

Description

This invention relates to a thermoplastic resin composition which is low in deformation degree when molded and has excellent mechanical properties, in particular, impact resistance.

Though crystalline thermoplastic resins are generally used per se as engineering plastics to be molded into machine parts for various purposes, they are used in the form of a composition containing reinforcing material such as glass fibers in the field requiring high mechanical strength or rigidity. However, a composition containing reinforcing fibers such as glass fibers is in general remarkably anisotropic and has the drawback of causing deformation of moldings during molding or annealing, though it has high mechanical strength and rigidity. Such deformation is particularly significant in resins of high crystallization degree, such as polyacetal and polybutylene terephthalate, or those of which crystallization is facilitated by annealing, such as polyethylene terephthalate. Therefore, the applicability of these resins as molding materials must be judged mainly on the basis of the balance between the mechanical properties such as impact resistance or rigidity and deformation, in addition to the chemical and thermal properties according to the purpose of use of the compound. This balance is particularly important when the resin is used as material for moldings of which dimensional accuracy is required, for example, substrate and cases. It is extremely difficult to improve the mechanical properties such as rigidity or impact resistance of moldings while suppressing the deformation thereof and, particularly, in the case of a crystalline thermoplastic resin, the manufacture of products having a high dimensional accuracy is nearly impossible.

Australian patent No. 522 577 discloses a composition which comprises a thermoplastic resin, reinforcing fibers and flaky fillers and teaches that the composition is fairly satisfactory. But the disclosed composition is not yet sufficient when it is used for molding.

US-A-4352907 discloses blends comprising for example, 92.5 parts of polyethyleneterephthalate, 2.5 parts of an aromatic polycarbonate 30% of fiberglass and 0.5% talc.

FR-A-2374368 discloses blends containing polybutyleneterephthalate, fiberglass, polycarbonate and talc.

US-A-4123415 discloses reinforced thermoplastic compositions comprising a high molecular weight polyester resin and glass fibers having an average diameter of 0.0005 inches. The composition may also contain a polycarbonate resin.

DE-A-2811795 discloses thermoplastic resins containing reinforcing fibers and plate-like fillers.

It is the object of the present invention to provide a thermoplastic resin composition having a reduced deformation degree and an improved impact resistance.

Said object is achieved by a thermoplastic resin composition having a reduced deformation degree and an improved impact resistance when molded which comprises

1) a crystalline thermoplastic resin and

(a) a reinforcing fiber having a staple length not greater than 1 mm and a ratio of length to diameter in the range of from 5 to 1000, said fiber being present in a concentration in the range of from 1 to 60 weight percent;

(b) a flaky filler having an average diameter in the range of from 100 to 1000 μm , an average thickness in the range of from 0.1 to 10 μm and a diameter/thickness ratio in the range of from 4 to 400, said filler being present in a concentration in the range of from 1 to 59 weight percent; and

(c) a polycarbonate in a concentration in the range of from 1 to 50 weight percent,

all based on the total quantity of the resin composition, and

2) an organic high molecular substance selected from ethylene/carboxylate ester copolymers and metallic salts thereof, polyacrylate resins and segment type thermoplastic copolyesters in a concentration of from 5 to 40 weight percent of said crystalline thermoplastic resin.

The crystalline thermoplastic resin used in this invention is an organic high molecular substance which has a crystalline structure at least partly in a solid state, such as, polyacetal (homo- or copolymer); polyalkylene terephthalate, e.g., polybutylene terephthalate, polypropylene terephthalate, or polyethylene terephthalate, and copolymers or mixtures thereof; or various polyamides. These crystalline resins are per se suitable for functional parts in respect of their chemical and thermal properties, but often insufficient when used as molding materials, mechanical strength and dimensional accuracy both of which are important factors, owing to a large degree of deformation during molding or annealing. However, a composition containing additional constituents as described below exhibits particularly high effects and provides a satisfactory function for the purpose.

The reinforcing fibers used in this invention include inorganic fibers such as glass fibers, carbon fibers, graphite fibers, metallic fibers, silicon carbide fiber, asbestos, wollastonite or fibrous potassium titanate, whiskers, and various organic fibers. The reinforcing material is preferably glass fiber, but various materials can be used in various ways according to the purpose such as reinforcement of mechanical

properties, impartment of electric conductivity, improvement in frictional characteristics, or increase in fire-proofness. These reinforcing fibers may be used alone or as a mixture thereof. According to this invention, the length/diameter ratio of the reinforcing fibers to be incorporated in the resin is within the range of from 5 to 1,000, in particular, from 10 to 100. For example, a glass fiber with a diameter of about 10 μm preferably has an average length ranging from 100 to 1,000 μm . Excessively long fibers degrade the moldability of the composition to be produced and, therefore, the staple length is preferably not larger than 1 mm. The quantity of the reinforcing fiber to be added ranges from 1 to 60% by weight of the total quantity of the resin composition, being appropriately determined according to the use, and is particularly from 2 to 30%.

The flaky fillers used in this invention include, for example mica (for example, muscovite, phlogopite or sericite), glass flakes, talc or metallic foil, among which glass flakes are particularly desirable. The proportion of the flaky fillers to be added ranges from 1 to 59% by weight of the total quantity of the resin composition, particularly from 2 to 40% by weight. These flaky fillers may be used alone or as a mixture thereof. The addition of flaky substances is effective for preventing deformation of the composition even when used alone, but is more effective when used in combination with fibrous additives for maintaining high mechanical properties, particularly, tensile strength and impact resistance as well as possessing high dimensional accuracy and low warpage as disclosed in the above Australian patent No. 522 577. However, since an excessive quantity of additives degrades the moldability of the resin composition, a practical upper limit of the total quantity of the flaky and fibrous additives is 60% by weight of the composition, preferably 30 to 50%. To reduce the deformation degree of the moldings, the diameter (the average length in the direction of spreading) of the flaky substance is preferably 40 μm or longer and the thickness thereof is from 0.1 to 10 μm , particularly from 1 to 5 μm . The diameter/thickness ratio is from 4 to 400 and most desirably from 30 to 400. Flaky substances which are low in diameters or diameter/thickness ratios exhibit a deformation preventive effect to a low degree only, whereas those which are too high tend to undesirably degrade the moldability of the composition. Above all, as regards glass flakes, thicknesses thereof range preferably from 2 to 5 μm and diameters (lengths in the direction of spreading) are from 100 to 1,000 μm in average.

Though these flaky fillers and reinforcing fibers may be incorporated without any particular treatment, they are capable of increasing the mechanical strength further when used after their surfaces have been treated with an appropriate surface-treating agent to improve the affinity and adhesiveness to synthetic resins. As surface-treating agents, various kinds of known ones may be used and there can be mentioned, for example, silanes, titanates, and epoxy compounds.

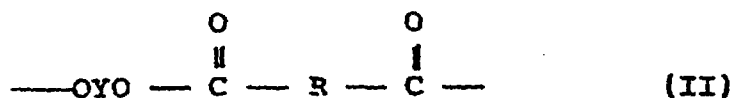
A characteristic of this invention is that a polycarbonate is incorporated therein, which provides synergistic effects for preventing deformation and warpage of the composition of the present invention as well as for improving the mechanical properties of said composition. The polycarbonate used in this invention is of a bisphenol type and obtained, for example, by the reaction of a bisphenol with a carbonate or with phosgene in the presence of an alkali. This polycarbonate is desired to have a high degree of fluidity and the quantity thereof to be added is preferably within the range of from 1 to 50% by weight of the total quantity of the resin composition, preferably from 2 to 25%, because the addition of too large a quantity of polycarbonate degrades the heat resistance of the composition.

The composition according to this invention is easily prepared by conventional methods of preparing reinforced resins or filler-containing resins. Any of the following methods is applicable, for example: a first method in which pellets to be used in this invention are prepared by mixing and extruding various additives using an extruder and then molded; a second method in which pellets containing different constituents from each other are blended together prior to molding and a composition containing constituents according to this invention is obtained after molding; and a third method in which every constituent is directly fed into the molding machine.

The composition according to this invention is used after organic high molecular substances are added thereto for adjusting or modifying the physical properties thereof according to the field of use of this composition. The organic high molecular substances are ethylene/carboxylate ester copolymers and metallic salts thereof, such as an ethylene/vinyl acetate copolymer, an ethylene/alkyl acrylate copolymer, and sodium salt of an ethylene/methacrylic acid copolymer; as well as a modifier comprising a polyacrylate resin, and a modifier comprising a segment type thermoplastic copolyester. The modifier is one in which the polyacrylate resin contains a unit derived from $\text{C}_1 - \text{C}_6$ alkyl acrylates, and the polyacrylate comprises a multistage copolymer having a rubber-like first stage and a final thermoplastic hard stage. A preferred multistage copolymer is, for example, butyl acrylate/butylene diacrylate/allyl methacrylate. The modifier comprising a segment type thermoplastic copolyester comprises a large number of repeating long-chain and short-chain ester units which are connected with each other through a head-to-tail bonding, the long-chain ester unit being represented by the following formula (I):



and the short-chain having the following formula (II):



In formulae (I) and (II), X represents a bivalent residue obtained by removing terminal hydroxy groups from polyalkylene oxide glycol having a melting point of not higher than about 60° C, a molecular weight of from about 400 to 4,000, and a carbon/oxygen ratio of from about 2.5 to 4.3; R represents a bivalent residue obtained by removing carboxyl groups from a dicarboxylic acid having a molecular weight of not larger than about 300; and Y denotes a bivalent residue obtained by removing hydroxyl groups from a diol having a molecular weight of not larger than about 250. These organic high molecular substances can be used alone or as a mixture of two or more of them according to the purpose. The quantity of these substances to be added is from 5 to 40% by weight of the crystalline thermoplastic resin. The composition according to this invention may be endowed with required properties according to the purpose of use by addition of known antistatic agents, coloring agents, lubricants, mold release agents, nucleating agents, stabilizers, fire-resistant agents, or surfactants.

The following examples illustrate the invention.

Examples 1 to 3 and Comparative Examples 1 to 12:

A composition was prepared by mixing polybutylene terephthalate (Duranex made by Polyplastics Co., Ltd.) with glass fibers, glass flakes (average diameter of 600 μm), and polycarbonate at the rate as shown in Table 1, and extruding the mixture into pellets by means of a 40 m/m uniaxial extruder. Then, test pieces were molded of said pellets by a molding machine for measurement of the deformation degree, tensile strength, and impact resistance. On the other hand, other examples for comparison which are devoid of polycarbonate or of any one of glass fiber and glass flake or an organic high molecular substance were measured with respect to the same items as above. The results of these measurements are shown in Table 1. For measurement of the deformation degrees, flat test pieces, 120 mm square (2 mm thick), were prepared and the most severely deformed part of the test piece was measured as a representative of the deformation degree.

Table 1

		Glass fiber	Glass flake	Poly- carbon- ate	Poly- butylene tere- phthalate	Deform- ation degree mm	Tensile strength	Izod (notched) kg.-cm/cm
Comparative	1	5	35	10	50	0.2	902	2.9
	2	10	30	10	50	0.5	1003	3.7
	3	20	20	10	50	1.7	1210	6.5
Example	1	20	20	10	50 *1)	1.8	1.69	8.5
	2	20	20	10	50 *2)	1.9	1175	9.6
	3	20	20	10	50 *3)	1.9	1157	8.6
Comp. Ex.	4	30	10	10	50	7.2	1402	8.0
	5	0	40		60	0.2	743	2.1
	6	5	35		60	0.4	815	2.9
	7	10	30		60	0.7	931	3.2
	8	20	20		60	13.6	1018	5.8
	9	30	10		60	25.3	1311	7.20
	10	40	0		60	25.7	1422	9.3
	11	0	40	10	50	0.2	790	2.6
	12	40	0	10	50	20.5	1543	9.7

Remarks:

*1) Polybutylene terephthalate (45% by weight) and ethylene/ethyl acrylate copolymer (5% by weight)

*2) Polybutylene terephthalate (45% by weight) and a modifier comprising polyacrylate resin (5% by weight) (Acryloid KM330: made by Rohm and Haas Co.)

*3) Polybutylene terephthalate (45% by weight) and a segment type copolyester (5% by weight) (Hytrel: made by Du Pont)

The quantity is denoted in terms of percent by weight against the total quantity of the composition.

Among the above examples, Examples 1 to 3 which specific high molecular substances were added, were able to give moldings which are low in the deformation degree and have an increased impact resistance. By using these resins, a high impact resistance can be obtained even if the quantity of glass fibers to be added is reduced, so that a further advantage of attaining reduction in the deformation degree is obtained.

Claims

1. A thermoplastic resin composition having a reduced deformation degree and an improved impact resistance when molded which comprises
 - 1) a crystalline thermoplastic resin and
 - (a) a reinforcing fiber having a staple length not greater than 1 mm and a ratio of length to diameter in the range of from 5 to 1000, said fiber being present in a concentration in the range of from 1 to 60 weight percent;
 - (b) a flaky filler having an average diameter in the range of from 100 to 1000 μm , an average thickness in the range of from 0.1 to 10 μm and a diameter/thickness ratio in the range of from 4 to 400, said filler being present in a concentration in the range of from 1 to 59 weight percent; and
 - (c) a polycarbonate in a concentration in the range of from 1 to 50 weight percent, all based on the total quantity of the resin composition, and
 - 2) an organic high molecular substance selected from ethylene/carboxylate ester copolymers and metallic salts thereof, polyacrylate resins and segment type thermoplastic copolyesters in a concentration of from 5 to 40 weight percent of said crystalline thermoplastic resin.
2. The thermoplastic resin composition of claim 1 wherein the total content of said reinforcing fiber and said flaky filler is not more than 60 weight percent.
3. The thermoplastic resin composition of claim 1 or 2, wherein said reinforcing fiber is present in a concentration of from 2 to 30 weight percent.
4. The thermoplastic resin composition of any of claims 1 to 3, wherein said flaky filler is present in a concentration of from 2 to 40 weight percent.
5. The thermoplastic resin composition of any of claims 1 to 4, wherein the total content of said reinforcing fiber and said flaky filler is in the range of from 30 to 50 weight percent.
6. The thermoplastic resin composition of any of claims 1 to 5, wherein said polycarbonate is present in a concentration of from 2 to 25 weight percent.
7. The thermoplastic resin composition of any of claims 1 to 6 wherein the crystalline thermoplastic resin is polybutylene terephthalate resin.
8. The thermoplastic resin composition of any of claims 1 to 7, wherein the flaky filler is glass.
9. The thermoplastic resin composition of any of claims 1 to 8, in which said reinforcing fiber is a fiber selected from the group consisting of glass, carbon, graphite, metals, silicon carbide, asbestos, wollastonite, potassium titanate and organic fibers.

Revendications

1. Composition de résine thermoplastique ayant un degré de déformation réduit et une résistance au choc améliorée lorsqu'elle est moulée, qui comprend
 - 1) Une résine thermoplastique cristalline et
 - (a) une fibre de renfort ayant une longueur non supérieure à 1 mm et un rapport de la longueur au diamètre dans l'intervalle de 5 à 1 000, cette fibre étant présente à une concentration dans l'intervalle de 1 à 60 % en poids ;
 - (b) une charge lamellaire ayant un diamètre moyen dans l'intervalle de 100 à 1 000 μm , une épaisseur moyenne dans l'intervalle 0,1 à 10 μm et un rapport diamètre/épaisseur dans l'intervalle

Among the above examples, Examples 1 to 3 which specific high molecular substances were added, were able to give moldings which are low in the deformation degree and have an increased impact resistance. By using these resins, a high impact resistance can be obtained even if the quantity of glass fibers to be added is reduced, so that a further advantage of attaining reduction in the deformation degree is obtained.

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 - (c) a polycarbonate in a concentration in the range of from 1 to 50 weight percent, all based on the total quantity of the resin composition, and
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5. The thermoplastic resin composition of any of claims 1 to 4, wherein the total content of said reinforcing fiber and said flaky filler is in the range of from 30 to 50 weight percent.
6. The thermoplastic resin composition of any of claims 1 to 5, wherein said polycarbonate is present in a concentration of from 2 to 25 weight percent.
7. The thermoplastic resin composition of any of claims 1 to 6 wherein the crystalline thermoplastic resin is polybutylene terephthalate resin.
8. The thermoplastic resin composition of any of claims 1 to 7, wherein the flaky filler is glass.
9. The thermoplastic resin composition of any of claims 1 to 8, in which said reinforcing fiber is a fiber selected from the group consisting of glass, carbon, graphite, metals, silicon carbide, asbestos, wollastonite, potassium titanate and organic fibers.

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 - 1) Une résine thermoplastique cristalline et
 - (a) une fibre de renfort ayant une longueur non supérieure à 1 mm et un rapport de la longueur au diamètre dans l'intervalle de 5 à 1 000, cette fibre étant présente à une concentration dans l'intervalle de 1 à 60 % en poids ;
 - (b) une charge lamellaire ayant un diamètre moyen dans l'intervalle de 100 à 1 000 μm , une épaisseur moyenne dans l'intervalle 0,1 à 10 μm et un rapport diamètre/épaisseur dans l'interval-



le de 4 à 400, cette charge étant présente à une concentration dans l'intervalle de 1 à 59 % en poids ; et

(c) un polycarbonate à une concentration dans l'intervalle de 1 à 50 % en poids,

le tout par rapport à la quantité totale de la composition de résine, et

2) Une substance organique de masse moléculaire élevée choisie parmi des copolymères éthylène ester carboxylique et des sels métalliques de ceux-ci, des résines de polyacrylate et des copolyesters thermoplastiques du type segmenté, à une concentration de 5 à 40 % de cette résine thermoplastique cristalline.

2. Composition de résine thermoplastique selon la revendication 1, dans laquelle la teneur totale de cette fibre de renfort et de cette charge lamellaire n'est pas supérieure à 60 % en poids.
3. Composition de résine thermoplastique selon la revendication 1 ou 2, dans laquelle cette fibre de renfort est présente à une concentration de 2 à 30 % en poids.
4. Composition de résine thermoplastique selon l'une quelconque des revendications 1 à 3, dans laquelle cette charge lamellaire est présente à une concentration de 2 à 40 % en poids.
5. Composition de résine thermoplastique selon l'une quelconque des revendications 1 à 4, dans laquelle la teneur totale de cette fibre de renfort et de cette charge lamellaire est dans l'intervalle de 30 à 50 % en poids.
6. Composition de résine thermoplastique selon l'une quelconque des revendications 1 à 5, dans laquelle ce polycarbonate est présent à une concentration de 2 à 25 % en poids.
7. Composition de résine thermoplastique selon l'une quelconque des revendications 1 à 6, dans laquelle la résine thermoplastique cristalline est une résine de polybutylène téréphtalate.
8. Composition de résine thermoplastique selon l'une quelconque des revendications 1 à 7, dans laquelle la charge lamellaire est du verre.
9. Composition de résine thermoplastique selon l'une quelconque des revendications 1 à 8, dans laquelle cette fibre de renfort est choisie parmi les fibres de verre, de carbure, de graphite, de métaux, de carbure de silicium, d'amiante, de wollastonite, de titanate de potassium et des fibres organiques.

Patentansprüche

1. Thermoplastische Harzmasse mit verringertem Deformationsgrad und verbesserter Schlagfestigkeit nach dem Formen, das
 - 1) ein kristallines, thermoplastisches Harz und
 - (a) eine Verstärkungsfasern mit einer Stapellänge von nicht mehr als 1 mm und einem Verhältnis von Länge zu Durchmesser im Bereich von 5 bis 1000, wobei die Faser in einer Konzentration im Bereich von 1 bis 60 Gew.-% vorliegt;
 - (b) ein flockenartiges Füllmittel mit einem durchschnittlichen Durchmesser im Bereich von 100 bis 1000 µm, einer durchschnittlichen Dicke im Bereich von 0,1 bis 10 µm und einem Durchmesser/Dicke-Verhältnis im Bereich von 4 bis 400, wobei das Füllmittel in einer Konzentration im Bereich von 1 bis 59 Gew.-% vorliegt; und
 - (c) ein Polycarbonat in einer Konzentration im Bereich von 1 bis 50 Gew.-%,
 jeweils bezogen auf die Gesamtmenge der Harzmasse, und
 - 2) eine organische Substanz mit hohem Molekulargewicht, gewählt aus Ethylen/Carboxylatester-Copolymeren und Metallsalzen davon, Polyacrylatharzen und thermoplastischen Copolyestern vom Segmenttyp in einer Konzentration von 5 bis 40 Gew.-% des kristallinen thermoplastischen Harzes umfaßt.
2. Thermoplastische Harzmasse nach Anspruch 1, worin der Gesamtgehalt der Verstärkungsfasern und des flockenartigen Füllmittels nicht mehr als 60 Gew.-% beträgt.
3. Thermoplastische Harzmasse nach Anspruch 1 oder 2, worin die Verstärkungsfasern in einer Konzentra-



tion von 2 bis 30 Gew.-% vorliegt.

4. Thermoplastische Harzmasse nach einem der Ansprüche 1 bis 3, worin das flockenartige Füllmittel in einer Konzentration von 2 bis 40 Gew.-% vorliegt.

5. Thermoplastische Harzmasse nach einem der Ansprüche 1 bis 4, worin die Gesamtmenge der Verstärkungsfasern und des flockenartigen Füllmittels im Bereich von 30 bis 50 Gew.-% liegt.

6. Thermoplastische Harzmasse nach einem der Ansprüche 1 bis 5, worin das Polycarbonat in einer Konzentration von 2 bis 25 Gew.-% vorliegt.

7. Thermoplastische Harzmasse nach einem der Ansprüche 1 bis 6, worin das kristalline thermoplastische Harz Polybutylenterephthalatharz ist.

8. Thermoplastische Harzmasse nach einem der Ansprüche 1 bis 7, worin das flockenartige Füllmittel Glas ist.

9. Thermoplastische Harzmasse nach einem der Ansprüche 1 bis 8, worin die Verstärkungsfasern eine Faser, gewählt aus der Gruppe, bestehend aus Glas, Kohlenstoff, Graphit, Metallen, Siliciumcarbid, Asbest, Wollastonit, Kaliumtitanat und organischen Fasern, ist.

