

DESCRIPTION

TRANSPARENT RUBBER-MODIFIED COPOLYMER RESIN AND RESIN

COMPOSITION THEREOF

TECHNICAL FIELD

5 The present invention relates to a rubber-modified
copolymer resin which is excellent in transparency,
impact resistance and rigidity and which has little
dependency of the transparency on molding conditions, and
a rubber-modified copolymer resin composition which has
10 the above characteristics and which further has high
practical strength.

BACKGROUND ART

Heretofore, transparent rubber-modified copolymer
resins were employed in various applications including
15 household electric products, packaging materials and
optical applications. However, they were inadequate in
transparency, impact resistance and rigidity, and they
had dependency of the transparency on molding conditions.
Thus, they were not satisfactory. Further, they were not
20 adequate against a demand in recent market place for high
practical strength.

For example, JP-A-4-180907 discloses a rubber-
modified copolymer resin having the toluene-insoluble
content, the swelling index, etc. adjusted within certain
25 specific ranges, but for such a resin, it was required to
use a specific styrene/butadiene copolymer or a specific
reactor, and there was a problem such that the balance of



the transparency, the impact resistance, the rigidity, etc. was not sufficient.

JP-A-8-269142 discloses a rubber-modified styrenic resin composition wherein a copolymer of a styrenic monomer and a (meth)acrylic ester monomer, constitutes a continuous phase, and rubber particles having two peaks constitute a dispersed phase, but its use was limited due to the facts that control of the rubber particle size distribution, the gel content, the swelling index, etc. was not sufficient, the dependency of the transparency on the molding conditions was large, and the practical strength was low.

JP-A-11-147993 discloses a rubber-modified styrenic resin composition wherein a copolymer of a styrenic monomer and a (meth)acrylic ester monomer constitutes a continuous phase and rubber particles having two peaks constitute a dispersed phase, and its molecular weight distribution is adjusted to be within a specific range. However, there was a problem that there were many particles having small particle diameters and low impact resistance, and the balance of the impact resistance and the rigidity was not sufficient.

It is an object of the present invention to provide a rubber-modified copolymer resin is excellent in transparency, impact resistance and rigidity and which has little dependency of the transparency on molding conditions, and a rubber-modified copolymer resin

composition which has the above-mentioned characteristics and which further has excellent practical strength.

DISCLOSURE OF THE INVENTION

The present inventors have conducted an extensive
5 study to solve such problems and as a result have arrived
at the present invention on the basis of discovery that a
rubber-modified copolymer resin having a specific rubber
particle size distribution is excellent in transparency,
impact resistance and rigidity and has little dependency
10 of the transparency on molding conditions. Further, it
has been found that among such rubber-modified copolymer
resins, a rubber-modified copolymer resin having a
specific gel content, swelling index and weight average
molecular weight is further excellent in transparency,
15 impact resistance and rigidity and has little dependency
of the transparency on molding conditions.

Further, it has been found that a rubber-modified
copolymer resin composition comprising such a rubber-
modified copolymer resin and an emulsion graft copolymer,
20 is excellent in transparency, impact resistance and
rigidity and has little dependency of the transparency on
molding conditions and further has high practical
strength, whereby the present invention has been
accomplished.

25 Namely, the present invention has the following
characteristics.

(1) A transparent rubber-modified copolymer resin

which is a rubber-modified copolymer resin comprising one type or a mixture of two or more types obtained by copolymerizing a styrenic monomer and a (meth)acrylic ester monomer in the presence of a rubbery polymer, and
5 which is characterized in that the volume mean particle diameter (d_v) of rubber particles dispersed in the resin, is from 0.4 to 2.0 μm , and in the cumulative rubber particle size distribution curve by volume, the difference between the diameter (d_{75}) at an integrated
10 value of 75% and the diameter (d_{25}) at an integrated value of 25%, is from 0.2 to 2.0 μm .

(2) The transparent rubber-modified copolymer resin according to the above (1), wherein in the cumulative rubber particle size distribution curve by volume, rubber
15 particles having particle diameters of less than 0.8 μm occupy from 95 to 30 vol%, and rubber particles having particle diameters of at least 0.8 μm occupy from 5 to 70 vol%.

(3) The transparent rubber-modified copolymer resin
20 according to the above (1) or (2), wherein the cumulative rubber particle size distribution curve by volume has at least one peak value at each of a particle diameter of less than 0.8 μm and a particle diameter of at least 0.8 μm .

25 (4) The transparent rubber-modified copolymer resin according to any one of the above (1) to (3), which has a gel content of from 5 to 25 mass%.

(5) The transparent rubber-modified copolymer resin according to any one of the above (1) to (4), which has a swelling index is from 9 to 17.

(6) The transparent rubber-modified copolymer resin
5 according to any one of the above (1) to (5), which has a weight average molecular weight (Mw) of 80,000 to 200,000.

(7) A rubber-modified copolymer resin composition characterized by comprising from 60 to 99.9 mass% of a transparent rubber-modified copolymer resin (A) which is
10 a rubber-modified copolymer resin comprising one type or a mixture of two or more types obtained by copolymerizing a styrenic monomer and a (meth)acrylic ester monomer in the presence of a rubbery polymer, and which is characterized in that the volume mean particle diameter
15 (dv) of rubber particles dispersed in the resin, is from 0.4 to 2.0 μm , and in the cumulative rubber particle size distribution curve by volume, the difference between the diameter (d75) at an integrated value of 75% and the diameter (d25) at an integrated value of 25%, is from 0.2
20 to 2.0 μm , and from 0.1 to 40 mass% of an emulsion graft copolymer (B).

(8) The transparent rubber-modified copolymer resin composition according to the above (7), wherein in the cumulative particle size distribution curve by volume of
25 rubber particles dispersed in the transparent rubber-modified copolymer resin (A), rubber particles having particle diameters of less than 0.8 μm occupy from 95 to

30 vol%, and rubber particles having particle diameters of at least 0.8 μm occupy from 5 to 70 vol%.

(9) The transparent rubber-modified copolymer resin composition according to the above (7) or (8), wherein
5 the cumulative particle size distribution curve by volume of rubber particles dispersed in the transparent rubber-modified copolymer resin (A), has at least one peak value at each of a particle diameter of less than 0.8 μm and a particle diameter of at least 0.8 μm .

10 (10) The rubber-modified copolymer resin composition according to any one of the above (7) to (9), wherein the difference in the refractive index at a temperature of 25°C as between the transparent rubber-modified copolymer resin (A) and the emulsion graft copolymer (B), is less
15 than 0.03.

In the present invention, the cumulative rubber particle size distribution curve by volume means a cumulative distribution curve by volume of the rubber particle size distribution showing the particle size on
20 the abscissa and the volume fraction on the ordinate. Further, a frequency rubber particle size distribution curve means a frequency distribution curve by volume of the rubber particle size distribution showing the particle diameter on the abscissa and the volume fraction
25 on the ordinate.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an example of the frequency rubber

particle size distribution curve by volume of the transparent rubber-modified copolymer resin (A).

BEST MODE FOR CARRYING OUT THE INVENTION

Now, the present invention will be described in
5 detail.

Firstly, the transparent rubber-modified copolymer resin of the present invention will be described.

The transparent rubber-modified copolymer resin of the present invention is obtained by copolymerizing a
10 styrenic monomer and a (meth)acrylic ester monomer in the presence of a rubbery polymer. The styrenic monomer to be used in the present invention may, for example, be styrene, α -methylstyrene, p-methylstyrene or p-t-butylstyrene, but is preferably styrene. Such styrenic
15 monomers may be used alone or in combination as a mixture of two or more of them.

The (meth)acrylic ester monomer to be used in the present invention may, for example, be methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl
20 acrylate, n-butyl acrylate, 2-methylhexyl acrylate, 2-ethylhexyl acrylate or octyl acrylate, but is preferably methyl methacrylate or n-butyl acrylate. Such (meth)acrylic ester monomers may be used alone or in combination as a mixture of two or more of them.
25 However, it is most preferred to use methyl methacrylate and n-butyl acrylate in combination.

In the present invention, monomers other than the

styrenic monomer and the (meth)acrylic acid ester monomer, such as acrylonitrile, maleic anhydride, methacrylic acid, etc., may be contained in an amount less than 50 parts by mass, per 100 parts by mass of the total amount of the styrenic monomer and the (meth)acrylic ester monomer.

The proportions of styrenic monomer and the (meth)acrylic ester monomer are preferably from 5 to 95 parts by mass of the styrenic monomer and from 95 to 5 parts by mass of the (meth)acrylic ester monomer, more preferably from 10 to 90 parts by mass of the styrenic monomer and from 90 to 10 parts by mass of the (meth)acrylic ester monomer. However, the total amount of the styrenic monomer and the (meth)acrylic ester monomer is 100 parts by mass. If the styrenic monomer and the (meth)acrylic ester monomer are outside such ranges, there may be a case where the transparency, etc. tend to be poor.

The rubbery polymer to be used in the present invention may, for example, be a polybutadiene, a styrene/butadiene rubber, a styrene/butadiene block rubber, a partially hydrogenated polybutadiene, a partially hydrogenated styrene/butadiene rubber or a partially hydrogenated styrene/butadiene block rubber, but is preferably a styrene/butadiene rubber or a styrene/butadiene block rubber having a styrene content of from 20 to 50 mass%. Further, the viscosity of a 5

mass% styrene solution of the rubbery polymer at a temperature of 25°C is preferably from 15 to 200 mPa·s, more preferably from 20 to 60 mPa·s. The proportion of a 1,2-vinyl bond among unsaturated bonds based on butadiene is preferably from 8 to 25 mol%, more preferably from 12 to 16 mol%.

In the present invention, a polymer other than the rubbery polymer, such as a styrene/butadiene/styrene resin, may be incorporated, if it is less than 50 parts by mass per 100 parts by mass of the rubbery polymer.

The proportion of the rubbery polymer is preferably from 0.1 to 30 parts by mass, more preferably from 3 to 15 parts by mass, per 100 parts by mass of the total amount of the styrenic monomer and the (meth)acrylic ester monomer. If the rubbery polymer is outside the above range, there may be a case where the object cannot be accomplished such that the impact resistance, etc. are poor.

In the present invention, when the styrenic monomer and the (meth)acrylic ester monomer are to be polymerized in the presence of the rubbery polymer, the rubbery polymer is dissolved in the styrenic monomer and the (meth)acrylic ester monomer, followed by polymerization. The polymerization is carried out at a high temperature. The polymerization temperature is preferably from 80 to 170°C, more preferably from 100 to 160°C. Further, at the time of the polymerization, it is preferred to add a

known polymerization initiator such as t-butylperoxy benzoate, t-butylperoxy-2-ethyl hexanoate, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(t-butylperoxy)-cyclohexane, 2,2-bis(4,4-di-
5 butylperoxycyclohexyl)propane, t-butylperoxyisopropyl monocarbonate, di-t-butylperoxide, dicumylperoxide, or ethyl-3,3-di-(t-butylperoxy) butylate, or a known molecular weight-controlling agent such as 4-methyl-2,4-diphenylpentene-1, t-dodecylmercaptan or n-
10 dodecylmercaptan.

The amount of the polymerization initiator or the molecular weight-controlling agent is preferably from 0.005 to 5 parts by mass, more preferably from 0.01 to 1 part by mass, per 100 parts by mass of the total amount
15 of the styrenic monomer and the (meth)acrylic ester monomer. If it is outside the above range, there may be a case where the object cannot be accomplished such that the impact resistance tends to be poor.

Further, at the time of the polymerization, a known
20 crosslinking agent such as divinyl benzene or a known antioxidant such as octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, may also be added.

In the present invention, at the time of the polymerization, an organic solvent such as ethylbenzene
25 or toluene is used preferably in an amount of from 0.1 to 50 parts by mass, more preferably in an amount of from 5 to 20 parts by mass, per 100 parts by mass of the total

amount of the styrenic monomer and the (meth)acrylic ester monomer. By the use of the solvent, there may be a desired case where the viscosity during the polymerization tends to be low, and the polymerization control can be improved. Further, as a system for the polymerization in the present invention, a continuous polymerization system is preferred.

As described above, a transparent rubber-modified copolymer resin containing rubber particles as dispersed, is produced. The rubber particles have the following characteristics in the transparent rubber-modified copolymer resin of the present invention. Further, a rubber-modified copolymer resin containing rubber particles having such characteristics, may be constituted by one type of a rubber-modified copolymer resin obtained by copolymerizing the styrenic monomer and the (meth)acrylic ester monomer in the presence of the rubbery polymer, but may otherwise be constituted by mixing and melting two or more rubber-modified copolymer resins obtained separately and being different in the particle diameters of the rubber particles.

In the transparent rubber-modified copolymer resin of the present invention, the volume mean particle diameter (d_v) of rubber particles contained as dispersed, is from 0.4 to 2 μm , preferably from 0.4 to 1.5 μm , more preferably from 0.5 to 1.2 μm . If the volume mean particle diameter (d_v) of rubber particles is less than

0.4 μm , the resin tends to be poor in impact resistance, and if it exceeds 2 μm , the resin tends to be poor in transparency.

The volume means particle diameter (dv) in the present invention is a mean particle diameter to be obtained by the following Formula 1 by measuring particle diameters $(=(\text{long diameter} + \text{short diameter})/2)$ of about 1000 rubber particles in a photograph of an ultrathin specimen of the resin taken by a transmission electron microscope.

Formula 1:

$$\text{Mean particle diameter} = \sum n_i \cdot D_i^4 / \sum n_i \cdot D_i^3$$

(wherein n_i is the number of rubber particles having a particle size D_i)

Further, rubber particles will be formed along with the progress of polymerization when the rubber-modified copolymer resin is produced, whereby control of the volume mean particle diameter (dv) of rubber particles is carried out by adjusting the stirring speed during the polymerization, the amount of the polymerization initiator or the molecular weight-controlling agent to be added or mixing of a rubber-modified copolymer resin having a different particle diameter.

Further, the rubber particles dispersed in the transparent rubber-modified copolymer resin of the present invention are characterized in that the difference between dv_{75} and dv_{25} (hereinafter represented

by $dv_{75}-dv_{25}$) is from 0.2 to 2.0 μm , preferably from 0.4 to 1.7 μm , more preferably from 0.5 to 1.5 μm . If $dv_{75}-dv_{25}$ is less than 0.2 μm , the balance of the impact resistance and the rigidity tends to be poor, and if it exceeds 2.0 μm , the balance of the transparency and the rigidity tends to be poor, and further, the dependency of the transparency on molding conditions tends to be large. The control of $dv_{75}-dv_{25}$ is carried out, for example, by the stirring condition during the polymerization, the type or the amount of the polymerization initiator or the molecular weight-controlling agent, or mixing of a rubber-modified copolymer resin having a different particle diameter.

Further, dv_{75} and dv_{25} are particle diameters corresponding to integrated values of 75% and 25%, respectively, in the above-mentioned cumulative distribution curve by volume of the rubber particle size distribution showing the particle diameter on the abscissa and the volume fraction on the ordinate. Further, the rubber particle diameters are ones obtained by measuring the particle diameters from a photograph of an ultrathin specimen of the resin taken by a transmission electron microscope, in the same manner as for the volume mean particle diameter (dv) of the rubber particles. Further, the volume fraction is one represented by the volume fraction when the rubber particles obtained with such particle diameters are

assumed to be spherical.

The rubber particles dispersed in the transparent rubber-modified copolymer resin of the present invention are preferably such that in the cumulative rubber
5 particle size distribution curve by volume, rubber particles having particle diameters of less than 0.8 μm occupy from 95 to 30 vol%, and rubber particles having particle diameters of at least 0.8 μm occupy from 5 to 70 vol%. More preferably, those having particle diameters
10 of less than 0.8 μm occupy from 80 to 40 vol%, and those having particle diameters of at least 0.8 μm occupy from 20 to 60 vol%. If those having particle diameters of less than 0.8 μm are from 95 to 30 vol%, and those having particle diameters of at least 0.8 μm are from 5 to 70
15 vol%, the resin will be further excellent in transparency, impact resistance and rigidity and will have less dependency of the transparency on molding conditions. The control of the ratio of those having particle diameters of less than 0.8 μm and those having
20 particle diameters of at least 0.8 μm , can be carried out by adjusting the stirring conditions during the polymerization, the amount of the polymerization initiator or the molecular weight-controlling agent, mixing of a rubber-modified copolymer resin having a
25 different particle diameter, etc.

The rubber particles dispersed in the transparent rubber-modified copolymer resin of the present invention

are preferably such that the frequency rubber particle size distribution curve by volume of the rubber particle size distribution showing the particle diameter on the abscissa and the volume fraction on the ordinate as
5 described above, has at least one peak value at each of a particle diameter of less than $0.8\text{ }\mu\text{m}$ and a particle diameter of at least $0.8\text{ }\mu\text{m}$. If the distribution curve has at least one peak value at each of a particle diameter of less than $0.8\text{ }\mu\text{m}$ and a particle diameter of
10 at least $0.8\text{ }\mu\text{m}$, the resin will be further excellent in transparency, impact resistance and rigidity and has a less dependency of the transparency on molding conditions. The control to let the frequency rubber particle size distribution curve by volume have at least
15 one peak value at each of a particle diameter of less than $0.8\text{ }\mu\text{m}$ and a particle diameter of at least $0.8\text{ }\mu\text{m}$, can be carried out by adjusting the stirring condition during the polymerization, the type or amount of the polymerization initiator or the molecular weight
20 controlling agent, mixing of a rubber-modified copolymer resin having a different particle diameter, etc.

As an example of the frequency rubber particle size distribution curve by volume, Fig. 1 shows an example of the frequency distribution by volume of the rubber
25 particle diameter against logarithm.

The gel content of the transparent rubber-modified copolymer resin of the present invention is preferably

from 5 to 25 mass%, more preferably from 15 to 23 mass%.
If the gel content is less than 5 mass%, the impact
resistance tends to be poor, and if the gel content
exceeds 25 mass%, the transparency and the rigidity tend
5 to be poor, and further, dependency of the transparency
on molding conditions tends to be large. The adjustment
of the gel content can be carried out by adjusting the
stirring condition during the polymerization, the type or
amount of the polymerization initiator or the molecular
10 weight-controlling agent, etc.

Further, in the present invention, the gel content
is measured as follows.

1 g of a sample is accurately weighed (a) and
dissolved in 100 ml of methyl ethyl ketone (MEK) at a
15 temperature of 25°C over a period of 24 hours. Then, the
solution is transferred to a centrifuging tube having the
mass (b) measured and centrifuged at a temperature of at
most 10°C at 14000 rpm for 40 minutes. After removing
the supernatant by decantation, the rest is dried in a
20 vacuum dryer at a temperature of 70°C for 24 hours. The
mass (c) of the centrifuging tube after the drying, is
measured, whereupon the gel content is calculated by the
following Formula 2.

Formula 2:

25 Gel content (mass%) = $\{(c-b)/a\} \times 100$

Further, the swelling index of the transparent
rubber-modified copolymer resin of the present invention

is preferably from 9 to 17, more preferably from 10 to 14. If the swelling index is less than 9, the impact resistance tends to be poor, and if the swelling index exceeds 17, the transparency and the rigidity tend to be poor, and further, the dependency of the transparency on molding conditions tends to be large. Control of the swelling index can be adjusted by an addition of an antioxidant, adjustment of the heating conditions in the devaporizer, etc.

Here, the swelling index in the present invention is measured as follows.

About 1 g of a sample is dissolved in 100 ml of toluene at a temperature of 25°C over a period of 24 hours. Then, the solution is transferred to a centrifuging tube having the mass (d) measured and centrifuged at a temperature of at most 10°C at 14000 rpm for 40 minutes. After removing the supernatant by decantation, the mass (e) of the centrifuging tube after drying is measured. It is dried in a vacuum dryer at a temperature of 70°C for 24 hours. The mass (f) of the centrifuging tube after the drying, is measured, and the swelling index is calculated by the following Formula 3.

Formula 3:

$$\text{Swelling index} = (e-d)/(f-d)$$

The weight average molecular weight (Mw) of the transparent rubber-modified copolymer resin of the present invention is preferably from 80,000 to 200,000,

more preferably from 100,000 to 160,000. If Mw is less than 80,000, the impact resistance tends to be poor, and if it exceeds 200,000, the transparency tends to decrease, and further, the dependency of the transparency on molding conditions tends to be large. Control of Mw can be adjusted by the type or amount of the polymerization initiator or the molecular weight-controlling agent, the temperature condition for polymerization, etc.

10 To the transparent rubber-modified copolymer resin of the present invention, it is possible to add additives such as an antioxidant, a weather-resistant agent, a lubricant, a plasticizer, a coloring agent, an antistatic agent, a mineral oil, a flame retardant, etc., as the case requires, and they may be added at an optional stage during the production. The method for adding such additives is not particularly limited. However, a method of adding during the polymerization, or a method of melt-kneading them by an extruder, may, for example, be
15 mentioned.

The transparent rubber-modified copolymer resin of the present invention will be pressed into various molded products by conventional methods such as injection molding, extrusion molding, compression molding, vacuum
25 molding, etc. and then, practically used. Now, a composition comprising the rubber-modified copolymer resin of the present invention will be described in

detail.

The rubber-modified copolymer resin composition in the present invention comprises the above-mentioned transparent rubber-modified copolymer resin (A) and an
5 emulsion graft copolymer (B).

The transparent rubber-modified copolymer resin (A) has already been described in detail, and, now, the emulsion graft copolymer (B) will be described.

As the emulsion graft copolymer (B), one readily
10 available in the market, for example, as Kureha BTA, manufactured by Kureha Chemical Industry Co., Ltd. or as カネエース manufactured by Kaneka Corporation, may be used. Otherwise, it may be one obtained by a conventional emulsion polymerization method.

15 For example, it is possible to employ a method for obtaining it by emulsion graft polymerizing a styrenic monomer and/or a (meth)acrylic ester monomer, to a latex of the rubbery polymer as described with respect to the transparent rubber-modified copolymer resin (A), i.e. a
20 butadiene or styrene/butadiene latex. Further, as the case requires, it is possible to employ a method for graft polymerizing a vinyl type monomer copolymerizable with such monomers.

Specifically, in the presence of a rubbery polymer
25 latex, emulsion graft polymerization is carried out by using a styrenic monomer and/or a (meth)acrylic ester monomer. The amount of the rubbery polymer may be one

obtained by using it in an amount of more than 30 parts by mass and not more than 500 parts by mass, per 100 parts by mass of the total of the styrenic monomer and/or the (meth)acrylic ester monomer.

5 If the rubbery polymer is less than 30 parts by mass, the practical strength of the rubber-modified copolymer resin composition tends to be low. Further, if the rubbery polymer exceeds 500 parts by mass, the dependency of the transparency on molding conditions is
10 more likely to result.

 The ratio of the transparent rubber-modified copolymer resin (A) to the emulsion graft copolymer (B) is from 99.9 to 60 mass% : from 0.1 to 40 mass%, preferably from 95 to 70 mass% : from 5 to 30 mass%, more
15 preferably from 90 to 75 mass% : from 10 to 25 mass%. If the emulsion graft copolymer (B) is less than 0.1 mass%, the practical strength tends to be poor, and if it exceeds 40 mass%, the rigidity tends to be low.

 The rubber-modified copolymer resin composition may
20 comprise two or more transparent rubber-modified copolymer resins (A) and two or more emulsion graft copolymers (B).

 Further, as the transparent rubber-modified copolymer resin (A) constituting the resin composition of
25 the present invention, a rubber-modified copolymer resin (A) is selected wherein the volume mean particle diameter ($\bar{d}_v$) of rubber particles dispersed in the rubber-modified

copolymer resin, is from 0.5 to 2.0 μm , and in the cumulative rubber particle size distribution curve by volume, the difference between the diameter (dv_{75}) at an integrated value of 75 and the diameter (dv_{25}) at an
5 integrated value of 25%, is from 0.2 to 2.0 μm .

The volume mean particle size of rubber particles dispersed in the transparent rubber-modified copolymer resin (A) is preferably from 0.6 to 1.7 μm , more preferably from 0.7 to 1.5 μm . If the volume mean
10 particle size of rubber particles is less than 0.5 μm , the impact resistance or the practical strength of the rubber-modified copolymer resin composition tends to be low, and if it exceeds 2.0 μm , the transparency tends to be poor.

15 Further, the difference between dv_{75} and dv_{25} is preferably from 0.4 to 1.7 μm , more preferably from 0.5 to 1.5 μm . If $dv_{75}-dv_{25}$ is less than 0.2 μm , the balance of the impact resistance and the rigidity, and the practical strength of the rubber-modified copolymer resin
20 composition tend to be poor, and if it exceeds 2.0 μm , the balance of the transparency and the rigidity, tends to be poor, and further, the dependency of the transparency on molding conditions tends to be large.

The rubber particles dispersed in the transparent
25 rubber-modified copolymer resin (A) are preferably such that in the cumulative rubber particle size distribution curve by volume, those having particle diameters of less

than 0.8 μm occupy from 95 to 30 vol%, and those having particle diameters of at least 0.8 μm occupy from 5 to 70vol%. More preferably, those having particle diameters of less than 0.8 μm occupy from 80 to 40 vol%, and those
5 having particle diameters of at least 0.8 μm occupy from 20 to 60 vol%. Still further, if those having particle diameters of less than 0.8 μm are from 95 to 30 vol%, and those having particle diameters of at least 0.8 μm are from 5 to 70 vol%, the rubber-modified copolymer resin
10 composition will be further excellent in transparency, impact resistance and rigidity, and has less dependency of the transparency on molding conditions, and its practical strength will be high.

Further, as mentioned above, the rubber particles
15 dispersed in the transparent rubber-modified copolymer resin (A) preferably have at least one peak value at each of a particle diameter of less than 0.8 μm and a particle diameter of at least 0.8 μm , in the frequency particle size distribution curve by volume of the rubber particle
20 size distribution showing the rubber particle diameter on the abscissa and the volume fraction on the ordinate. If it has at least one peak value at each of a particle diameter of less than 0.8 μm and a particle diameter of at least 0.8 μm , the rubber-modified copolymer resin
25 composition will be further excellent in transparency, impact resistance and rigidity and will have less dependency of the transparency on molding conditions and

higher practical strength.

Further, the difference in the refractive index at a temperature of 25°C as between the transparent rubber-modified copolymer resin (A) and the emulsion graft
5 copolymer (B) is preferably less than 0.03, more preferably less than 0.02. If the difference in the refractive index is at least 0.03, the transparency deteriorates substantially, such being undesirable.

Here, for the refractive index of the present
10 invention, the compositional ratio of the constituting monomer units is measured by a compositional analysis, and the refractive index is obtained by calculation by means of the following Formula 4.

Formula 4:

15
$$n = X_A \times n_A + X_B \times n_B + X_C \times n_C + \dots$$

Namely, in a case where the composition of monomer units comprises Am monomer: X_A , Bm monomer: X_B and Cm monomer: X_C (provided that $X_A + X_B + X_C = 1$ by mass ratio), n_A represents the refractive index of a polymer
20 made of the Am monomer, n_B the refractive index of a polymer made of the Bm monomer, and n_C the refractive index of a polymer made of the Cm monomer, and they are substituted for the above Formula to obtain the refractive index by calculation. Here, the analysis of
25 the composition can be carried out by a known method such as pyrolytic gas chromatography.

The transparent rubber-modified copolymer resin (A)

and the emulsion graft copolymer (B) may be mixed by a known method to obtain a rubber-modified copolymer resin composition. For example, a method of melt kneading them by means of an extruder may be mentioned.

5 To the rubber-modified copolymer resin composition of the present invention, it is possible to add additives such as an antioxidant, a weather resistant agent, a lubricant, a plasticizer, a coloring agent, an antistatic agent, a mineral oil, a flame retardant, etc., as the
10 case requires, and they may be added at an optional stage during the production. A method for adding such additives, is not particularly limited. However, there may, for example, be mentioned a method of adding them during polymerization of each resin or copolymer, or a
15 method of melt-kneading them by an extruder during the production of the resin composition.

The rubber-modified copolymer resin composition of the present invention may be processed into various molded products by a known method such as injection
20 molding, extrusion molding, compression molding or vacuum forming.

EXAMPLES

Now, the present invention will be described with reference to Examples, but it should be understood that
25 the present invention is by no means restricted to such Examples.

(1) Examples for transparent rubber-modified

copolymer resins

REFERENCE EXAMPLE 1

A first completely mixing type reactor having a capacity of about 5L and equipped with a stirrer, a
5 second completely mixing type reactor having a capacity of 15L and equipped with a stirrer, a column plug flow type reactor having a capacity of about 40L and a devaporizer equipped with a preheater, were connected in series. A starting material solution was prepared by
10 mixing 14 parts by mass of ethylbenzene, 0.05 part by mass of t-butylperoxyisopropyl monocarbonate (the temperature for a half life period of one hour: 118°C), 0.1 part by mass of t-dodecylmercaptan and 0.1 part by mass of octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)
15 propionate to a monomer solution comprising 8 parts by weight of Asaprene 670A manufactured by Asahi Kasei Corporation as a rubbery polymer (a styrene/butadiene rubber, styrene content: 40 mass%, viscosity of a 5 mass% styrene solution at a temperature of 25°C: 33 mPa·s, and
20 proportion of 1,2-vinyl bond: 13.9 mol%), 56 parts by mass of styrene, 39 parts by mass of methyl methacrylate (hereinafter MMA), and 5 parts by mass of n-butyl acrylate (hereinafter n-BA). This starting material solution was introduced into the first completely mixing
25 type reactor controlled at a temperature of 110°C at a rate of 7 kg/hr and then continuously supplied to the second completely mixing type reactor controlled at a

temperature of 130°C. Then, the polymerized solution was continuously withdrawn from the second completely mixing type reactor and introduced into the column plug flow type reactor adjusted so that the temperature gradient would be from 130°C to 150°C in the flow direction. While heating this polymerized solution by the preheater, it was introduced into the devaporizer having the pressure reduced to 1.3 kPa, whereby a vapor content such as an unreacted monomer, was removed at a devaporizer internal temperature of 230°C. This resin solution was withdrawn by a gear pump, extruded in the form of a strand and cut to obtain a resin in the form of pellets. By controlling the rubber particle diameters by changing the stirring speed in the second completely mixing type reactor, samples A to E were obtained. Table 1 shows the results of evaluation of the physical properties.

REFERENCE EXAMPLE 2

The operation was carried out in the same manner as in Reference Example 1 except that the first completely mixing type reactor was not used, and the starting material solution having no t-butylperoxyisopropylmonocarbonate added, was directly supplied to the second completely mixing type reactor. By controlling the rubber particle diameters by changing the stirring speed in the second completely mixing type reactor, samples F to G were obtained. Table 1 shows the results of evaluation of the physical properties.

REFERENCE EXAMPLE 3

The operation was carried out in the same manner as in Reference Example 1 except that t-dodecylmercaptan was changed to 0.02 part by mass, and the starting material
 5 solution was prepared by mixing 0.1 part by mass of 4,6-bis(octylthiomethyl)-o-cresol instead of octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, whereby sample H was obtained. Table 1 shows the results of evaluation of the physical properties.

10 Table 1

	Sample identification	Average particle diameter (μm) of rubber particles
Reference Example 1	A	0.2
	B	0.5
	C	0.7
	D	1.1
	E	2.8
Reference Example 2	F	0.5
	G	1.1
Reference Example 3	H	0.5

EXAMPLES 1 to 6 and COMPARATIVE EXAMPLES 1 to 4

The blend as shown in Table 2, 3 or 4 was extruded in the form of a strand at a temperature of 230°C by means of a 40 mm single screw extruder and then cut by a
 15 pelletizer to obtain a rubber-modified copolymer resin in the form of pellets. Further, the results of evaluation of the physical properties are shown in Tables 2, 3 and 4.

Table 2

		Example 1	Example 2	Example 3
Blend type		B/D	B/D	B/D
Blend ratio (parts by mass)		60/40	40/60	80/20
dv (μm)		0.8	1.0	0.7
dv75 (μm)		1.1	1.2	1.0
dv25 (μm)		0.4	0.5	0.4
dv75-dv25 (μm)		0.7	0.7	0.6
Less than 0.8 μm (vol%)		70	45	82
At least 0.8 μm (vol%)		30	55	18
Peak at less than 0.8 μm		One peak	One peak	One peak
Peak at at least 0.8 μm		One peak	One peak	Nil
Gel content (mass%)		16	17	15
Swelling index		12	12	12
Weight average molecular weight (Mw)		140,000	140,000	140,000
200°C molded product	Total light trans- mittance (%)	91	91	91
	Haze (%)	2.8	3.9	2.6
230°C molded product	Total light trans- mittance (%)	91	91	91
	Haze (%)	1.9	2.5	1.9
Izod impact strength (J/m)		111	120	99
Flexural modulus (MPa)		2560	2520	2570

Table 3

		Example 4	Example 5	Example 6
Blend type		F/G	H/D	B/D/E
Blend ratio (parts by mass)		60/40	80/20	60/20/20
dv (μm)		0.8	0.7	1.0
dv75 (μm)		1.1	1.0	1.6
dv25 (μm)		0.4	0.4	0.4
dv75-dv25 (μm)		0.7	0.6	1.2
Less than 0.8 μm (vol%)		70	82	65
At least 0.8 μm (vol%)		30	18	35
Peak at less than 0.8 μm		One peak	One peak	One peak
Peak at at least 0.8 μm		One peak	Nil	Two peaks
Gel content (mass%)		14	14	17
Swelling index		12	16	12
Weight average molecular weight (Mw)		140,000	170,000	140,000
200°C molded product	Total light trans- mittance (%)	91	90	90
	Haze (%)	3.9	4.5	4.5
230°C molded product	Total light trans- mittance (%)	91	91	91
	Haze (%)	1.9	2.8	2.8
Izod impact strength (J/m)		92	113	128
Flexural modulus (MPa)		2560	2570	2550

Table 4

		Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Blend type		C	E	A/E	A/D
Blend ratio (parts by mass)		100	100	60/40	95/5
dv (μm)		0.7	2.8	0.9	0.3
dv75 (μm)		0.7	2.9	2.6	0.4
dv25 (μm)		0.6	2.7	0.2	0.2
dv75-dv25 (μm)		0.1	0.2	2.4	0.1
Less than 0.8 μm (vol%)		70	1	60	96
At least 0.8 μm (vol%)		30	99	40	4
Peak at less than 0.8 μm		One peak	Nil	One peak	One peak
Peak at at least 0.8 μm		Nil	One peak	One peak	One peak
Gel content (mass%)		15	16	16	13
Swelling index		12	12	12	12
Weight average molecular weight (Mw)		140,000	140,000	140,000	140,000
200°C molded product	Total light trans- mit- tance (%)	91	89	89	91
	Haze (%)	2.6	15.5	9.1	2.6
230°C molded product	Total light trans- mit- tance (%)	91	90	90	91
	Haze (%)	1.9	9.8	4.3	1.9
Izod impact strength (J/m)		58	97	104	52
Flexural modulus (MPa)		2550	2550	2550	2560

Each of Examples relating to the transparent rubber-modified copolymer resin of the present invention, was excellent in transparency, impact resistance and rigidity and had little dependency of the transparency on molding conditions, while each of Comparative Examples which do not meet the conditions of the present invention, was poor in some physical property among transparency, impact resistance, rigidity and dependency of the transparency on molding conditions.

(2) Examples for the rubber-modified copolymer resin composition

REFERENCE EXAMPLE 4

A first completely mixing type reactor having a capacity of about 5L and equipped with a stirrer, a second completely mixing type reactor having a capacity of about 15L and equipped with a stirrer, a column plug flow type reactor having a capacity of about 40L and a devaporizer equipped with a preheater, were connected in series. A starting material solution was prepared by mixing 15 parts by mass of ethylbenzene, 0.05 part by mass of t-butylperoxyisopropyl monocarbonate, 0.15 part by mass of t-dodecylmercaptan, and 0.1 part by mass of octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate to a monomer solution comprising 10 parts by mass of Asaprene 670A manufactured by Asahi Kasei Corporation as a rubbery polymer (styrene/butadiene rubber, styrene content: 40 mass%, viscosity of a 5 mass% styrene

solution at a temperature of 25°C: 33 mPa·s, proportion of 1,2-vinyl bond: 13.9 mol%), 56 parts by mass of styrene, 39 parts by mass of methyl methacrylate (hereinafter (MMA)), and 5 parts by mass of n-butyl acrylate (hereinafter n-BA). This starting material solution was introduced into the first completely mixing type reactor controlled at a temperature of 110°C at a rate of 7 kg/hr and then continuously supplied to the second completely mixing type reactor controlled at a temperature of 130°C. The rubber particle diameters were controlled by the stirring speed in the second completely mixing type reactor. Then, the polymerized solution was continuously withdrawn from the second completely mixing type reactor and introduced into the column plug flow type reactor adjusted so that the temperature gradient would be from 130°C to 150°C in the flow direction. While heating this polymerized solution by the preheater, it was introduced into the devaporizer having the pressure reduced to 1.3 kPa, and a vapor content such as an unreacted monomer was removed at a devaporizer internal temperature of 230°C. This resin solution was withdrawn by a gear pump, extruded in the form of a strand and cut to obtain a resin in the form of pellets. By controlling the rubber particle diameters by changing the stirring speed in the second completely mixing type reactor, samples A' to E' were obtained. Table 5 shows the results of evaluation of the physical properties.

REFERENCE EXAMPLE 5

The operation was carried out in the same manner as in Reference Example 4 except that the first completely mixing type reactor was not used, and the starting
5 material solution having no t-butylperoxyisopropyl monocarbonate added, was directly supplied to the second completely mixing type reactor. By controlling the rubber particle diameters by changing the stirring speed in the second completely mixing type reactor, samples F'
10 to G' were obtained. Table 5 shows the results of evaluation of the physical properties.

REFERENCE EXAMPLE 6

The operation was carried out in the same manner as in Reference Example 4 except that the starting material
15 solution was prepared by mixing 0.1 part by mass of 4,6-bis(octylthiomethyl)-o-cresol instead of octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, whereby sample H was obtained. Table 5 shows the results of evaluation of the physical properties.

Table 5

	Sample identification	Average particle diameter (μm) of rubber particles
Reference Example 4	A'	0.2
	B'	0.5
	C'	0.7
	D'	1.1
	E'	2.8
Reference Example 5	F'	0.5
	G'	1.1
Reference Example 6	H'	0.5

REFERENCE EXAMPLE 7

The blend as identified in Table 6 or 7 was extruded in the form of a strand at a temperature of 230°C by means of a 40 mm single screw extruder and cut by a pelletizer to obtain a rubber-modified copolymer resin (A) in the form of pellets. The results of evaluation of the physical properties are shown in Tables 6 and 7.

Here, the refractive index calculated from the composition of monomer units constituting the obtained resin, was obtained in such a manner that the compositional ratio of monomer units constituting the rubber-modified copolymer resin (A) was measured by the analysis of the composition, and the refractive index was obtained by calculation by means of the above-mentioned Formula 4 on the basis that the refractive indices of styrene, methyl methacrylate, n-butyl acrylate and

butadiene monomers are 1.595, 1.494, 1.463 and 1.518, respectively. In each case, the refractive index was 1.548.

Table 6

Test number	2-1	2-2	2-3	2-4	2-5
Blend type	B' / D'	B' / D'	B' / D'	F' / G'	H' / D'
Blend ratio (parts by mass)	60/40	40/60	80/20	60/40	80/20
dv (μm)	0.8	1.0	0.7	0.8	0.7
dv75 (μm)	1.1	1.2	1.0	1.1	1.0
dv25 (μm)	0.4	0.5	0.3	0.4	0.3
dv75-dv25 (μm)	0.7	0.7	0.7	0.7	0.7
Less than 0.8 μm (vol%)	68	45	83	68	83
At least 0.8 μm (vol%)	32	55	17	32	17
Peak at less than 0.8 μm	One peak	One peak	One peak	One peak	One peak
Peak at at least 0.8 μm	One peak	One peak	Nil	One peak	Nil
Gel content (mass%)	18	19	18	17	17
Swelling index	12	12	12	12	16
Mw	130,000	130,000	130,000	130,000	160,000

Table 7

Test number	2-6	2-7	2-8	2-9	2-10
Blend type	B'/D'/E'	C'	E'	A'/E'	A'/D'
Blend ratio (parts by mass)	60/20/20	100	100	60/40	95/5
dv (μm)	1.0	0.7	2.8	0.9	0.3
dv75 (μm)	1.6	0.7	2.9	2.6	0.4
dv25 (μm)	0.4	0.6	2.7	0.2	0.2
dv75-dv25 (μm)	1.2	0.1	0.2	2.4	0.1
Less than 0.8 μm (vol%)	65	68	1	60	96
At least 0.8 μm (vol%)	35	32	99	40	4
Peak at less than 0.8 μm	One peak	One peak	Nil	One peak	One peak
Peak at at least 0.8 μm	Two peaks	Nil	One peak	One peak	One peak
Gel content (mass%)	19	17	18	18	15
Swelling index	12	12	12	12	12
Mw	130,000	130,000	130,000	130,000	130,000

REFERENCE EXAMPLE 8

Into an autoclave having a capacity of 200 liter, 115 kg of pure water, 500 g of potassium oleate, 75 g of sodium pyrophosphate, 1.5 g of ferrous sulfate, 2.2 g of sodium ethylenediamine tetraacetate and 22 g of Rongalite were added and uniformly dissolved with stirring. Then, 20.0 kg of styrene, 30.0 kg of butadiene, 148 g of t-dodecylmercaptan, 30 g of divinyl benzene and 96 g of diisopropylbenzene hydroperoxide were added, and a reaction was carried out at a temperature of 50°C for 16 hours with stirring to complete polymerization thereby to obtain a rubbery polymer latex. To the obtained rubbery polymer latex, 45 g of sodium sulfosuccinate was added and sufficiently stabilized, whereupon a 0.2% hydrochloric acid aqueous solution and a 2% sodium hydroxide aqueous solution were added from separate nozzles so as to maintain the pH of the latex to be from 8 to 9, whereby the latex was flocculated and grown to obtain a rubbery elastomer latex having an average particle diameter of 0.42 μm . This rubbery elastomer latex was weighed to be 30 kg as calculated as the solid content and transferred to an autoclave having a capacity of 200L, whereupon 80 kg of pure water was added, and the temperature was raised to 50°C in a nitrogen stream with stirring. Added thereto was 2 kg of pure water having 1.25 g of ferrous sulfate, 2.5 g of sodium ethylenediamine tetraacetate and 100 g of Rongalite

dissolved. A mixture comprising 16 kg of styrene, 14 kg of methyl methacrylate and 60 g of t-dodecylmercaptan, and a solution having 120 g of diisopropylbenzene hydroperoxide dispersed in 8 kg of pure water containing
5 450 g of potassium oleate, were separately continuously added over a period of 6 hours. After completion of the addition, the temperature was raised to 70°C, and 30 g of diisopropylbenzene hydroperoxide was further added. Then, the mixture was left to stand for 2 hours to
10 complete the polymerization.

To the obtained emulsion, an antioxidant was added, followed by dilution with pure water to a solid content of 15 mass%. Then, the temperature was raised to 60°C, and while vigorously stirring, dilute sulfuric acid was
15 added for salting out. Thereafter, the temperature was raised to 90°C for coagulation, followed by dehydration, washing with water and drying to obtain a powdery emulsion graft copolymer (B).

The compositional ratio of the monomer units
20 constituting the obtained emulsion graft copolymer (B) was measured, and the refractive index calculated by means of the above-mentioned Formula 4, was 1.548.

EXAMPLES 7 to 13 and COMPARATIVE EXAMPLES 5 to 9

The blend as shown in Table 8 or 9 was extruded in
25 the form of a strand at a temperature of 230°C by means of a 35 mm twin screw extruder and cut by a pelletizer to obtain a rubber-modified copolymer resin composition in

the form of pellets. The results of evaluation of the physical properties are shown in Tables 8 and 9.

Table 8

		Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13
Rubber-modified copolymer resin	Test number	2-1	2-2	2-3	2-4	2-5	2-6	2-1
	Mass%	90	90	90	90	90	90	80
Emulsion graft amount (mass%)		10	10	10	10	10	10	20
200°C molded product	Total light transmittance (%)	90	90	90	90	89	90	90
	Haze (%)	3.2	4.5	3.0	4.5	4.9	3.9	3.0
230°C molded product	Total light transmittance (%)	91	90	91	91	90	91	91
	Haze (%)	2.4	3.0	2.3	2.5	3.3	2.7	2.2
Izod impact strength (J/m)		152	154	134	130	141	150	195
Falling weight strength (cm)		45	47	38	35	40	43	75
Flexural modulus (MPa)		2410	2380	2400	2450	2450	2380	2280

Table 9

		Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9
Rubber- modified copolymer resin	Test number	2-1	2-7	2-8	2-9	2-10
	Mass%	100	90	90	90	90
Emulsion graft amount (mass%)		0	10	10	10	10
200°C molded product	Total light trans- mit- tance (%)	90	90	88	88	90
	Haze (%)	3.2	3.2	17.3	10.3	3.2
230°C molded product	Total light trans- mit- tance (%)	91	91	89	89	91
	Haze (%)	2.4	2.4	8.6	5.6	2.4
Izod impact strength (J/m)		112	61	95	105	58
Falling weight strength (cm)		8	23	29	30	23
Flexural modulus (MPa)		2410	2400	2380	2370	2400

As shown in Table 8, each of Examples relating to the rubber-modified copolymer resin composition of the present invention, is excellent in transparency, impact resistance and rigidity and has little dependency of the transparency on molding conditions, and it is excellent in practical strength. As shown in Table 9, each of Comparative Examples which do not meet the conditions of the present invention, was poor in some physical property among transparency, impact resistance, rigidity, dependency of the transparency on molding conditions and practical strength.

Here, evaluation was made in accordance with the following methods.

(1) Volume mean particle diameter ($\bar{d}_v$) of rubber particles

From a photograph by a transmission electron microscope by an ultrathin specimen method of the resin dyed with osmic acid, particle diameters $(=(\text{long diameter} + \text{short diameter})/2)$ of about 1000 particles in the photograph were measured, and it was obtained as a mean particle diameter obtainable by the following Formula 5. For the measurement of the particle size diameters, an image-treating measuring apparatus KS300, manufactured by Carl Zeiss Vision Company was used.

Formula 5:

$$\text{Mean particle diameter} = \sum n_i \cdot D_i^4 / \sum n_i \cdot D_i^3$$

(wherein n_i is the number of rubber particles having

a particle diameter D_i)

Further, the $dv_{75\%}$ diameter and the $dv_{25\%}$ diameter were also obtained by organizing the particle diameters obtained by the above measurements by means of the image-treating measuring apparatus.

(2) The gel content and the swelling index were measured by the above-mentioned methods.

(3) Weight average molecular weight (M_w)

Measured under the GPC measuring conditions as follows:

Name of apparatus: SYSTEM-21 Shodex (manufactured by SHOWA DENKO K.K.)

Column: Three columns of PL gel MIXED-B were connected in series

Temperature: 40°C

Detection: Differential refractive index

Solvent: Tetrahydrofuran

Concentration: 2 mass%

calibration curve: Prepared by means of standard polystyrene (PS) (manufactured by PL Company), and the weight average molecular weight was represented by the PS-calculated value.

(4) Transparency

By means of an injection molding machine (IS-50EPN) manufactured by Toshiba Machine Co., Ltd., a three-stepped plate having thicknesses of 1 mm, 2 mm and 3 mm was molded at a cylinder temperature of 200°C or 230°C.

By using the 2 mm portion of such a three-stepped plate, the total light transmittance and the haze were measured (unit: %) by means of HAZE meter (NDH-1001DP model), manufactured by NIPPON DENSHOKU INDUSTRIES CO., LTD.

5 (5) Impact resistance

By means of an injection molding machine (IS-80CNV) manufactured by Toshiba Machine Co., Ltd., a test specimen of $12.7 \times 64 \times 6.4$ mm was molded at a cylinder temperature of 200°C. By using this test specimen, the
10 Izod impact strength was measured in accordance with ASTM D256 (unit: J/m).

(6) Rigidity

By means of an injection molding machine (IS-80CNV) manufactured by Toshiba Machine Co., Ltd., a test
15 specimen of $12.7 \times 127 \times 6.4$ mm was molded at a cylinder temperature of 200°C. By using this test specimen, the flexural modulus was measured in accordance with ASTM D790 (unit: MPa).

(7) Practical strength

20 By means of an injection molding machine (IS-80CVN) manufactured by Toshiba Machine Co., Ltd., a three-stepped plate having thicknesses of 1 mm, 2 mm and 3 mm was molded at a cylinder temperature of 230°C. By using the 1 mm portion of this test specimen, the 50% breaking
25 height was measured (unit: cm) by using a weight having a weight of 200 gf and having a forward end of 5R and a weight diameter of 14 mm.

INDUSTRIAL APPLICABILITY

The rubber-modified copolymer resin of the present invention is excellent in transparency, impact resistance and rigidity and has little dependency of the
5 transparency on molding conditions.

Further, the rubber-modified copolymer resin composition of the present invention is excellent in transparency, impact resistance and rigidity and has little dependency of the transparency on molding
10 conditions, and it further has high practical strength. Thus, it is useful for various applications including home electric appliances and packaging materials.

CLAIMS

1. A transparent rubber-modified copolymer resin which is a rubber-modified copolymer resin comprising one type or a mixture of two or more types obtained by
5 copolymerizing a styrenic monomer and a (meth)acrylic ester monomer in the presence of a rubbery polymer, and which is characterized in that the volume mean particle diameter (d_v) of rubber particles dispersed in the resin, is from 0.4 to 2.0 μm , and in the cumulative rubber
10 particle size distribution curve by volume, the difference between the diameter (d_{75}) at an integrated value of 75% and the diameter (d_{25}) at an integrated value of 25%, is from 0.2 to 2.0 μm .
2. The transparent rubber-modified copolymer resin
15 according to Claim 1, wherein in the cumulative rubber particle size distribution curve by volume, rubber particles having particle diameters of less than 0.8 μm occupy from 95 to 30 vol%, and rubber particles having particle diameters of at least 0.8 μm occupy from 5 to 70
20 vol%.
3. The transparent rubber-modified copolymer resin according to Claim 1 or 2, wherein the cumulative rubber particle size distribution curve by volume has at least one peak value at each of a particle diameter of less
25 than 0.8 μm and a particle diameter of at least 0.8 μm .
4. The transparent rubber-modified copolymer resin according to any one of Claims 1 to 3, which has a gel

content of from 5 to 25 mass%.

5. The transparent rubber-modified copolymer resin according to any one of Claims 1 to 4, which has a swelling index is from 9 to 17.

5 6. The transparent rubber-modified copolymer resin according to any one of Claims 1 to 5, which has a weight average molecular weight (Mw) of 80,000 to 200,000.

7. A rubber-modified copolymer resin composition characterized by comprising from 60 to 99.9 mass% of a
10 transparent rubber-modified copolymer resin (A) which is a rubber-modified copolymer resin comprising one type or a mixture of two or more types obtained by copolymerizing a styrenic monomer and a (meth)acrylic ester monomer in the presence of a rubbery polymer, and which is
15 characterized in that the volume mean particle diameter (dv) of rubber particles dispersed in the resin, is from 0.4 to 2.0 μm , and in the cumulative rubber particle size distribution curve by volume, the difference between the diameter (d75) at an integrated value of 75% and the
20 diameter (d25) at an integrated value of 25%, is from 0.2 to 2.0 μm , and from 0.1 to 40 mass% of an emulsion graft copolymer (B).

8. The transparent rubber-modified copolymer resin composition according to Claim 7, wherein in the
25 cumulative particle size distribution curve by volume of rubber particles dispersed in the transparent rubber-modified copolymer resin (A), rubber particles having

particle diameters of less than 0.8 μm occupy from 95 to 30 vol%, and rubber particles having particle diameters of at least 0.8 μm occupy from 5 to 70 vol%.

9. The transparent rubber-modified copolymer resin
5 composition according to Claim 7 or 8, wherein the cumulative particle size distribution curve by volume of rubber particles dispersed in the transparent rubber-modified copolymer resin (A), has at least one peak value at each of a particle diameter of less than 0.8 μm and a
10 particle diameter of at least 0.8 μm .

10. The rubber-modified copolymer resin composition according to any one of Claims 7 to 9, wherein the difference in the refractive index at a temperature of 25°C as between the transparent rubber-modified copolymer
15 resin (A) and the emulsion graft copolymer (B), is less than 0.03.