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THERMOPLASTIC RESIN COMPOSITION, MOLDED PRODUCT AND
METHOD FOR ITS PRODUCTION

The present invention relates to a thermoplastic
5 resin composition, a thermoplastic resin molded product
made thereof and a method for producing such a molded
product. Particularly, the present invention relates to
a thermoplastic resin composition comprising, as
essential components, a maleimide copolymer essentially
10 comprising residues of an unsaturated dicarboxylic acid
anhydride monomer and residues of an unsaturated
dicarboxylic acid imide monomer, a graft copolymer
essentially comprising a rubbery polymer, residues of an
aromatic vinyl monomer and residues of a vinyl cyanide
15 monomer, a polyamide resin, and an elastomer of ethylene-
 α -olefin containing residues of an unsaturated
dicarboxylic acid monomer and/or residues of an
unsaturated dicarboxylic acid anhydride monomer, in a
specific ratio, and such a thermoplastic resin.
20 composition is capable of imparting excellent chemical

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resistance to an ABS resin. Further, it relates to a thermoplastic resin molded product comprising such a thermoplastic resin composition and an ABS resin, which has heat resistance and chemical resistance, particularly
5 a thermoplastic resin molded product having excellent impact resistance, heat resistance and chemical resistance, which is obtained by a method which comprises simultaneously supplying to and molding by a molding machine (hereinafter referred to as direct molding) such
10 a thermoplastic resin composition and an ABS resin.

Heretofore, a so-called ABS resin prepared by graft copolymerizing a mixture of styrene and acrylonitrile to a rubbery polymer, has been used for various applications, as it has excellent impact resistance,
15 moldability and surface gloss. On the other hand, the material having chemical resistance is desired depending upon the particular application. Particularly, for automobile parts, electric and electronic parts, parts of office appliances, heating instruments, kitchen utensils,
20 refrigerator parts, bathtub parts, shower instrument parts, water cleaning instrument parts or toilet seat parts, which are subject to contact with chemicals such as cleaning agents, oils or organic solvents, chemical resistance is required for safety and durability.

25 As a method for improving chemical resistance of ABS resins, it has heretofore been known to incorporate and acrylic rubbery polymer or a polyamide resin to ABS

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resins.

However, ABS resins containing an acrylic rubbery polymer have problems such that they are poor in heat resistance and heat stability, although they have high
5 chemical resistance and impact resistance. On the other hand, a resin composition having a polyamide resin blended to an ABS resin has a drawback that the compatibility between the blended resins is inadequate, and when formed into a molded product, delamination is
10 likely to result, and it is difficult to obtain a good balance of the impact resistance and the chemical resistance.

When an acrylic rubbery polymer or a polyamide resin is to be kneaded with an ABS resin, it has been common to
15 employ a kneader such as a single screw extruder, a twin screw extruder or a Banbury mixer to obtain resin pellets having the desired chemical resistance or other physical properties and to mold the obtained resin pellets by a means such as injection molding to produce a molded
20 product.

In order to obtain molded products having different levels of physical properties such as chemical resistance and heat resistance by such a conventional method, it has been necessary to obtain resin pellets which are
25 respectively different corresponding to the required levels of physical properties, whereby the quality control has been cumbersome.





Further, in order to obtain resin pellets corresponding to the respective levels of physical properties, kneading operations have been required independently, whereby especially the ABS resin has
5 tended to deteriorate, thus leading to deterioration of the impact strength. Further, the kneading operations require substantial costs and are economically disadvantageous.

It is an object of the present invention to provide a
10 thermoplastic resin composition which is capable of imparting excellent chemical resistance to an ABS resin and to solve also the above-mentioned problem involved in obtaining a molded product, to provide a thermoplastic resin molded product excellent in chemical resistance,
15 which comprises the thermoplastic resin composition of the present invention and an ABS resin, particularly a thermoplastic resin molded product excellent in impact resistance, heat resistance and chemical resistance, which is obtained by directly molding the thermoplastic
20 resin composition of the present invention and an ABS resin, and a method for its production.

The present inventors have conducted an extensive study for the purpose of developing a thermoplastic resin composition which is capable of imparting chemical
25 resistance to a molded product when an ABS resin is injection molded and as a result, have found it possible to accomplish such an object by blending a maleimide





copolymer comprising residues of an unsaturated
dicarboxylic acid anhydride monomer and residues of an
unsaturated dicarboxylic acid imide monomer in a certain
specific ratio, a graft copolymer, a polyamide resin, an
5 elastomer of ethylene- α -olefin containing residues of an
unsaturated dicarboxylic acid monomer and/or residues of
an unsaturated dicarboxylic acid anhydride monomer in a
certain specific ratio, and an optional vinyl copolymer
essentially comprising residues of an aromatic vinyl
10 monomer and residues of a vinyl cyanide monomer, in a
certain specific ratio. The present invention has been
accomplished on the basis of this discovery.

Namely, the present invention provides a
thermoplastic resin composition comprising from 3 to 50
15 parts by weight of component (A) which is a maleimide
copolymer comprising from 40 to 80 wt% of residues of an
aromatic vinyl monomer, at most 20 wt% (excluding 0 wt%)
of residues of an unsaturated dicarboxylic acid anhydride
monomer, at least 10 wt% and less than 60 wt% of residues
20 of an unsaturated dicarboxylic acid imide derivative and
from 0 to 20 wt% of residues of a vinyl monomer
copolymerizable therewith; from 0 to 50 parts by weight
of component (B) which is a vinyl copolymer comprising
from 60 to 80 wt% of residues of an aromatic vinyl
25 monomer, from 20 to 40 wt% of residues of a vinyl cyanide
monomer and from 0 to 20 wt% of residues of a vinyl
monomer copolymerizable therewith; from 3 to 50 parts by





weight of component (C) which is a graft copolymer
obtained by graft polymerizing from 35 to 65 parts by
weight of a monomer mixture comprising from 50 to 80 wt%
of an aromatic vinyl monomer, from 20 to 40 wt% of a
5 vinyl cyanide monomer and from 0 to 30 wt% of a vinyl
monomer copolymerizable therewith, to from 35 to 65 parts
by weight of a rubbery polymer; more than 20 parts by
weight and not more than 56 parts by weight of component
(D) which is a polyamide resin; and more than 12 parts by
10 weight and not more than 40 parts by weight of component
(E) which is an elastomer copolymer of ethylene- α -olefin
containing at most 5 wt% (excluding 0 wt%) of residues of
an unsaturated dicarboxylic acid monomer and/or residues
of an unsaturated dicarboxylic acid anhydride monomer;
15 provided that the total of components (A) to (E) is 100
parts by weight; said thermoplastic resin composition
having a melt flow rate (MFR) of from 3 to 40 g/10
minutes at 265°C under a load of 10 kg.

The feature of the thermoplastic resin composition of
20 the present invention is that when formed into a molded
product, chemical resistance can be imparted simply and
at a low cost without remarkably lowering various
physical properties such as heat resistance and impact
resistance of the base ABS resin.

25 Now, the maleimide copolymer of component (A) to be
used for the thermoplastic resin composition of the
present invention will be described.





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The aromatic vinyl monomer constituting component (A) is at least one monomer selected from the group consisting of styrene monomers such as styrene, α -methyl styrene, vinyl toluene, t-butyl styrene and chloro
5 styrene. Among them, styrene is particularly preferred.

The copolymer comprising the aromatic vinyl monomer, the unsaturated dicarboxylic acid imide derivative, the unsaturated dicarboxylic acid anhydride, and the optional vinyl monomer copolymerizable therewith, may be prepared
10 by copolymerizing the unsaturated dicarboxylic acid anhydride with the aromatic vinyl monomer and the optional copolymerizable vinyl monomer, followed by reacting with ammonia and/or a primary amine to obtain a maleimide copolymer having residues of an unsaturated
15 dicarboxylic acid anhydride monomer and residues of an unsaturated dicarboxylic acid imide monomer. Otherwise, at least one imide monomer selected from the group consisting of maleimide, N-methylmaleimide, N-ethylmaleimide, N-cyclohexylmaleimide, N-phenylmaleimide,
20 N-naphthylmaleimide and glutarimide, may be directly copolymerized with the aromatic vinyl monomer, the unsaturated dicarboxylic acid anhydride monomer and the optional vinyl monomer copolymerizable therewith, to obtain a maleimide copolymer. The unsaturated
25 dicarboxylic acid anhydride may be at least one member selected from anhydrides of maleic acid, itaconic acid, citraconic acid and aconitic acid. Maleic anhydride is





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particularly preferred. The ammonia or the primary amine to be used for the reaction for imide-formation may be in an anhydrous state or in the form of an aqueous solution. The primary amine may be at least one member selected
5 from alkylamines such as methylamine, ethylamine and cyclohexylamine, and aromatic amines such as aniline, toluidine and naphthylamine.

When the reaction for imide-formation is conducted in a solution state or in a suspension state, a usual
10 reactor such as an autoclave may preferably be used. When it is conducted in a bulky molten state, an extruder equipped with a deaerator may be employed.

The temperature for the reaction for imide-formation is usually from about 80 to 350°C, preferably from 100 to
15 300°C. If the temperature is lower than 80°C, the reaction rate tends to be slow, and it takes a long time for the reaction, such being not practical. On the other hand, if it exceeds 350°C, the physical properties tend to deteriorate due to heat decomposition of the polymer.
20 A catalyst may be used for the reaction for imide-formation, and in such a case, a tertiary amine such as triethylamine, is preferably employed.

The residues of an aromatic vinyl monomer used for component (A) are from 40 to 80 wt%, preferably from 45
25 to 60 wt%. If they are less than 40 wt%, the moldability tends to be poor, and if they exceed 80 wt%, the heat resistance of the thermoplastic resin composition tends





to be low, such being undesirable. The residues of an unsaturated dicarboxylic acid imide derivative to be used for component (A) are at least 10 wt% and less than 60 wt%. If they are less than 10 wt% or at least 60 wt%,
5 the resulting thermoplastic resin composition tends to be poor in the compatibility, and the impact resistance tends to be substantially low. The residues of an unsaturated dicarboxylic acid imide derivative are particularly preferably from 25 to 55 wt%.

10 Further, the residues of an unsaturated dicarboxylic acid anhydride monomer, are at most 20 wt% (excluding 0 wt%), preferably from 0.5 to 15 wt%. If residues of an unsaturated dicarboxylic acid anhydride are not incorporated, the compatibility between the maleimide
15 copolymer for component (A) and the polyamide resin for component (D) tends to be poor, which not only causes cleavage of the molded product but also causes deterioration of the impact strength. If they exceeds 20 wt%, crosslinking with terminal amino groups in the
20 polyamide resin of component (D) tends to proceed, whereby the fluidity (melt flow rate: MFR) tends to be low, and the surface appearance tends to be impaired, and at the same time the moldability tends to be poor. The residues of a copolymerizable vinyl monomer is from 0 to
25 20 wt%, preferably from 0 to 10 wt%. If they exceed 20 wt%, the compatibility with other components, tends to be poor, whereby the impact resistance tends to be poor, and





when formed into a molded product, delamination is likely to result.

The weight average molecular weight of the maleimide copolymer of component (A) is not particularly limited, but is preferably from 70,000 to 160,000, more preferably from 80,000 to 150,000.

Now, the vinyl copolymer (B) to be used for the thermoplastic resin composition of the present invention will be described.

10 The aromatic vinyl monomer to be used for component (B) of the present invention is at least one member selected from styrene monomers such as styrene, α -methyl styrene, vinyl toluene, t-butyl styrene, and chloro styrene. Particularly preferred is styrene. The vinyl
15 cyanide monomer may be at least one member selected from acrylonitrile, methacrylonitrile and α -chloroacrylonitrile. Particularly preferred is acrylonitrile.

The vinyl monomer copolymerizable therewith may be at
20 least one member selected from acrylates such as methyl acrylate, ethyl acrylate and butyl acrylate, methacrylates such as methyl methacrylate and ethyl methacrylate, vinyl carboxylic acid monomers such as acrylic acid and methacrylic acid, acrylic acid amide,
25 methacrylic acid amide, and N-vinyl carbazole. Among them, a monomer such as a methacrylate, acrylic acid or methacrylic acid is particularly preferred.





The residues of an aromatic vinyl monomer in component (B) are from 60 to 80 wt%, preferably from 68 to 78 wt%. If they are less than 60 wt% or more than 80 wt%, the moldability tends to be poor. The residues of a vinyl cyanide monomer are from 20 to 40 wt%, preferably from 22 to 32 wt%. If they are less than 20 wt% or more than 40 wt%, the compatibility with component (A) tends to be poor, thus leading to delamination of the molded product or deterioration of the impact strength. The residues of a copolymerizable vinyl monomer are from 0 to 20 wt%, preferably from 0 to 10 wt%. If they exceed 20 wt%, the compatibility with other components tends to be poor, whereby the impact resistance tends to be poor, and when formed into a molded product, delamination is likely to result. Component (B) may also be produced by a conventional polymerization method. For example, a polymerization method such as suspension polymerization, solution polymerization or emulsion polymerization may be employed.

Now, the graft copolymer of component (C) to be used for the thermoplastic resin composition of the present invention will be described.

The rubbery polymer to be used for component (C) may be at least one member selected from a butadiene polymer, a copolymer of butadiene with a polymerizable vinyl monomer, an ethylene-propylene copolymer and an ethylene-propylene-diene copolymer.





The aromatic vinyl monomer to be used for component (C) may be at least one member selected from styrene monomers such as styrene, α -methyl styrene, vinyl toluene, t-butyl styrene and chloro styrene.

5 Particularly preferred is styrene. The vinyl cyanide monomer may be at least one member selected from acrylonitrile, methacrylonitrile and α -chloroacrylonitrile. Particularly preferred is acrylonitrile.

10 Further, the vinyl monomer copolymerizable therewith may be at least one member selected from acrylate monomers such as methyl acrylate, ethyl acrylate and butyl acrylate, methacrylate monomers such as methyl methacrylate and ethyl methacrylate, vinyl carboxylic
15 acid monomers such as acrylic acid and methacrylic acid, acrylic acid amide, methacrylic acid amide, and N-vinyl carbazole. Among them, a monomer such as an acrylate, a methacrylate, acrylic acid or methacrylic acid, is particularly preferred.

20 Any conventional polymerization technique may be employed for the production of the graft polymer of component (C). For example, aqueous non-homogeneous polymerization such as suspension polymerization or emulsion polymerization, bulk polymerization, solution
25 polymerization, or non-homogeneous polymerization wherein formed polymer is precipitated in a poor solvent, or a combination thereof, may be mentioned.





The rubber particle size, the graft ratio and the weight average molecular weight of non-graft copolymer, of the graft copolymer of component (C), are not particularly limited. However, the rubber particle size is preferably within a range of from 0.1 to 0.6 μm , from the viewpoint of impact resistance. Further, the graft ratio is preferably from 20 to 80%, more preferably from 30 to 50%, and the weight average molecular weight of non-graft copolymer is preferably within a range of from 50,000 to 200,000, more preferably from 60,000 to 100,000, whereby the balance of the impact resistance and the moldability will be good.

The graft copolymer of component (C) is the one prepared by graft copolymerizing from 35 to 65 parts by weight of a monomer mixture comprising from 50 to 80 wt% of an aromatic vinyl monomer, from 20 to 40 wt% of a vinyl cyanide monomer and from 0 to 30 wt% of a vinyl monomer copolymerizable therewith, in the presence of from 35 to 65 parts by weight of a rubbery polymer, provided that the total of the rubbery polymer and the monomer mixture is 100 parts by weight. Particularly preferred is the one comprising from 65 to 72 wt% of an aromatic vinyl monomer, from 22 to 32 wt% of a vinyl cyanide monomer and from 0 to 13 wt% of a vinyl monomer copolymerizable therewith. If the aromatic vinyl monomer is less than 50 wt%, the direct moldability of the thermoplastic resin composition of the present invention





and an ABS resin, tends to be poor, and if it exceeds 80 wt%, the heat resistance of the thermoplastic resin composition of the present invention tends to be poor. If the vinyl cyanide monomer is less than 20 wt% or more than 40 wt%, the compatibility with component (A) tends to be poor, and delamination or deterioration of the impact strength tends to be caused with a molded product of the thermoplastic resin composition of the present invention and the ABS resin. If the residues of the copolymerizable vinyl monomer exceeds 30 wt%, the compatibility with other components tends to be poor, the impact resistance tends to be poor, and when formed into a molded product, delamination tends to result. Further, if the rubbery polymer in component (C) is less than 35 parts by weight, the impact resistance of the thermoplastic resin composition of the present invention tends to be poor, and if it exceeds 65 parts by weight, the heat resistance of the thermoplastic resin composition of the present invention tends to be poor, and the direct moldability of the thermoplastic resin composition of the present invention and an ABS resin tends to be poor.

In graft polymerization, it is usually difficult to graft the entire amount of monomers to the rubbery polymer, and non-graft copolymer will be produced as a by-product. In the present invention, it is of course possible to use a real graft copolymer having such non-





graft copolymer positively separated and removed, or a graft polymer containing such non-graft copolymer. Either one may be used as the graft copolymer for the purpose of the present invention.

5 Now, the polyamide resin of component (D) to be used for the thermoplastic resin composition of the present invention, will be described.

 The polyamide resin of component (D) may, for example, be nylon-6, nylon-6,6, nylon-4,6, nylon-6,10,
10 nylon-12 or nylon 11. These resins may be used alone or in combination as a mixture.

 Now, the elastomer of ethylene- α -olefin of component (E) to be used for the thermoplastic resin composition of the present invention will be described. As the
15 elastomer of ethylene- α -olefin containing an unsaturated dicarboxylic acid and/or its anhydride for component (E), preferred is the one having a number average molecular weight within a range of from 10,000 to 1,000,000 and an ethylene content of from 50 to 80 mol%. The α -olefin may
20 be at least one member selected from propylene, 1-butene and 1-pentene. Particularly preferred is propylene.

 The residues of an unsaturated dicarboxylic acid monomer and/or residues of an unsaturated dicarboxylic acid anhydride monomer, used for modification, as
25 functional groups of component (E), may be at least one member selected from maleic acid, itaconic acid, citraconic acid and aconitic acid, and anhydride monomers





of such acids. Particularly preferred is maleic anhydride.

The content of residues of an unsaturated dicarboxylic acid monomer and/or residues of an unsaturated dicarboxylic acid anhydride monomer, is at most 5 wt% (excluding 0 wt%), preferably from 0.5 to 5 wt%. If the content exceeds 5 wt%, gelation or the like tends to occur in the composition. On the other hand, if it is less than 0.5 wt%, the compatibility of the thermoplastic resin composition tends to be inadequate, whereby when formed into a molded product, delamination is likely to result, and adequate impact strength can not be obtained. Such a modified elastomer of ethylene- α -olefin can be prepared by using the preparation method disclosed in Example of JP-B-58-445.

The blend ratio of components (A), (B), (C), (D) and (E) in the thermoplastic resin composition of the present invention is such that component (A) is from 3 to 50 parts by weight, component (B) is from 0 to 50 parts by weight, component (C) is from 3 to 50 parts by weight, component (D) is more than 20 parts by weight and not more than 56 parts by weight, and component (E) is more than 12 parts by weight and not more than 40 parts by weight, particularly preferably, component (A) is from 5 to 30 parts by weight, component (B) is from 0 to 30 parts by weight, component (C) is from 5 to 20 parts by weight, component (D) is from 30 to 50 parts by weight,

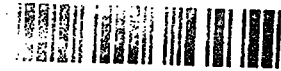




and component (E) is from 20 to 40 parts by weight,
provided that the total of components (A) to (E) is 100
parts by weight. If component (A) is less than 3 parts
by weight, the compatibility tends to be inadequate, and
5 if it exceeds 50 parts by weight, the impact resistance
and moldability of the thermoplastic resin composition
will be substantially poor. Further, if component (B)
exceeds 50 parts by weight, the moldability tends to be
poor. If component (C) is less than 3 parts by weight,
10 the impact resistance tends to be poor, and it exceeds 50
parts by weight, the moldability tends to be poor. If
component (D) is not more than 20 parts by weight,
chemical resistance tends to be inadequate, and it
exceeds 56 parts by weight, the dimensional stability
15 tends to be poor. If component (E) is not more than 12
parts by weight, the impact resistance tends to be
inadequate. If it exceeds 40 parts by weight, the
moldability tends to be poor. Further, the ratio of
component (E) to (D) in the thermoplastic resin
20 composition of the present invention is not particularly
limited, but it is preferably $(E)/(D) = 30/70$ to $50/50$
in a weight ratio.

The method for mixing components (A) to (E) to obtain
the thermoplastic resin composition of the present
25 invention is not particularly limited, and any
conventional means may be employed. Such a conventional
means may, for example, be a Banbury mixer, a tumbler





mixer, a mixing roll, or a single screw or twin screw extruder. With respect to the mixing manner, usual melt mixing, multi-stage melt mixing employing e.g. master pellets, or blending in a solution to obtain the composition, may be mentioned. In particular, components (D) and (E) may be preliminarily melt mixed, and the rest of components (A) to (C) may then be mixed thereto. It is particularly preferred to preliminarily melt mix a resin composition comprising components (D) and (E) and then mix components (A), (B) and (C) so that the weight ratio of components (A), (B) and (C) to components (D) and (E) will be $[(A)+(B)+(C)]/[(D)+(E)] = 60/40$ to 20/80, particularly preferably 40/60 to 20/80, to obtain a thermoplastic resin composition, which is then directly molded together with an ABS resin to obtain a molded product, whereby the heat resistance, chemical resistance, impact resistance and moldability of the obtained molded product will be further improved. Further, the melt flow rate (MFR) of the thermoplastic resin composition of the present invention is required to be within a range of from 3 to 40, preferably from 3 to 25, more preferably from 3 to 10. If the melt flow rate is less than 3, the molded product obtained by direct molding together with the ABS resin tends to have poor surface appearance, and if it exceeds 40, the impact strength and the heat resistance of the molded product tend to be poor.





To the thermoplastic resin composition of the present invention, a stabilizer, a plasticizer, a lubricant, an ultraviolet absorber or a coloring agent may further be incorporated depending upon the particular purpose.

5 Such an additive may be supplied simultaneously at the time of supplying the thermoplastic resin composition of the present invention and the ABS resin directly to a molding machine.

10 The ABS resin to be used in the present invention, may, for example, be a resin obtained by polymerizing at least two monomers selected from an aromatic vinyl monomer, a vinyl cyanide monomer, a maleimide monomer and a vinyl monomer copolymerizable therewith, in the presence of at least one rubbery polymer selected from a
15 butadiene polymer, a butadiene-styrene copolymer, an ethylene-propylene copolymer, an ethylene-propylene-diene copolymer and an acrylate polymer.

20 The aromatic vinyl monomer, the vinyl cyanide monomer and a vinyl monomer copolymerizable therewith may, for example, be the aromatic vinyl monomer, the vinyl cyanide monomer and a vinyl monomer copolymerizable therewith as described above for component (B) of the thermoplastic resin composition. The maleimide monomer may, for example, be maleimide, N-methyl maleimide, N-ethyl
25 maleimide, N-propyl maleimide, N-cyclohexyl maleimide or N-phenyl maleimide.

Further, to adjust the amount of the rubber component





in the resin, a polymer made of the same monomer components as the monomers constituting the resin may be mixed thereto. However, such a polymer may not necessarily be made of the same monomer components. For
5 example, when styrene and an acrylonitrile monomer are used as the monomer components, a polymer of a monomer mixture comprising styrene, acrylonitrile and α -methylstyrene, may be mixed thereto.

Specific examples of the ABS resin to be used in the
10 present invention include ABS (acrylonitrile-butadiene-styrene) resin, α -methyl-styrene heat resistant ABS (acrylonitrile-butadiene- α -methyl styrene; acrylonitrile-butadiene- α -methylstyrene-styrene) resin, maleimide heat resistant ABS (acrylonitrile-butadiene-N-phenylmaleimide-
15 styrene) resin, AES (acrylonitrile-EPDM-styrene) resin, AAS (acrylonitrile-acrylate-styrene) resin, MBS (methylemethacrylate-butadiene-styrene) resin, and MABS (methyl methacrylate-acrylonitrile-butadiene-styrene) resin. However, the ABS resin is not particularly
20 limited to such specific examples.

The blend ratio of the thermoplastic resin composition of the present invention to the ABS resin is not particularly limited. However, the blend preferably comprises from 10 to 50 wt% of the thermoplastic resin
25 composition and from 50 to 90 wt% of the ABS resin, preferably from 15 to 40 wt% of the thermoplastic resin composition and from 60 to 85 wt% of the ABS resin,





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particularly preferably from 15 to 30 wt% of the thermoplastic resin composition and from 70 to 85 wt% of the ABS resin.

5 If the thermoplastic resin composition is less than 10 wt%, the chemical resistance of a molded product obtainable by direct molding together with the ABS resin, tends to be inadequate. On the other hand, if it exceeds 50 wt%, the direct moldability together with the ABS resin tends to be poor.

10 To the thermoplastic resin composition of the present invention, the ABS resin may be preliminarily incorporated within a range not to impair the purpose of the present invention, specifically within a range of from 0 to 20 wt%.

15 The molding machine to be used in the present invention may be an injection molding machine, a sheet-forming machine, a blow molding machine, an injection-blow molding machine. However, the molding machine is not particularly limited to such specific examples.

20 The method for supplying the thermoplastic resin composition of the present invention and the ABS resin to a molding machine, may be a method wherein a mixture preblended by means of a conventional apparatus such as a tumbler mixer or a V-blender, is supplied, a method
25 wherein the two materials are quantitatively separately supplied to the supply inlet of the molding machine, or a method wherein the thermoplastic resin composition and





the ABS resin are preliminarily melt-kneaded to form pellets, which are then supplied to the molding machine. However, the supply method is not particularly limited.

5 The temperature set for the cylinder of the molding machine is determined to be the optimum temperature depending upon the composition of the thermoplastic resin composition. Specifically, it is preferably from 240 to 280°C in the present invention.

10 In the case of injection molding, a conventional stationary mixer of e.g. Sulzer type, Kenics type or Toray type may be installed between the molding machine cylinder and the nozzle, whereby it is possible to obtain a molded product of higher quality.

15 Further, as a screw for an injection molding machine, a full-flighted screw which is most commonly used, may be employed. However, a screw of dumble type, pin type or Maddock type, which has higher kneading efficiency, may also be employed.

20 Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted to such specific examples. Further, in the following Examples and Comparative Examples, "parts" and "%" mean "parts by weight" and "% by weight",
25 respectively, unless otherwise specified.

TEST EXAMPLES 1 AND 2

Maleimide copolymer of component (A) (A-1, A-3)





Into an autoclave equipped with a stirrer, 60 parts of styrene, 0.05 part of α -methyl styrene dimer and 100 parts of methyl ethyl ketone were charged, and the interior of the system was replaced by nitrogen gas.

- 5 Then, the temperature was raised to 85°C, and a solution having 40 parts of maleic anhydride and 0.15 part of benzoyl peroxide dissolved in 200 parts of methyl ethyl ketone, was continuously added thereto over a period of 8 hours. After the addition, the temperature was
- 10 maintained at 85°C for further 3 hours. To the copolymer solution thereby obtained, 38 parts of aniline and 0.6 part of triethylamine were added and reacted at 140°C for 7 hours. The reaction solution was supplied to a vented twin-screw extruder and deaerated to obtain a maleimide
- 15 copolymer. From the C-13NMR analysis, the conversion of acid anhydride groups to imide groups was 92 mol%. This maleimide copolymer was a copolymer containing 51% of units of N-phenylmaleimide as an unsaturated dicarboxylic acid imide derivative, and it was designated as copolymer
- 20 A-1. Maleimide copolymer A-3 was prepared in the same manner as for A-1 except that the amount of aniline was adjusted to adjust the ratio of imide groups added to maleic anhydride.

TEST EXAMPLE 3

25 Maleimide copolymer of component (A) (A-2)

Into an autoclave equipped with a stirrer, 60 parts of styrene and 100 parts of methyl ethyl ketone were





charged, and the interior of the system was replaced by nitrogen gas. Then, the temperature was raised to 85°C, and stirring was carried out thoroughly while maintaining the temperature. Except that 1 part of α -methyl styrene dimer was added thereto, maleimide copolymer A-2 was prepared in the same manner as for A-1. In Table 1, the results of analyses of the compositions of A-1 to A-3 and the weight average molecular weights are shown.

Table 1

	Composition (%)			Weight average molecular weight ($\times 10^{-4}$)
	St	NPMI	MAH	
A-1	46.5	51.0	2.5	14.5
A-2	46.5	51.0	2.5	8.0
A-3	47.5	46.0	6.5	14.5

St: Styrene, NPMI: N-phenylmaleimide,
MAH: Maleic anhydride

For the GPC measurement to determine the weight average molecular weight, "SHODEX GPC SYSTEM-21" manufactured by Showa Denko K.K., was used, and the weight average molecular weight calculated as polystyrene, was obtained by using a calibration curve prepared by employing polystyrene having a standard molecular weight.

TEST EXAMPLE 4

Preparation of a vinyl copolymer of component (B) (B-1)



Into a reactor equipped with a stirrer, 70 parts of styrene, 30 parts of acrylonitrile, 2.5 parts of calcium tertiary phosphate, 0.5 part of t-dodecylmercaptane, 0.2 part of benzoyl peroxide and 250 parts of water were
5 charged, and the temperature was raised to 70°C to initiate polymerization. Upon expiration of 7 hours from the initiation of polymerization, the temperature was raised to 75°C and maintained for 3 hours to complete the polymerization. The degree of polymerization reached
10 97%. The obtained reaction solution was neutralized with hydrochloric acid, dehydrated and dried to obtain a copolymer as white beads. This copolymer was designated as copolymer B-1.

TEST EXAMPLE 5

15 Preparation of a graft copolymer of component (C) (C-1)

Into a reactor equipped with a stirrer, 143 parts of a polybutadiene latex (solid content: 35%, weight average particle size: 0.25 μ m, gel content: 90%), 1 part of sodium stearate, 0.1 part of sodium formaldehyde
20 sulfoxylate, 0.03 part of tetrasodium ethylene diamine tetraacetate, 0.003 part of ferrous sulfate and 150 parts of pure water were charged and heated to 50°C. Then, 50 parts of a monomer mixture comprising 70% of styrene and 30% of acrylonitrile, 0.2 part of t-dodecylmercaptan and
25 0.15 part of cumen hydroperoxide were continuously added thereto over a period of 6 hours. After the addition, the temperature was raised to 65°C, and the mixture was





further polymerized for 2 hours. The degree of
polymerization reached 97%. To the obtained latex, 0.3
part of an antioxidant (Irganox 1076) was added,
followed solidification with calcium chloride, washing
5 with water and drying to obtain a graft copolymer as
white powder. This copolymer was designated as copolymer
C-1.

Then, to measure the graft ratio and the molecular
weight of non-graft copolymer, of C-1, 3 g of C-1 was
10 taken and swelled with a methyl ethyl ketone solution,
followed by centrifugal separation, whereupon the
molecular weight of a non-graft styrene-acrylonitrile
copolymer in the supernatant was measured by gel
permeation chromatography, whereby the weight average
15 molecular weight was 82,000. Further, the composition of
the gel content precipitated by the centrifugal
separation (graft copolymer and rubbery polymer) was
analyzed by a Kieldahl nitrogen quantitative analysis and
the thermal decomposition gas chromatography, whereupon
20 the weight of the graft copolymer was determined from the
amounts of styrene and acrylonitrile. Further, by a
bromine-addition method, polybutadiene rubber was
analyzed, whereby the weight of the rubbery polymer was
determined. The graft ratio was obtained by the
25 following formula from the weight of the graft copolymer
and the weight of the rubbery polymer, thus obtained,
whereby the graft ratio was 33%.





Graft ratio=(Weight of graft copolymer/weight of
rubbery polymer) × 100 (%)

As a polyamide resin of component (D), nylon-6 i.e.
nylon-6 (CM-1017, manufactured by Toray Industries, Inc.)
5 having a relative viscosity of 2.65 (as measured at a
temperature of 25°C using concentrated sulfuric acid as a
solvent at a concentration of 0.5 g/100 ml), obtained by
condensation polymerization of ε-caprolactone, was used
as D-1.

10 TEST EXAMPLE 6

Preparation of an elastomer component (E) of modified
ethylene-α-olefin (E-1)

In accordance with the process disclosed in JP-A-52-
49289 (Examples), 1.3% of maleic anhydride was grafted to
15 an ethylene-propylene copolymer having a number average
molecular weight of 500,000 (modified EPR having a MFR of
0.5 g/10 minutes at 230°C under a load of 10 kg: Tafmer
MP-0430, manufactured by Mitsui Petrochemical Co., Ltd.),
and the obtained elastomer was designated as E-1.

20 TEST EXAMPLE 7

Mixing of components (D) and (E)

60 parts of components (D) and 40 parts of component
(E) were blended, and this blend product was extruded at
280°C by a 35 mm vented same rotational direction twin-
25 screw extruder and pelletized to obtain resin composition
(F-1). In the same manner, resin composition (F-2)
comprising 80 parts of component (D) and 20 parts of





component (E) was obtained.

TEST EXAMPLE 8

Preparation of a thermoplastic resin composition

Component (A), component (B), component (C) and F-1
5 or F-2 were blended in a ratio as shown in Table 2, and
the blend product was extruded at 280°C by a 35 mm vented
same rotational direction twin-screw extruder and
pelletized to obtain a thermoplastic resin composition
MB-1 to MB-9. The melt flow rate (MFR) of the
10 thermoplastic resin composition was measured and shown in
Table 2.



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Table 2

	MB-1	MB-2	MB-3	MB-4	MB-5	MB-6	MB-7	MB-8	MB-9
A-1				5		5			
A-2					5				
A-3	10	5	5				10	20	30
B-1	40	25	10	10	10	10	20	10	0
C-1	20	10	5	5	5	5	10	10	10
F-1	30	60	80	80	80		60	60	60
F-2						80			
MFR	43	9.4	2.2	8.9	7.5	10	7.0	3.2	0.8

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As the ABS resin, commercially available ABS resin
"GT-R, manufactured by Denki Kagaku Kogyo K.K."
(hereinafter referred to as ABS-1) or commercially
available heat resistant ABS resin "K-090, manufactured
5 by Denki Kagaku Kogyo K.K." (hereinafter referred to as
ABS-2) was used.

EXAMPLES 1 TO 7

The thermoplastic resin composition MB-2, MB-4, MB-5,
MB-7 or MB-8 and the ABS resin ABS-1 or ABS-2, were
10 supplied to an injection molding machine, respectively,
by quantitative feeders in the ratio as identified in
Table 3, to mold a test specimen. The molding was
carried out by attaching a stationary kneader (mixing
nozzle) TMN-16-06, manufactured by Toray Engineer K.K. to
15 an injection molding machine K-125 manufactured by
Kawaguchi Tekko K.K. Other molding conditions were as
follows.

Temperature set for cylinder: 260°C

Injection pressure: minimum filling pressure + 5
20 kg/cm²G

Injection rate: 70%

Mold temperature: 60°C

Screw: Full-flighted type

Using the test specimen thus obtained, various
25 physical properties were measured, and the results are
shown in Table 3. ABS-1 and ABS-2 were evaluated without
addition of the thermoplastic resin composition, and the





results are shown as Reference Examples 1 and 2 in Table
4.

EXAMPLE 8

20 parts of the thermoplastic resin composition MB-2
5 and 80 parts of the ABS resin ABS-2 were extruded at
260°C by a 40 mm Φ single screw extruder to obtain
pellets. Using the pellets, a test specimen was prepared
under the same molding conditions as in Example 1. The
physical properties were measured, and the results are
10 shown in Table 3.





Table 3

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
ABS-1	80 20	85 15	85 15	80 20	80 20	80 20	70 30	80 20
ABS-2								
MB-2								
MB-4								
MB-5								
MB-7								
MB-8								
Izod impact strength (kg·cm/cm)	26	25	25	20	26	25	27	23
HDT (°C)	97	97	97	91	97	97	98	97
MFR (g/10 min.)	65	65	70	58	65	60	52	68
Critical strain (%)	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Dimensional stability	○	○	○	○	○	○	○	○
Surface appearance	○	○	○	○	○	○	○	○





Table 4

	Reference Example 1	Reference Example 2
ABS-1	100	100
ABS-2		
Izod impact strength (kg·cm/cm)	20	25
HDT (°C)	91	97
Critical strain (%)	0.6	0.6

COMPARATIVE EXAMPLES 1 TO 8

The operation was carried out in the same manner as in the Examples except that the thermoplastic resin composition MB-1, MB-3, MB-6, MB-9 or F-1 and the ABS resin ABS-1 or ABS-2 were used in a ratio as identified in Table 5.





Table 5

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
ABS-1	60	85				85		
ABS-2			60	85	90		85	80
MB-1	40		40					
MB-3		15		15		15	15	20
MB-6					10			
MB-9								
F-1								
Izod impact strength (kg·cm/cm)	15	14	15	14	7	12	13	24
HDT (°C)	90	91	95	97	97	91	97	98
MFR (g/10 min.)	73	60	80	80	80	72	88	55
Critical strain (%)	0.9	0.9	0.9	0.9	0.9	1.1	1.1	1.1
Dimensional stability	○	○	○	○	○	○	○	○
Surface appearance	○	×	○	×	○	○	○	×



Test methods for measuring the physical properties

1) HDT (heat deformation temperature): Measured in accordance with ASTM D-648 under a load of 18.6 kg/cm².

2) Izod impact strength: Measured in accordance with
5 ASTM-D-256 using a notched test specimen having a thickness of 1/4 inch

3) MFR: Measured in accordance with ASTM-D-6874 at 265°C under a load of 10 kg.

4) Critical strain (chemical resistance): Using a
10 test specimen having a shape of 330 × 20 × 2 mm, the critical strain after 24 hours at 23°C, was measured by a 1/4 ellipse method with a long radius of 248 mm and a short radius of 148 mm. To remove the influence of the molding strain, the test specimen was prepared by press
15 molding pellets at 270°C and cutting out the test specimen therefrom. As the reagent, salad oil was used.

5) Dimensional stability: No. 1 dumbbell in accordance with ASTM-D-368, was immersed in a warm water of 80°C for 24 hours, and the dimensional change in the
20 longitudinal direction of the dumbbell between before and after the immersion was measured.

Symbol ○ indicates that the dimensional change was not more than 0.5%, and symbol × indicates that the dimensional change exceeded 0.5%.

25 6) Appearance: A square plate having a size of 127 × 127 mm with a thickness of 2 mm, was molded by a side gate (two points) under the above-mentioned injection





molding conditions, whereupon the appearance of the molded product was visually inspected and evaluated under the following standards.

○: No defects (such as flaw marks, silver streaks, flash) were observed on the surface

x: Defects (such as flaw marks, silver streaks, flash) were observed on the surface.

As shown by the Examples in Table 3, by directly molding the thermoplastic resin composition of the present invention and an ABS resin, it is possible to obtain a molded product having chemical resistance and high quality appearance without deteriorating various physical properties of the ABS resin as a base material.

Whereas, as shown by the Comparative Examples in Table 5, if a thermoplastic resin composition departing from the range of the present invention, is employed, it is impossible to obtain a molded product having such excellent properties.

As described in the foregoing, a molded product obtained by molding the thermoplastic resin composition of the present invention and an ABS resin, is excellent in chemical resistance and heat resistance. Especially, the thermoplastic resin composition of the present invention can be directly molded together with an ABS resin, and the molded product has excellent chemical resistance, heat resistance and impact resistance, and yet it is excellent in the moldability without





deteriorating various properties of the base ABS resin.
According to the direct molding of the present invention,
by changing the blend ratio of the specific thermoplastic
resin composition and a base ABS resin described to have
5 chemical resistance imparted, it is possible to obtain a
molded product having the desired chemical resistance
imparted, simply and at a low cost without deteriorating
the properties of the base ABS resin. Further, it is
thereby possible to employ such an economically excellent
10 method as direct molding, and the value for industrial
application is significant as a material for automobile
parts, electric or electronic parts, parts of office
appliances, heating instruments, kitchen utensils,
refrigerator parts, bathtub parts, shower instrument
15 parts, water cleaning parts or toilet seat parts.





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CLAIMS:

1. A thermoplastic resin composition comprising from 3 to 50 parts by weight of component (A) which is a maleimide copolymer comprising from 40 to 80 wt% of
5 residues of an aromatic vinyl monomer, at most 20 wt% (excluding 0 wt%) of residues of an unsaturated dicarboxylic acid anhydride monomer, at least 10 wt% and less than 60 wt% of residues of an unsaturated dicarboxylic acid imide derivative and from 0 to 20 wt%
10 of residues of a vinyl monomer copolymerizable therewith; from 0 to 50 parts by weight of component (B) which is a vinyl copolymer comprising from 60 to 80 wt% of residues of an aromatic vinyl monomer, from 20 to 40 wt% of residues of a vinyl cyanide monomer and from 0 to 20 wt%
15 of residues of a vinyl monomer copolymerizable therewith; from 3 to 50 parts by weight of component (C) which is a graft copolymer obtained by graft polymerizing from 35 to 65 parts by weight of a monomer mixture comprising from 50 to 80 wt% of an aromatic vinyl monomer, from 20 to 40
20 wt% of a vinyl cyanide monomer and from 0 to 30 wt% of a vinyl monomer copolymerizable therewith, to from 35 to 65 parts by weight of a rubbery polymer; more than 20 parts by weight and not more than 56 parts by weight of component (D) which is a polyamide resin; and more than
25 12 parts by weight and not more than 40 parts by weight of component (E) which is an elastomer copolymer of ethylene- α -olefin containing at most 5 wt% (excluding 0

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- wt%) of residues of an unsaturated dicarboxylic acid monomer and/or residues of an unsaturated dicarboxylic acid anhydride monomer; provided that the total of components (A) to (E) is 100 parts by weight; said
- 5 thermoplastic resin composition having a melt flow rate (MFR) of from 3 to 40 g/10 minutes at 265°C under a load of 10 kg.
2. The thermoplastic resin composition according to Claim 1, wherein the weight ratio of component (E) to
- 10 component (D) is $(E)/(D) = 30/70$ to $50/50$.
3. The thermoplastic resin composition according to Claim 1 or 2, which is prepared by preliminarily melt mixing a composition comprising components (D) and (E), and adding components (A), (B) and (C) thereto so that
- 15 the weight ratio of components (A), (B) and (C) to components (D) and (E) is $[(A)+(B)+(C)]/[(D)+(E)] = 60/40$ to $20/80$.
4. A thermoplastic resin molded product obtained by supplying to and molding by a molding machine, from 10 to
- 20 50 wt% of the thermoplastic resin composition as defined in Claim 1, 2 or 3, and from 50 to 90 wt% of an ABS resin.
5. A thermoplastic resin molded product obtained by supplying to and molding by an injection molding machine,
- 25 from 10 to 50 wt% of the thermoplastic resin composition as defined in Claim 1, 2 or 3, and from 50 to 90 wt% of an ABS resin.

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6. A method for producing a thermoplastic resin molded product, which comprises simultaneously supplying to and molding by a molding machine, from 10 to 50 wt% of the thermoplastic resin composition as defined in Claim 1, 2
5 or 3, and from 50 to 90 wt% of an ABS resin.

7. A method for producing a thermoplastic resin molded product, which comprises simultaneously supplying to and molding by an injection molding machine, from 10 to 50 wt% of the thermoplastic resin composition as defined in
10 Claim 1, 2 or 3, and from 50 to 90 wt% of an ABS resin.

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