DESCRIPTION

PRODUCTION METHOD FOR MOLDED ARTICLE OF POLYPHENYLENE ETHER-BASED RESIN COMPOSITION

TECHNICAL FIELD

[0001]

The present invention relates to a production method for molded article of a polyphenylene ether-based resin composition, and more particularly, to a production method for molded article of a polyphenylene ether-based resin composition enabling the production of a polyphenylene ether resin-based composition having a favorable color tone and free of decreases in physical properties, at high production efficiency.

BACKGROUND ART

[0002]

Although polyphenylene ether resin is an engineering plastic having superior heat resistance, electrical characteristics and chemical resistance, it conversely also has shortcomings consisting of poor fluidity and being difficult to mold. Consequently, a material incorporating a polystyrene-based resin was developed for the purpose of improving the moldability, fluidity and impact resistance of polyphenylene ether (see Patent Document 1), this is typically referred to as a modified polyphenylene ether resin, and is used in numerous fields as a type of engineering plastic.

[0003]

However, since polyphenylene ether resin has a high glass

transition temperature, it requires a high molding temperature, thereby resulting in increased susceptibility to discoloration caused by thermal degradation. This problem of discoloration is also a significant problem in the case of attempting to improve fluidity by incorporating a polystyrene-based resin and the like, and is an important issue to be overcome.

This problem of discoloration during molding is known to be primarily caused by oxidative deterioration by oxygen, and a method is sought that enables extrusion molding to be carried out efficiently while preventing oxidative deterioration.

[0004]

In order to produce a pellet (molded article) as a molding material from the above-mentioned polyphenylene ether resin, a mixture of polyphenylene ether resin, polystyrene-based resin, and an additive as necessary, is supplied to an extruder followed by melting and kneading inside the extruder, extruding into strands, cooling, cutting the strands and pelletization.

When incorporating the polystyrene-based resin into a polyphenylene ether resin powder, supplying to an extruder, extruding and molding, air is entrained with the resin and is entrapped therein, thereby resulting in susceptibility of the polyphenylene ether resin to oxidative deterioration.

[0005]

Although a method consisting of adding an antioxidant to the raw materials is ordinarily used to prevent this oxidative deterioration (see Patent Document 2), the effect of this alone

is not adequate, and although a method involving supplying an inert gas such as nitrogen gas to the extruder has also been deployed (see Patent Document 3), the effect of simply supplying an inert gas is also not adequate.

[0006]

In the case of using a so-called powder obtained directly from a polymerization device for the polyphenylene ether resin in particular, since polyphenylene ether resin powder has a low apparent density in a powdered state and contains a large amount of air, the problem of oxidative deterioration becomes even more serious.

Moreover, when supplying a polyphenylene ether resin powder to an extruder, air incorporated in the resin from the cylinder of the extruder flows back towards the hopper, resulting in increased susceptibility to the occurrence of so-called feed neck phenomenon, thereby also resulting in the problem of a sudden decrease in productivity.

[0007]

Under such circumstances, there has been a strong desire to develop a method for efficiently producing a resin molded article (pellet) having favorable color tone and free of decreases in physical properties from a polyphenylene ether resin powder and a polystyrene-based resin.

CITATION LIST

PATENT LITERATURE

[0008]

Patent Document 1: U.S. Patent No. 3383435

Patent Document 2: Japanese Patent Application Laid-Open No. 2003-246865

Patent Document 3: Japanese Patent Application Laid-Open No. H06-206216

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0009]

With the foregoing in view, an object of the present invention is to provide a production method for molded article of a polyphenylene ether-based resin composition enabling the production of a polyphenylene ether resin-based composition molded article (pellet) having a favorable color tone and free of decreases in physical properties at high production efficiency.

SOLUTION TO PROBLEM

[0010]

As a result of conducting detailed analyses and extensive studies on phenomena that occur during melting and kneading to achieve the above-mentioned object, the inventors of the present invention found that the problems can be solved by using a specific polyphenylene ether resin powder and treating the specific powder with a special method, thereby leading to completion of the present invention. In addition, nearly all problems were able to be solved by using the polystyrene-based resin incorporated in the polyphenylene ether resin powder in a specific form that demonstrates little entrainment of air, and incorporating using

a special method that does not cause defective dispersion.

[0011]

Namely, according to a first invention of the present invention, a production method for a pellet of a polyphenylene ether-based resin composition is provided, wherein

in the production of a polyphenylene ether-based resin composition pellet by melting and kneading a polyphenylene ether resin, a polystyrene-based resin which is used at 5 parts by weight to 100 parts by weight based on 100 parts by weight of the polyphenylene ether resin and, as necessary, an additive with an extruder, which comprises that,

1) a polyphenylene ether resin having an intrinsic viscosity of 0.3 dl/g to 0.6 dl/g, a number of terminal hydroxyl groups of 0.3 to 1.5 groups per 100 phenylene ether units, a residual toluene concentration of 0.05% by weight to 0.5% by weight, a copper content of 0.02 ppm to 0.2 ppm,

and a powder having a mean particle diameter of 50 μm to 600 μm, a maximum peak of particle size distribution of within the range of 30 μm to 300 μm, and a half width of the maximum peak of 500 μm or less, is used for the polyphenylene ether resin, and

2) the polyphenylene ether resin powder is treated with an inert gas by allowing the powder to flow down in a flowing state over a distance of 1 m or more through an inert gas having an oxygen concentration of 10% or less before introducing the powder into the extruder,

wherein a pellet having a mean particle diameter of 1 mm to

5 mm and an apparent density of 110% to 140% with respect to the apparent density of the polyphenylene ether resin powder is used for the polystyrene-based resin, and

wherein the polyphenylene ether resin powder and the polystyrene-based resin pellet are supplied to the extruder by adjusting the blending ratio thereof using separate quantitative feeders, and the gaseous oxygen concentration in a supply unit of the extruder is held to 10% or less.

[0012]

In addition, according to a second invention of the present invention, a production method for molded article of a polyphenylene ether-based resin composition is provided wherein, in the first invention, the filling ratio of the polyphenylene ether resin and the polystyrene-based resin in a solid transporting zone of the extruder is 30% or less.

[0013]

According to a third invention of the present invention, a production method for molded article of a polyphenylene ether-based resin composition is provided wherein, in the first or second invention, a vent-type extruder is used for the extruder, and molding is carried out by forming gas sealing portions using molten resin in a screw on an upstream side and a downstream side of a vent port.

[0014]

In addition, according to a fourth invention of the present invention, a production method for molded article of a

polyphenylene ether-based resin composition is provided wherein, in the third invention, the extruder is a vent-type extruder, and the degree of pressure reduction of a pressure reduction vent thereof is -0.099 MPa to -0.06 MPa.

[0015]

In addition, according to a fifth invention of the present invention, a production method for molded article of a polyphenylene ether-based resin composition is provided wherein, in any of the first to fourth inventions, a phosphorous-based flame retardant is added as the additive.

[0016]

In addition, according to a sixth invention of the present invention, a production method for molded article of a polyphenylene ether-based resin composition is provided wherein, in the fifth invention, the phosphorous-based flame retardant is supplied further downstream from a gas sealing portion downstream of a vent port.

[0017]

In addition, according to a seventh invention of the present invention, a production method for molded article of a polyphenylene ether-based resin composition is provided wherein, in the sixth invention, the phosphorous-based flame retardant is supplied downstream of the pressure reduction vent in a liquid state having a viscosity of 0.001 Pa·s to 3 Pa·s.

[0018]

In addition, according to an eighth invention of the present

invention, a production method for molded article of a polyphenylene ether-based resin composition is provided wherein, in any of the first to seventh inventions, a polyphenylene ether-based resin composition is extruded from the extruder in the form of strands, and the strands are cooled by being introduced into cooling water within 2 seconds after coming out of the extruder.

[0019]

In addition, according to a ninth invention of the present invention, a production method for molded article of a polyphenylene ether-based resin composition is provided wherein, in the eighth invention, the strand temperature is adjusted to 90°C to 150°C by cooling, and the strands are cut in this temperature range.

ADVANTAGEOUS EFFECTS OF INVENTION

[0020]

According to the production method of a polyphenylene ether-based resin composition pellet of the present invention, a molding method can be provided that enables the production of a polyphenylene ether-based resin composition pellet having favorable color tone and free of decreases in physical properties at high production efficiency.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021]

FIG. 1 is a schematic cross-sectional view showing an embodiment of an extruder and screw used in the present invention;

FIG. 2 is a schematic cross-sectional view showing an

embodiment of a raw material supply unit of an extruder used in the present invention; and

FIG. 3 is a schematic cross-sectional view showing an embodiment of a raw material supply unit of an extruder used in the present invention.

DESCRIPTION OF EMBODIMENTS

[0022]

Although the following provides a detailed explanation of the present invention by indicating embodiments and examples thereof, the present invention is not limited to the following embodiments and examples, but rather can be arbitrarily modified within a range that does not deviate from the gist of the present invention.

[0023]

The present invention relates to a production method for molded article of a polyphenylene ether-based resin composition by melting and kneading a polyphenylene ether resin, a polystyrene-based resin and, as necessary, an additive with an extruder, which comprises that

1) a powder having a mean particle diameter of 50 μm to 600 μm is used for the polyphenylene ether resin, and

2) the powder is treated with an inert gas by allowing the powder to flow down in a flowing state over a distance of 1 m or more through an inert gas having an oxygen concentration of 10% or less before introducing the powder into the extruder.

[0024]

The following provides a detailed explanation of the present invention with reference to the drawings.

FIG. 1 is a schematic cross-sectional view showing an embodiment of an extruder and screw used in the present invention.

FIG. 2 is schematic cross-sectional view showing an embodiment of a treatment device used in the present invention.

FIG. 3 is a schematic cross-sectional view showing an embodiment of a treatment device used in the present invention.

[0025]

As shown in FIG. 1, hoppers (raw material supply units) 4 and 4' are arranged on the rear side of a cylinder 1 of an extruder, and raw materials consisting of a polyphenylene ether resin 10 and a polystyrene-based resin 11 are weighed by weighing feeders 5 and 5' and then supplied to the cylinder 1 by passing through a raw material supply port 3 provided in the rear end of the cylinder 1.

In the present invention, the polyphenylene ether resin (also referred to as "PPE") raw material 10 is a powder, and although the form of the polystyrene-based resin is arbitrary such as a powder or pellet, that in the form of a pellet is used preferably for the reasons indicated below.

Although the terms, “powder” and “powdered body” are used in the present specification, they both indicate the same thing. In addition, the PPE powder exhibits an appearance and behavior in the manner of powdered starch or cornstarch and the like, and is resistant to penetration into the screw of the extruder when

carrying out pelletization.

[0026]

An inert gas injection port 9 is provided in the raw material supply port 3, and an inert gas is supplied therein. The amount of inert gas supplied is only required to be an amount that enables the oxygen concentration measured in the vicinity of the lower end of the raw material supply port 3 to be 10% or less, and is not required to be blown in excess.

An inert gas refers to a gas that is inert (not having substantially any reactivity) with respect to PPE such as nitrogen gas and argon gas, and normally nitrogen gas is used.

The polyphenylene ether resin powder 10 supplied from the weighing feeder 5 contacts an inert gas while descending towards the raw material supply port 3 of the extruder, and air (oxygen) contained in the powder is replaced with the inert gas.

[0027]

In order to ensure that the oxygen content of the polyphenylene ether resin powder 10 is adequately replaced (treated) with the inert gas, the polyphenylene ether resin powder 10 is required to be in a flowing state since favorable replacement is unable to be carried out if the powder is compacted (solidified).

A flowing state of the powder normally refers to a state in which the powder is in a dispersed state as a result of having been agitated by the quantitative feeders (weighing feeders) 5 and 5' as shown in FIG. 1, or in a free-falling state thereafter, and particularly favorable treatment can be carried out if the powder

10 contacts the inert gas while allowing it to fall freely.

[0028]

In the case of a free-falling, flowing state as shown in FIG. 1, treatment capacity is affected by the particle diameter of the powder, falling distance and the like.

A general indicator of falling distance is a minimum distance of 1 m in the case of the powder 10 having a mean particle diameter of 50 μm to 600 μm.

If the powder particle diameter is excessively small, it becomes difficult to handle (extrusion mold), while if the particle diameter is excessively large (excessively large pellet), the effects of treatment are diminished.

[0029]

FIGS. 2 and 3 indicate other forms of treatment of the polyphenylene ether resin powder 10 with inert gas.

FIG. 2 indicates the providing of mutually different plates 13 inclined on the inner surface of a cylinder 12 such that the polyphenylene ether resin powder 10 falls in a zigzag pattern. As a result of employing this structure, movement (flow) is imparted to the powder and the falling distance is substantially increased, or in other words, the distance over which the powder falls in a zigzag pattern becomes the falling distance.

Although two weighing feeders 5 and 5' are provided in FIGs. 1 and 2, pellets of the polyphenylene ether resin powder 10 and the polystyrene-based resin 11 are supplied corresponding to their individual blended amounts by using separate weighing feeders 5

and 5'.

[0030]

As a result of employing this type of supply method, in the case of using the polyphenylene ether resin 10 in the form of a powder and the polystyrene-based resin 11 in the form of pellets, uneven dispersion caused by classification attributable to differences in apparent density between the powder and pellets, which occur when supplying the powder and pellets after mixing in advance, can be prevented.

An inert gas is supplied from the inert gas injection port 9, and both the polyphenylene ether resin powder 10 and pellets of the polystyrene-based resin 11 in a flowing state are treated with the inert gas.

In the present invention, although the polyphenylene ether resin powder 10 that composes the main component of the molded article (pellet) is required to be treated with an inert gas, it is naturally also preferable to treat the polystyrene-based resin 11, which is added to improve fluidity, with the inert gas.

[0031]

FIG. 3 shows another example of a mechanism for treating with inert gas. In FIG. 3, a structure is employed in which a spiral-shaped sliding plate 15 is provided around a shaft 14 in the cylinder 12. The polyphenylene ether resin powder 10 sent from the weighing feeder 5 flows downward while flowing along the upper surface of the spiral-shaped sliding plate 15, and is treated with an inert gas from the inert gas injection port 9 so as to reduce

the amount of oxygen contained therein. At this time, the flowing state (such as the downward flow rate) of the polyphenylene ether resin powder 10 can be controlled by oscillating the shaft 14 in the vertical direction 16.

In FIG. 3, although a tank 17 is provided in the lower portion to recover the treated polyphenylene ether resin powder 10, the recovered powder may be supplied directly to a hopper and the like and used for molding, or another feeding device (such as a weighing feeder) may naturally also be provided at this location to enable the powder to be supplied to an extruder.

[0032]

As a result of treating the polyphenylene ether resin with an inert gas as described above while in the state of a powder, the oxygen contained therein decreases considerably. Although favorable replacement (removal) of oxygen does not normally occur even if an inert gas is blown onto a powdered polyphenylene ether resin housed in a container (and not in a flowing state), by treating the powdered polyphenylene ether resin in a flowing state (state in which it is flowing) with an inert gas as previously described, removal of the internal oxygen was found to be carried out efficiently. A raw material polyphenylene ether resin powder having a mean particle diameter of 50 μm to 600 μm is suitable for treatment with inert gas in consideration of fluidity, surface area and the like.

[0033]

On the other hand, the polystyrene resin is preferably used

in the form of pellets (having a mean particle diameter of about 1 mm to 5 mm). In the case of blending into a polyphenylene ether resin in the form of a powder, by also blending the polystyrene resin in the form of a powder having roughly the same apparent density normally enables both components to be uniformly dispersed and mixed, thereby making it possible to prevent the occurrence of classification during molding and the formation of a non-uniform composition. Thus, it is matter of common technical knowledge to match the particle diameter and apparent density thereof, and this technique is not ruled out in the present invention as well.

[0034]

However, in the present invention, it is recommended to blend pelletized polystyrene resin with a powdered polyphenylene ether resin.

The reason for this is related to the difference in melting point (softening point).

Polystyrene resin has a lower softening point than polyphenylene ether resin and is inferior thereto with respect to heat resistance. Thus, in the case of using as a powder having an apparent density roughly equal to that of polyphenylene ether resin, it is thought to be necessary to carry out deoxygenation treatment (inert gas treatment) to a degree greater than that of the polyphenylene ether resin, thereby making this unreasonable in terms of both equipment and production work.

[0035]

Thus, a method is preferably used in which the polystyrene

resin is first molded into pellets having a small surface area (outer surface area per unit weight) at a temperature that is low enough so as not to cause deterioration or discoloration, and used in a form that has a less of a need for deoxygenation treatment.

When considering the behavior in the extruder, since polystyrene resin having a low softening point, namely that which is easily melted, is introduced into an extruder in a state having a smaller surface area per unit weight than a powder (state in which it is difficult to conduct heat), melting time is comparatively slow, thereby demonstrating the effect of preventing deterioration and discoloration of the polystyrene-based resin.

[0036]

However, in the case of mixing pellets into a powder, classification (phenomenon by which the pellets and powder separate more easily due to vibrations and the like) ends up occurring, and this causes problems such as the composition ratio during molding deviating from a prescribed range or being unable to obtain a molded product. The present invention is also able to overcome these problems.

Namely, a quantitative feeder is used at a precise location.

Classification occurs in the case a powder and pellets are allowed to stand to a certain degree after mixing. Thus, in the present invention, the weighing feeders 5 and 5' for separately supplying powder and pellets are individually provided immediately before (directly above) the resin supply port 3 of the extruder 1, and prescribed amounts thereof are respectively supplied. As

a result, both resins are supplied to the extruder at a prescribed blending ratio at all times, thereby solving the problem of classification.

The use of pellets having an apparent density of 110% to 140% of the apparent density of the polyphenylene ether resin powder is preferable in terms of handling.

[0037]

The screw 2 is rotatably arranged in the cylinder 1, and carries out smooth transport, mixing and finally melting of the resin raw materials, after which they are finally extruded from a discharge die 6. In the case the molded article is a pellet, the molten resin is extruded in the form of strands. A cooling water bath is normally provided in front of the discharge die 6, and following cooling treatment, the strands are cut with cutting means such as a pelletizer to obtain molded products (pellets) having a mean particle diameter of about 1 mm to 5 mm. When cutting with the pelletizer, cutting becomes difficult if the strands are completely cooled (to about room temperature), and since problems such as the generation of fine powder occur, the strands are preferably cut when the strand temperature is within the range of 90°C to 150°C.

Although the temperature when the strands are cut refers to the temperature obtained by measuring strand temperature immediately before entering the pelletizer with a non-contact thermometer, for the sake of simplicity, it is sufficient to collect a suitable amount of the cut pellets and measure their temperature

by inserting a thermometer.

[0038]

As shown in FIG. 1, the inside of the cylinder 1 is composed of at least three zones consisting of a transporting zone a, a mixing zone b and a melting zone c in the order of those steps.

[0039]

The transporting zone a, the mixing zone b and the melting zone c are demarcated into three zones according to the element configuration of the screw 2. As shown in FIG. 1, the screw configuration in the transporting zone a is composed of a forward conveying screw, and this is rotated to send unmelted or molten resin from the supply port to the subsequent mixing zone b. Since the screw 2 in the transporting zone a increases the amount of plasticization by improving penetration in order to transport and melt the pellets, the depth of the grooves thereof is deeper than those of other zones, and the length thereof is preferably 5 times to 18 times the inner diameter of the cylinder.

[0040]

The mixing zone b is composed of a kneading disc, a mixing screw or a backward conveying screw, and unmelted or semi-melted polyphenylene ether resin/polystyrene resin transported from the transporting zone a is retained therein and then melted by heat, pressure and high shearing force.

The melting zone c is composed of a forward conveying screw, and sends the molten resin composition to the subsequent front of the cylinder. A vent port 7 is preferably provided in the melting

zone c for carrying out removal of low-volatile components in the resin raw materials. At this time, the vent port 7 is preferably used as a pressure reduction vent through which pressure is reduced using a vacuum pump, and the degree of pressure reduction thereof is more preferably -0.099 MPa to -0.06 MPa.

[0041]

Although the transporting zone a, which begins starting directly below the resin supply port 3, fulfills the role of stably transporting a prescribed amount of resin, it is inherently difficult to transport a powder with a screw. This is because the fed amount becomes unstable as a result of the powder containing more space (gas) as it becomes finer, thereby resulting in greater susceptibility to the occurrence of so-called "breathing".

The present invention is able to eliminate this problem as well.

Namely, this objective was found to be able to be achieved by making the filling ratio of the supplied amounts of resin in the solid transport portion (transporting zone a) within the extruder to 30% or less.

Filling ratio refers to ratio of the supplied amount of resin (volume according to true density) to the spatial volume per pitch of the screw of the transporting zone a.

The above-mentioned problem is solved by supplying a considerably smaller amount of resin than the supply capacity of the extruder through the use of a quantitative feeder and the like to reliably feed the resin in this manner.

[0042]

Since the function of the mixing zone b has little involvement with sending the molten resin forward, it retains the molten resin at this location. Namely, this portion is a gas sealing portion that prevents the distribution of gas.

In addition, a gas sealing portion such as a sealing ring 18 and the like is preferably provided on the downstream side (die side) of the above-mentioned vent port 7. The sealing ring 18 is a metal ring that blocks 70% to 80% of the flow path and fulfills the role of preventing distribution of gas by forcing molten resin to be retained in this portion.

Namely, by forming gas sealing portions on the upstream side and downstream side on both sides of the vent port 7, the vent portion is isolated with respect to gas, and by reducing the pressure of this portion (including an open state), volatile components and the like in the molten resin can be effectively removed.

In the case of adding an additive such as a flame retardant, the additive is preferably injected further downstream from this gas sealing portion (sealing ring 18) on the downstream side thereof. This can be said to be a contrivance for preventing the injected additive from dissipating from the vent portion.

[0043]

In order to uniformly mix the powdered polyphenylene ether resin and the pelletized polystyrene resin, a polyphenylene ether resin powder having a mean particle diameter of 50 μm to 600 μm is used for the raw material polyphenylene ether resin powder, while

pellets having a mean particle diameter of 1 mm to 5 mm and an apparent density equal to 110% to 140% of the apparent density of the polyphenylene ether resin powder are used for the polystyrene-based resin.

Although the polyphenylene ether resin and the polystyrene resin are compatible in terms of the entire composition, they are respectively used within the above-mentioned ranges in order to carry out uniform mixing of the powdered polyphenylene ether resin and the pellets of polystyrene resin. If the mean particle diameter of the polyphenylene ether resin powder is less than 50 μm, there is increased susceptibility to the occurrence of a situation that prevents the resin from being supplied to the occurrence of feed neck phenomenon, thereby resulting in poor color tone due caused by generation of heat. If the mean particle diameter exceeds 600 μm, the amount of residua toluene to be subsequently described increases, resulting in an increased likelihood of poor color tone. Although previously described, in terms of carrying out favorable inert gas treatment as well, the preferable mean particle diameter of the polyphenylene ether resin powder is 60 μm to 300 μm.

In consideration of favorable dispersibility in the polyphenylene ether resin powder and thermal behavior within the extruder, the preferable mean particle diameter of the polystyrene-based resin pellets is 2 mm to 4 mm. The blended amount of the polystyrene-based resin pellets is 5 parts by weight to 100 parts by weight, and preferably 5 parts by weight to 30 parts by weight, based on 100 parts by weight of the polyphenylene ether

resin powder.

[0044]

In addition, in consideration of the effect of favorable color tone, the maximum peak of the particle size distribution of the polyphenylene ether resin powder is preferably within the range of 30 μm to 300 μm, and the half width value of the maximum peak is preferably 500 μm or less. Particle size distribution can be measured with particle size distribution analyzer using the laser diffraction/scattering method to be subsequently described.

Moreover, the polyphenylene ether resin powder preferably has a residual toluene concentration attributable to toluene used as polymerization solvent of 0.05% by weight to 0.5% by weight. If the residual toluene concentration exceeds 0.5% by weight, color tone easily becomes poor, while the lower limit thereof is about 0.05% by weight.

[0045]

The intrinsic viscosity of the polyphenylene ether resin powder is preferably 0.3 dl/g to 0.6 dl/g, and the number of terminal hydroxyl groups is preferably 0.3 groups to 1.5 groups per 100 phenylene ether units. If the intrinsic viscosity is 0.3 dl/g or less, impact strength of the resin composition becomes inadequate, while if the intrinsic viscosity exceeds 0.6 dl/g, moldability becomes inadequate while also causing the occurrence of defective appearance of molded products.

In addition, if the number of terminal hydroxyl groups per 100 phenylene ether units is 0.3 groups or less, compatibility with

styrene-based resin decreases resulting in the occurrence of defective appearance, and color tone may also worsen in a high-temperature atmosphere. In addition, if the number of terminal hydroxyl groups exceeds 1.5 groups, thermal stability decreases.

[0046]

In the present invention, when supplying the polyphenylene ether resin powder 10 and the polystyrene-based resin pellets 11 to the extruder, the gaseous oxygen concentration in the supply unit 3 of the extruder is held to 10% or less.

Although the gaseous oxygen concentration can be held to 10% or less by providing the inert gas supply port 9 in the bottom of the hopper 4 and supplying an inert gas such as nitrogen gas, since the oxygen concentration may end up exceeding 10% as a result of entrapment of air that has been introduced from the polyphenylene ether resin powder in the case of simply retaining nitrogen gas alone, the amount of inert gas supplied is increased if the oxygen concentration becomes high while monitoring oxygen concentration in the resin supply port 3 with an oxygen concentration meter and the like (not shown). The preferable gaseous oxygen concentration is 3% or less, while the lower limit thereof is about 0.1% in consideration of the balance between the effect of improving color tone and economy.

[0047]

Although the set temperature and time in the extruder can be arbitrarily selected according to the resin composition, type

of extruder and the like, normally the kneading temperature is 200°C to 350°C and preferably 220°C to 320°C, while the kneading time is preferably 3 minutes or less. If kneading exceeds 350°C or 3 minutes, it becomes difficult to prevent thermal deterioration of the polyphenylene ether resin and styrene-based resin, resulting in increased susceptibility to the occurrence of decreases in physical properties and defective appearance.

[0048]

In addition, when supplying the polyphenylene ether resin powder 10 and the polystyrene resin pellets 11 to the extruder, the polyphenylene ether resin powder 10 and the polystyrene resin pellets 11 are preferably supplied quantitatively by providing a quantitative supplying a quantitative feeder (weighing feeder) 5 in the lower portion of the hoppers 4 and 4'.

As shown in FIG. 1, hoppers 4 and 4' and quantitative feeders 5 and 5' are provided in the upper portion of the resin supply port 3 of the extruder, and polyphenylene ether resin and polystyrene-based resin are supplied from their respective quantitative feeders 5 and 5' corresponding to their blending ratio. At this time, a height H of the upper portion of the supply port 3 is 1 m or more, and the polyphenylene ether resin powder and polystyrene resin-based pellets are allowed to fall, or in other words, the polyphenylene ether resin powder is allowed to flow downward in a flowing state for 1 m or more. At this time, as a result of supplying an inert gas (such as nitrogen gas) having a gaseous oxygen concentration of 10% or less from the inert gas supply

port 9 in the resin supply port 3, the polyphenylene ether resin powder is treated with the inert gas.

[0049]

Inert gas is naturally filled into the hoppers 4 and 4'. In addition, polyphenylene ether resin powder (raw material resin) that has been preliminarily treated with inert gas can be introduced into the hoppers 4 and 4' and quantitatively supplied. In such a case, it is naturally not necessary to make the height of the supply port 3 to be 1 m or more.

By quantitatively supplying (supplying after weighing) each of the resins immediately prior to being introduced into the extruder, both resins (powder and pellets) are mixed in advance, thereby allowing the obtaining of a composition having a more stable blending ratio.

[0050]

Moreover, the supplied amounts of the polyphenylene ether resin and the polystyrene-based resin in the transporting zone a of the extruder are preferably controlled so that their filling ratio is maintained at 30% or less. Filling ratio (%) is defined as the occupied area of the resin relative to the effective spatial area in a cross-section of the cylinder. By making the filling ratio 30% or less, the resins can be supplied stably and as a result thereof, a resin composition pellet having favorable color tone is easily obtained.

With respect to the configuration of the screw 2 in the extruder, the mixing zone b, composed of a backward conveying screw

or kneading element and the like, is provided between the transporting zone a and the melting zone c.

Since the mixing zone has little force that causes the resin to be sent forward, the resin is retained in this portion to a certain degree, and the internal space of the cylinder 1 is partially blocked by this retained resin. Namely, a gas sealing portion is formed by this retained resin. The mixing zone b is located on the upstream side of a vent port.

[0051]

The sealing ring 18 is provided on the downstream side (die side) of the vent port 7 of the melting zone c. Although a structure can also be provided that causes the resin to be retained, such as a backward conveying screw or backward conveying kneading element, normally the sealing ring 18 is used that only requires a shorter width (lengthwise direction relative to the screw).

The sealing ring 18 is in the form of a ring that fits onto the screw, and forms a gas sealing portion by blocking about 70% to 80% of the flow path and interrupting the flow of resin.

The effects of the vent are further improved and volatile components and the like in the resin are favorably removed by gas sealing portions provided upstream and downstream of the vent port 7.

[0052]

A second supply port 8 may be provided downstream of the vent port 7 and further downstream from the sealing ring 18, and an additive is injected (introduced under pressure) as necessary from

this second supply port 8.

For example, a volatile additive such as a phosphorous-based flame retardant is preferably injected from this location. This is because there is less susceptibility to the effect of reduced pressure of the vent due to the sealing ring 18, enabling the additive to be added favorably.

Reference symbols 19, 19' and 19" are band heaters that control the temperature of the extruder.

[0053]

The polyphenylene ether resin used in the present invention is a polymer having phenylene ether units for the main chain thereof, and may be a homopolymer or a copolymer.

Specific examples of homopolymers include polymers of 2,6-dialkylene ether such as poly(2,6-dimethyl-1,4-phenylene) ether, poly(2,6-diethyl-1,4-phenylene) ether, poly(2,6-dipropyl-1,4-phenylene) ether, poly(2-methyl-6-ethyl-1,4-phenylene) ether or poly(2-methyl-6-propyl-1,4-phenylene) ether, while specific examples of copolymers include various types of 2,6-dialkylphenol/2,3,6-trialkylphenol copolymers, although poly(2,6-dimethyl-1,4-phenylene) ether and 2,6-dimethylphenol/2,3,6-trimethylphenol copolymer are particularly preferable.

[0054]

Although there are no particular limitations on the production method of the polyphenylene ether resin, it can be easily

produced by carrying out oxidative polymerization of a 2,6 xylenol in the presence of a cuprous salt and an amine compound as indicated in, for example, Japanese Patent Publication No. S61-20576, and specific production methods are indicated in the production examples to be subsequently described.

[0055]

The number of terminal hydroxyl groups of the polyphenylene ether resin used in the present invention is preferably 0.3 groups or more per 100 phenylene ether units.

Specific examples of units having terminal hydroxyl groups include a 3,5-dimethyl-4-hydroxyphenyl group, 3,5-diethyl-4-hydroxyphenyl group, 3,5-dipropyl-4-hydroxyphenyl group, 3-methyl-5-ethyl-4-hydroxyphenyl group, 3-methyl-5-propyl-4-hydroxyphenyl group and 2,3,5-trimethyl-4-hydroxyphenyl group. Since polyphenylene ether in which the number of terminal hydroxyl groups is less than 0.3 demonstrate decreased compatibility with styrene-based resins, defective appearance or layer separation of molded products may occur, and have increased susceptibility to decreases in rupture elongation and impact strength. In addition, there is also increased susceptibility to the poor color tone due to decreased thermal stability in a high-temperature atmosphere.

[0056]

Although a method for obtaining polyphenylene ether resin in which the number of terminal hydroxyl groups is 0.3 or more is also described in the above-mentioned Japanese Patent Publication

No. S61-20576, a polyphenylene ether resin in which the number of terminal hydroxyl groups is 0.3 or more can be obtained by deactivating a catalyst followed by stirring a polyphenylene ether solution in an atmosphere that avoids mixing with oxygen by a method consisting of, for example, carrying out an oxidative polymerization reaction on 2,6-dimethyl xylenol in the presence of oxygen in a solvent such as toluene while using a cuprous salt and an amine compound as catalysts, and adding a compound that forms a chelate compound with copper to the resulting polyphenylene ether solution.

Furthermore, the temperature of the solution during stirring is maintained at 50°C or higher and preferably at about 70°C. More preferably, the number of terminal hydroxyl groups is 0.4 groups to 2 groups per 100 phenylene ether units. If the number of terminal hydroxyl groups exceeds 2, strength and thermal stability decrease easily.

[0057]

The intrinsic viscosity of the polyphenylene ether resin at 30°C when measured in chloroform is preferably 0.3 dl/g to 0.6 dl/g. If the intrinsic viscosity is less than 0.3 dl/g, impact strength of the resin composition becomes inadequate, while if the intrinsic viscosity exceeds 0.6 dl/g, moldability becomes inadequate and the appearance of molded products may be poor. The intrinsic viscosity is more preferably 0.35 dl/g to 0.55 dl/g.

[0058]

Moreover, the copper content attributable to residual

catalyst of the polyphenylene ether resin used in the present invention is preferably 0.02 ppm to 0.2 ppm based on the weight of the polyphenylene ether resin. If the copper content exceeds 0.2 ppm, thermal stability decreases and there is increased susceptibility to the occurrence of defective appearance and decreased mechanical strength of molded products.

It is important to effectively remove the copper salt used for the catalyst of the oxidative polymerization reaction from the solution in order to make the copper content 0.2 ppm or less. Although not necessarily limited to the following method, the copper salt can be effectively removed by adding an aqueous solution of sodium ethylenediamine tetraacetate, which forms a chelate compound with copper, to the polyphenylene ether solution obtained by the oxidative polymerization reaction and stirring efficiently followed by effectively separating the aqueous solution from the polyphenylene ether solution. In general, repeating the stirring and separation procedures increases the effect of reducing the copper content of the polyphenylene ether. If these procedures are carried out inadequately, it is difficult to reduce the copper content of the polyphenylene ether even if the polyphenylene ether that has separated as a solid following addition of methanol and the like to the polyphenylene ether solution is adequately washed with methanol or water and the like.

The copper content of the polyphenylene ether is preferably 0.15 ppm or less.

[0059]

Examples of the styrene-based resin (B) used as one of the components in the present invention include copolymers of styrene-based monomers, copolymers of styrene-based monomers and other copolymerizable monomers, and styrene-based graft copolymers.

Examples of styrene-based monomers include styrene, α-methylstyrene and p-methylstyrene, with styrene being preferable. Examples of monomers copolymerizable with styrene-based monomers include cyanated vinyl monomers such as acrylonitrile or methacrylonitrile, (meth)acrylic acid alkyl ester monomers such as methyl acrylate, ethyl acrylate, propyl acrylate, methyl methacrylate or ethyl methacrylate, and monomers such as maleimide or N-phenylmaleimide, with cyanated vinyl monomers and (meth)acrylic acid alkyl ester monomers being preferable.

[0060]

Examples of copolymers of styrene-based monomers and other copolymerizable monomers include AS resin (acrylonitrile-styrene copolymer), while examples of styrene-based graft copolymers include HIPS resin (high impact polystyrene resin), ABS resin, AES resin (acrylonitrile/EPDM/styrene copolymer) and AAS resin (acrylonitrile/acrylonitrile rubber/styrene copolymer). Examples of methods for producing styrene-based copolymers include known methods such as emulsification polymerization, solution polymerization, suspension polymerization or bulk polymerization.

[0061]

The blended amount of the polystyrene-based resin pellets

is 5 parts by weight to 100 parts by weight, and preferably 5 parts by weight to 30 parts by weight, based on 100 parts by weight of the polyphenylene ether resin powder. If the blended amount of the polystyrene-based resin is less than 5 parts by weight, chemical resistance of the resin composition is inadequate, while if the blended amount exceeds 100 parts by weight, heat resistance and impact resistance decrease. The blended amount of the polystyrene-based resin pellets is more preferably 10 parts by weight to 50 parts by weight and particularly preferably 15 parts by weight to 45 parts by weight.

[0062]

Although a phosphorous-based flame retardant for imparting flame resistance is preferably added to the polyphenylene ether/polystyrene-based resin composition in the present invention, the method used to add the phosphorous-based flame retardant preferably consists of providing a pressure reduction vent 7 in the extruder, and supplying the phosphorous-based flame retardant from the second supply port 8 provided on the downstream side of the pressure reduction vent 7. Moreover, the phosphorous-based flame retardant is more preferably supplied by arranging the sealing ring 18 and a backward conveying screw or backward conveying kneading element on the screw 2 on the downstream side of the pressure reduction vent 7, and providing the second supply port 8 further downstream from the backward conveying screw or backward conveying kneading element.

[0063]

As a result of using such an addition method, the phosphorous-based flame retardant having a low melt viscosity can be prevented from undergoing phase separation from the polyphenylene ether resin. At this time, the viscosity of the phosphorous-based flame retardant when fed from the second supply port 8 is preferably that of a liquid state of 0.001 Pa·S to 3 Pa·s (pascal seconds, 1 centipoise to 3 centipoises). If the viscosity of the phosphorous-based flame retardant is excessively high, the feeding thereof becomes unstable thereby making uniform mixing difficult.

[0064]

Preferable examples of phosphorous-based flame retardants that can be used include phosphazene-based compounds, phosphate-based compounds and condensed phosphate esters.

Examples of phosphazene-based compounds include cyclic phenoxyphosphazene compounds, linear phenoxyphosphazene compounds and crosslinked phenoxyphosphazene compounds.

Examples of phosphate-based flame retardants include triphenyl phosphate, tricresyl phosphate, diphenyl-2-ethylcresyl phosphate, tri(isopropylphenyl) phosphate, diphenylcresyl phosphate and tributyl phosphate.

[0065]

Preferable examples of condensed phosphate ester-based flame retardants include phenyl resorcin polyphosphate, cresyl resorcin polyphosphate, phenyl cresyl resorcin polyphosphate, xylyl resorcin polyphosphate, phenyl p-tert-butylphenyl resorcin

polyphosphate, phenyl isopropylphenyl resorcin polyphosphate, cresyl xylyl resorcin polyphosphate, and phenyl isopropylphenyl diisopropylphenyl resorcin polyphosphate.

In addition, other preferable examples include phenyl bisphenol polyphosphate, cresyl bisphenol polyphosphate, phenyl cresyl bisphenol polyphosphate, xylyl bisphenol polyphosphate, phenyl p-tert-butylphenyl bisphenol polyphosphate, phenyl isopropylphenyl bisphenol polyphosphate, cresyl xylyl bisphenol polyphosphate and phenyl isopropylphenyl diisopropylphenyl bisphenol polyphosphate.

[0066]

Preferable examples of commercially available phosphorous-based flame retardants that can be used include “TPP” (triphenyl phosphate), “CR733S” (resorcinol bis(diphenylphosphate)), “CR741” (bisphenol A bis(diphenylphosphate)) and “PX200” (resorcinol bis(dixylenylphosphate)) manufactured by Daihachi Chemical Industry Co., Ltd.), and “ADK STB FP700” (bisphenol A bis(diphenylphosphate)) manufactured by Adeka Corp..

[0067]

In the present invention, other components can be added as necessary in addition to the above-mentioned components.

Examples of other components include weather resistance improvers, foaming agents, lubricants, fluidity improvers, impact resistance improvers, dyes, pigments, fillers, reinforcing materials and dispersants. Examples of fillers and reinforcing

materials include organic or inorganic fillers and organic or inorganic reinforcing materials, specific examples of which include glass fiber, mica, talc, wollastonite, potassium titanate, calcium carbonate and silica. Incorporation of fillers and reinforcing materials is effective for improving rigidity, heat resistance, dimensional accuracy and the like. The blending ratio of fillers and reinforcing materials is preferably 1 part by weight to 80 parts by weight and more preferably 5 parts by weight to 60 parts by weight based on 100 parts by weight of the total weight of the resin components.

[0068]

The resin composition pellet obtained according to the method of the present invention is used as a molded product by molding into an arbitrary shape by molding according to various molding methods typically used for modified polyphenylene ether resins, namely injection molding, injection compression molding, blow molding, extrusion molding, sheet molding, heat molding, rotational molding, laminating molding or press molding.

Examples of molded products include components of electrical and electronic devices, OA equipment, information terminal devices, mechanical parts, home appliances, vehicle parts, construction materials, various types of containers, recreational articles and general merchandise, and lighting equipment. Among these, molded products are used particularly preferably in components of electrical and electronic devices, OA equipment, information terminal devices, home appliances, vehicle parts and lighting

equipment.

EXAMPLE

[0069]

The following provides a more detailed explanation of the present invention by indicating examples thereof. However, the present invention is not limited to the following examples, but rather can be arbitrarily modified within a range that does not deviate from the gist thereof.

[0070]

Methods used to evaluate the polyphenylene ether resin in the following examples and comparative examples are as indicated below.

(1) Intrinsic Viscosity:

0.5 g of polyphenylene ether are dissolved in chloroform to bring to 100 ml or more (concentration of 0.5 g/dl or less) as solution followed by measuring specific viscosity at 30°C at a different concentration using an Ubbelohde viscometer and calculating the ratio between specific viscosity and concentration as intrinsic viscosity by extrapolating the temperature to 0.

[0071]

(2) Types and Numbers of Terminal Groups:

^{13}C-nuclear magnetic resonance spectrum was measured with the JNM-A400 manufactured by JEOL Ltd. using $CDCl_3$ as solvent, using tetramethylsilane as reference standard and using the ^{13}C-NMR complete decoupling mode for the measurement mode, followed by determining the types and numbers of terminal hydroxyl groups

(number per 100 groups) according to the method described in Macromolecules, 1990, Vol. 23, pp. 1318-1329.

(3) Copper Content:

Polyphenylene ether resin was decomposed with nitric acid followed by quantifying the copper in the residue by atomic absorption spectrophotometry and calculating the copper content (ppm) in the polyphenylene ether resin.

[0072]

(4) Residual Toluene Concentration:

2 g of polyphenylene ether resin were dissolved in 10 ml of chloroform followed by analyzing the supernatant resulting from precipitation with ethanol by gas chromatography to obtain the residual toluene concentration (%).

(5) Mean Particle Diameter and Particle Size Distribution:

Volume mean particle diameter was measured by a wet method and at a flow rate of 70% using a particle size analyzer based on the laser diffraction/scattering method in the form of the MT3300 particle size analyzer manufactured by Nikkiso Co., Ltd. and used as the value of mean particle diameter (μm), followed by confirming the maximum peak (μm) of the particle size distribution and the half width value (μm) of the maximum peak.

[0073]

In addition, measurement of color tone and glass transition temperature of pellets obtained in the examples and comparative examples was carried out in the manner described below.

(6) Color Tone:

The YI color tone value was determined with the Spectro Color Meter S2000 manufactured by Nippon Denshoku Industries Co., Ltd.

(7) Glass Transition Temperature (Tg):

Temperature was raised from 25°C to 250°C at the rate of 20°C/min using the DSC 220U thermal analyzer manufactured by Seiko Instruments Inc., followed by determination of glass transition temperature based on the point of backward curvature thereof.

[0074]

(8) Apparent Density

Apparent density was measured in compliance with JIS K5101 (bulk density).

(9) Viscosity of Phosphorous-Based Flame Retardant

Viscosity was measured in compliance with JIS K2283 using the TV-5NS constant-temperature liquid bath for measurement of kinematic viscosity manufactured by Thomas Kagaku Co., Ltd. Viscosity was measured while changing temperature and a viscosity curve was obtained from the values thereof. The temperature at which the phosphorous-based flame retardant is supplied to the extruder (set temperature) was then applied to the viscosity curve and used as the viscosity of the phosphorous-based flame retardant.

[0075]

[Polyphenylene Ether Production Example A (PPE-A)]

42.5 g of cuprous oxide, 255.7 g of a 47% aqueous solution of hydrogen bromide, 495.8 g of N,N-di-n-butylamine (DBA), 1257.6 g of N,N-dimethyl-n-butylamine (BD), 102.4 g of N,N'-di-t-butylethylenediamine (Dt), 30.0 g of trioctylmethyl

ammonium chloride (TOM) and 83.109 g of toluene were placed in a 30 liter reactor provided with a sparger for introducing oxygen-containing gas into the bottom of the reactor, and a reflux condenser equipped with a stirring vane, a baffle, and a decanter for separating condensed liquid in a vent gas line of the upper portion of the reactor in the bottom thereof to produce an initially charged liquid. Next, nitrogen was introduced into the gas phase portion of the reactor followed by controlling the absolute pressure of the gas phase portion of the reactor to 0.108 MPa.

[0076]

Continuing, gas prepared by diluting oxygen with nitrogen and having an absolute pressure of 0.108 MPa and oxygen concentration of 70% was introduced through the sparger, and the absolute pressure of the gas phase portion of the reactor was controlled by nitrogen and the above-mentioned gas to be maintained at 0.108 MPa with a control valve while introducing nitrogen into the gas phase portion of the reactor, including during the subsequent polymerization. The introduction rate of the above-mentioned gas was 103.5 Nl/min. Immediately after beginning introduction of the above-mentioned gas, a solution obtained by dissolving 33,000 g of 2,6-dimethylphenol in 31,707 g of toluene was begun to be added at a rate at which the entire amount is able to be finished being added within 30 minutes using a plunger pump. A heating medium was passed through a jacket to regulate the polymerization temperature so as to be held at 40°C.

At about 140 minutes after having begun introduction of gas,

in addition to introducing nitrogen instead of oxygen-containing gas, 15,000 g of a 5% aqueous solution of ethylenediamine tetraacetic acid sodium salt(tetrasodium EDTA) were added to the reactor and stirred. Subsequently, stirring was continued for 2 hours while controlling the temperature of the reaction solution at 70°C with the heating medium.

[0077]

After discontinuing stirring, the aqueous solution that separated as a result of being allowed to stand undisturbed was discharged outside the system. Further, 500 g of pure water was added to the reaction liquid, the resulting product was stirred for 10 minutes, and the aqueous layer that separated as a result of being allowed to stand undisturbed for 10 minutes was discharged outside the system.

Subsequently, a nearly equal volume of methanol was then added to the resulting reaction liquid to precipitate polyphenylene ether. The precipitated PPE was then filtered and the polyphenylene ether was washed twice with a suitable amount of methanol followed by forced air drying for 1 hour at about 140°C to obtain a powdered polyphenylene ether (to also be abbreviated as "PPE-A").

[0078]

The evaluation results of the resulting polyphenylene ether (PPE-A) were as indicated below.

Intrinsic viscosity: 0.48 dl/g

Number of terminal hydroxyl groups: 0.62 groups per 100 phenylene ether units

Copper content: 0.1 ppm

Mean particle diameter: 91 μm, particle size distribution peak: 79 μm, half width value: 110 μm

Residual toluene concentration: 0.14%

Apparent density: 0.49

[0079]

[Polyphenylene Ether Production Example B (PPE-B)]

The above-mentioned polyphenylene ether (PPE-A) was applied to a 160 mesh sieve to obtain a polyethylene ether powder that passed through the 160 mesh sieve (to also be abbreviated as "PPE-B").

Differences between this PPE-B and PPE-A were as indicated below.

Mean particle diameter: 55 μm, particle size distribution peak: 28 μm, half width value: 50 μm

[0080]

[Polyphenylene Ether Production Example C (PPE-C)]

The following polyphenylene ether powder (to also be abbreviated as "PPE-C") was obtained in the same manner as the above-mentioned polyphenylene ether production method A with the exception of washing with methanol only once.

Intrinsic viscosity: 0.48 dl/g

Number of terminal hydroxyl groups: 0.62 groups per 100 phenylene ether units

Copper content: 0.1 ppm

Mean particle diameter: 91 μm, particle size distribution peak: 76 μm, half width value: 105 μm

Residual toluene concentration: 0.63%

Apparent density: 0.49

[0081]

[Polyphenylene Ether Production Example D (PPE-D)]

A powdered polyphenylene ether powder (to also be abbreviated as "PPE-D") was obtained in the same manner as the above-mentioned polyphenylene ether production method A with the exception of not carrying out the washing procedure consisting of adding 7,500 g of pure water to the reaction liquid, stirring and separating. The evaluation results are shown below.

Intrinsic viscosity: 0.48 dl/g

Number of terminal hydroxyl groups: 0.59 groups per 100 phenylene ether units

Copper content: 0.5 ppm

Mean particle diameter: 93 μm, particle size distribution peak: 72 μm, half width value: 120 μm

Residual toluene concentration: 0.22%

Apparent density: 0.49

[0082]

[Polyphenylene Ether Production Example E (PPE-E)]

Two stages of condensers were connected in series to a polymerization reactor provided with an air blowing tube. Temperature was adjusted by allowing a coolant to flow through so that the temperature of the condensers was about 0°C, and the toluene phase of the bottoms product was made to continuously return to the polymerization reactor. Polymerization was carried out at 40°C

by dropping a solution obtained by dissolving 23,500 g of 2, 6-dimethylphenol in 54,000 g of toluene into a catalyst solution consisting of 220 g of cupric bromide, 4,000 g of dibutylamine and 98,000 g of toluene over the course of 60 minutes while supplying air at the rate of 10 NL/min per 1 kg of monomer.

An aqueous solution obtained by dissolving 1.5 times moles tetrasodium EDTA in catalyst copper (the amount of the aqueous solution was 0.2 times the total weight of polymerization reaction liquid) was added to the reaction liquid while stirring 120 minutes after dropping in the monomer to stop the reaction.

[0083]

After discontinuing stirring, the aqueous solution that separated as a result of being allowed to stand undisturbed was discharged outside the system. Further, 5,500 g of pure water was added to the reaction liquid, the resulting product was stirred for 10 minutes, and the aqueous layer that separated as a result of being allowed to stand undisturbed for 10 minutes was discharged outside the system. A similar procedure was then repeated. Namely, in the second procedure, an aqueous solution obtained by dissolving 0.5 times moles of tetrasodium EDTA in the catalyst copper used (0.2 times the total weight of the polymerization reaction liquid) was added to the reaction liquid while stirring, followed by standing undisturbed and separation.

Subsequently, 6,000 g of pure water were added to the reaction liquid in the same manner as previously described followed by stirring for 10 minutes and discharging the aqueous layer that

separated after being allowed to stand undisturbed for 10 minutes outside the system. A nearly equal volume of methanol was then added to the resulting reaction liquid to precipitate polyphenylene ether. The precipitate of PPE was then filtered and the polyphenylene ether was further washed with a suitable amount of methanol followed by forced air drying for more 1 hour at about 140°C to obtain the following powdered polyphenylene ether (to also be abbreviated as "PPE-E").

[0084]

Intrinsic viscosity: 0.48 dl/g

Number of terminal hydroxyl groups: 0.24 groups per 100 phenylene ether units

Copper content: 0.1 ppm

Mean particle diameter: 85 μm, particle size distribution peak: 68 μm, half width value: 90 μm

Residual toluene concentration: 0.23%

Apparent density: 0.49

[0085]

[Polyphenylene Ether Production Example F (PPE-F)]

The polyphenylene ether produced in the above-mentioned polyphenylene ether production method E was applied to a 50 mesh sieve and those particles of polyphenylene ether that remained on the sieve were gathered to obtain the following polyphenylene ether F (to also be abbreviated as "PPE-F").

Intrinsic viscosity: 0.48 dl/g

Number of terminal hydroxyl groups: 0.62 groups per 100

phenylene ether units

Copper content: 0.1 ppm

Mean particle diameter: 810 μm

Particle size distribution peak: 780 μm, half width value: 570 μm

Residual toluene concentration: 0.72%

Apparent density: 0.55

A list of analysis values of the PPE-A to PPE-F described above is shown in Table 1.

[0086]

[Table 1]

	Intrinsic viscosity	Terminal OH	Copper content	Mean particle diameter	Max. particle size distri-bution peak	Half width value	Residual toluene	Apparent density
	dl/g	number /100 units	ppm	μm	μm	μm	%	g/cc
PPE-A	0.48	0.62	0.1	91	79	110	0.14	0.49
PPE-B	0.48	0.62	0.1	55	28	50	0.14	0.49
PPE-C	0.48	0.62	0.1	91	76	105	0.63	0.49
PPE-D	0.48	0.59	0.5	93	72	120	0.22	0.49
PPE-E	0.48	0.24	0.1	85	68	90	0.23	0.49
PPE-F	0.48	0.62	0.1	810	780	570	0.72	0.55

[0087]

[Polystyrene-Based Resin Pellets]

The following polystyrene resin pellets were used.

Polystyrene A (abbreviated as "PS-A"):

Polystyrene HT478 manufactured by A&M Styrene Co., Ltd.

Mean pellet weight: 23 mg, mean particle diameter: 3.3 mm, apparent density: 0.62 g/cc

[0088]

Polystyrenes B to D (abbreviated as "PS-B", "PS-C" and "PS-D"):

The above-mentioned PS-A pellets were used after freezing and crushing, and the duration of freezing and crushing was adjusted to obtain the following PS-B to PS-D.

PS-B

Mean particle diameter: 1.2 mm, apparent density: 0.59 g/cc

PS-C

Mean particle diameter: 200 μm, apparent density: 0.56 g/cc

PS-D

Mean particle diameter: 80 μm, apparent density: 0.53 g/cc

[0089]

[Phosphorous-Based Flame Retardant]

The following phosphorous-based flame retardants were used.

Phosphorous-based flame retardant A: Triphenyl phosphate (Daihachi Chemical Industry Co., Ltd.)

Phosphorous-based flame retardant B: Aromatic condensed phosphate ester (CR733S, Daihachi Chemical Industry Co., Ltd.)

[0090]

(Example 1)

The screw configuration described in detail below was employed using an intermeshed co-rotating twin screw head extruder (TEX30α, Japan Steel Works Ltd.) having a cylinder length of 52.5 D (D represents the inner diameter of the cylinder).

a) Transporting zone: length 12.75 D (portion indicated with

a in FIG. 1), feed screw lead: 1.5 D

b) Mixing zone: length 3.0 D (portion indicated with b in FIG. 1), composed of a forward conveying kneading element 1D, a neutral kneading element 1D and a backward conveying kneading element 1D moving in the direction of feeding

c) Melting zone: length 25.75 D (portion indicated with c in FIG. 1)

Moreover, the melting zone contains a 0.5 D sealing ring 18 after a 19.5 D forward conveying screw.

Moreover, the pressure reduction vent 7 is provided between the mixing zone b and the sealing ring 18, and the degree of pressure reduction of the pressure reduction vent 7 was made to be -0.090 MPa.

The injection port 8 for injecting an additive such as a phosphorous-based flame retardant is provided between the sealing ring 18 and the die 6.

[0091]

100 parts by weight of PPE-A and 30 parts by weight of PS-A pellets were supplied to the hoppers 4 and 4' and extruded. The weighing feeders 5 and 5' were provided below the hoppers 4 and 4', and the materials were supplied quantitatively. An inert gas replacement tower having a height (H) of 2 m was installed below the weighing feeders 5 and 5', and nitrogen gas was fed into the resin supply unit 3 in the lower portion of the replacement tower from the inert gas supply tube 9 to reduce the oxygen concentration in the inert gas replacement tower (bottom of the replacement tower)

to 2.6%.

The inside of the inert gas replacement tower was filled with inert gas, and a structure was employed in which the PPE powder was treated with inert gas as a result of falling through the inert gas replacement tower.

[0092]

The set temperature of the cylinder was then set to 280°C, and the screw rotating speed was set to 150 rpm. Supplied amount was incrementally increased from 10 kg/hr at the rate of 10 kg/hr to determine the supplied amount at which feed neck occurs. The supplied amount at which feed neck occurred was 40 kg/hr. The supplied amount was then decreased to 30 kg/hr at which feed neck does not occur followed by extrusion of strands. The resin filling rate in the transporting zone a was 24.2%.

(Furthermore, the purpose of the inert gas replacement tower is to effectively replace oxygen in the PPE powder with inert gas. Since powders contain numerous microvoids, allowing the powder to fall through an inert gas atmosphere is considered to be an easy and effective method for replacing oxygen contained therein with inert gas.)

[0093]

Here, the filling rate of the transporting zone a was determined according to the method indicated below.

Transporting zone filling rate: Value obtained by dividing the volume of resin fed to the hopper (l/hr) by the theoretical transport volume of the screw (l/hr) (%)

Screw theoretical transport volume: (spatial area of cross-section of extruder cylinder - screw cross-sectional area in direction perpendicular to screw axis × 2) × screw lead length × screw rotating speed (/hr)

Here, the volume of resin fed to the hopper refers to the sum of the value (l/hr) obtained by dividing the weight of the fed polyphenylene ether resin powder (kg/hr) by the apparent density, and the value (l/hr) obtained by dividing the weight of the fed polystyrene-based resin (kg/hr) by the apparent density of PS.

[0094]

The extruded strands were cooled in a water bath and then cut into pellets. 0.4 seconds were required to place the extruded strands in the water bath.

(If 2 seconds or more are required for the strands to be placed in the water bath, oxidation caused by air progresses and causes the pellets to easily become yellowed. The time until cooling is preferably 1 second or less.)

The strands were cut by inserting into a pelletizer at 110°C. If the strand temperature exceeds 150°C, the strands wrap around the cutter thereby preventing the obtaining of a favorable pellets. In addition, if the strand temperature is below 90°C, problems such as cracking of the pellets occur during cutting thereby a decrease in appearance. Pellets cut at 110°C have an attractive cut surface and a favorable shape.

[0095]

The resulting pellets were dried for 4 hours at 120°C, and

a molded product measuring 100 mm × 100 mm × 2 mm was molded using the SH100 Injection Molding Machine manufactured by Sumitomo Heavy Industries, Ltd. under conditions of a cylinder temperature of 290°C and mold temperature of 100°C, followed by measuring the yellow index (YI) color tone value and glass transition temperature (Tg).

[0096]

The results of Example 1 are shown in the following Table 2.

In Table 2, the charged amount (kg/hr) refers to the sum of the polyphenylene ether resin powder and polystyrene-based resin fed to the base of the extruder. In addition, charged volume (l/hr) refers to the sum of values obtained by dividing the respective weights by the respective apparent densities. The symbols ⊗, O, Δ and × used to indicate overall evaluation were determined based on the criteria indicated below.

⊗: Feed neck discharge amount of 40 kg/hr or more and YI color tone value of less than 40

O: Feed neck discharge amount of 40 kg/hr or more and YI color tone value of 40 or more to less than 60

Δ: Feed neck discharge amount of 30 kg/hr or more to less than 40 kg/hr and YI color tone value of 40 or more to less than 60

×: YI color tone value of 60 or more

[0097]

(Example 2)

Molding was carried out in the same manner as Example 1 with

the exception of changing the tower height to 1.3 m. The results are shown in Table 2.

(Examples 3 to 6)

Molding was carried out in the same manner as Example 1 with the exception of changing the type and amount of polystyrene resin as shown in Table 2 and changing the supplied amount as shown in Table 2. The results are shown in Table 2.

[0098]

(Example 7)

Molding was carried out in the same manner as Example 1 with the exception of setting the degree of pressure reduction of the vent to -0.05 MPa. The results are shown in Table 2.

(Example 8)

Molding was carried out in the same manner as Example 1 with the exception of increasing the strand cooling distance and introducing the strands into the pelletizer at a strand temperature of 80°C. Cracks formed in the resulting pellets and the size of the pellets was uneven.

[0099]

(Example 9)

Pellets were produced in the same manner as Example 1 with the exception of reducing the amount of nitrogen fed to the bottom of the hoppers and maintaining the oxygen concentration at the bottom of the hoppers at 7.2%. The results are shown in Table 2.

(Comparative Example 8)

Pellets were produced in the same manner as Example 1 with

the exception of using PPE-B instead of PPE-A. Since feed neck occurred at 30 kg/hr, the charged amount was set to 20 kg/hr. The results are shown in Table 2.

[0100]

(Comparative Example 9)

Pellets were produced in the same manner as Example 1 with the exception of using PPE-C instead of PPE-A. Since feed neck occurred at 30 kg/hr, the charged amount was set to 20 kg/hr. The results are shown in Table 2.

(Comparative Examples 10-11)

Pellets were obtained in the same manner as Example 1 with the exception of using PPE-D and PPE-E shown in Table 2. The results are shown in Table 2.

[0101]

(Comparative Example 12)

Molding was carried out in the same manner as Example 1 with the exception of using PS-D shown in Table 2 and changing the supplied amount to the amount shown in Table 2. The results are shown in Table 2.

(Example 10)

a) Molding was carried out in the same manner as Example 1 with the exception of changing screw configuration A to screw configuration B in which the lead (screw pitch relative to cylinder inner diameter) of the forward conveying screw of the transporting zone was changed to that having a length of 1.0 D, and changing the degree of pressure reduction to that shown in Table 2. The

results are shown in Table 2.

[0102]

(Comparative Example 1)

Molding was carried out in the same manner as Example 1 with the exception of changing the height of the insert gas replacement tower to 50 cm. The results are shown in Table 2.

(Comparative Examples 2 and 3)

Pellets were produced in the same manner as Example 1 with the exception of lowering the amount of nitrogen fed to the bottom of the hoppers or interrupting the feed and maintaining the oxygen concentration at the bottom of the hoppers at 11% or 21%. The results are shown in Table 2.

(Comparative Example 4)

Pellets were produced in the same manner as Example 1 with the exception of not using polystyrene resin and maintaining the oxygen concentration at the bottom of the hoppers at 21%. The results are shown in Table 2.

(Comparative Example 5)

Pellets were produced in the same manner as Example 1 with the exception of using PPE-F instead of PPE-A. The results are shown in Table 2.

[0103]

[Table 2]

			Examples															Comparative Examples				
		Units	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	1	2	3	4	5
Raw materials (Weight parts)	PPE-A	Weight parts	100	100	100	100	100	100	100	100	100					100	100	100	100	100	100	
	PPE-B											100										
	PPE-C												100									
	PPE-D													100								
	PPE-E														100							
	PPE-F																					100
	PS-A		30	30	8	70			30	30	30	30	30	30	30		30	30	30	30		30
	PS-B						30															
	PS-C							30														
	PS-D															30						
Extrusion	Replacement tower oxygen conc.	%	2.6	3	2.6	2.6	2.6	2.6	2.6	2.6	7.2	2.6	2.6	2.6	2.6	2.6	2.6	2.6	11	21	21	2.6
	Tower height	m	2	1.3	2	2	2	2	2	2	2	2	2	2	2	2	2	0.5	2	2	2	2
	Screw config.		A	A	A	A	A	A	A	A	A	A	A	A	A	A	B	A	A	A	A	A
	Vent pressure reduction	MPa	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
	Feed neck supplied amount	Kg/hr	40	40	30	40	50	40	40	40	40	30	30	40	40	30	40	40	40	40	40	40
	Solid transport zone supplied amount	Kg/hr	30	30	20	30	40	30	30	30	30	20	20	30	30	20	30	30	30	30	30	30
		l/hr	58.3	58.3	40.2	55.9	58.8	59.4	58.3	58.3	58.3	38.9	38.9	58.3	58.3	38.9	58.3	58.3	58.3	58.3	61.2	53.1
	Solid transport zone filling rate	%	24.2	24.2	16.7	23.2	24.2	24.7	24.2	24.2	24.2	16.1	16.1	24.2	24.2	16.1	36.2	24.2	24.2	24.2	38.1	22
Evaluation	YI		39	42	56	17	43	44	43	39	54	49	51	52	51	50	46	60	61	65	85	61
	Tg	℃	184	184	197	155	184	184	184	184	184	184	184	184	184	184	184	184	184	184	210	184
	Overall evaluation		⊗	O	Δ	⊗	O	O	O	Δ	O	Δ	Δ	O	O	Δ	O	×	×	×	×	×

[0104]

(Examples 16 to 25 and Comparative Examples 6 and 7)

Pellets were produced in the same manner as Example 1 with the exception of using the raw materials containing phosphorous-based flame retardant shown in Table 3 in the amounts described in Table 3 and setting the oxygen concentration to the concentrations described in Table 3. Any of the following three addition methods indicated below were used to add the phosphorous-based flame retardant.

[0105]

Addition method A: A heated molten liquid was added from the supply port 8 provided downstream of a sealing ring. The liquid was heated to 70°C and a gear pump was used to supply the liquid. Viscosity of the phosphorous-based flame retardant A at 70°C was 0.006 Pa·s (6 centipoise), while the viscosity of the phosphorous-based flame retardant B at 70°C was 0.04 Pa·s (40 centipoise) as read from a viscosity curve.

Addition method B: Phosphorous-based flame retardant was added downstream of a sealing ring using a gear pump. The temperature of the liquid was 10°C. The viscosity of the phosphorous-based flame retardant at this time was 3.2 Pa·s (3200 centipoise).

Addition method C: Phosphorous-based flame retardant was added from the hopper side together with the resin raw materials in the form of a powder.

[0106]

The results are shown in Table 3.

In Table 3, the charged amount (kg/hr) refers to the sum of the PPE powder and PS fed from the base of the extruder. In addition, the charged volume (l/hr) refers to the sum of values (l/hr) obtained by dividing the respective weights by the respective apparent densities. In the case of feeding phosphorous-based flame retardant from the base of the extruder, the amount fed is the value obtained by adding the charged amount (kg/hr) and charged volume (l/hr) of the phosphorous-based flame retardant.

The symbols ⊗, O, Δ and × used to indicate overall evaluation were determined based on the criteria indicated below.

⊗: Feed neck discharge amount of 40 kg/hr or more and YI color tone value of less than 30

O: Feed neck discharge amount of 40 kg/hr or more and YI color tone value of 30 or more to less than 40

Δ: Feed neck discharge amount of 30 kg/hr or more to less than 40 kg/hr and YI color tone value of 30 or more to less than 40

×: YI color tone value of 40 or more

[0107]

[Table 3]

			Examples										Comparative Examples	
		Units	16	17	18	19	20	21	22	23	24	25	6	7
Raw Materials	PPE-A	Weight parts	100	100	100					100	100	100	100	100
	PPE-B					100								
	PPE-C						100							
	PPE-D							100						
	PPE-E								100					
	PS-A		30	30	30	30	30	30	30		30	30	30	30
	PS-D									30				
	P-based flame retardant A		10		10	10	10	10	10	10		10	10	10
	P-based flame retardant B			10							10			
Extrusion	P-based flame retardant addition method		A	A	A	A	A	A	A	A	B	C	A	A
	Replacement tower O_2 conc.	%	2.7	2.7	5.3	2.7	2.7	2.7	2.7	2.7	2.7	2.7	11	21
	Feed neck supplied amount	kg/hr	40	40	40	30	30	40	40	30	40	40	40	40
	Solid transporting zone supplied amount	kg/hr	30	30	30	20	20	30	30	20	30	30	30	30
		l/hr	58.3	58.3	58.3	38.9	38.9	58.3	58.3	38.9	58.3	57.2	58.3	58.3
	Solid transporting zone filling rate	%	24.2	24.2	24.2	16.1	16.1	24.2	24.2	16.1	24.2	23.7	24.2	24.2
Evaluation	YI color tone		29	28	34	37	36	35	37	38	32	36	47	52
	Tg	°C	173	169	173	173	173	173	173	173	172	178	173	173
	Overall evaluation		⊗	⊗	O	Δ	Δ	O	Δ	O	O	O	×	×
	P-based flame retardant residual rate	%	94	97	94	94	94	94	94	94	92	52	94	94

[0108]

On the basis of each of the examples, using a powder having a mean particle diameter of 50 μm to 600 μm, and allowing the powder to fall in a flowing state through an inert gas having an oxygen concentration of 10% or less over a distance of 1 m or more prior to introduction into the extruder was determined to make it possible to produce pellets having favorable color tone and free of decreases in physical properties at high production efficiency.

INDUSTRIAL APPLICABILITY

[0109]

According to the production method of polyphenylene ether-based resin composition pellets of the present invention, since pellets having favorable color tone and free of decreases in physical properties can be produced from a polyphenylene ether resin powder and a polystyrene-based resin raw material at high production efficiency, molded products of favorable quality can be obtained from the resulting pellets, and the molded products can be applied to a wide range of fields such as electrical and electronic devices, OA equipment, information terminal devices, home appliances, vehicle parts and lighting equipment, thereby demonstrating an extremely high level of industrial applicability.

REFERENCE SIGNS LIST

[0110]

1 Extruder cylinder

2 Screw

3 Supply port

4 Hopper

9 Inert gas injection port

CLAIMS

1. A production method for a pellet of a polyphenylene ether-based resin composition by melting and kneading a polyphenylene ether resin, a polystyrene-based resin which is used at 5 parts by weight to 100 parts by weight based on 100 parts by weight of the polyphenylene ether resin and, as necessary, an additive with an extruder, which comprises that,

1) a polyphenylene ether resin having an intrinsic viscosity of 0.3 dl/g to 0.6 dl/g, a number of terminal hydroxyl groups of 0.3 to 1.5 groups per 100 phenylene ether units, a residual toluene concentration of 0.05% by weight to 0.5% by weight, a copper content of 0.02 ppm to 0.2 ppm,

and a powder having a mean particle diameter of 50 μm to 600 μm, a maximum peak of particle size distribution of within the range of 30 μm to 300 μm, and a half width of the maximum peak of 500 μm or less, is used for the polyphenylene ether resin, and

2) the polyphenylene ether resin powder is treated with an inert gas by allowing the powder to flow down in a flowing state over a distance of 1 m or more through an inert gas having an oxygen concentration of 10% or less before introducing the powder into the extruder,

wherein a pellet having a mean particle diameter of 1 mm to 5 mm and an apparent density of 110% to 140% with respect to the apparent density of the polyphenylene ether resin powder is used for the polystyrene-based resin, and

wherein the polyphenylene ether resin powder and the polystyrene-based resin pellet are supplied to the extruder by adjusting the blending ratio thereof using separate quantitative feeders, and the gaseous oxygen concentration in a supply unit of the extruder is held to 10% or less.

2. The production method for molded article of a polyphenylene ether-based resin composition according to claim 1, wherein the filling ratio of the polyphenylene ether resin and the polystyrene-based resin in a solid transporting zone of the extruder is maintained at 30% or less.

3. The production method for molded article of a polyphenylene ether-based resin composition according to claim 1 or 2, wherein a vent-type extruder is used for the extruder, and extruding is carried out by forming gas sealing portions using molten resin in a screw on an upstream side and a downstream side of a vent port.

4. The production method for molded article of a polyphenylene ether-based resin composition according to claim 3, wherein the extruder is a vent-type extruder, and the degree of pressure reduction of a pressure reduction vent thereof is -0.099 MPa to -0.06 MPa.

5. The production method for molded article of a polyphenylene ether-based resin composition according to any of claims 1 to 4, wherein a phosphorous-based flame retardant is added as the additive.

6. The production method for molded article of a polyphenylene

ether-based resin composition according to claim 5, wherein the phosphorous-based flame retardant is supplied further downstream from a gas sealing portion downstream of a vent port.

7. The production method for molded article of a polyphenylene ether-based resin composition according to claim 6, wherein the phosphorous-based flame retardant is supplied downstream of the pressure reduction vent in a liquid state having a viscosity of 0.001 Pa·s to 3 Pa·s.

8. The production method for molded article of a polyphenylene ether-based resin composition according to any of claims 1 to 7, wherein the polyphenylene ether-based resin composition is extruded from the extruder in the form of strands, and the strands are cooled by being introduced into cooling water within 2 seconds after coming out of the extruder.

9. The production method for molded article of a polyphenylene ether-based resin composition according to claim 8, wherein the strand temperature is adjusted to 90°C to 150°C by cooling, and the strands are cut in this temperature range.