

DESCRIPTION

DEVOLATILIZING EXTRUDER, AND DEVOLATILIZING EXTRUSION
METHOD OF POLYMER COMPOSITION USING THE SAME AND METHOD OF
5 PRODUCING METHACRYLIC POLYMER

Technical Field

[0001]

The present invention relates to a devolatilizing
extruder to be used in a production of a methacrylic
10 polymer, and a method for devolatilizing extrusion of a
polymer composition using the same, and a method for
producing a methacrylic polymer.

Background Art

[0002]

15 There have been known, as a method for producing a
polymer such as a methacrylic polymer, methods in which a
polymer composition containing a methacrylic polymer and a
volatile component is obtained by a solution polymerization
method or a bulk polymerization method, and then the
20 obtained polymer composition is supplied to a screw type
devolatilizing extruder to remove a volatile component,
thus obtaining a methacrylic polymer (see, for example,
Patent Documents 1 and 2).

[0003]

25 A screw inserted into a devolatilizing extruder used

in the aforementioned method is supported by a shaft seal bearing portion of a devolatilizing extruder, and a shaft seal portion is provided around a screw in the shaft seal bearing portion. Various types of seal structures are known as a seal structure that forms this shaft seal portion, and a mechanical seal is known as one of typical seal structures.

Prior Art Documents

Patent Documents

10 [0004]

Patent Document 1: JP-A-3-49925

Patent Document 2: JP-A-2003-96105

Disclosure of the Invention

15 Problems to be Solved by the Invention

[0005]

In a mechanical seal, a mechanical seal liquid is used as a lubricating liquid of a sealing face. Therefore, a conventional devolatilizing extruder using the mechanical seal had a problem that a part of the mechanical seal liquid leaks out through a shaft seal portion when an operation is continuously carried out over a long period and thus a polymer composition and a methacrylic polymer to be produced may be contaminated. When the polymer composition and the methacrylic polymer to be produced are

20

25

contaminated, there arises a problem that transparency of a methacrylic polymer deteriorates and the methacrylic polymer is likely to be colored during molding.

[0006]

5 In light of the problems of the prior art, the present invention has been made and an object thereof is to provide a devolatilizing extruder that can suppress contamination of a polymer composition and a methacrylic polymer to be produced, and a method for devolatilizing
10 extrusion of a polymer composition using the same, and a method for producing a methacrylic polymer.

Means for Solving the Problems

[0007]

 In order to achieve the aforementioned object, the
15 present invention provides a devolatilizing extruder for producing a methacrylic polymer, including a cylinder that includes a polymer composition supply port, a gas discharge port, a polymer outlet and a through-hole; a rotatable screw inserted into the cylinder through the through-hole;
20 and a shaft seal bearing portion that supports a shaft portion of the screw extending from the through-hole to the outside of the cylinder; wherein the shaft seal portion of the shaft seal bearing portion is formed of a mechanical seal using at least one kind selected from the group
25 consisting of an adipate ester, a phthalate ester, a

diisobutyrate ester and acetylated glyceride as a mechanical seal liquid.

[0008]

At least one kind selected from the group consisting of an adipate ester, a phthalate ester, a diisobutyrate ester and acetylated glyceride, used as the aforementioned mechanical seal liquid, has a property of being less likely to exert an adverse influence such as deterioration of transparency of a methacrylic polymer or coloration during molding even if mixed in a polymer composition. Therefore, in the aforementioned devolatilizing extruder, since a shaft seal portion is formed of a mechanical seal and also at least one kind selected from the group consisting of an adipate ester, a phthalate ester, a diisobutyrate ester and acetylated glyceride is used as a mechanical seal liquid, it is possible to suppress contamination of a polymer composition and a methacrylic polymer to be produced even if the mechanical seal liquid leaks out into a cylinder by a continuous operation over a long period. Accordingly, according to the aforementioned devolatilizing extruder, it is possible to efficiently produce a methacrylic polymer whose contamination has been suppressed even if an operation is continuously carried out over a long period.

[0009]

The present invention also provides a method for

devolatilizing extrusion of a polymer composition, which includes supplying a polymer composition containing a methacrylic polymer and a volatile component into the cylinder through the polymer composition supply port in the devolatilizing extruder of the present invention; and then discharging the volatile component through the gas discharge port and discharging a methacrylic polymer after devolatilization through the polymer outlet, respectively.

[0010]

According to such the devolatilizing extrusion method, since the aforementioned devolatilizing extruder of the present invention is used, contamination of a polymer composition and a methacrylic polymer to be produced can be suppressed. Therefore, according to the aforementioned devolatilizing extrusion method, it is possible to efficiently produce a methacrylic polymer whose contamination has been suppressed even if an operation is continuously carried out over a long period.

[0011]

The present invention further provides a method for producing a methacrylic polymer, which include the steps of continuously supplying a raw material that contains a monomer component containing a methacrylic monomer as a main component, a radical polymerization initiator and a chain transfer agent into a polymerization reaction vessel;

polymerizing the monomer component in the polymerization
reaction vessel to obtain a polymer composition that
contains a methacrylic polymer and a volatile component
containing an unreacted monomer; and supplying the polymer
5 composition into the cylinder through the polymer
composition supply port in the devolatilizing extruder
according to claim 1, and then discharging the volatile
component through the gas discharge port and discharging a
methacrylic polymer after devolatilization through the
10 polymer outlet, respectively.

[0012]

According to such the methacrylic a method for
producing a polymer, since the aforementioned
devolatilizing extruder of the present invention is used,
15 contamination of a polymer composition and a methacrylic
polymer to be produced can be suppressed. Therefore,
according to the aforementioned devolatilizing extrusion
method, it is possible to efficiency produce a methacrylic
polymer whose contamination has been suppressed even if an
20 operation is continuously carried out over a long period.

Effects of the Invention

[0013]

According to the present invention, it is possible to
provide a devolatilizing extruder that can suppress
25 contamination of a polymer composition and a methacrylic

polymer to be produced, and a method for devolatilizing
extrusion of a polymer composition using the same, and a
method for producing a methacrylic polymer.

Brief Description of the Drawings

5 [0014]

Fig. 1 is a schematic view showing an internal
structure of a devolatilizing extruder according to
preferred embodiment of the present invention.

Fig. 2 is a partial sectional view of a shaft seal
10 bearing portion of a devolatilizing extruder according to
preferred embodiment of the present invention.

Fig. 3 is a schematic block diagram showing a
production system of a methacrylic polymer using a
devolatilizing extruder of the present invention.

15 Mode for Carrying Out the Invention

[0015]

Preferred embodiments of the present invention will
be described in detail with reference to the accompanying
drawings. The same numerals are used for the same or
20 identical portions in the drawings, and repetitive
descriptions are omitted. Also, dimensional ratios of the
drawings are not limited to the illustrated ratios.

[0016]

Fig. 1 is a schematic view showing an internal
25 structure of a devolatilizing extruder according to

preferred embodiment of the present invention. As shown in Fig. 1, a devolatilizing extruder 100 is provided with a cylinder 10 including a polymer composition supply port 12 for supplying a polymer composition containing a methacrylic polymer and a volatile component, a gas discharge port 14 for discharging a volatile component, a polymer outlet 16 for discharging a methacrylic polymer after devolatilization, and a through-hole 18; a rotatable screw 20 inserted into the cylinder 10 through the through-hole 18; and a shaft seal bearing portion 30 that supports a shaft portion 20a of the screw 20 extending from the through-hole 18 to the outside of the cylinder 10. The cylinder 10 is provided with four gas discharge ports 14, and one gas discharge port (back vent) 14a is provided at the side of the shaft seal bearing portion 30 when viewed from the polymer composition supply port 12, and three gas discharge ports (fore vents) 14b, 14c, 14d are respectively provided at the side of the polymer outlet 16. The shaft seal bearing portion 30 includes a shaft seal portion 32.

[0017]

Fig. 2 is a partial sectional view of a shaft seal bearing portion of a devolatilizing extruder according to preferred embodiment of the present invention. As shown in Fig. 2, a shaft seal portion 32 is formed of a mechanical seal. A driving device (not shown) for rotationally

driving the screw 20 is provided on the opposite side of the shaft seal portion 32.

[0018]

There is no particular limitation on the type of the mechanical seal that form the shaft seal portion 32, and a known type mechanical seal can be used. For example, as shown in Fig. 2, the mechanical seal includes a rotating ring 32a fixed on the side of a screw 20 and a fixed ring 32b fixed on the side of a shaft seal bearing portion body (casing), and is constituted so that the rotating ring 32a and the fixed ring 32b are pressed by a given force using a spring (not shown) or the like and thus they tightly adhere to each other. In order to decrease friction of a contact surface between the rotating ring 32a and the fixed ring 32b, a mechanical seal liquid 32c is filled into the mechanical seal 32. In Fig. 2, a constitution of a mechanical seal including two pair of combinations of the rotating ring 32a and the fixed ring 32b, namely, a double mechanical seal is shown. Usually, the mechanical seal liquid 32c is continuously supplied through a mechanical seal liquid introduction port (not shown) using a pump or the like, and then continuously discharged through a mechanical seal liquid discharge port (not shown). It is preferred that the mechanical seal liquid is circulatorily supplied. The filling pressure is appropriately set

according to the size, extrusion conditions and the like of the devolatilizing extruder, and is set to a pressure higher than that of the gas discharge port 14a of the devolatilizing extruder 100. Since the devolatilizing
5 extruder is provided with a pressure gauge and a safety valve according to a maximum working pressure, the filling pressure is adjusted so that the safety valve does not operate.

[0019]

10 As the mechanical seal liquid 32c, at least one kind selected from the group consisting of an adipate ester, a phthalate ester, a diisobutyrate ester and acetylated glyceride is used. Examples of the adipate ester include
15 bis(2-ethylhexyl) adipate, diisononyl adipate, diisodecyl adipate and the like. Examples of the phthalate ester include bis(2-ethylhexyl) phthalate, diisononyl phthalate, diisodecyl phthalate and the like. Examples of the diisobutyrate ester include 2,2,4-trimethyl-1,3-pentanediol diisobutyrate and the like. Examples of the acetylated
20 glyceride include glycerin diacetomonolaurate, glycerin diacetomonostearate, glycerin diacetomonooleate, glycerin diacetomonolinoleate, glycerin diacetomono 12-hydroxystearate, glycerin diacetomonomyristate, glycerin diacetomonopalmitate, glycerin monoacetomonostearate,
25 glycerin monoacetomonomyristate, glycerin

monoacetomonopalminate, glycerin monoacetomonoricinoleate,
glycerin monoacetomono 12-hydroxystearate, glycerin
monoacetomonobehenate, glycerin monoacetomonooleate,
glycerin monoacetomonolaurate, glycerin monoacetodioleate,
5 glycerin monoacetodiricinoleate, glycerin
monoacetodicaprylate, glycerin monoacetodilaurate, glycerin
monoacetodistearate and the like. Among these, an adipate
ester and a diisobutyrate ester are preferred, and an
adipate ester is particularly preferred. The adipate ester,
10 phthalate ester, diisobutyrate ester and acetylated
glyceride have a merit that they do not accelerate a
polymerization reaction of a monomer containing an
unreacted methacrylic monomer as a main component even if
mixed in a polymer composition, and are also less likely to
15 cause an adverse influence such as coloration of the
obtained methacrylic polymer.

[0020]

There is no particular limitation on the material of
the rotating ring 32a and the fixed ring 32b, and these
20 rings may be constituted from a known material. Examples
of the material of the rotating ring 32a and the fixed ring
32b include carbon, silicon carbide, cemented carbide,
chromium oxide coating and the like.

[0021]

25 In the devolatilizing extruder 100, a polymer

composition is supplied through a polymer composition supply port 12. At this time, the liquid polymer composition is converted into a vapor mist by adjusting the pressure in the vicinity of the polymer composition supply port 12 and at least a part of the volatile component contained in the polymer composition is discharged through gas discharge ports 14a, 14b close to the polymer composition supply port 12. The polymer composition goes forward to the side of the polymer outlet 16 by rotation of the screw 20 and most of the volatile component contained in the polymer composition is vaporized until the polymer composition reaches the polymer outlet 16, and then is discharged through gas discharge ports 14b, 14c, 14d. In addition to the unreacted monomer, a solvent and additives used optionally and a volatile by-product produced during the polymerization process are contained in the volatile component that is discharged through the gas discharge port 14. Thus, it is possible to obtain a methacrylic polymer after devolatilization, in which most of the volatile component has been removed, through the polymer outlet 16. The methacrylic polymer can be obtained, for example, in a state of pellets.

[0022]

The aforementioned devolatilizing extruder 100 can be suitably used to produce a methacrylic polymer that is

obtained by polymerizing a monomer mixture containing methyl methacrylate as a main component among methacrylic polymers.

[0023]

5 In the devolatilizing extruder 100, there is no particular limitation on the number of gas discharge ports 14 formed in the cylinder 10. While the constriction in which four gas discharge ports 14 are provided was described in Fig. 1, the number of gas discharge ports 14
10 may be from 1 to 3, or 5 or more. From the viewpoint of efficiently discharging the volatile component in the polymer composition, the cylinder 10 preferably includes one or more of gas discharge ports (back vents) provided between the polymer composition supply port 12 and the
15 shaft seal bearing portion 30, and one or more of gas discharge ports (fore vents) provided between the polymer composition supply port 12 and the polymer outlet 16, and more preferably one back vent and one to three fore vent.

[0024]

20 There is no particular limitation on the number of screws 20 used in the devolatilizing extruder 100. The number of screws is preferably one to two, and more preferably two. A twin-screw devolatilizing extruder including two screws 20 is preferred since a methacrylic
25 polymer can be efficiently produced. There is no

particular limitation on the diameter of the screw 20, and is usually from $\phi 100$ to 450 mm.

[0025]

5 The method for devolatilizing extrusion of a polymer composition and the method for producing a methacrylic polymer of the present invention will be described below.

[0026]

10 The method for producing a methacrylic polymer of the present invention is a method comprising: a step of continuously supplying a raw material containing a monomer component containing as a main component a methacrylic monomer, a radical polymerization initiator and a chain transfer agent into a polymerization reaction vessel; a step of polymerizing the monomer component in the
15 polymerization reaction vessel to obtain a polymer composition containing a methacrylic polymer and a volatile component containing an unreacted monomer; and a step of supplying the polymer composition into a cylinder through a polymer composition supply port in the devolatilizing
20 extruder of the present invention to discharge the volatile component through the gas discharge port and to discharge the methacrylic polymer after devolatilization through a polymer outlet , respectively. The respective steps will be described in detail below.

25 [0027]

Fig. 3 is a schematic block diagram showing a production system of a methacrylic polymer. As shown in Fig. 3, first, an initiator composition and a monomer composition are blended in an initiator blending vessel 101 and a monomer blending vessel 102, respectively. The initiator composition is prepared by mixing a radical polymerization initiator, a monomer component containing as a main component a methacrylic monomer and a chain transfer agent. The monomer composition is prepared by mixing a monomer and a chain transfer agent. Then, the blended initiator composition and monomer composition are continuously supplied to a polymerization reaction vessel 103, where a polymerization reaction is carried out.

[0028]

Herein, the monomer component containing as a main component a methacrylic monomer, the radical polymerization initiator and the chain transfer agent are selected according to a methacrylic polymer to be produced. Each component will be described below as preferred embodiment. In the present description, "(meth)acryl" means "acryl" and "methacryl" corresponding thereto.

[0029]

The monomer component containing a methacrylic monomer as a main component is a methacrylic monomer alone, or a mixture of a methacrylic monomer and the other monomer

that is copolymerizable with the methacrylic monomer. When the monomer other than the methacrylic monomer is mixed, the content of the methacrylic monomer is 50% by mass or more, and preferably 75% by mass or more, based on the entire monomer amount.

[0030]

There is no particular limitation on the methacrylic monomer, and examples thereof include alkyl methacrylate (an alkyl group has 1 to 4 carbon atoms). Examples of the alkyl of the alkyl methacrylate (an alkyl group has 1 to 4 carbon atoms) include methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl and the like and, among alkyl methacrylates, methyl methacrylate is preferred. These methacrylic monomers can be used alone, or two or more kinds of them can be used in combination. When two or more kinds of them are used in combination, the monomer component containing the methacrylic monomer as a main component is a mixture of two or more kinds of methacrylic monomers, or a mixture of two or more kinds of methacrylic monomers and the other monomer that is copolymerizable with the methacrylic monomer. When two or more kinds of methacrylic monomers are mixed with the other monomer that is copolymerizable with the methacrylic monomer, the total content of two or more kinds of methacrylic monomers is 50% by mass or more, and preferably 75% by mass or more, based

on the entire monomer amount.

[0031]

Examples of the other monomer, which can be used in combination with the methacrylic monomer, include other vinyl monomer that is copolymerizable with the methacrylic monomer. Examples of the other vinyl monomer include alkyl acrylates having an alkyl group of 1 to 18 carbon atoms, such as methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate and stearyl acrylate; unsaturated carboxylic acids and acid anhydrides thereof, such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, maleic anhydride and itaconic anhydride; hydroxyl group-containing monomers such as 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, monoglycerol acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate and monoglycerol methacrylate; nitrogen-containing monomers such as acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, diacetoneacrylamide and dimethylaminoethyl methacrylate; epoxy group-containing monomers such as allyl glycidyl ether, glycidyl acrylate and glycidyl methacrylate; and styrenic monomers such as styrene and α -methylstyrene.

[0032]

In the present invention, examples of the polymerization initiator to be supplied to a reaction

vessel include a radical polymerization initiator.

Examples of the radical polymerization initiator include
azo compounds such as azobisisobutyronitrile,
azobisdimethylvaleronitrile, azobiscyclohexanenitrile,
5 1,1'-azobis(1-acetoxy-1-phenylethane), dimethyl 2,2'-
azobisisobutylate and 4,4'-azobis-4-cyanovaleric acid; and
organic peroxides such as benzoyl peroxide, lauroyl
peroxide, acetyl peroxide, capryl peroxide, 2,4-
dichlorobenzoyl peroxide, isobutyl peroxide,
10 acetylcyclohexylsulfonyl peroxide, t-butyl peroxy-pivalate,
t-butylperoxy-2-ethyl hexanoate, 1,1-di-t-
butylperoxycyclohexane, 1,1-di-t-butylperoxy-3,3,5-
trimethylcyclohexane, 1,1-di-t-hexylperoxy-3,3,5-
trimethylcyclohexane, isopropyl peroxydicarbonate, isobutyl
15 peroxydicarbonate, s-butyl peroxydicarbonate, n-butyl
peroxydicarbonate, 2-ethylhexyl peroxydicarbonate, bis(4-t-
butylcyclohexyl) peroxydicarbonate, t-amylperoxy-2-ethyl
hexanoate, 1,1,3,3-tetramethylbutyl peroxy-ethyl hexanoate,
1,1,2-trimethylpropyl peroxy-2-ethylhexanoate, t-butyl
20 peroxyisopropyl monocarbonate, t-amyl peroxyisopropyl
monocarbonate, t-butyl peroxy-2-ethyl hexylcarbonate, t-
butyl peroxyallyl carbonate, t-butyl peroxyisopropyl
carbonate, 1,1,3,3-tetramethylbutyl peroxyisopropyl
monocarbonate, 1,1,2-trimethylpropyl peroxyisopropyl
25 monocarbonate, 1,1,3,3-tetramethylbutyl peroxyisononanoate,

1,1,2-trimethylpropyl peroxyisononanoate and t-butyl peroxybenzoate. These polymerization initiators may be used alone, or a mixture of two or more kinds may be used.
[0033]

5 There is no particular limitation on the blend amount of the radical polymerization initiator, and the blend amount is usually from 0.001 to 1 part by mass based on 100 parts by mass of the monomer component as a raw material. When a mixture of two or more kinds of radical
10 polymerization initiators is used, the total used amount may be within this range. The polymerization initiator supplied into the reaction vessel is selected according to the methacrylic polymer to be produced and the kind of a raw monomer component used and is not particularly limited
15 in the present invention. For example, the radical polymerization initiator is preferably a radical polymerization initiator in which a half-life at a polymerization temperature is within 1 minute. When the half-life at the polymerization temperature is more than 1
20 minute, the reaction rate decreased, and thus the radical polymerization initiator may be unsuited for the polymerization reaction in a continuous polymerization device. A relationship between the temperature of the radical polymerization initiator and the half-life is
25 described in various documents and technical data of

manufacturers for each kind of the radical polymerization initiator. In the present invention, values described in a known products catalog of Wako Pure Chemical Industries, Ltd., KAYAKU AKZO CO., LTD. or the like were used.

5 [0034]

In the present invention, a chain transfer agent can be blended in a reaction vessel so as to adjust the molecular weight of the methacrylic polymer to be produced. The chain transfer agent may be either a monofunctional or
10 polyfunctional chain transfer agent. Specific examples thereof include alkylmercaptans such as propylmercaptan, butylmercaptan, hexylmercaptan, octylmercaptan, 2-ethylhexylmercaptan and dodecylmercaptan; aromatic mercaptans such as phenylmercaptan and thiocresol;
15 mercaptans having not more than 18 carbon atoms, such as ethylene thioglycol; polyhydric alcohols such as ethylene glycol, neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol and sorbitol; those obtained by esterifying a hydroxyl group
20 with thioglycolic acid or 3-mercaptopropionic acid, 1,4-dihydronaphthalene, 1,4,5,8-tetrahydronaphthalene, β -terpinene, terpinolene, 1,4-cyclohexadiene, hydrogen sulfide and the like. These chain transfer agents may be used alone, or two or more kinds may be used in combination.

25 [0035]

Since the blend amount of the chain transfer agent varies depending on the kind of the chain transfer agent used and the like, there is no particular limitation on the blend amount. For example, when mercaptans are used, the
5 blend amount is preferably from 0.01 to 3 parts by mass, and more preferably from 0.05 to 1 part by mass, based on 100 parts by mass of the monomer component as a raw material. The use amount within this range is preferred since thermostability is satisfactorily maintained without
10 impairing mechanical properties of the methacrylic polymer. When two or more kinds of chain transfer agents are used in combination, the total use amount may be adjusted within this range.

[0036]

15 A polymerization reaction vessel 103 used in the present embodiment is a vessel type reactor equipped with a stirrer. The stirrer enables a solution in a vessel to convert into a substantially completely mixed state. It is possible to use, as a stirring impeller, a Maxblend
20 impeller manufactured by Sumitomo Heavy Industries, Ltd., a paddle impeller, a double helical ribbon impeller, an MIG impeller, a full zone impeller manufactured by Shinko Pantech Co Ltd. and the like, however, there is no particular limitation. It is preferred to attach a baffle
25 so as to increase the stirring effect.

[0037]

As a matter of course, it is preferred that the stirring efficiency is as high as possible. The stirring power that is more than the necessity is not preferred since only surplus heat is applied to a reaction vessel. Therefore, the stirring power is from 0.5 to 20 kW/m³, and preferably from 1 to 15 kW/m³. It is necessary that this stirring power is increased as the viscosity of a content liquid, namely, the content of the polymer becomes larger.

10 [0038]

The polymerization reaction vessel 103 is preferably in a state of being filled with a liquid, which is substantially free from a vapor phase. When the polymerization reaction vessel is in a state of being filled with a liquid, adhesion and production of the polymer on a vapor phase portion and a vessel inner wall face as a gas-liquid interface are suppressed, and thus deterioration in quality due to mixing of them in the product can be suppressed. Moreover, since the entire volume of the polymerization reaction vessel 103 can be effectively utilized, productivity can be improved.

[0039]

In order to fill the polymerization reaction vessel 103 with a liquid, it is most simple to dispose an outlet of a solution in a vessel on the top portion of a reaction

vessel. In this case, a supply port of a raw material (an initiator composition and a monomer composition) is preferably provided at the lower portion of the polymerization reaction vessel 103. It is desired to prevent a gas of a monomer from generating in the polymerization reaction vessel 103. For that purpose, it is preferred to adjust the pressure in the vessel to a vapor pressure or more at a temperature of a content liquid. This pressure is generally from about 10 to 20 kg/cm².

10 [0040]

The interior of the polymerization reaction vessel 103 is preferably in an insulated state that is substantially free from inflow/outflow of heat from the outside. Namely, it is preferred to adjust the temperature in the reaction vessel and the temperature on the side of the reaction vessel outer wall face to about the same temperature. Specifically, a jacket is disposed, for example, at the side of the reaction vessel outer wall face and the temperature of the reaction vessel outer wall is allowed to follow the temperature in the reaction vessel using steam, other heat medium or the like, and thus nearly the same temperature can be achieved.

[0041]

The polymerization reaction vessel 103 is kept in an insulated state since a formation of a polymer on the

reaction vessel inner wall face can be prevented and self-controllability of being capable of suppressing a runaway reaction by stabilizing the polymerization reaction is imparted. It is not preferred to adjust the temperature of the reaction vessel inner wall face to a temperature that is excessively higher than that of the content liquid since surplus heat is applied to the interior of the reaction vessel. It is preferred that a temperature difference between the interior of the reaction vessel and the reaction vessel outer wall is as small as possible. However, the temperature may be actually adjusted to a variation within a range of about $\pm 5^{\circ}\text{C}$.

[0042]

In the present embodiment, heat generated in the polymerization reaction vessel 103, namely, polymerization heat and stirring heat is preferably well-balanced with quantity of heat taken by a liquid (syrup-like) polymer composition that is discharged from the polymerization reaction vessel 103. Quantity of heat taken by the polymer composition is determined by the amount, specific heat and temperature (polymerization temperature) of the polymer composition.

[0043]

The polymerization temperature varies depending on the kind of the radical polymerization initiator used and

is preferably from about 120 to 180°C, and more preferably from 130 to 180°C. When this temperature is too high, the obtained methacrylic polymer exhibits low syndiotacticity, and thus the amount of oligomer produced may increase and heat resistance of the resin may deteriorate.

[0044]

The average residence time in the polymerization reaction vessel 103 is preferably not less than 15 minutes nor more than 2 hours, and more preferably not less than 20 minutes nor more than 1.5 hours. When the average residence time is longer than the necessity, the amount of an oligomer such as dimer or trimer produced increases and thus heat resistance of the product may deteriorate. The average residence time can be adjusted by changing the supply amount of the monomer per unit time.

[0045]

It is possible to use, as the initiator blending vessel 101 and the monomer blending vessel 102 used in the present embodiment, a blending vessel equipped with the same stirrer as that of the aforementioned polymerization reaction vessel 103. In the initiator blending vessel 101, a radical polymerization initiator is completely dissolved in a monomer to obtain an initiator solution. The temperature in the initiator blending vessel 101 is maintained at a temperature at which a polymerization

reaction does not proceed, and preferably maintained at -20 to 10°C. In contrast, the temperature in the monomer blending vessel 102 is maintained at a temperature at which the monomer is not volatilized, and is preferably maintained at -20 to 10°C. An initiator composition and a monomer composition as raw materials of the methacrylic polymer are continuously supplied into the polymerization reaction vessel 103 from the initiator blending vessel 101 and the monomer blending vessel 102 by a pump or the like.

10 [0046]

The amount of the initiator composition supplied from the initiator blending vessel 101 to the polymerization reaction vessel 103 varies depending on the capacity or the like of the polymerization reaction vessel 103 and the amount is, for example, preferably from 0.1 to 10 kg/hr, and more preferably from 0.5 to 5 kg/hr, when the capacity of the polymerization reaction vessel 103 is 10 L. The amount of the monomer composition supplied from the monomer blending vessel 102 to the polymerization reaction vessel 103 varies depending on the capacity or the like of the polymerization reaction vessel 103 and the amount is, for example, preferably from 4 to 40 kg/hr, and more preferably from 10 to 30 kg/hr, when the capacity of the polymerization reaction vessel 103 is 10 L.

25 [0047]

There may be used, as the monomer blended in the monomer blending vessel 102, not only a fresh monomer, but also a monomer separated and recovered in an unreacted state as shown in Fig. 3. When the monomer is blended, it is common that an inert gas is bubbled into the monomer blending vessel 102 or dissolved oxygen is removed by pressure reducing deaeration, so as to prevent an influence by dissolved oxygen. In the method of the present embodiment, it is not necessarily required to strictly remove dissolved oxygen, and a polymerization reaction can be stably carried out even though about 1.5 to 3 ppm of dissolved oxygen exist. When the blended monomer composition is supplied into the polymerization reaction vessel 103, it is particularly preferred to filter with a filter having an appropriate size selected according to the purposes so as to remove foreign matters in the case of using the obtained methacrylic polymer in the material for an optical equipment.

[0048]

In the method for producing a methacrylic polymer of the present embodiment, as described above, an initiator composition and a monomer composition as raw materials of the methacrylic polymer are continuously supplied into the polymerization reaction vessel 103 from the initiator blending vessel 101 and the monomer blending vessel 102,

and then at least a part of a monomer is polymerized in the polymerization reaction vessel 103 to obtain a polymer composition containing the methacrylic polymer and the unreacted monomer. In the polymerization reaction vessel 5 103, a polymerization method of the methacrylic polymer may be either a bulk polymerization using no solvent or a solution polymerization using a solvent, and a bulk polymerization method is particularly preferred.

[0049]

10 The polymerization is carried out by a continuous solution polymerization method in the same manner as in the aforementioned continuous bulk polymerization method, except that the solvent is used in the polymerization reaction. The solvent used in the polymerization reaction 15 may be appropriately set according to a raw monomer component of the continuous solution polymerization reaction or the like and is not particularly limited, and examples thereof include toluene, xylene, ethylbenzene, methyl isobutyl ketone, methyl alcohol, ethyl alcohol, 20 octane, decane, cyclohexane, decalin, butyl acetate, pentyl acetate and the like. Among these solvents, toluene, methanol, ethylbenzene and butyl acetate are preferred. The solvent can be added to one or both of an initiator composition and a monomer composition. There is no 25 particular limitation on the proportion of the solvent, and

the proportion is preferably from 5 to 30% by mass, and more preferably from 1 to 20% by mass, based on the entire polymer composition.

[0050]

5 The content of the polymer in the polymer composition is preferably from 40 to 70% by mass. When the content of the polymer is too high, efficiency of mixing and heat transfer may decrease and thus stability may become worse. In contrast, when the content of the polymer is too low, it
10 may become difficult to separate a volatile component containing an unreacted monomer as a main component.

[0051]

 The polymer composition produced in the polymerization reaction vessel 103 is continuously
15 extracted from the polymerization reaction vessel 103 and then optionally lead to a heater 104. In the heater 104, a liquid polymer composition is preheated for the purpose of increasing efficiency of subsequent devolatilization in a devolatilizing extruder 100. At this time, the preheating
20 temperature is preferably adjusted within a range of 180 to 220°C. When the preheating temperature is higher than the aforementioned range, a volatile component may be gasified and thus it may become difficult to deliver a liquid at a given flow rate.

25 [0052]

Next, the polymer composition is supplied to the devolatilizing extruder 100. As the devolatilizing extruder 100, the aforementioned devolatilizing extruder 100 of the present invention is used. The devolatilizing extrusion is carried out by continuously supplying a polymer composition into a cylinder 10 through a polymer composition supply port 12 in the devolatilizing extruder 100 to discharge a volatile component containing an unreacted monomer as a main component through a gas discharge port 14 and to discharge a methacrylic polymer after devolatilization through a polymer outlet 16, respectively.

[0053]

The devolatilizing extrusion is carried out by heating a polymer composition to be continuously supplied at 200 to 290°C thereby continuously separating and removing most of the volatile component containing an unreacted monomer as a main component. With respect to the pressure condition at the time of devolatilizing extrusion, the pressure of a gas discharge port (back vent) 14a is adjusted within a range of about -0.05 to 0.15 MPaG (in terms of gauge pressure) and the pressures of gas discharge ports (fore vents) 14b, 14c, 14d are respectively adjusted within a range of about -0.09 to -0.02 MPaG (in terms of gauge pressure). The gasified volatile component and

methacrylic polymer enter into the devolatilizing extruder 100 through the polymer composition supply port 12. At this time, when the pressure of the back vent is decreased to -0.05 MPaG, an entrainment phenomenon arises at the back vent, and thus it is preferred to adjust the pressure within the aforementioned range. In order to remove the volatile component, the pressures of four vents are preferably adjusted within the aforementioned range. Usually, a pressure regulating valve is disposed between the heater 104 and the devolatilizing extruder 100, thereby adjusting the pressure at the time of devolatilizing extrusion.

[0054]

On or after the aforementioned devolatilizing extrusion, lubricants such as higher alcohols and higher fatty acid esters, an ultraviolet absorber, a heat stabilizer, a coloring agent, an antistatic agent and the like can be added to the methacrylic polymer.

[0055]

The volatile component containing an unreacted monomer as a main component discharged through the gas discharge port 14 is sent to a monomer recovery tower 105. The volatile component containing an unreacted monomer as a main component contains impurities contained originally in a monomer, oligomers such as a dimer and a trimer, and impurities such as a radical polymerization initiator

residue. When the polymerization is carried out by the continuous solution polymerization method, a solvent can be contained in addition to these impurities. When impurities are accumulated, the obtained methacrylic polymer undergoes coloration. Therefore, impurities are removed from the unreacted monomer by a means such as distillation or adsorption in the monomer recovery tower 105, and then the obtained monomer is recycled as a monomer for polymerization. For example, in the monomer recovery tower 105, the monomer is recovered as a distillatory solution from a tower top of the monomer recovery tower 105 by continuous distillation, and then recycled to the monomer blending vessel 102. Impurities removed in the monomer recovery tower 105 are discarded as wastes. The volatile component containing an unreacted monomer as a main component usually refers to those in which not less than 30% by mass of the unreacted monomer is contained in the volatile component.

[0056]

According to the method for devolatilizing extrusion of a polymer composition and the method for producing a methacrylic polymer as described above, it is possible to efficiently produce a methacrylic polymer with contamination suppressed even when continuously operated for a long term.

[0057]

The aforementioned method for devolatilizing extrusion of a polymer composition and method for producing a methacrylic polymer can be suitably used in the
5 production of a methacrylic polymer obtained by polymerizing a monomer mixture containing methyl methacrylate as a main component among some methacrylic polymers.

[0058]

10 The methacrylic polymer obtained by the aforementioned method can be suitably in various fields such as illuminations, signboards and vehicles since excellent transparency and weatherability can be obtained. The methacrylic polymer can be used particularly suitably
15 in materials for an optical disk substrate; materials for an optical equipment such as Fresnel lens, lenticular lens, a light guide plate and a diffuser panel used in a backlight system of a liquid crystal display, and a protective front panel of a liquid crystal display; vehicle
20 members such as a tail lamp cover, a head lamp cover, a visor and a meter panel; and the like.

Description of Reference Symbols

[0059]

10: Cylinder

25 12: Polymer composition supply port

- 14: Gas discharge port
- 16: Polymer outlet
- 18: Through-hole
- 20: Screw
- 5 20a: Shaft portion
- 30: Shaft seal bearing portion
- 32: Shaft seal portion
- 100: Devolatilizing extruder

CLAIMS

1. A devolatilizing extruder for producing a methacrylic polymer, comprising:
 - 5 a cylinder having a polymer composition supply port, a gas discharge port, a polymer outlet and a through-hole;
 - a rotatable screw inserted into the cylinder through the through-hole; and
 - a shaft seal bearing portion supporting a shaft
 - 10 portion of the screw extending from the through-hole to the outside of the cylinder; wherein
 - the shaft seal portion of the shaft seal bearing portion is formed of a mechanical seal using at least one kind selected from a group consisting of an adipate ester,
 - 15 a phthalate ester, a diisobutyrate ester and acetylated glyceride as a mechanical seal liquid.
2. A method for devolatilizing extrusion of a polymer composition, comprising: supplying a polymer composition
- 20 containing a methacrylic polymer and a volatile component into the cylinder through the polymer composition supply port in the devolatilizing extruder according to claim 1 to discharge the volatile component through the gas discharge port and to discharge a methacrylic polymer after
- 25 devolatilization through the polymer outlet, respectively.

3. A method for producing a methacrylic polymer,
comprising the steps of:

continuously supplying a raw material that contains a
5 monomer component containing a methacrylic monomer as a
main component, a radical polymerization initiator and a
chain transfer agent into a polymerization reaction vessel;

polymerizing the monomer component in the
polymerization reaction vessel to obtain a polymer
10 composition that contains a methacrylic polymer and a
volatile component containing an unreacted monomer; and

supplying the polymer composition into the cylinder
through the polymer composition supply port in the
devolatilizing extruder according to claim 1 to discharge
15 the volatile component through the gas discharge port and
to discharge a methacrylic polymer after devolatilization
through the polymer outlet, respectively.