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DESCRIPTION

PROCESS FOR PRODUCING STABILIZED OXYMETHYLENE COPOLYMER

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an economical process for producing an oxymethylene copolymer having excellent thermal stability.

Description of the Related Art

Since a polyoxymethylene copolymer (which may hereinafter be abbreviated as "POM copolymer") has excellent mechanical properties, heat resistance, chemical resistance, electrical properties and sliding properties and at the same time has excellent moldability or formability, it is used as an engineering plastic for a wide variety of applications such as machine parts, automobile parts or electrical/electronic parts.

It is known that a stabilized POM copolymer provided for practical use is generally produced in accordance with a process as described below.

First, a crude POM copolymer is obtained by using, as a principal monomer, a cyclic acetal such as trioxane and, as a comonomer, a cyclic acetal or cyclic ether having an adjacent

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carbon atom; adding thereto, depending upon the purpose, a chain transfer agent for the regulation of the polymerization degree; and then copolymerizing in the presence of a cationic active catalyst. In general, such a crude POM copolymer contains a large amount of unstable end parts. When heat is applied to the polymerization catalyst which has remained active, depolymerization of the copolymer or an increase in unstable end parts occurs.

Accordingly, next, the crude POM copolymer which is a polymerization product is provided for a decomposition and removal step of the unstable end parts after the catalyst contained in the copolymer is neutralized or deactivated with an organic or inorganic basic compound such as alkylamine, alkoxyamine or hindered amine, or a hydroxide of an alkali metal or alkaline earth metal. Then, the copolymer so treated is heated in the presence of a basic compound, for example, the above-exemplified compound, and water or an alcohol which is used in combination as needed, whereby unstable end parts are removed by decomposition.

Then, to the POM copolymer from which unstable end parts have been removed by decomposition in this way, suitable additives are added to impart the copolymer with thermal stability and long-term stability, and besides, depending upon

the purpose, various additives or reinforcing agents are added to impart the copolymer with desired properties, followed by melt-kneading, whereby a stabilized POM copolymer suitable for practical use is prepared.

On the contrary, various investigations have been carried out to prepare a stabilized POM copolymer more economically. Examples of the known measures for the economical production include improvement of a polymerizer, polymerization catalyst or the like in a polymerization step, an improvement in a deactivator, deactivating method or the like in a catalyst deactivation step and an improvement in a decomposition accelerator, a decomposition and removal apparatus in a decomposition and removal step of unstable end parts.

However, any one of the above measures is only for a specific step so that improvements brought by it spontaneously have limitations. There is accordingly a demand for the provision of a more economical process for the production of a POM copolymer in consideration of the whole step from polymerization until final stabilization of a POM copolymer. Particularly, among the above-described steps, the step for the decomposition and removal of unstable end parts requires a cumbersome operation for the treatment and needs much energy for the treatment. If a POM copolymer can be provided for the

final stabilization step substantially without the decomposition and removal step, an extremely economically advantageous production can be carried out. For exclusion of the decomposition and removal step, it is necessary to prepare a high-quality (crude) POM copolymer in the polymerization step and/or catalyst deactivation step. As a method for the improvement of the catalyst deactivation, it is known to deactivate the crude POM copolymer, which is a polymerization product, by pulverization from the viewpoint of heightening a catalyst deactivation efficiency and also a subsequent decomposition and removal efficiency of unstable ends. From such viewpoints, the pulverized copolymer with a shorter particle size has been regarded to be preferable (JP-A-57-80414 and JP-A-58-34819).

Still, as a result of investigation, the present inventors have found the problem that, although such deactivation treatment of the crude POM copolymer by pulverization improves the quality of the resulting POM copolymer, but if the resulting POM copolymer is provided for a stabilization step, in which the resulting copolymer is added with a stabilizer, and then melt-kneaded without a decomposition and removal step of unstable end parts, the resulting POM copolymer inevitably has markedly inferior operability.

As described above, no effective and simplified process for economically producing a stabilized POM copolymer by providing a POM copolymer for a final stabilization step without a decomposition and removal step of unstable end parts has so far been found.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an extremely economically advantageous and simple process for producing a stabilized POM copolymer suitable for practical use, thereby overcoming the above-described problem.

With a view to attaining the above object, the present inventors have carried out a total investigation on the process from a polymerization step of a POM copolymer until a stabilization step. As a result, it has been found that the pulverization of the crude POM copolymer, which is a polymerization product, is an important factor and the above-described object can be attained by appropriately controlling the particle size distribution of the copolymer. That leads to the completion of the present invention.

namely, in the present invention is a process for producing a stabilized oxymethylene copolymer, characterized by pulverizing a crude oxymethylene copolymer discharged from

a polymerizer into a powder satisfying the following requirements (1) to (4) of the particle size distribution and simultaneously deactivating the polymerization catalyst and then melt-kneading the pulverized oxymethylene copolymer together with a stabilizer substantially without a treatment for stabilizing the ends of the polymer molecules by removing the unstable end parts by decomposition:

- (1) the average particle diameter is 0.3 to 0.7 mm,
 - (2) 3 to 20% by weight of the particles have a diameter of longer than 1.0 mm,
 - (3) 50 to 97% by weight of the particles have a diameter of 0.18 to 1.0 mm, and
 - (4) 0 to 30% by weight of the particles have a diameter of shorter than 0.18 mm
- (the total being 100% by weight).

In other words, the invention is directed to a process for producing an oxymethylene copolymer which comprises the steps of polymerizing an oxymethylene polymer, crashing a crude copolymer product into powder having the size distributions (1), (2), (3) and (4), deactivating the catalyst remaining in the powder and melt-kneading the powder with a stabilizer, provided that the powder has not been treated to remove unstable terminals of the molecules by decomposing them. The invention



moreover provides a method for stabilizing the oxymethylene polymer by conducting the above shown step.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will hereinafter be described more specifically.

First, the (crude) oxymethylene copolymer (POM copolymer) to which the present invention is applied is available by the copolymerization of, as a principal monomer, a cyclic acetal such as trioxane and, as a comonomer, a cyclic ether or cyclic formal in the presence of a cationic active catalyst.

The cyclic ether or cyclic formal employed here as a comonomer is a cyclic compound containing at least a pair of coupling carbon atom and oxygen atom. Examples include ethylene oxide, 1,3-dioxolane, 1,3,5-trioxepane, diethylene glycol formal, 1,4-butanediol formal, 1,3-dioxane and propylene oxide. Among them, preferred comonomers are ethylene oxide, 1,3-dioxolane, diethylene glycol formal and 1,4-butanediol formal. The comonomer is used in an amount of 0.1 to 20 mole%, preferably 0.2 to 10 mole%, relative to the trioxane which is a principal monomer.

Upon the production of the (crude) POM copolymer by the copolymerization of such a monomer and a comonomer, an

ordinarily employed cationic catalyst is used as a polymerization catalyst. Examples of the cationic catalyst include Lewis acids such as halides of boron, tin, titanium, phosphorus, arsenic and antimony, more particularly, boron trifluoride, tin tetrachloride, titanium tetrachloride, phosphorus pentachloride, phosphorus pentafluoride, arsenic pentafluoride and antimony pentafluoride, compounds such as complex or salt thereof; a protonic acid such as trifluoromethanesulfonic acid and perchloric acid, esters of a proton acid such as an ester of perchloric acid and a lower aliphatic alcohol (ex. a tertiary butyl ester of perchloric acid), anhydrides of a proton acid, especially a mixed anhydride of perchloric acid and a lower aliphatic carboxylic acid (ex. acetyl perchlorate), isopoly acid, heteropoly acid (for example, phosphomolybdic acid), triethyloxonium hexafluorophosphate, triphenylmethyl hexafluoroarsenate and acetyl hexafluoroborate.

Among them, boron trifluoride and a coordination compound between boron trifluoride and an organic compound (for example, an ether) are most commonly used as catalysts. In addition, since a proton acid such as heteropoly acid or isopoly acid has high activity as a catalyst, it easily provides a high-quality crude POM copolymer in a small catalytic amount and is easily

deactivated. It is therefore preferred to prepare a crude POM copolymer by polymerizing in the presence of a catalyst selected from such compounds or a mixture of two or more of them. When a Lewis acid such as boron trifluoride is used as a catalyst, it is preferably added in an amount of 15 to 25 ppm relative to the raw material monomers. It is desired to use a monomer having a water content not higher than 10 ppm in order to obtain a high-quality crude POM copolymer.

For the adjustment of the molecular weight of the crude POM copolymer available by copolymerization, it is also possible to carry out polymerization, if necessary, by adding a proper amount of a suitable chain transfer agent, for example, an acetal compound such as methylal or dioxymethylene dimethyl ether.

Alternatively, it is possible to produce such a crude POM copolymer in the presence of a hindered phenol compound which is an antioxidant. This method is effective for controlling the oxidative destruction of the resulting POM copolymer during polymerization or suppressing the oxidative destruction of the POM copolymer caused by heating treatment in the subsequent step, which makes it possible to provide the final stabilization step with a high-quality-maintained POM copolymer. The crude POM copolymer so obtained is therefore

preferably employed for the present invention.

The crude POM copolymer can be copolymerized by using the conventionally known equipment and process, for example, either of a batch or continuous process, or either of melt polymerization or melt bulk polymerization. From the industrial viewpoint, generally-employed and preferred is the continuous bulk method in which a liquid monomer is used and a polymer is obtained in the form of a solid powdery mass with the progress of the polymerization. In this case, the polymerization can be conducted in the presence of an inert liquid medium as needed. Examples of the polymerization apparatus usable in the present invention include Ko-Kneader, twin-screw continuous extrusion mixer and twin-puddle type continuous mixer.

The process of the present invention is characterized by pulverizing the crude POM copolymer, which has been obtained as described above, into a powder having a certain particle size distribution and simultaneously deactivating the polymerization catalyst contained in the powder, and then melt-kneading the pulverized POM copolymer together with a stabilizer substantially without a treatment for stabilizing the ends by removing the unstable end parts by decomposition.

Here, the POM copolymer so pulverized is required to

satisfy the particle size distribution prescribed below in (1) to (4):

- (1) the average particle diameter is 0.3 to 0.7 mm,
 - (2) 3 to 20% by weight of the particles have a diameter of longer than 1.0 mm,
 - (3) 50 to 97% by weight of the particles have a diameter of 0.18 to 1.0 mm, and
 - (4) 0 to 30% by weight of the particles have a diameter of shorter than 0.18 mm
- (the total being 100% by weight).

The above particle size distribution is found by the present inventors, as a result of an extensive investigation with a view to satisfying both the quality, specifically the amount of unstable ends, of the POM copolymer available by the pulverization and deactivation of the catalyst; and operability of the stabilization step for melt-kneading the pulverized POM copolymer together with a stabilizer, thereby stabilizing the copolymer.

Among the above requirements, the upper limit (0.7 mm) of the average particle diameter in (1) and the upper limit of the ratio of the particles having a diameter exceeding 1.0 mm in (2) are important requirements mainly for determining the quality of the POM copolymer. On the other hand, the lowest

limit (0.3 mm) of the average particle diameter in (1), the lowest limit of the ratio of the particles having a diameter exceeding 1.0 mm in (2) and the upper limit of the ratio of the particles having a diameter smaller than 0.18 mm in (4) are important requirements mainly for determining the operability in the stabilizing step by a stabilizer.

When the particle size exceeds the above particle size distribution, for example, the average particle size exceeds its upper limit or the ratio of the particles having a particle size longer than 1.0 mm exceeds its upper limit, the resulting pulverized POM copolymer becomes deteriorated in its quality, particularly the amount of unstable ends increases, and a stable POM copolymer which can be provided on the market cannot be obtained only by stabilization with a stabilizer without a treatment for stabilizing the ends by removing the unstable end portions by decomposition. On the other hand, when the particle size is below the above particle size distribution, for example, the average particle size is below its lowest limit, the ratio of the particles having a particle size longer than 1.0 mm is below its lowest limit, or the ratio of the particles shorter than 0.18 mm exceeds its upper limit, the operability of the stabilization step by kneading with a stabilizer becomes markedly inferior instead of satisfactory quality of the POM

copolymer so that it becomes difficult to economically produce a stabilized POM copolymer.

With the forgoing in view, the preferred particle size distribution which can satisfy both the better quality of the POM copolymer and operability of the stabilization step is as follows:

- (1)' the average particle diameter is 0.4 to 0.7 mm,
 - (2)' 5 to 15% by weight of the particles have a diameter of longer than 1.0 mm,
 - (3)' 60 to 95% by weight of the particles have a diameter of 0.18 to 1.0 mm, and
 - (4)' 0 to 25% by weight of the particles have a diameter of shorter than 0.18 mm
- (the total being 100% by weight).

Upon pulverization as described above, no particular limitation is imposed on the pulverizer to be employed. Examples include rotary mill, hammer mill, jaw crusher, feather mill, rotary cutter mill, turbo mill and classifying type impact pulverizer. The particle size distribution can be controlled by the rotation frequency of a pulverizer, clearance or screen mesh attached to a pulverizer and/or a shift attached separately as needed.

Upon deactivation of the catalyst contained in the crude

POM copolymer, a conventionally known method can be employed. In the present invention, it is preferred that deactivation is effected by using an aqueous solution of an organic or inorganic basic compound typified by triethylamine, triethanolamine, sodium carbonate or calcium hydroxide as a deactivator, and that, at the same time, the crude POM copolymer is pulverized by wet pulverization into powder having the above-described particle size distribution. Above all, it is preferred to add the deactivator on the way from the position immediately before the outlet of the polymerizer to the inlet of the pulverizer, whereby a high quality POM copolymer can be obtained.

After the deactivation of the catalyst and pulverization, the POM copolymer is subjected to washing, drying and the like as needed.

In the present invention, a high quality POM copolymer with less unstable ends can be obtained by deactivating the catalyst of the crude POM copolymer, which is a polymerization product, as described above and at the same time pulverizing it into powder having a certain particle size distribution. It is particularly preferred to subject the resulting copolymer having unstable end amount of 0.3 to 0.8 to the subsequent stabilizing step.

Incidentally, the term "unstable end amount" of the POM

copolymer as used herein means an amount of formaldehyde in wt. % relative to the copolymer, said amount being determined by charging 1 g of a POM copolymer to a closed pressure bottle together with 100 ml of a 50% aqueous methanol solution containing 0.5% of ammonium hydroxide, heating the resulting mixture at 180°C for 45 minutes, cooling, taking out of the bottle, and then analyzing the amount of formaldehyde decomposed and dissolved in the liquid.

The pulverized POM copolymer which has been pulverized to have a certain particle size distribution as described above, followed by deactivation treatment of the catalyst contained therein, is then melt-kneaded together with a stabilizer substantially without a conventional treatment for removing the unstable end parts by decomposition, whereby a stabilized POM copolymer can be obtained.

No particular limitation is imposed on the stabilizer usable here. Any known stabilizer can be employed, but generally, an antioxidant and thermal stabilizer are used in combination.

Examples of the antioxidant include 1,6-hexanediol-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], pentaerythrityltetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], triethyleneglycol-bis[3-(3-t-butyl-5-methyl-4-

hydroxyphenyl)propionate] and N,N'-hexamethylenebis(3,5-di-t-butyl-4-hydroxy-cyannamide).

Examples of the thermal stabilizer include triazine compounds such as melamine and melamine-formaldehyde condensate, polyamides such as nylon 12 and nylon 6·10; hydroxides, carbonates, phosphates, acetates and oxalates of an alkali metal or alkaline earth metal; and metallic salts of a higher fatty acid such as stearic acid or a higher fatty acid having a substituent such as a hydroxyl group.

To the POM copolymer of the present invention, various additives can be added depending upon the purpose. Examples include, weather-(or light-)resistant stabilizer, lubricant, nucleating agent, mold release agent, antistatic, dyestuff, pigment, other organic high-molecular materials, inorganic or organic fibrous, plate or powdery fillers.

The melt-kneading with a stabilizer and the like is generally carried out in an extruder.

Examples and comparative examples will now be described. It is obvious that the present invention is not limited to them. Examples 1 to 5 and Comparative Examples 1 to 4

In each example, a twin-puddle type continuous polymerizer was continuously fed with trioxane (containing 15 ppm or 8 ppm of water) and 2.5 wt.% (based on the whole monomer) of 1,3-dioxolane, and polymerization was effected in the

presence of boron trifluoride or phosphomolybdic acid (supplied as a mixture with a comonomer) as a catalyst. The crude POM copolymer discharged from the outlet at the end of the polymerizer was subjected to wet pulverization or dry pulverization in a manner described below and at the same time, deactivation treatment of the catalyst was carried out, followed by dehydration and drying, whereby powdery POM copolymer having a particle size distribution as shown in Table 1 was obtained. The particle size distribution was controlled by changing the rotation frequency of the pulverizer or size or shape of the screen mesh.

Wet pulverization:

An aqueous solution containing 500 ppm of triethylamine was supplied as a catalyst deactivator to the outlet of the polymerizer. While it was brought into contact with the crude POM copolymer just discharged from the outlet to cause deactivation of the catalyst, the resulting mixture was introduced into a ball mill equipped with a screen mesh and pulverized therein. The slurry containing the powdery POM copolymer and the catalyst deactivator was discharged from the pulverizer and then introduced into a storage tank, wherein further deactivation was effected, followed by dehydration and drying.

Dry pulverization:

The crude POM copolymer discharged from the outlet of the polymerizer was introduced into the pulverizer through a line which had been sealed hermetically to avoid the contact with water and air, followed by pulverization. The powdery POM copolymer discharged from the pulverizer was then introduced into a storage tank of an aqueous solution containing 500 ppm of triethylamine and was subjected to deactivation treatment, followed by dehydration and drying.

The powdery POM copolymer obtained in the above-described way was not subjected to the conventional treatment for the decomposition and removal of unstable end portions, but was melt-kneaded in an extruder after mixed with, as a stabilizer, 0.5 wt.% of pentaerythrityltetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] and 0.1 wt.% of calcium stearate, whereby a stabilized POM copolymer was obtained in the pellet form. The evaluation results are shown in Table 1.

Incidentally, the evaluation method and standards are as follows:

[Thermal stability of stabilized POM]

The weight loss of the stabilized POM copolymer (5 g) when heated at 220°C for 45 minutes in the air is weighed and it is indicated by a weight reduction ratio (%) per minute.

[Extrudability]

- Biting of raw materials

Observed are the biting condition of the raw materials into an extruder and discharged condition of stabilized POM from the extruder at the time when a stabilizer is incorporated in the powdery POM copolymer and the resulting mixture is melt-kneaded in an extruder. They are evaluated in accordance with the following four ranks A to D;

A: Both biting condition and discharged strands are stable.

B: Inferior biting condition sometimes occurs and fluctuations in the thickness of the strands appear.

C: Fluctuations in the biting condition are slightly large, fluctuations in the thickness of strands are large and strand breaking sometimes occurs.

D: Fluctuations in the biting condition are intense and a biting amount is totally low and no strands can be formed.

- Motor load amplitude

Difference between the maximum and minimum current values of the motor at the time of extrusion (unit: ampere)

- Difference in the fluctuations of the resin pressure

Difference between the maximum and minimum values indicated by the resin manometer disposed immediately after the tip of the screw of the extruder (unit: kg/cm^2).

Table 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comp.Ex.1	Comp.Ex.2	Comp.Ex.3	Comp.Ex.4
Water content of monomer (ppm)	15	8	8	8	8	15	8	8	8
Catalyst Kind Concentration (ppm)	BF ₃ 30	BF ₃ 20	BF ₃ 20	BF ₃ 20	HPA 5	BF ₃ 30	BF ₃ 20	BF ₃ 20	BF ₃ 20
Pulverizing method	wet	wet	wet	dry	wet	wet	wet	wet	dry
Particle size distribution									
Average particle size	0.45	0.46	0.59	0.47	0.46	0.72	0.72	0.17	0.74
D>1.0 mm (%)	8	7	18	10	8	38	37	2	42
1.0 mm ≥ D ≥ 0.18 mm (%)	71	70	77	72	69	57	58	43	55
0.18 mm > D (%)	21	23	5	18	23	5	5	55	3
Amount of unstable ends after deactivation (%)	0.78	0.68	0.70	0.85	0.68	1.10	1.07	0.68	1.10
Thermal stability of stabilized POM	0.013	0.005	0.006	0.011	0.005	0.040	0.032	0.005	0.037
Extrudability									
Biting condition of raw material	A	A	A	A	A	A	A	D	A
Motor load amplitude	2	2	2	2	2	4	5	18	4
Fluctuation difference of resin pressure	3	3	2	2	3	5	4	17	5

BF₃: boron trifluoride

HPA: phosphomolybdic acid

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What we claim is:

1. A process for producing a stabilized oxymethylene copolymer, characterized by pulverizing a crude oxymethylene copolymer discharged from a polymerizer into a powder satisfying the following requirements (1) to (4) of the particle size distribution and simultaneously deactivating the polymerization catalyst and then melt-kneading the pulverized oxymethylene copolymer together with a stabilizer substantially without a treatment for stabilizing the ends by removing the unstable end parts by decomposition:

- (1) the average particle diameter is 0.3 to 0.7 mm,
- (2) 3 to 20% by weight of the particles have a diameter of longer than 1.0 mm,
- (3) 50 to 97% by weight of the particles have a diameter of 0.18 to 1.0 mm, and
- (4) 0 to 30% by weight of the particles have a diameter of shorter than 0.18 mm

(the total being 100% by weight).

2. The process for producing a stabilized oxymethylene copolymer according to claim 1, wherein the pulverized oxymethylene copolymer has 0.3 to 0.8% by weight (based on the copolymer) of unstable ends.

3. The Process for producing a stabilized oxymethylene



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copolymer according to claim 1 or 2, wherein the crude oxymethylene copolymer is one obtained by the polymerization conducted in the presence of a proton acid as the catalyst.

4. The process for producing a stabilized oxymethylene copolymer according to claim 1 or 2, wherein the crude oxymethylene copolymer is one obtained by the polymerization conducted in the presence of 15 to 25 ppm, based on the starting monomer, of a Lewis acid as the catalyst.

5. The process for producing a stabilized oxymethylene copolymer according to any of claims 1 to 4, wherein the crude oxymethylene copolymer is one obtained by the polymerization conducted in the presence of a hindered phenolic compound.

6. The process for producing a stabilized oxymethylene copolymer according to any of claims 1 to 5, wherein the crude oxymethylene copolymer is one obtained by the polymerization of a monomer having a water content of 10 ppm or below.

7. The process for producing a stabilized oxymethylene copolymer according to any of claims 1 to 6, wherein the pulverization is conducted by the wet pulverization method and the deactivation treatment is conducted with an aqueous solution of a basic compound as the deactivating agent for the polymerization catalyst.

8. The process for producing a stabilized oxymethylene



copolymer according to claim 7, wherein the deactivation treatment is conducted by adding the deactivating agent for the polymerization catalyst between the point immediately before the outlet for the polymer of the polymerizer and the inlet of the pulverizer.

