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(54) **COMPOSITION DE RESINE THERMOPLASTIQUE**
(54) **THERMOPLASTIC RESIN COMPOSITION**

(57) The present invention is directed to a thermoplastic resin composition comprising (A) 5 to 50 parts by weight of a saturated polyester resin, (B) 10 to 70 parts by weight of a graft polymer obtainable by polymerizing an aromatic vinyl compound and an unsaturated nitrile in the presence of a conjugated diene base rubber, (C) 10 to 70 parts by weight of an α -alkylstyrene-unsaturated nitrile copolymer comprising 50 to 85 % by weight of the α -alkylstyrene and 50 to 15 % by weight of the unsaturated nitrile, provided that the total amount of the components (A), (B) and (C) is 100 parts by weight, wherein the content of the conjugated diene base rubber in the composition is from 5 to 30 % by weight. The composition provides a molded article having improved properties, e.g. chemical resistance, impact resistance, flexural modulus, heat resistance and dimensional stability.

2012265

Abstract

The present invention is directed to a thermoplastic resin composition comprising (A) 5 to 50 parts by weight of a saturated polyester resin, (B) 10 to 70 parts by weight of a graft polymer obtainable by polymerizing an aromatic vinyl compound and an unsaturated nitrile in the presence of a conjugated diene base rubber, (C) 10 to 70 parts by weight of an α -alkylstyrene-unsaturated nitrile copolymer comprising 50 to 85 % by weight of the α -alkylstyrene and 50 to 15 % by weight of the unsaturated nitrile, provided that the total amount of the components (A), (B) and (C) is 100 parts by weight, wherein the content of the conjugated diene base rubber in the composition is from 5 to 30 % by weight. The composition provides a molded article having improved properties, e.g. chemical resistance, impact resistance, flexural modulus, heat resistance and dimensional stability.

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Thermoplastic Resin Composition

The present invention relates to a thermoplastic resin which gives a molded article having good impact resistance, flexural modulus, chemical resistance, heat 5 resistance and dimensional stability.

ABS resins have well balanced physical properties and dimensional stability and are used in various fields. However, if corrosive materials, e.g. gasoline, brake fluids or rust preventive oils adhere to the ABS resin, the 10 resin tends to crack. Therefore, it would be desirable to improve the resistance of ABS resin against various chemical materials.

A saturated polyester resin is known as a resin having good chemical resistance, but it has inferior impact 15 resistance. In particular, notched Izod impact strength is poor and it has poor dimensional stability.

Japanese Patent Kokai Publication No. 219362/1984 proposes the addition of a small amount of a saturated polyester resin to a specific ABS resin composition 20 comprising a styrene-acrylonitrile base copolymer having a specific intrinsic viscosity to provide a resin composition having improved chemical resistance, dimensional stability and weld strength without deteriorating the good physical properties of the ABS resin. However, the obtained resin 25 composition is not necessarily satisfactory in heat

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resistance and the balance between flexural modulus and impact resistance. To improve only the heat resistance, Japanese Patent Kokai Publication No. 11347/1984 proposes a composition comprising a saturated polyester resin and an α -methylstyrene-methacrylate copolymer which is optionally reinforced with a rubber. But, the balance between flexural modulus and impact resistance of such a resin composition is inferior. In addition, silver streaks are generated on the molded article surfaces. Such a resin composition is not a practically attractive material.

An object of the present invention is to provide a resin composition comprising a saturated polyester resin and an ABS resin, which has not only good chemical resistance and heat resistance but also good dimensional stability and balance between flexural modulus and impact resistance.

This and other objects are achieved by a thermoplastic resin composition comprising (A) 5 to 50 parts by weight of a saturated polyester resin, (B) 10 to 70 parts by weight of a graft polymer obtainable by polymerizing an aromatic vinyl compound and an unsaturated nitrile in the presence of a conjugated diene base rubber, (C) 10 to 70 parts by weight of an α -alkylstyrene-unsaturated nitrile copolymer comprising 50 to 85 % by weight of the α -alkylstyrene and 50 to 15 % by weight of the unsaturated nitrile, provided that the total amount of

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the components (A), (B) and (C) is 100 parts by weight, wherein the content of the conjugated diene base rubber in the composition is from 5 to 30 % by weight.

5 If the α -alkylstyrene-unsaturated nitrile copolymer alone is added to the ABS resin, the impact resistance and processability of the resin composition deteriorates although the heat resistance of the composition is improved. However, when the composition comprises the saturated polyester resin, the ABS resin and 10 the α -alkylstyrene-unsaturated nitrile copolymer, it has not only good heat resistance but also good impact resistance.

15 To improve the impact resistance of the composition comprising the ABS resin and polyester, it has been contemplated to increase the content of the rubber in the composition, namely to use the ABS resin containing the rubber in a high proportion. However, the flexural modulus of the resin composition deteriorates greatly.

20 In the composition of the present invention, the addition of the α -alkylstyrene-unsaturated nitrile copolymer improves the flexural modulus. Therefore, even the resin composition containing the rubber in a low content can have good flexural modulus and impact resistance.

25 The components of the resin composition of the present invention will now be explained in detail.

Saturated polyester resin (A)

As the saturated polyester resin (A) to be contained in the resin composition of the present invention, are exemplified polyethylene terephthalate, polytetramethylene terephthalate, polybutylene terephthalate and mixtures thereof. Among them, polybutylene terephthalate is preferred.

There is no limitation on the structure of the saturated polyester resin (A). Preferably, the saturated polyester resin (A) has a viscosity average molecular weight of 18,000 to 88,000 (in a mixed solvent of phenol and tetrachloroethane in a weight ratio of 1:1, at room temperature) from the viewpoint of balance among the physical properties. The saturated polyester resin (A) may be prepared by any of the conventional methods.

Graft polymer (B)

As the conjugated diene base rubber in the graft polymer (B), are exemplified polybutadiene, butadiene-styrene copolymer, butadiene-acrylonitrile copolymer and mixtures thereof. Particle size, gel content and other properties of the conjugated diene base rubber are not critical.

Examples of the aromatic vinyl compound are styrene, α -methylstyrene, dimethylstyrene, vinyltoluene and mixtures thereof. Among them, styrene is preferred.

2012265

Examples of the unsaturated nitrile are acrylonitrile, methacryloyl nitrile and mixtures thereof. Among them, acrylonitrile is preferred.

5 A composition, a graft ratio, a particle size and the like of the graft polymer (B) are not critical. From the viewpoint of balance among the physical properties of the resin composition and the content of the conjugated diene base rubber in the resin composition being 5 to 30 % by weight, preferably the graft polymer (B) has a weight average particle size of 0.05 to 5 μm and comprises 20 to 70 % by weight of the conjugated diene base rubber, 60 to 15 % by weight of the aromatic vinyl compound and 10 to 40 % by weight of the unsaturated nitrile.

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15 The graft polymer (B) may be prepared by any of the conventional methods, e.g. emulsion polymerization, suspension polymerization, bulk polymerization, solution polymerization and combinations thereof.

α -Alkylstyrene-unsaturated nitrile base copolymer
(C)

20 Examples of the α -alkylstyrene in the copolymer (C) are α -methylstyrene, α -ethylstyrene, methyl- α -methylstyrene and mixtures thereof. Among them, α -methylstyrene is preferred.

25 Examples of the unsaturated nitrile are acrylonitrile, methacrylonitrile and mixtures thereof. Among them, acrylonitrile is preferred.

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The copolymer comprises 50 to 85 % by weight of the α -alkylstyrene, 50 to 15 % by weight of the unsaturated nitrile and 0 to 25 % by weight of styrene. Outside these ranges, the resin composition does not achieve the objects of the present invention.

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The properties of the copolymer (C), e.g. an intrinsic viscosity, are not critical. From the viewpoint of the processability of the obtained resin composition, the intrinsic viscosity of the copolymer (C) is preferably from 0.3 to 1.0 (in dimethylformamide at 30°C). The copolymer may be prepared by any of the conventional methods, e.g. emulsion polymerization, bulk polymerization, suspension polymerization, solution polymerization and combination thereof.

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Composition

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The resin composition comprises 5 to 50 parts by weight of the saturated polyester resin (A), 10 to 70 parts by weight of the graft polymer and 10 to 70 parts by weight of the copolymer (C) provided that the total of the components (A), (B) and (C) is 100 parts by weight. Outside these ranges, the resin composition cannot achieve the objects of the present invention. In view of chemical resistance, heat resistance, the balance between flexural modulus and impact resistance and processability, the resin composition of the present invention preferably comprises 10 to 45 parts by weight of the saturated polyester resin (A),

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20 to 50 parts by weight of the graft polymer (B) and 15 to 60 parts by weight of the copolymer (C).

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In the resin composition of the present invention, the content of the conjugated diene base rubber is from 5 to 30 % by weight based on the weight of the resin composition. Outside this range, the objects of the present invention cannot be achieved. From the viewpoint of balance between flexural modulus and impact resistance and the processability, the content of the conjugated diene base rubber is preferably from 10 to 25 % by weight.

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The resin composition of the present invention may be prepared by mixing the saturated polyester resin (A), the graft polymer (B) and the copolymer (C) by a per se conventional method with a known kneading apparatus, e.g. a Banbury mixer, an extruder and the like. The three components may be mixed at once, or two of them can be mixed first and then the remaining component can be added and mixed further.

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During mixing of the components, conventionally used additives, e.g. a stabilizer, a dye or a pigment, a plasticizer, an antistatic agent, an ultraviolet light absorbing agent, a lubricant and a filler, or other thermoplastic resins, e.g. polycarbonate, polyamide, polyphenylene ether may be added.

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The present invention will be illustrated by the following Examples, in which "parts" are by weight unless otherwise indicated.

2012265

Examples and Comparative Examples

A saturated polyester, a graft polymer and a copolymer were kneaded in a single-screw extruder in a composition shown in Tables 1 and 2.

5 The properties of the prepared compositions are shown Tables 3 and 4.

In the Examples and Comparative Examples, the following saturated polyesters, graft polymers and copolymers were used:

10 Saturated polyester resin (A)

(i) Commercially available polybutylene terephthalate

(Viscosity average molecular weight: 31,000)

(ii) Commercially available polyethylene terephthalate

(Viscosity average molecular weight: 34,000)

15 Graft polymer (B)

(i) A graft polymer (B-1) was prepared by polymerizing styrene (37.5 parts) and acrylonitrile (12.5 parts) in a polybutadiene latex (gel content: 85 %, a particle size: 0.41 μm) (50 parts of the solid component) by conventional emulsion polymerization.

20 (ii) A graft polymer (B-2) was prepared by polymerizing styrene (20 parts), α -methylstyrene (22 parts) and acrylonitrile (18 parts) in a polybutadiene latex (gel content: 80 %, a particle size: 0.35 μm) (40 parts of the

2012265

solid component) by conventional emulsion polymerization.

5 (iii) A graft polymer (B-3) was prepared by polymerizing styrene (50 parts) and acrylonitrile (20 parts) in a styrene-butadiene copolymer latex (gel content: 87 %, a particle size: 0.40 μm , styrene content: 10 % by weight) (30 parts of the solid component) by conventional emulsion polymerization.

Copolymer

10 (i) A copolymer (C-1) having an intrinsic viscosity of 0.50 was prepared by copolymerizing α -methylstyrene (75 parts) and acrylonitrile (25 parts) by conventional emulsion polymerization.

15 (ii) A copolymer (C-2) having an intrinsic viscosity of 0.65 was prepared by copolymerizing α -methylstyrene (65 parts), acrylonitrile (25 parts) and styrene (10 parts) by conventional emulsion polymerization.

20 (iii) A copolymer (X-1) having an intrinsic viscosity of 0.80 was prepared by copolymerizing α -methylstyrene (40 parts), acrylonitrile (25 parts) and styrene (35 parts) by conventional emulsion polymerization.

25 (iv) A copolymer (X-2) having an intrinsic viscosity of 0.70 was prepared by copolymerizing styrene (75 parts) and acrylonitrile (25 parts) by conventional emulsion polymerization.

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2012265

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(v) A copolymer (X-3) was prepared by polymerizing α -methylstyrene (51 parts) and methylstyrene (34 parts) in a polybutadiene latex (gel content: 85 %, a particle size: 0.41 μm) (15 parts of the solid component) by conventional emulsion polymerization.

Table 1

Example No.	C. 1	C. 2	1	2	C. 3	C. 4	3	4	C. 5	5	C. 6
Saturated polyester resin (A)											
PBT (parts)			20	20							
PET (parts)					30	30					
Graft polymer (B)											
B-1 (parts)	30	30									
B-2 (parts)											
B-3 (parts)					55	35					
Copolymer (C)											
C-1 (parts)	70		25	45							
C-2 (parts)											
Copolymer (X)											
X-1 (parts)							45	5			
X-2 (parts)											
X-3 (parts)											
Rubber content (% by weight)	15.0	15.0	16.5	10.5	10.5	19.5	18.0	14.0	14.0	10.0	2.0

2012265

Table 2

Example No.	C. 7	6	C. 8	7	C. 9	8	C.10	C.11	C.12	C.13
Saturated polyester resin (A)										
PBT (parts)	40	40	40	40	40	40	40	40	60	60
PET (parts)										
Graft polymer (B)										
B-1 (parts)	35	35	35	25	25	15	15		5	25
B-2 (parts)										
B-3 (parts)	55									
Copolymer (C)										
C-1 (parts)	25		35				45			15
C-2 (parts)										
Copolymer (X)										
X-1 (parts)	5		25							
X-2 (parts)					35					
X-3 (parts)							45		60	
Rubber content (% by weight)	16.5	17.5	17.5	10.0	10.0	7.5	7.5	9.0	2.5	12.5

2012265

Table 3

Example No.	C. 1	C. 2	1	2	C. 3	C. 4	3	4	C. 5	5	C. 6
Chemical resistance *1) (presence of cracks)											
Brake fluid	Yes	Yes	No	No	Yes	Yes	No	No	Yes	No	Yes
Rust preventive oil	Yes	Yes	No	No	No	No	No	No	No	No	No
Heat resistance *2) (°C)	108	88	93	98	82	78	90	94	78	96	80
(Flexural modulus) x 10 ⁴ *3) (kg/cm ²) (C)	2.3	2.3	2.0	2.3	2.3	2.0	2.1	2.2	2.2	2.4	2.5
Impact resistance *4) (kg.cm/cm)	10	20	17	12	3	8	19	16	4	10	2
Dimensional stability (mm)	0	0	0	0	0.1	0.11	0.05	0.06	0.21	0.08	0.32

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2012265

Table 4

Example No.	C. 7	6	C. 8	7	C. 9	8	C. 10	C. 11	C. 12	C. 13
Chemical resistance*1) (presence of cracks)										
Brake fluid	NO	NO	NO	NO						
Rust preventive oil	NO	NO	NO	NO						
Heat resistance*2) (°C)	78	96	93	97	77	98	65	93	65	68
Toughness x 10 ³ *3) (kg/cm ²) (C)	2.2	2.2	2.2	2.3	2.3	2.3	2.3	2.3	2.4	2.3
Impact resistance*4) (kg.cm/cm)	6	18	5	13	5	10	3	4	2	5
Dimensional*5) stability (mm)	0.33	0.13	0.39	0.12	0.37	0.20	0.43	0.45	0.51	0.48*6)

Note: *1) A disc plate of 130 mm in diameter and 3 mm in thickness which has, at its center, a boss of 3.2 mm in inner diameter, 9.0 mm in outer diameter and 25 mm in height was injection molded.

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In the boss, a self tapping screw (JIS type 2, M 4 x 12 mm) and a washer of 1 mm in thickness were screwed at a torque of 15 kg/cm and the plate having the screw and the washer was completely dipped in the brake fluid or the rust preventive oil at room temperature for one hour. Then, the article was removed from the test fluid and the formation of cracks was inspected.

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*2) ASTM D-648; thickness of 1/4 inch and load of 18.6 kg/cm².

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*3) ASTM D-790.

*4) ASTM D-256; thickness of 1/4 inch, notched Izod impact strength.

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*5) A disc of 100 mm in diameter and 2 mm in thickness was injection molded at the resin temperature of 280 to 285°C and degree of warp was observed on a base plate.

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*6) On the surface of the test disc, many silver streaks were found.

As can be understood from the results in the Tables, the addition of the α -methylstyrene-acrylonitrile copolymer to the graft polymer improved the heat resistance but decreased the impact strength in comparison to the 5 addition of the styrene-acrylonitrile copolymer to the graft copolymer.

The addition of the α -methylstyrene-acrylonitrile copolymer to the saturated polyester resin and the graft polymer improved not only the heat resistance but also 10 greatly improved the impact strength.

2012265

Claims:

1. A thermoplastic resin composition comprising
(A) 5 to 50 parts by weight of a saturated polyester resin,
(B) 10 to 70 parts by weight of a graft polymer obtainable
5 by polymerizing an aromatic vinyl compound and an unsatu-
rated nitrile in the presence of a conjugated diene base
rubber, (C) 10 to 70 parts by weight of an α -alkylstyrene-
unsaturated nitrile copolymer comprising 50 to 85 % by
weight of the α -alkylstyrene and 50 to 15 % by weight of the
10 unsaturated nitrile, provided that the total amount of the
components (A), (B) and (C) is 100 parts by weight, wherein
the content of the conjugated diene base rubber in the com-
position is from 5 to 30 % by weight.

2. The thermoplastic resin composition according
15 to claim 1, wherein the saturated polyester resin (A) has a
viscosity average molecular weight of 18,000 to 88,000.

3. The thermoplastic resin composition according
to claim 1, wherein the saturated polyester resin (A) is
polybutylene terephthalate.

20 4. The thermoplastic resin composition according
to claim 1, wherein the graft polymer (B) has a weight ave-
rage particle size of 0.05 to 5 μm .

25 5. The thermoplastic resin composition according
to claim 1, wherein the graft polymer (B) comprises 20 to 70
% by weight of the conjugated diene base rubber, 60 to 15 %
by weight of the aromatic vinyl compound and 10 to 40 % by
weight of the unsaturated nitrile.

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2012265

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6. The thermoplastic resin composition according to claim 1, wherein the α -alkylstyrene-unsaturated nitrile copolymer comprises 50 to 85 % by weight of the α -alkylstyrene, 50 to 15 % by weight of the unsaturated nitrile and 0 to 25 % by weight of styrene.

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7. The thermoplastic resin composition according to claim 1, which comprises 10 to 45 parts by weight of the saturated polyester resin (A), 20 to 50 parts by weight of the graft polymer (B) and 15 to 60 parts by weight of the copolymer (C).