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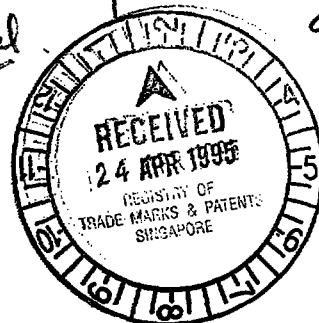


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TITLE OF THE INVENTION

LIQUID CRYSTAL POLYESTER RESIN BLEND

FIELD OF THE INVENTION

The present invention relates to a liquid crystal polyester resin blend in which a liquid crystal polyester material is stably plasticized during a molding process, which can be stably molded and which gives a molded material having excellent mechanical properties and thermal stability. The present invention also relates to a method for molding a liquid crystal polyester material wherein said liquid crystal polyester resin blend is used as the liquid crystal polyester material.

RELATED ART

A liquid crystal polyester is generally referred to as a thermotropic liquid crystal polymer, since it has a rigid molecule which has no intertwist during a melted state, it forms a polydomain having a liquid crystal state and it exhibits a behavior that a molecular chain is remarkably oriented in a flow direction at a low shear rate. The liquid crystal polyester has an extremely excellent melt flowability due to said unique behavior and has the thermal deformation resistance at a temperature of at least 300°C depending on a structure. The liquid crystal polyester is used as a molded material such as an electronic part, an OA (office automation) part, an AV (audiovisual) part, a thermal resistant tableware and the like.

A method for obtaining the molded material generally uses an extruder having a screw as in an injection molding and an extrusion. In this case, the liquid crystal polyester often has a problem of non-stability during a plasticizing process. Namely, the plasticization time is not constant and stable. In the case of the injection molding, a



plasticization does not sometimes come to an end during a cooling time so that the molding cannot be completed at a constant cycle and the productivity and quality of the molded material are often adversely affected.

The reasons why the plasticization time of the liquid crystal polyester is unstable are unclear. One of the reasons is believed to be that, since the liquid crystal polyester has a high dependency of a melt viscosity of the liquid crystal polyester itself on the shear rate and the temperature, only a particle surface of the liquid crystal polyester is selectively plasticized so that the cohesion easily occurs.

In order to prevent such phenomenon, Japanese Patent Kokai Publication No. 125259/1993 discloses the use of a composition in which a higher aliphatic acid and a metal salt of higher aliphatic acid are mixed with the thermotropic liquid crystal polymer. Japanese Patent Kokai Publication No. 125258/1993 discloses that the use of a particle mixture comprising thermotropic liquid crystal polymer particles and a metal salt of higher aliphatic acid gives a stable plasticization.

However, in every case, the higher aliphatic acid or the metal salt thereof having a decomposition at a high temperature is used together with the liquid crystal polymer having the high thermal resistance. When the molded material of the liquid crystal polymer is obtained, a large amount of gas evolves in a molding machine so that it is difficult to conduct the stable molding and the thermal stability of the molded material is decreased, whereby sometimes resulting in the insufficiency for an advanced application.

SUMMARY OF THE INVENTION

An object of the present invention is to solve the above

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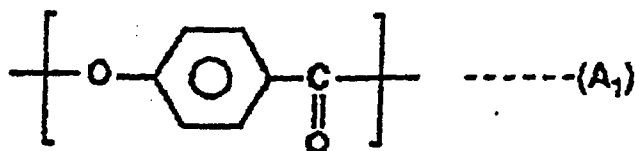
problems and to provide a liquid crystal polyester resin blend which is stably plasticized during a molding process, which can be stably molded and which gives a molded material having excellent mechanical properties and thermal stability.

Another object of the present invention is to provide a method for molding a liquid crystal polyester material wherein the above liquid crystal polyester resin blend is used as the liquid crystal polyester material.

The present inventors intensively studied a solution of the above problems and then found that a liquid crystal polyester resin composition comprising a liquid crystal polyester and an optional filler as the main components is mixed with a fluorinated resin to give a liquid crystal polyester resin blend achieving the above objects and that a liquid crystal polyester material can be stably plasticized during the molding process by the use of said liquid crystal polyester resin blend.

The present invention provides a liquid crystal polyester resin blend comprising 100 parts by weight of a liquid crystal polyester resin composition and 0.01 to 20 parts by weight of a fluorinated resin which are blended in a solid state, wherein the liquid crystal polyester resin composition comprises 100 parts by weight of a liquid crystal polyester and 0 to 150 parts by weight of a filler.

In the liquid crystal polyester resin blend, the liquid crystal polyester may comprise at least 30 % by mole, based on the liquid crystal polyester, of a repeating unit of the formula (A₁):





The present invention also provides a method for molding a liquid crystal polyester material, wherein the above liquid crystal polyester resin blend is used as the liquid crystal polyester material.

DETAILED DESCRIPTION OF THE INVENTION

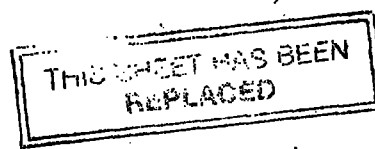
The liquid crystal polyester used in the present invention is a polyester referred to as a thermotropic liquid crystal polymer.

Specific examples of the liquid crystal polyester are

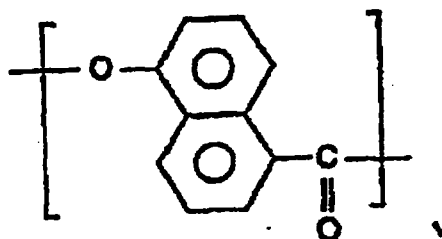
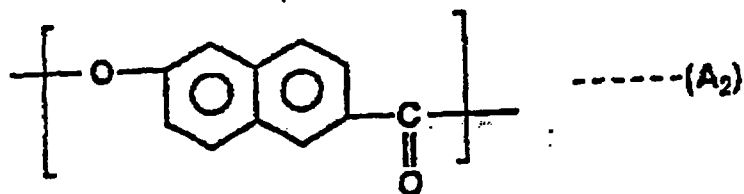
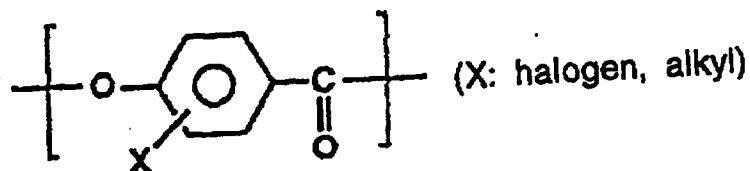
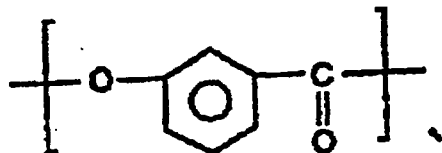
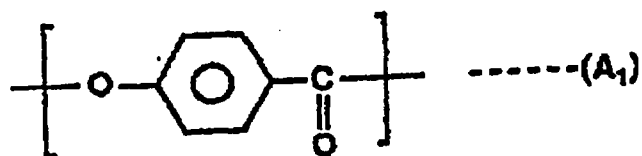
- (1) a combination of an aromatic dicarboxylic acid, an aromatic diol and an aromatic hydroxycarboxylic acid;
- (2) a combination of different aromatic hydroxycarboxylic acids;
- (3) a combination of an aromatic dicarboxylic acid and an aromatic diol; and
- (4) a product of the reaction between an aromatic hydroxycarboxylic acid and a polyester such as polyethylene terephthalate

and form an anisotropic melted material melting at a temperature of at most 400°C. Instead of the aromatic dicarboxylic acid, aromatic diol and aromatic hydroxycarboxylic acid, an ester-forming derivative thereof may be used.

Specific non-limiting examples of the repeating unit of the liquid crystal polyester are as follows:

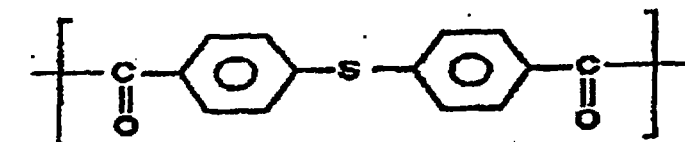
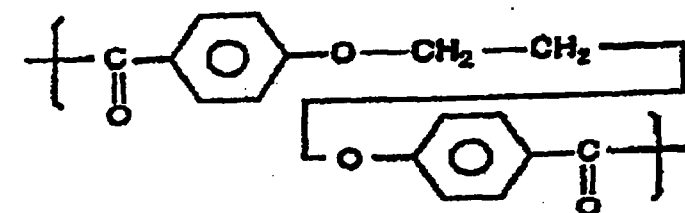
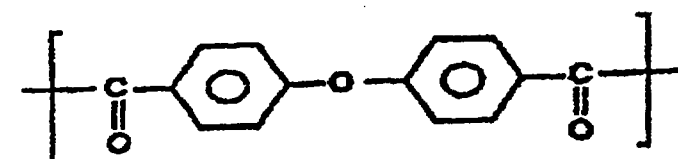
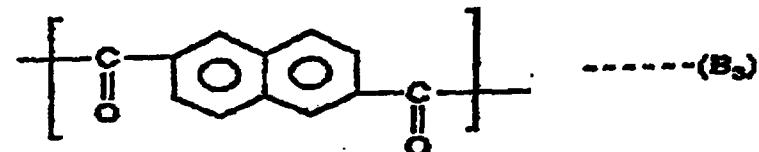
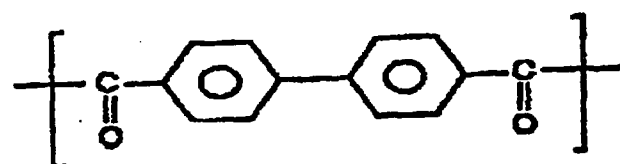
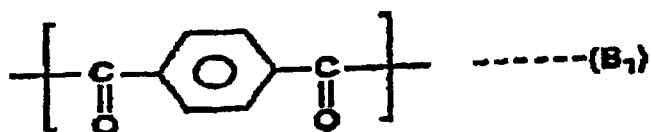


The repeating units derived from the aromatic hydroxy-carboxylic acid:



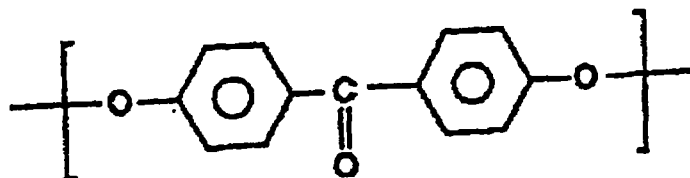
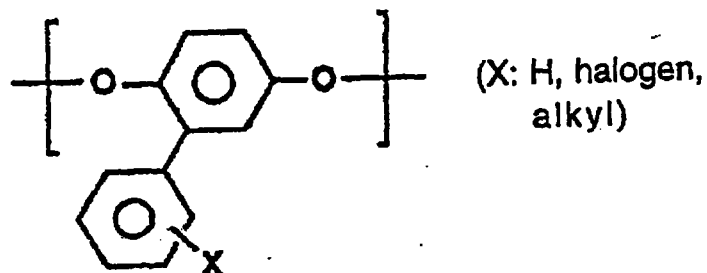
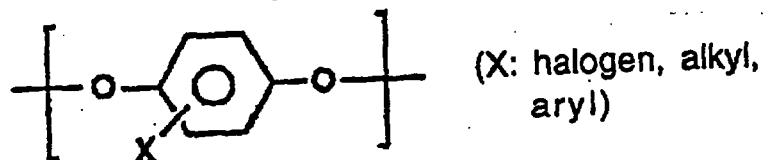
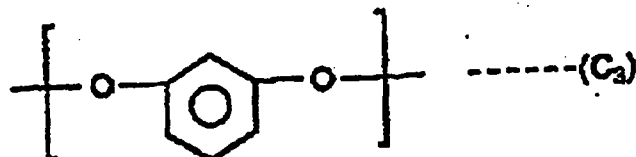
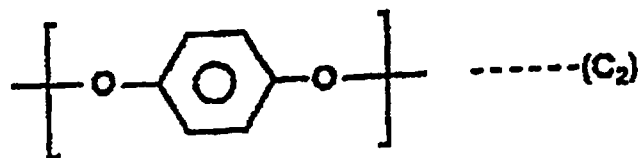
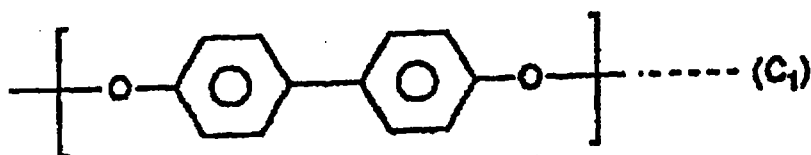


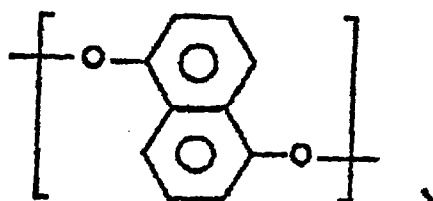
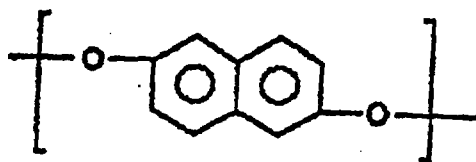
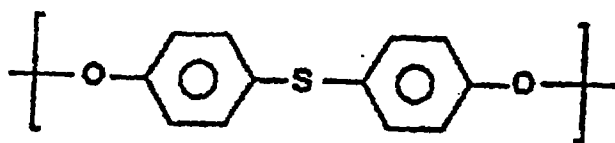
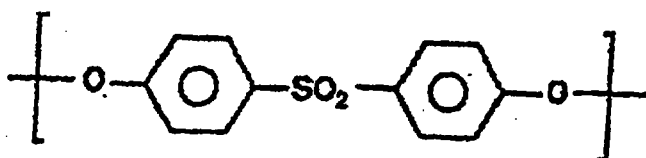
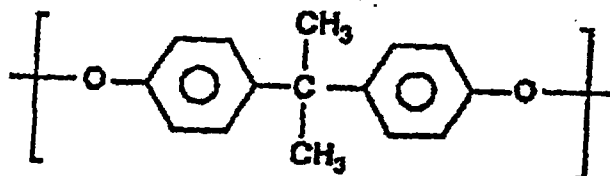
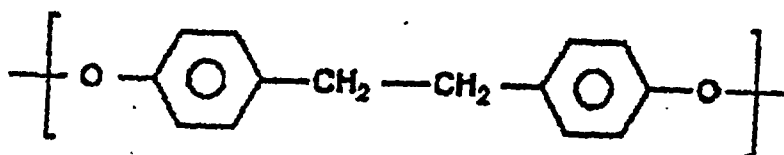
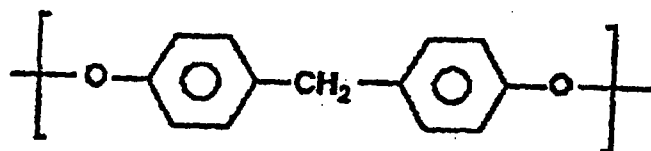
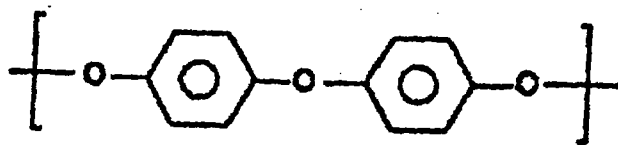
Repeating units derived from the aromatic dicarboxylic acid:





Repeating units derived from the aromatic diol:







In view of the balance of a thermal resistance, mechanical properties and a processability, a particularly preferred liquid crystal polyester is a liquid crystal polyester containing at least 30 % by mole, based on the liquid crystal polyester, of the repeating unit of the formula (A_1).

The following combinations (a)-(f) of the repeating units are preferable:

- (a): (A_1), (B_1) or a combination of (B_1) and (B_2), and (C_1);
- (b): (A_1) and (A_2);
- (c): in the combination (a), a part of (A_1) is replaced with (A_2);
- (d): in the combination (a), a part of (B_1) is replaced with (B_3);
- (e): in the combination (a), a part of (C_1) is replaced with (C_3);
- (f): the repeating units (B_1) and (C_1) are added to the combination (b).

The liquid crystal polyesters having the basic structure combinations (a) and (b) are described in, for example, Japanese Patent Kokoku Publication Nos. 47870/1972 and 3888/1988, respectively.

In the present invention, the filler is optionally added to the liquid crystal polyester. When the filler is added, an amount of the added filler is at most 150 parts by weight, preferably 20 to 100 parts by weight per 100 parts by weight of the liquid crystal polyester. If the amount of the added filler is larger than 150 parts by weight, the composition has a high melt viscosity to give the decreases of granulating ability and moldability, so that the effect of stabilizing the plasticization during the molding process is decreased even if the fluorinated resin is added to the liquid crystal polyester resin composition in a solid state.



The liquid crystal polyester resin composition used in the present invention is generally in a particulate form such as a pellet or a chip form. The preferable form of liquid crystal polyester resin composition is a cylinder or sphere having an average particle size of 1 mm to 10 mm. When the average particle size is smaller than 1 mm, the resultant product has a bad surface, since a gas is easily caught in the product when the resin is plasticized by a screw during the molding process. When the average particle size is larger than 10 mm, the plasticization during the molding process is difficult and a rotation torque of screw increases.

A procedure for obtaining the particle or chip of the liquid crystal polyester resin composition is not limited. Generally, it is a method comprising mixing the liquid crystal polyester with the filler, optionally a mold release modifier, a thermally stabilizing agent, a colorant and the like in a Henschel mixer, a tumbler or the like, conducting the melt incorporation by an extruder, and cutting the melted resin extruded from a hole of die with a rotating blade to give particles; or a method comprising cooling and solidifying a stand of resin extruded from a hole of die and cutting the stand with a rotating blade to give particles. In addition, an extruder may be directly connected with a downstream of a reactor for the polymerized liquid crystal polyester to give liquid crystal polyester particles or chips.

The liquid crystal polyester resin composition is preferably a particulate shape such as pellets, a chip shape or a powdery shape so as to facilitate the mixing of the liquid crystal polyester resin composition with the fluorinated resin.

The filler used in the present invention includes a fibrous or acicular reinforcing material such as a glass fiber, a silica-alumina



fiber, wollastonite, a carbon fiber, a potassium titanate whisker, a aluminum borate whisker and a titanium oxide whisker; an inorganic filler such as calcium carbonate, dolomite, talc, mica, clay and a glass bead, and the combination thereof can be used.

Specific examples of the fluorinated resin used in the present invention are polytetrafluoroethylene, a tetrafluoroethylene/hexafluoropropylene copolymer, polytrichlorofluoroethylene, a tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer, a tetrafluoroethylene/ethylene copolymer, a perfluoroalkyl group-containing acrylate or methacrylate polymer or copolymer. Among them, polytetrafluoroethylene (hereinafter referred to as PTFE) is preferable.

The fluorinated resin used in the present invention is preferably in the powdery or particulate form so as to facilitate the mixing the fluorinated resin with the liquid crystal polyester resin composition.

PTFE is preferably PTFE powder having an average particle size of smaller than 20 μm . Specific examples of commercially available PTFE are Cefral Lube I, Cefral Lube IP and Cefral Lube F (manufactured by CENTRAL GLASS CO., LTD.); Fluon 169J, L170 and L171 (manufactured by ASAHI GLASS COMPANY); Lubron L-2, L-5 and LD-1 (manufactured by DAIKIN INDUSTRIES LTD.); Teflon TLP-10 and TLP-10F-1 (manufactured by MITSUI DUPONT FLUOROCHEMICAL) and the like.

In the liquid crystal polyester resin blend according to the present invention, the amount of the fluorinated resin is 0.01 to 20 parts by weight, preferably 0.03 to 10 parts by weight per 100 parts by weight of the liquid crystal polyester resin composition comprising the liquid crystal polyester and the optionally present filler. If the amount of the fluorinated resin is larger than 20 parts by weight, the



moldability is undesirably deteriorated because of the high melt viscosity of the blend. If the amount of the fluorinated resin is smaller than 0.01 parts by weight, the effect of stabilizing the plasticization during the molding process which must be achieved by the present invention is undesirably insufficient.

As far as the object of the present invention is not adversely affected, at least one usual additive, for example, a colorant such as a dye and a pigment; an antioxidant; a thermal stabilizing agent; a UV absorber; an antistatic agent; and a surfactant may be added to the liquid crystal polyester resin composition or the liquid crystal polyester resin blend according to the present invention.

A small amount of a thermoplastic resin, for example, a polyamide, a polyester, a polyphenylenesulfide, a polyetherketone, a polycarbonate, a polyphenyleneether and a modified product thereof, a polysulfone, a polyethersulfone and a polyetherimide; a small amount of a thermosetting resin, for example, a phenol resin, an epoxy resin, a polyimide resin may be added alone or in combination.

In addition to the fluorinated resin, an additive having an external lubricating effect such as a higher fatty acid and a metal salt of higher aliphatic acid may be added to the liquid crystal polyester resin composition.

The mixing procedure for preparing the liquid crystal polyester resin blend is not limited, as far as the liquid crystal polyester resin composition comprising the liquid crystal polyester and the optional filler is mixed with the fluorinated resin in the solid state. For example, the particles of the liquid crystal polyester resin composition in the solid state are mixed with the powder or particles of the fluorinated resin by the use of a Henschel mixer or tumbler.



PREFERRED EMBODIMENT OF THE INVENTION

The present invention will be illustrated by the following Examples which do not limit the present invention. The measurement of various properties and the test used in the Examples are conducted as follows:

(1) Meterage property during the injection molding

An average meterage time for continuous 50 shots and a standard deviation thereof are calculated.

(2) Tensile properties

An ASTM No. 4 tensile dumbbell is molded, and tensile properties are measured according to ASTM D638.

(3) Relative amount of low-boiling point gas evolving from the molded material

A JIS 1 (1/2) dumbbell (thickness: 0.8 mm) is molded, and the resultant molded material is cut into chips having a length of 5 mm, a width of 5 mm and a thickness of 0.8 mm. Four grams of the chips are precisely weighted and washed with distilled water. The chips are placed in a vacuum-dried 25 cc vial and the vial is sealed with a packing of polytetrafluoroethylene. The vial is heated in a hot air dryer adjusted at 120°C for 20 hours so that a gas evolves from the molded material. The vial is mounted in a head space gas chromatography (GC-15A/HS-3A) manufactured by SHIMADZU CORPORATION, and a gas is injected in a column having a length of 15 m and filled with a filler DB-WAX (manufactured by J & W SCIENTIFIC) while keeping the vial at 120°C. A column temperature is increased from 80°C at a rate of 2°C/min simultaneously with the injection, and a total amount of the gas is detected by a detector until a retention time of 25 minutes. The detector is FID type one, and a carrier gas is helium.



A relative amount of the gas is indicated by a value of a total area of various gases. The relative amount of gas evolving from the molded material is compared by the use of said value. When the sample is not placed in the vial, namely for the empty vial, the measured value is 3,000. The larger the measured value is, the larger the amount of the low-boiling point gas evolving from the molded material is.

A gas chromatography mass analysis revealed that the gas until the retention time of 25 minutes includes an aromatic hydrocarbon, an aliphatic hydrocarbon, acetic acid, a phenol analogue and the like.

(4) Flow temperature

A temperature at which the sample resin shows a melt viscosity of 48,000 poises when it is melted by heating at a heating rate of 4 °C/min and extruded from a nozzle of 1 mm in internal diameter and 10 mm in length under a load of 100 kg/cm².

Examples 1-7 and Comparative Examples 1-3

A liquid crystal polyester having the above repeating units (A1), (B1), (B2) and (C1) wherein a molar ratio of (A1):(B1):(B2):(C1) is 60:15:5:20 and having a flow temperature of 323°C was mixed with a milled glass fiber (EFH 75-01 manufactured by CENTRAL GLASS CO., LTD.) in an ratio shown in Table 1 in a Henschel mixer. The mixture was converted into particles by the use of a biaxial extruder (PCM-30 manufactured by IKEGAI CORPORATION) at a cylinder temperature of 340°C to give a liquid crystal polyester resin composition. The resultant liquid crystal polyester resin composition was cylinder particles having an average diameter of 2 mm and an average length of 2.5 mm.

The resultant liquid crystal polyester resin composition was



mixed with PTFE powder (Cefral Lube I manufactured by CENTRAL GLASS CO., LTD.) in a ratio shown in Table 1 at a room temperature by the use of a tumbler to give a liquid crystal polyester resin blend.

After the liquid crystal polyester resin blend was dried at 120°C for 3 hours, JIS 1 (1/2) dumbbells were prepared at a cylinder temperature of 350°C and a mold temperature of 130°C by the use of an injection molding machine (PS40E5ASE manufactured by NISSEI PLASTIC CO., LTD.). Meterage times for 50 continuous shots were measured to evaluate the stability. The tensile properties and the evolved gas were measured by the use of the resultant dumbbell.

In the similar manner, the stability of the meterage time, the tensile properties and the amount of the evolved gas were measured as to a liquid crystal polyester resin mixture containing no fluorinated resin (Comparative Example 1). The results are shown in Table 1.

As shown in Table 1, the mixture (Examples 1-7) comprising the liquid crystal polyester resin composition and the fluorinated resin in the solid state has a smaller difference of the meterage time among the shots and a smaller meterage time than the mixture (Comparative Example 1) comprising no fluorinated resin, is stably plasticized, has excellent mechanical properties and gives a low amount of gas evolving from the molded material.

The mixture (Comparative Example 2) in which the amount of the fluorinated resin mixed with the liquid crystal polyester resin composition in the solid state was 0.005 parts by weight had an insufficient effect of stable plasticization during the molding process. The mixture (Comparative Example 3) in which 25 parts by weight of the fluorinated resin was mixed with the liquid crystal polyester resin composition in the solid state had the significantly decrease of the



tensile properties.

Comparative Example 4

The same manner as in Example 1 was repeated, except that the fluorinated resin together with the milled glass fibers was premixed with the liquid crystal polyester, and the particles were formed from the mixture by the use of the biaxial extruder. The results are shown in Table 1. The mixture (Comparative Example 4) in which the fluorinated resin composition was previously incorporated in the liquid crystal polyester resin at the melted state had a large value of the meterage time and a large change among the shots to give an unstable plasticization during the molding process.

Comparative Examples 5-8

The same manner as in Example 1 was repeated, except that barium stearate or calcium stearate was used instead of the fluorinated resin. The results are shown in Table 1. The mixtures (Comparative Examples 5, 6 and 8) in which barium stearate or calcium stearate was mixed with the liquid crystal polyester resin composition had the good effect of stabilizing the plasticization, but had a very large amount of gas evolving from the molded material. The mixture containing 5 parts by weight of barium stearate could not be molded, since it violently evolved a gas in the cylinder of the injection molding machine.

Example 8

The same manner as in Example 1 was repeated, except that Fluon 169 J (manufactured by ASAHI GLASS COMPANY) was used instead of Cefral Lube I. The results are shown in Table 1. As in the mixture containing Cefral Lube, the mixture (Example 8) in which Fluon 169 J was mixed with the liquid crystal polyester resin composition in the

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solid state also had a small change of the meterage time among the shots and a short meterage time to give the stable plasticization, and had excellent mechanical properties and a small amount of gas evolving from the molded material.

Table 1

	Liquid crystal polyester resin blend					Meterage property		Tensile properties		Relative amount of evolved gas	Remarks
	Liquid crystal polyester resin composition			Blend		Average meterage time (sec)	Standard deviation (sec)	Strength (kg/cm ²)	Elastic modulus (kg/cm ²)		
	Liquid crystal polyester (wt%)	Glass fiber (wt%)	Fluorinated resin (Cefral Lube I) (pbw)	Type	pbw						
Ex. 1	60	40	-	Cefral Lube I	0.05	17.3	1.0	1510	142000	52000	
2	60	40	-	Cefral Lube I	0.3	16.3	1.0	1490	141000	49000	
3	60	40	-	Cefral Lube I	0.5	14.1	0.6	1500	140000	56000	
4	60	40	-	Cefral Lube I	0.8	12.3	0.5	1520	141000	53000	
5	60	40	-	Cefral Lube I	1.0	11.0	0.6	1500	137000	55000	
6	60	40	-	Cefral Lube I	5.0	9.3	0.2	1450	134000	65000	
7	60	40	-	Cefral Lube I	10.0	8.9	0.2	1380	132000	69000	
8	60	40	-	Fluon 169J	0.5	15.2	0.4	1500	141000	50000	
Com. Ex. 1	60	40	-	-	-	22.5	11.6	1540	140000	53000	Remarkable discoloring of molded material
2	60	40	-	Cefral Lube I	0.005	22.0	5.9	1530	139000	53000	
3	60	40	-	Cefral Lube I	25.0	7.8	0.2	870	94000	72000	
4	60	40	1.0	-	-	25.7	11.4	1440	136000	95000	
5	60	40	-	Barium stearate	0.05	15.2	0.8	1360	133000	133000	
6	60	40	-	Barium stearate	0.5	15.1	0.9	1110	112000	326000	
7	60	40	-	Barium stearate	5.0	>40	17.2	-	-	-	
8	60	40	-	Calcium stearate	0.5	10.5	0.5	1190	123000	265000	

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The liquid crystal polyester resin blend according to the present invention has a stability of plasticizing the liquid crystal polyester material during the molding process, can be stably molded and gives a molded material having excellent mechanical properties and thermal stability. The method for molding the liquid polyester resin blend of the present invention is useful in a molding process using an extruder having a screw, such as an injection molding process and an extrusion process.

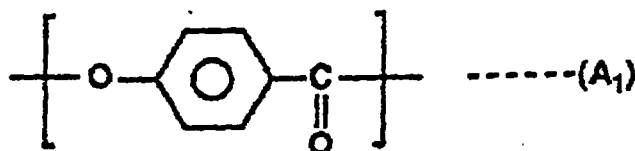


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What is claimed is:

1. A liquid crystal polyester resin blend comprising 100 parts by weight of a liquid crystal polyester resin composition and 0.01 to 20 parts by weight of a fluorinated resin which are blended in a solid state, wherein the liquid crystal polyester resin composition comprises 100 parts by weight of a liquid crystal polyester and 0 to 150 parts by weight of a filler.

2. The liquid crystal polyester resin blend according to claim 1, wherein the liquid crystal polyester comprises at least 30 % by mole, based on the liquid crystal polyester, of a repeating unit of the formula (A₁):



3. A method for molding a liquid crystal polyester material, wherein a liquid crystal polyester resin blend according to claim 1 or 2 is used as the liquid crystal polyester material.

4. A liquid crystal polyester resin blend substantially as hereinbefore described with reference to any one of the examples, excluding the comparative examples.

5. A method for molding a liquid crystal polyester material, wherein a liquid crystal polyester resin blend according to claim 4 is used as the liquid crystal polyester material.

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