in the first injection volume measurement step. The ratio (Φ_s/Φ_n) was changed to 6, and the maximum injection volume for which blisters do not generate was obtained by the same method as in the first injection volume measurement step. The ratio (Φ_s/Φ_n) was changed to 7.3, and the maximum injection volume for which blisters do not generate was obtained by the same method as in the first injection volume measurement step. The results of these are also shown in Table 1. Furthermore, graphs of the results of Table 1 are shown in FIG. 3.

Relational Expression Derivation Step

The relationship between the ratio (Φ_s/Φ_n) and injection volume ($V_{C_{max}}$) showed the same behavior for both of the liquid crystalline resin compositions 1 and 2. Therefore, an approximation formula representing the relationship between the ratio (Φ_s/Φ_n) and the injection volume ($V_{C_{max}}$) was obtained as a linear function by a method using Microsoft Excel spreadsheet software, using the data of the liquid crystalline resin compositions 1 and 2 with values for the ratio (Φ_s/Φ_n) of 2, 3.3 and 4.7. The linear function acquired was $V_{C_{max}} = -45(\Phi_s/\Phi_n) + 240$ (dotted line in FIG. 3).

[Table.1]

		ϕ_s/ϕ_n	$V_{c_{max}}$ (cm^3/sec)
Example 1	liquid crystalline resin compositions 1	2	159.2
		3.3	92.9
		4.7	53.1
		6	26.5
		7.3	26.5
	liquid crystalline resin compositions 2	2	159.2
		3.3	106.1
		4.7	26.5
		6	26.5
		7.3	26.5

By using the method of manufacturing of the present invention as mentioned above, it is possible to increase the condition of injection volume to the utmost extent. In addition, the method of manufacturing of the present invention can be applied irrespective of the type of liquid crystalline resin composition to be used. As a result, it is possible to suppress the generation of blisters, while being able to easily raise the productivity of molded articles to near the limit, without making modifications such as a change in materials.

CLAIMS

1. A method of manufacturing a molded article characterized in comprising:

a step of measuring a maximum injection volume $(V_{c_{max}})_1$ which does not generate a blister on a surface of the molded article when a liquid crystalline resin composition is injection molded under a predetermined molding condition,

a step of measuring a maximum injection volume $(V_{c_{max}})_2$ which does not generate a blister on the surface of the molded article when the liquid crystalline resin composition is injection-molded changing a ratio (Φ_s/Φ_n) of an exit diameter (Φ_s) of a sprue and an exit diameter (Φ_n) of a nozzle, and

a step of deriving the relation between a maximum injection volume $(V_{c_{max}})$ which does not generate a blister and the ratio (Φ_s/Φ_n) of the sprue exit diameter and the nozzle exit diameter by a function $(V_{c_{max}} = f(\Phi_s/\Phi_n))$ of a predetermined form; wherein

the liquid crystalline resin composition is injection molded under conditions satisfying $V_{c_{max}} \text{ (cm}^3\text{/sec)} < f(\Phi_s/\Phi_n)$, and wherein the exit diameter (Φ_n) of said nozzle is no more than 3 mm.

2. The method of manufacturing a molded article according to claim 1 characterized in that the function of predetermined form is represented by the following Equation (I), and

the liquid crystalline resin composition is injection molded under molding conditions satisfying the following Equation (II):

$$V_{C_{\max}} (\text{cm}^3/\text{sec}) < -45 (\Phi_s/\Phi_n) + 240 \cdots (I)$$

$$\Phi_n < 3 \text{ mm} \cdots (II)$$

3. The method of manufacturing a molded article according to claim 1 or 2 characterized in that the nozzle exit diameter (Φ_n) is no more than 2 mm.

4. The method of manufacturing a molded article according to any one of claims 1 to 3 characterized by that the liquid crystalline resin composition contains a glass fiber.

5. The method of manufacturing a molded article according to any one of claims 1 to 4 wherein the ratio (Φ_s/Φ_n) of the exit diameter of the sprue and the exit diameter of the nozzle is no more than 4.5.

6. A method of suppressing blister generation when injection molding a liquid crystalline resin composition by making a ratio of an exit diameter (mm) of a sprue and an exit diameter (mm) of a nozzle (Φ_s/Φ_n) no more than a predetermined value.

7. The method of suppressing blister generation according to claim 6 wherein the predetermined value is no more than 4.5 and the exit diameter (Φ_n) of the abovementioned nozzle is no more than 3 mm.