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**A PROCESS FOR MANUFACTURING A RUBBER-MODIFIED STYRENE RESIN
COMPOSITION**

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for manufacturing a rubber-modified styrene resin composition. In particular, it relates to a process for manufacturing a rubber-modified styrene resin composition with high fluidity which is improved in impact resistance by conducting polymerization in particular conditions.

2. Description of the Related Art

Polystyrene is a transparent and hard resin with good dimensional stability and electric insulation, but has poor impact resistance. For resolving the problem, there has been developed high impact styrene resins in which a rubbery polymer is incorporated. Known high impact styrene resins include a simple blend of polystyrene and a rubbery polymer, which is, however, inadequately improved in impact resistance. Thus, it is common to manufacture a rubber-modified styrene resin composition with good impact resistance by adding a rubbery polymer during polymerization of styrene to graft styrene to the rubbery polymer for improving dispersibility of the rubbery polymer.

It is well known that the physical properties of the rubber-modified styrene resin composition manufactured as

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described above substantially depend on the size and the structure of the rubbery polymer particles. Thus, preparation of a rubber-modified styrene resin composition with good physical properties has been attempted by controlling a particle morphology of the rubbery polymer.

Currently, such impact-resistant polystyrene resins are industrially manufactured by a polymerization process such as bulk polymerization, solution polymerization, suspension polymerization, bulk-suspension polymerization and emulsion polymerization.

Among these, continuous bulk polymerization has been commonly employed in a large scale production because it can provide a large amount of product with uniform physical properties at a low cost.

In continuous bulk polymerization, a synthetic rubbery polymer is used as a modifier for manufacturing a impact-resistant styrene resin. Usually, the rubbery polymer is crushed by a mill into chips, which are then added and dissolved in styrene monomer. To the mixture are added additives such as polymerization initiators, molecular weight regulators and antioxidants, and then the resulting mixture is polymerized to provide a styrene resin with good impact resistance in which the rubbery polymer particles occluding polystyrene are dispersed by grafting styrene molecules in the double bonds of the rubbery polymer.

Since impact-resistant styrene resins thus

manufactured have a good balance between impact resistance and hardness, ABS resins have been increasingly replaced with rubber-modified styrene resins, in a number of industrial parts such as those in household electrical appliances, OA equipment or automobiles. For example, they have been used in a large and thin molding with a more complex shape formed by injection molding. Recently, resin materials with higher fluidity have been desired for improving their formability.

Increasing the amount of a rubbery polymer added in a rubber-modified styrene resin composition may be, however, more effective in improving impact resistance, while reducing fluidity.

Reducing the molecular weight of the matrix using a large amount of chain transfer agent is known as a method for improving fluidity. The method may, however, reduce impact resistance.

USP-4493922 and JP-A 63-112846 have disclosed procedures for improving impact resistance, where a rubber-modified styrene resin composition containing rubbery-polymer particles with a single occlusion structure formed from a styrene-butadiene copolymer rubber is blended with a common rubber-modified styrene resin composition containing a small amount of rubbery-polymer particles with a salami structure. These procedures may give a resin with improved impact resistance, but make the production process more complicated and cannot realize sufficient physical

properties.

JP-A 52-86444 has disclosed a impact-resistant polystyrene(HIPS) prepared using a polybutadiene rubber in which at least 90 molar % of butadiene units in the polymer chain are of cis-1,4-bond, as a rubbery polymer. In addition, JP-B 55-30525 has disclosed a procedure for increasing a gel content in a resin, using a particular rubbery polymer obtained using an organic peroxide. Both of these procedures may, however, reduce fluidity.

JP-As 60-130613 and 60-130614 have disclosed a resin composition in which the particle size and its distribution of a dispersed rubbery polymer are adjusted by using a particular rubbery polymer, but not disclosed a technique for manufacturing a rubber-modified styrene resin composition which can improve fluidity of a product, keeping its impact resistance high.

JP-B 6-99531 has disclosed a process for manufacturing a styrene resin with high impact resistance where a styrene compound is polymerized, adjusting a ratio between an organic peroxide and a chain transfer agent. This process may provide a styrene resin with high impact resistance, which is, however, not highly fluid.

It is well known that in general a polymerization rate is proportional to a square root of an initiator concentration in radical polymerization. However, the relationship is not appropriate when a chain transfer agent which reduces the

molecular weight of the matrix is added for improving fluidity of the resin. It is also known that a mercaptan type of molecular weight regulator as a chain transfer agent may have a reduced effect in reducing the particle size of the rubbery polymer when it is used in combination with an organic peroxide.

Using an organic peroxide alone may make the particle size distribution broader in proportion to its amount. In any case, the relationship between the concentrations of the organic peroxide as an initiator and of the chain transfer agent has little understood. Furthermore, relationship of the ratio and physical properties of a resin produced has not been understood at all.

Thus, a process for manufacturing a rubber-modified styrene resin which may be, for example, formed by injection molding and which is suitable as a resin material for a large and thin molding with a complex shape, has been desired.

SUMMARY OF THE INVENTION

An objective of this invention is to provide a process for manufacturing a rubber-modified styrene resin composition which has high fluidity during a forming process and having a high impact resistance in a good balance of physical properties.

We have intensively attempted to solve the above problems, investigating influence of various factors related

to polymerization on physical properties in detail. Consequently, we have discovered that a rubber-modified styrene resin composition with high fluidity and impact resistance can be prepared by a manufacturing process completely novel in the light of previous findings, i.e., determining the relationship between concentrations of an initiator and a chain transfer agent for increasing an amount of styrene grafting to a rubbery polymer and controlling the particle size and its distribution of the dispersed rubbery polymer even when molecular weight reduction is effected aiming at improving fluidity, by which we can achieve the above objective.

This invention provides a process for manufacturing a rubber-modified styrene resin composition in which a continuous phase consists of a styrene resin and a dispersed phase consists of a diene polymer type of rubbery polymer occluding a styrene resin by bulk or solution polymerization using a continuous polymerization apparatus consisting of at least two reactors including at least one complete-mixing type of reactor, comprising

converting 20 to 35% of a styrene compound monomer to a polymer in the first complete mixing type reactor in the polymerization system to form a dispersed phase consisting of the rubbery polymer, charging a material in the first complete mixing type reactor (hereinafter, referred to as the "polymerization material solution")

(1) having the following composition:

- (a) a styrene-compound monomer: 60 to 85 parts by weight
- (b) an aromatic solvent: 5 to 35 parts by weight; and
- (c) the diene rubbery polymer whose 5 wt% solution in styrene has a viscosity of 30 to 90 centipoise at 25 °C: 3 to 20 parts by weight, when the total amount of the styrene-compound monomer, the aromatic solvent and the diene rubbery polymer is 100 parts by weight;

(2) containing, in relation to the styrene-compound monomer,

- (a) 20 to 300 wt.ppm of an organic peroxide and
 - (b) 0 to 350 wt.ppm of a molecular weight regulator; and
- (3) meeting the following equation:

$$9 \leq 15[I]^{1/2}/[E]+[S]^{1/3} \leq 21 \dots [1]$$

wherein [I], [E] and [S] are the concentrations of the organic peroxide (wt.ppm), the aromatic solvent (wt.%) and the molecular weight regulator (wt.ppm), respectively;

increasing the conversion of the styrene-compound monomer ratio to 50 to 95 % in the subsequent reactors; and

separating the resulting product from the remaining monomer and the solvent, to provide a rubber-modified styrene resin composition in which the rubbery polymer as a dispersed phase has a volume-average particle size of 1 to 4 μm and the ratio(D1/D2) of 10 % value(D1) to 90 % value(D2) of the cumulative particle size distribution by volume ranges 3 to 20.

The process of this invention requires,

firstly, maintaining the relationship represented by Equation [1] with respect to the amounts of the organic peroxide and molecular weight regulator (the chain transfer agent) and the concentration of the aromatic solvent added in the polymerization system; and

secondly, converting 20 to 35% of a styrene compound monomer to a polymer in the first complete mixing type of reactor to attain a desirable relationship between the particle size and its distribution of the diene rubbery polymer including the styrene resin since the size and the distribution affect improvement of the balance between fluidity and impact resistance of the styrene resin composition.

DETAILED DESCRIPTION OF THE INVENTION

Styrene-compound monomers herein include styrene; side-chain alkylated styrenes such as α -methylstyrene and α -ethylstyrene; nuclear alkylated styrenes such as vinyltoluene, vinylxylenes, o-t-butylstyrene and p-t-butylstyrene; halogenated styrenes such as monochlorostyrene, dichlorostyrenes, tribromostyrenes and tetrabromostyrenes; p-hydroxystyrene; and o-methoxystyrene; particularly, styrene, α -methylstyrene and vinyltoluene. These styrene-compound monomers can be used alone or in combination of two or more.

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Other radical-polymerizable monomers such as methyl methacrylate, acrylic acid, phenyl maleimide, acrylonitrile, acrylamide and maleic anhydride may be added in an amount of up to 25 wt% to the styrene-compound monomers.

In this invention, it is essential to use an organic peroxide as a polymerization initiator during granulation of a rubbery polymer. The amount of the organic peroxide is preferably in the range of 20 to 300 wt.ppm, more preferably 30 to 250 wt.ppm to styrene-compound monomers in a solution of the rubbery polymer.

If the amount is less than 20wt.ppm, graft reaction of the styrene-compound monomer to the rubbery polymer does not proceed to adequately improve impact resistance. If it is more than 300 wt.ppm, it may adequately increase a graft rate of the styrene-compound monomer to the rubbery polymer to prepare a rubber-modified styrene resin composition with high impact resistance, but may inappropriately reduce fluidity.

Organic peroxides generally used in polymerization of a styrene-compound monomer may be used in this invention, which include peroxy ketals such as 2,2-bis(t-butylperoxy)butane, 2,2-bis(t-butylperoxy)octane, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(t-butylperoxy)cyclohexane and 4,4-bis(t-butylperoxy)valerate; dihydrocarbyl peroxides such as di-t-butyl peroxide, t-butyl cumyl peroxide, dicumyl

peroxide, α,α -bis(t-butylperoxyisopropyl)benzene, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane and 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3; diacyl peroxides such as acetyl peroxide, isobutyryl peroxide, octanoyl peroxide, decanoyl peroxide, lauroyl peroxide, 3,5,5-trimethylhexanoyl peroxide, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide and m-toluoyl peroxide; peroxy dicarbonates such as diisopropylperoxy dicarbonate, diethylhexylperoxy dicarbonate, di-n-propylperoxy dicarbonate, dimyristylperoxy dicarbonate, diethoxyethylperoxy dicarbonate, dimethoxyisopropylperoxy dicarbonate and di(3-methyl-3-methoxybutyl)peroxy dicarbonate; peroxy esters such as t-butyl peroxyacetate, t-butyl peroxyisobutyrate, t-butyl peroxy-pivalate, t-butyl peroxyneodecanoate, t-butyl peroxy-2-ethylhexanoate, t-butyl peroxy-3,5,5-trimethylhexanoate, t-butyl peroxy-nourate, t-butyl peroxybenzoate, t-butyl peroxyisophthalate, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane and t-butyl peroxyisopropylcarbonate; ketone peroxides such as acetylacetone peroxide, methyl ethyl ketone peroxide, cyclohexanone peroxide, 3,3,5-trimethylcyclohexanone peroxide and methylcyclohexanone peroxide; and hydroperoxides such as t-butyl hydroperoxide, cumene hydroperoxide, diisopropylbenzene hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide and 1,1,3,3-

tetramethyl-butyl hydroperoxide. Among these, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane is most preferable. These peroxides may be used alone or in combination of two or more.

The process of this invention may provide a resin with an adequate fluidity without using a molecular weight regulator. A molecular weight regulator is generally used in an amount of 0 to 350 wt.ppm, preferably 0 to 250 wt.ppm to a styrene-compound monomer. Any molecular weight regulator generally used in polymerization reaction of a styrene compound may be used, which includes mercaptan compounds, preferably alkylmercaptan compounds and α -methylstyrene dimer.

This invention is characterized in that an aromatic solvent is used in an amount of 5 to 35 parts by weight, preferably 15 to 35 parts by weight, to a polymerization material solution. If the amount is less than 5 wt.parts, fluidity may be reduced, while if it is more than 35 wt.parts the organic peroxide may not be adequately effective to improve impact resistance.

Aromatic solvents which may be used include benzene, toluene, ethylbenzene, n- and i-propylbenzenes, o-, m- and p-xylenes, o-, m- and p-diethylbenzenes and their mixtures.

It is also known that aromatic solvents have an effect as a chain transfer agent. Thus, these aromatic solvents may be used in combination with a molecular weight regulator

to perform molecular weight adjustment. In this invention, the concentration of the aromatic solvent is, therefore, taken into account in terms of a relationship between the concentrations of an initiator and a molecular weight regulator.

We have found that an organic peroxide, an aromatic solvent and a molecular weight regulator can be used in a ratio represented by Equation [1] to reduce the particle size of the rubbery polymer and to keep the particle size distribution relatively narrower while keeping a graft rate of styrene to the rubbery polymer, to provide a rubber-modified styrene resin composition with a good balance between impact resistance and fluidity.

In this invention, it is essential to use a polymerization material solution in which the concentrations of the organic peroxide [I] (wt.ppm), the aromatic solvent [E] (wt.%) and the molecular weight regulator [S] (wt.ppm) meet Equation [1]:

$$9 \leq 15[I]^{1/2}/[E]+[S]^{1/3} \leq 21 \dots [1],$$

preferably Equation [2]:

$$9 \leq 15[I]^{1/2}/[E]+[S]^{1/3} \leq 15 \dots [2]$$

Using the polymerization material solution, a rubber-modified styrene resin composition with high fluidity and impact resistance which has a good balance of its physical properties, can be prepared by converting 20 to 35% of a styrene compound monomer to a polymer in first mixing reactor

to form a dispersed phase of the rubbery polymer; increasing the reaction ratio to 50 to 95 % in the subsequent continuous reactors; and separating the resulting product from the remaining monomer and the solvent, to form rubbery-polymer dispersed particles in which a volume-average particle size ranges 1 to 4 μm , preferably 1.5 to 4 μm and the ratio of 10 % value to 90 % value of the cumulative particle size distribution by volume ranges 3 to 20, preferably 3 to 15.

In particular, when a polymerization material solution meeting Equation [2] is used, a molding may have the above-mentioned high fluidity and impact resistance, may be improved in damping property, i.e., reduction of vibration when the molding is vibrated, and may reduce an impact sound, i.e., a sound when an impact is applied to the molding. Utilizing these properties, for example, a plate formed by laminating an iron plate and a sheet from a resin composition of this invention can be used as a vibration-absorbing plate or a soundproof plate for reducing an impact sound.

It should be emphasized that a molding from a conventional HIPS may be broken when a nail is driven on it, while a molding from a rubber-modified styrene resin composition of the present invention can be satisfactorily nailed.

In this invention, a rubbery polymer is preferably a diene type, and the above styrene-compound monomer or monomer mixture containing a given amount of the rubbery polymer may

be polymerized to form dispersed particles of the rubbery polymer in the resulting styrene polymer.

Herein, a 5 wt% solution of the rubbery polymer in styrene has a viscosity of 20 to 100, preferably 30 to 90 centipoise as measured at 25 °C. The diene rubbery polymer may be a homopolymer or a rubbery copolymer of the diene compound with another monomer; particularly a butadiene polymer in which at least 90 molar % of butadiene units in the polymer chain are of cis-1,4-bond or styrene/butadiene copolymer.

The diene rubbery polymer may be used preferably in a proportion of 3 to 20, more preferably 5 to 20 parts by weight to 100 parts by weight of the polymerization material solution.

In this invention, it is necessary that a volume-average particle size of the rubbery polymer formed as described above is 1 to 4 μm . A volume-average particle size herein is determined as follows. A resin is sliced into an ultrathin section sample by an ultrathin sectioning method, whose electron micrograph is then taken. Then, 500 to 700 particles of the rubbery polymer in the photograph are measured for their shorter and longer axes, whose average is determined as a particle size, and then a volume-average particle size is calculated according to the following equation.

$$\text{Volume-average particle size } \Sigma nD^4 / \Sigma nD^3$$

where n is the number of rubbery polymer particles with a size of D μm .

When the volume-average particle size is less than 1 μm , a resulting rubber-modified styrene resin has reduced impact resistance, while when the size is more than 4 μm , a molding may have a poor appearance, in particular a poor surface gloss.

The volume-averaged particle size may depend on an agitation power of the agitator, a reaction temperature and an amount of an organic peroxide in a reactor. Specifically, stronger agitation may make the particle size smaller; a higher reaction temperature may make the particle size larger; and an increased amount of the organic peroxide makes the particle size smaller. The particle size can be controlled by adjusting these values within the range of this invention.

In this invention, a rubber-modified styrene resin composition with a good balance between fluidity and impact resistance can be prepared by adjusting a ratio of D_1/D_2 (hereinafter, referred to as a "distribution coefficient") within the range of 3 to 20, where D_1 and D_2 represent particle sizes whose cumulative particle size distributions by volume are 10 % and 90 % when counting the number of particles of the rubbery polymer from those with the largest size.

Preferably, the ratio should be within the range of 3 to 15 for improving impact resistance, an appearance,

specifically gloss, of a molding. The distribution coefficient may be controlled by adjusting factors such as the molecular weight distribution of the rubbery polymer, the mixing ratio of the rubbery polymer, an agitation power and an average resident time during polymerization and the amount of the organic peroxide. The stronger agitation is, the smaller the distribution coefficient is, while the longer the resident time, the smaller the distribution coefficient is. The distribution coefficient may be controlled by adjusting these factors.

A ratio outside the range is not preferable due to generation of particles with a significantly large volume-average particle size or an unusual shape, leading to reduction of impact resistance and poor appearance of a molding.

In this invention, a convert ratio of styrene-compound monomers can be controlled by adjusting known factors such as a polymerization temperature, a type and a concentration of a polymerization initiator used and a resident time.

The polymerization temperature in the process of this invention is generally 50 to 200 °C, preferably 80 to 150 °C.

The convert ratio may be increased by increasing the polymerization temperature, the concentration of the organic peroxide, the polymerization duration and the resident time. The convert ratio can be, therefore, controlled by adjusting

these parameters.

It is necessary that the polymerization process is controlled by dividing it, conducting continuous bulk or solution polymerization, into at least two steps comprising forming a dispersed phase of a rubbery polymer to control the particle size and its distribution of the rubbery polymer and improving the conversion of monomer ratio. In brief, in the first step starting monomers are continuously supplied in the polymerization reaction system, polymerizing 20 to 35% of the styrene compound in a complete mixing type of reactor to form a dispersed phase of the rubbery polymer; increasing the reaction ratio to 50 to 95 % in the subsequent continuous reactors while controlling the particle size and its distribution of the rubbery polymer; and removing the resulting polymer from the polymerization reaction system, to provide a product with considerably high fluidity and impact resistance.

In the first step, as polymerization is proceeded from the polymerization material solution containing the rubbery polymer, leading to increase of the amount of the styrene polymer, the rubbery polymer which has been in a continuous phase in the polymerization material solution is gradually separated to give particles by shearing force generated by agitation, during which the size and its distribution of the particles can be adjusted. The reactor used in the first step must be a complete mixing type. If the reactor is not

a complete mixing type or the reaction ratio is less than 20 % or more than 35 %, it may be difficult to adjust the particle size of the rubbery polymer, giving undesirable results such as generation of rubbery polymer particles with a large particle size or an unusual shape, which may cause reduction in impact resistance or fluidity.

The complete mixing type of reactor herein should not be necessarily a reactor which can perform an ideal complete mixing; any reactor equipped with an agitator which can generate shearing force by agitating to form rubber particles may be used. Such reactors have been described in, for example, Figs 7.3, 7.4, 7.5 and 7.6 (p.182 - 187) in Yasuharu Saeki, Koji Saeki and Shinzo Omi, "Novel Processes for Manufacturing Polymers", Kogyo Chosa Kai.

After the first step in which the rubbery polymer particles have been formed, a postpolymerization step in which polymerization is further proceeded maintaining the shape of the rubbery polymer particles should be conducted for improving the conversion of monomer ratio. In the postpolymerization step, any type of reactor may be used; a complete mixing type or tower type of agitation tank as well as a tube type reactor may be used. The convert ratio of the monomers to the polymer at the end of the postpolymerization step should be 50 to 90 wt%, preferably 50 to 85 wt%, more preferably 50 to 80 wt%.

A molding from a rubber-modified styrene resin

manufactured by the process of this invention shows higher impact resistance than one from a conventional resin, while being significantly improved in fluidity during molding. Increase of fluidity of a rubber-modified styrene resin may generally cause reduction of impact resistance, while impact resistance can be kept high in the process of this invention. Although it has not been clearly understood, it may be assumed that even when a large amount of catalyst (organic peroxide) is used for improvement in grafting, the particle size may be reduced and the size distribution may be kept narrow in spite of reduction in the molecular weight of the styrene resin if the relationship represented by Equation [1] is maintained, and thus the rubbery polymer particles become relatively uniform, resulting in significant improvement in fluidity during molding.

In a rubber-modified styrene resin according to the process of this invention, a styrene polymer occluded in a diene rubbery polymer as a dispersed phase is grafted to the rubbery polymer. It has been confirmed by the fact that the polystyrene cannot be separated from the rubbery polymer by GPC-IR analysis of the polymerization reaction solution after completion of polymerization.

To a rubber-modified styrene resin composition of this invention may be added, if necessary, antioxidants such as phenolic compound, phosphorous compound and sulfur compound antioxidants; fluidity modifiers such as mineral oils; mold

lubricants such as stearic acid, zinc stearate and organopolysiloxanes, in a polymerization material solution or during or after polymerization reaction.

Example

The following examples will specifically describe, but not limit, this invention. Physical properties in Examples and Comparative Examples were evaluated as follows.

(1) MFI: JIS K-7210(Temperature : 200 °C, Load: 49 N)

(2) Izod impact strength : determined according to JIS K-7110(6.4 mm with a notch)

(3) Nailing property: A nail with a diameter of 1 mm was driven at the center of a circular test piece with a thickness of 3.2 mm and a diameter of 5 cm, and then evaluation was performed according to the following criteria;

Good: without cracks or chips

Poor: with cracks and/or chips

Example 1

A rubber-modified styrene resin was prepared, using a continuous bulk polymerization apparatus comprising four serial complete mixing type reactors equipped with an agitator, whose outlet was connected with a preheater and then a vacuum chamber. To the first complete mixing type of reactor equipped with an agitator was continuously supplied a polymerization material solution consisting of a butadiene polymer as a rubbery polymer (I) whose 5 wt% styrene solution has a viscosity of 32 centipoise at 25 °C

and 98 % of which units in the polymer chain was of cis-1,4-bond (9 wt.parts), ethylbenzene (22 wt.parts), styrene (69 wt.parts) and 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane as an organic peroxide (200 wt.ppm to styrene), while reacting them at an agitation rate of 95 rpm.

The reaction temperatures and the resident times were as follows; the first reactor: 142 °C and 1.5 hours; the second reactor: 145 °C and 2 hours; and the third reactor: 145 °C and 2.5 hours. The temperature of the preheater was kept at 210 to 240 °C. The vacuum chamber was kept at a pressure of 40 Torr. The results are shown in Table 1.

Example 2

Polymerization was conducted as described in Example 1, except that the ratios of ethylbenzene, styrene and 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane as an organic peroxide were 30 wt.parts, 61 wt.parts and 200 wt.ppm, respectively and the agitation rate in the first reactor was 400 rpm. The results are shown in Table 1.

Comparative Example 1

Polymerization was conducted as described in Example 1, except that no organic peroxide were used and the ratio of the butadiene polymer was 2.5 wt.parts. A resulting product showed a low Izod impact value of 4.5 kJ/m².

Example 3

A rubber-modified styrene resin was prepared as described in Example 1, except that the ratios of the

butadiene polymer, ethylbenzene and styrene were 5 wt.parts, 22 wt.parts and 73 wt.ppm, respectively, and t-butyldodecylmercaptan was used as a molecular weight regulator in an amount of 200 wt.ppm to styrene. The results are shown in Table 1.

Example 4

Polymerization was conducted as described in Example 1, except that the ratios of the butadiene polymer, ethylbenzene and styrene were 15 wt.parts, 22 wt.parts and 63 wt.parts, respectively. The results are shown in Table 1.

Example 5

Polymerization was conducted as described in Example 1, except that the ratios of the butadiene polymer, ethylbenzene and styrene were 9 wt.parts, 22 wt.parts and 69 wt.ppm, respectively, and t-butyldodecylmercaptan and 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane were used as organic peroxides in amounts of 50 wt.ppm and 200 wt.ppm to styrene, respectively. The results are shown in Table 1.

Example 6

Polymerization was conducted as described in Example 5, except that the ratios of the butadiene polymer, ethylbenzene and styrene were 9 wt.parts, 22 wt.parts and 69 wt.ppm, respectively, and 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane was used as an organic peroxide

in an amount of 100 wt.ppm, but t-butyl dodecyl mercaptan was not used. The results are shown in Table 1.

Example 7

A rubber-modified styrene resin was prepared, using a continuous bulk polymerization apparatus comprising three serial complete mixing type reactors equipped with an agitator, whose outlet was connected with a preheater and then a vacuum chamber. To the first complete mixing type of reactor equipped with an agitator was continuously supplied a polymerization material solution consisting of a styrene/butadiene block copolymer as a rubbery polymer (I) whose 5 wt% styrene solution has a viscosity of 32 centipoise at 25 °C (12 wt.parts), ethylbenzene (18 wt.parts), styrene (70 wt.parts) and 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane as an organic peroxide (200 wt.ppm). The reaction temperatures and the resident times were as follows; the first reactor: 142 °C and 1.5 hours; the second reactor: 145 °C and 2 hours; and the third reactor: 145 °C and 2.5 hours. The temperature of the preheater was kept at 210 to 240 °C. The vacuum chamber was kept at a pressure of 40 Torr. The results are shown in Table 1.

Example 8

Polymerization was conducted as described in Example 1, except that the ratios of styrene, the rubbery polymer, ethylbenzene and the organic peroxide were 74 wt.parts, 6 wt.parts, 20 wt.parts and 200 wt.ppm, respectively, and a

molecular weight regulator was used in an amount of 250 wt.ppm. The results are shown in Table 1.

Comparative Example 2

Polymerization was conducted as described in Example 1, except that the temperature of the first reactor was lowered and the convert ratio of styrene was 10 %. In the first reactor, the particle size was not adequately controlled, causing the particle size to be larger. The resulting resin composition showed the following physical properties; a rubber particle size: 4.2 μm , a distribution coefficient: 25, MFI: 2.8, an Izod impact value: 11 kJ/m^3 . Thus, due to such a lower MFI value, the resulting resin composition was not acceptable in the light of the objective of this invention.

As illustrated above, it may be concluded that a rubber-modified styrene resin composition according to this invention has a good balance between impact resistance and fluidity or appearance (in particular, gloss), and thus may be significantly useful in the sector of component materials for, for example, electrical appliances and electronic devices.

Table 1

		Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Ex.8
Styrene	wt. %	69	61	73	63	69	69	70	74
Ethylbenzene[E]	wt. %	22	30	22	22	22	22	18	20
Rubbery polymer	wt. %	9	9	5	15	9	9	12	6
Organic peroxide[I]	wt.ppm	200	60	200	200	50	100	200	200
Molecular weight regulator[S]	wt.ppm	0	0	200	0	100	0	0	250
$15[I]^{1/2}/E+[S]^{1/3}$		9.6	9.5	15.5	9.6	9.5	10	11.8	16.9
Conversion of monomer ratio in the first reactor	%	28	26	26	26	28	28	28	22
Rubber particle size	μm	3.0	3.5	2.0	3.8	3.2	2.8	2.0	2.0
Distribution coefficient		3.5	4.0	4.5	6.5	3.5	4.0	4.0	4.5
MFI	g/10min	4.4	5.8	7.0	3.8	4.2	4.0	3.7	8.2
Izod impact strength	kJ/m^2	16	15	8.5	19	16	15	18	7.5
Nailing property		Good	Good	Poor	Good	Good	Good	Good	Poor



What is claimed is:

1. A process for manufacturing a rubber-modified styrene resin composition in which a continuous phase consists of a styrene resin and a dispersed phase consists of a diene polymer type of rubbery polymer occluding a styrene resin by bulk or solution polymerization using a continuous polymerization apparatus consisting of at least two reactors including at least one complete-mixing type of reactor, comprising

converting 20 to 35% of a styrene compound monomer to a polymer in the first complete mixing type reactor in the polymerization system to form a dispersed phase consisting of the rubbery polymer, charging a material in the first complete mixing type reactor (hereinafter, referred to as the "polymerization material solution")

(1) having the following composition:

(a) a styrene-compound monomer: 60 to 85 parts by weight
(b) an aromatic solvent: 5 to 35 parts by weight; and
(c) the diene rubbery polymer whose 5 wt% solution in styrene has a viscosity of 30 to 90 centipoise at 25 °C: 3 to 20 parts by weight, when the total amount of the styrene-compound monomer, the aromatic solvent and the diene rubbery polymer is 100 parts by weight;

(2) containing, in relation to the styrene-compound monomer,

(a) 20 to 300 wt.ppm of an organic peroxide and



- (b) 0 to 350 wt.ppm of a molecular weight regulator; and
(3) meeting the following equation:

$$9 \leq 15[I]^{1/2}/[E]+[S]^{1/3} \leq 21 \dots [1]$$

wherein [I], [E] and [S] are the concentrations of the organic peroxide (wt.ppm), the aromatic solvent (wt.%) and the molecular weight regulator (wt.ppm), respectively;

increasing the reaction ratio of the styrene-compound monomer to 50 to 95 % in the subsequent reactors; and

separating the resulting product from the remaining monomer and the solvent, to provide a rubber-modified styrene resin composition in which the rubbery polymer as a dispersed phase has a volume-average particle size of 1 to 4 μm and the ratio(D1/D2) of 10 % value(D1) to 90 % value(D2) of the cumulative particle size distribution by volume ranges 3 to 20.

2. A process for manufacturing a rubber-modified styrene resin composition as claimed in Claim 1, where the styrene polymer occluded in the diene rubbery polymer as a dispersed phase is grafted to the diene rubbery polymer.

3. A process for manufacturing a rubber-modified styrene resin composition as claimed in Claim 1, where [I], [E] and [S] meet Equation [2]:

$$9 \leq 15[I]^{1/2}/[E]+[S]^{1/3} \leq 15 \dots [2]$$



4. A process for manufacturing a rubber-modified styrene resin composition as claimed in Claim 1, where the styrene-compound monomer is styrene.

5. A process for manufacturing a rubber-modified styrene resin composition as claimed in Claim 1, where the aromatic solvent is at least one selected from the group consisting of benzene, toluene and ethylbenzene.

6. A process for manufacturing a rubber-modified styrene resin composition as claimed in Claim 1, where the diene rubbery-polymer is at least one selected from the group consisting of butadiene polymer and styrene/butadiene copolymer.

7. A process for manufacturing a rubber-modified styrene resin composition as claimed in Claim 1, where the organic peroxide is 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane.

8. A process for manufacturing a rubber-modified styrene resin composition as claimed in Claim 1, where the molecular weight regulator is a mercaptan compound.

9. A process for manufacturing a rubber-modified styrene resin composition as claimed in Claim 1, where the



ratio(D1/D2) of 10 % value(D1) to 90 % value(D2) of the cumulative particle size distribution by volume ranges 3 to 15 for the rubbery polymer particles.

10. A process for manufacturing a rubber-modified styrene resin composition as claimed in Claim 1, where the diene rubbery polymer is a polybutadiene rubber in which at least 90 molar % of butadiene units in the polymer chain are of cis-1,4-bond.