

HIGH-EXPANSIBILITY FOAMED POLYPROPYLENE BEAD AND PREPARATION METHOD THEREOF

Field of the Invention

The present invention relates to a foamed polypropylene bead, and in particular to a high-expansibility foamed polypropylene bead and a preparation method thereof.

Background of the Invention

Foamed polypropylene is a chemical material with excellent performance, and has the advantages of light weight, high strength, high temperature resistance and excellent energy absorption characteristics and the like, thereby being widely used in automobiles, packaging, construction, aerospace and other fields. At present, the production process of foamed polypropylene beads mainly includes three procedures of particle prepressing, forming and bonding, and drying and setting. The entire production cycle is relatively long, and a lot of time and energy sources are consumed in the two procedures of particle prepressing and the drying and setting.

In terms of particle prepressing, since there is no in-depth study on the pore walls of bead pores at present, a required internal pressure in the particles is ensured just by purely prolonging the time in the particle prepressing process. The higher the internal pressure required in the particles is, the longer the prepressing time is.

In terms of drying and setting, since a foamed polypropylene granule is a thermoplastic material, there is a phenomenon of thermal expansion and contraction, and most of the interior of the foamed polypropylene bead is air, and the phenomenon of thermal expansion and contraction of the air is more obvious, such that a foamed polypropylene product occurs obvious shrinkage in a cooling process and is easily peeled off from a mold. The more severe the shrinkage is, the longer the drying and setting time is required, the more energy is consumed, and the turnover efficiency becomes lower.

At present, the prepressing time for producing foamed polypropylene takes about 12 hours, and the drying time takes 8 to 16 hours. Therefore, if the time consumed in the two procedures of particle prepressing and the drying and setting can be shortened, not only the production efficiency can be improved, but also the energy consumption in the drying and setting process can be greatly reduced. This is also the focus and concern of downstream customers of the foamed polypropylene beads in the production process.

Summary of the Invention

The technical problem to be solved by the present invention is to overcome the defects in the prior art, improve the production efficiency of foamed polypropylene and reduce the energy consumption. In order to achieve the above objective, the present invention provides the following technical solutions:

A high-expansibility foamed polypropylene bead, having a formulation including the following ingredients in parts by weight:

87-100 parts of random propylene-butene copolymer polypropylene, 0-13 parts of homo-polypropylene, 1-5 parts of blowing promoter, 0.01-2 parts of special porous auxiliary agent, and 5-14 parts of other auxiliary agent. The molar ratio of monomer butene of the random propylene-butene copolymer polypropylene is 3-5%, the melting point is 140-147 °C, the melt index is 6- 8 g/10 min, and the bending modulus is greater than 900 MPa. The melting point of the homo-polypropylene is 160-165 °C.

Further, the blowing promoter is one or more of zinc borate, kaolin, montmorillonite, calcium carbonate, barium sulfate, white carbon black, carbon nanotube, graphene, talcum powder, citric acid and metal powder. More preferably, the blowing promoter is one or two of talcum powder and zinc borate.

Further, the special porous auxiliary agent is one or two of porous silicon dioxide and porous titanium dioxide. More preferably, the porous silicon dioxide or the porous titanium dioxide

has an aperture of 70-80 nm and a porosity of 65-86%.

Further, the other auxiliary agent is one or more of fire retardant, color master batch, dispersing agent, antioxidant, lubricant, antistatic agent, coupling agent, stabilizer and ultraviolet light absorber. More preferably, the fire retardant is 500-2000ppm, the color master batch is 6%-10%, the antistatic agent is 1%-3%, the stabilizer is 200-1000 ppm, and the antioxidant is 500-1000 ppm.

Another aspect of the present invention discloses a preparation method of a high-expansibility foamed polypropylene bead, including the following steps:

step 1, performing mixing, extrusion and wire drawing on random propylene-butene copolymer polypropylene, homo-polypropylene and auxiliary agents according to a proportion of parts by weight via an extruding machine, and performing grain cutting via a grain cutting device to form modified polypropylene microparticles, wherein the random propylene-butene copolymer polypropylene accounts for 87-100 parts, the homo-polypropylene accounts for 0-13 parts, a blowing promoter accounts for 1-5 parts, a special porous auxiliary agent accounts for 0.01-2 parts, and other auxiliary agent accounts for 5-14 parts. In the step 1, the molar ratio of monomer butene of the random propylene-butene copolymer polypropylene is 3-5%, the melting point is 140-147 °C, the melt index is 6- 8 g/10 min, and the bending modulus is greater than 900 MPa. The melting point of the homo-polypropylene is 160-165 °C.

Further, the blowing promoter in the step 1 is one or more of zinc borate, kaolin, montmorillonite, calcium carbonate, barium sulfate, white carbon black, carbon nanotube, graphene, talcum powder, citric acid and metal powder. More preferably, the blowing promoter is one or two of talcum powder and zinc borate.

Further, the special porous auxiliary agent in the step 1 is one or two of porous silicon dioxide and porous titanium dioxide. More preferably, the porous silicon dioxide or the porous titanium dioxide has an aperture of 70-80 nm and a porosity of 65-86%.

Further, the other auxiliary agent in the step 1 is one or more of fire retardant, color master batch, dispersing agent, antioxidant, lubricant, antistatic agent, coupling agent, stabilizer and ultraviolet light absorber. More preferably, 500-2000ppm of fire retardant, 6%-10% of color master batch, 1%-3% of antistatic agent, 200-1000 ppm of stabilizer and 500-1000 ppm of antioxidant are added according to performance requirements.

Further, in the step 1, the wire drawing diameter is 1 mm, and the grain cutting length is 1.8-2.5 mm. The single grain mass is 0.5-2 mg.

Step 2, throwing the modified polypropylene microparticles into a reaction kettle, adding a dispersion medium, and then performing heating pressurization, so that the polypropylene microparticles generate an outwardly expanding internal pressure under high temperature and high pressure and release the same to the atmospheric pressure instantly, and obtaining a high-expansibility foamed polypropylene material by treating the foamed particles in a constant temperature environment at a certain temperature for a certain time, wherein the finally formed pore size is 250-450 μm .

Further, in the step 2, the temperature of the reaction kettle is 145-160 $^{\circ}\text{C}$, the pressure is 1.5-2.4 MPa, and the heating time is 60-100 minutes. More preferably, the temperature of the reaction kettle is 149-157 $^{\circ}\text{C}$, the pressure is 1.8-2.3 MPa, and the heating time is 65-97 minutes.

Further, in the step 2, the dispersion medium is one or two of kaolin and butter. More preferably, the ratio of the dispersion medium of kaolin: butter is 1:1 to 4:1.

Further, in the step 2, the selected pressurization gas is one or more of air, nitrogen, water vapor and carbon dioxide. More preferably, the selected pressurization gas is carbon dioxide.

Further, in the step 2, the foaming tube is 2-4 meters, and the temperature of the foaming tube

is controlled at 90-110 °C. The foaming tube has the functions of keeping warm, adjusting the pore size and prolonging the pore increase time.

The foamed polypropylene bead prepared according to the present invention has a large-size pore structure, the size of the pore structure is about 250-450 μm , the pore wall is relatively thick, the particle supportability is high, and the foamed polypropylene bead is unlikely to shrink in the forming process. Moreover, due to the addition of the auxiliary agent of the porous structure, the compressed air can enter more easily to achieve the internal pressure for forming. Therefore, the present invention can shorten the prepressing time of the foamed polypropylene bead by more than 1/4.

In addition, the drying procedure in the production process of the foamed polypropylene bead mainly plays the role of setting and removing moisture, a formed product is easy to shrink after the production process, and the greater the shrinkage is, the longer the drying time is. The foamed polypropylene bead prepared according to the present invention can increase the wall thickness of the pore and improve the supportability, and at the same time, the heat convection inside and outside the pores are improved by the porous structure to quickly restore the shape of the shrunk product, thereby achieving the effect of shortening the drying time by 1/3.

Since the process method of the present invention has the characteristics of reducing the steam pressure and shortening the heating time required for forming, and shortening the setting and drying time and the like, the production energy consumption can be reduced by about 40% in the actual production. A DSC thermodynamic curve of the process method according to the present invention can refer to Fig.2.

Brief Description of the drawings

The drawings are used for providing a further understanding of the present invention and constitute a part of the specification. The drawings, together with the following specific embodiments, are used for explaining the present invention, but are not intended to limit the

present invention. In the drawings:

Fig.1 is a schematic diagram of a scanning electron microscope picture of a section structure of a high-expansibility foamed polypropylene bead prepared in the present invention.

Fig.2 is a calorific value (DSC) analysis curve chart of a high-expansibility foamed polypropylene bead prepared in the present invention.

Detailed Description of the Embodiments

The preferred embodiments of the present invention are described below in combination with the drawings. It should be understood that, the preferred embodiments described herein are merely used for illustrating and explaining the present invention, rather than limiting the present invention.

Embodiment 1

A preparation method of a high-expansibility foamed polypropylene bead according to the present invention includes the following steps:

step 1, performing mixing, extrusion and wire drawing on random propylene-butene copolymer polypropylene, homo-polypropylene and auxiliary agents according to a proportion of parts by weight via an extruding machine, and performing grain cutting via a grain cutting device to form modified polypropylene microparticles, wherein the random propylene-butene copolymer polypropylene accounts for 87 parts and the homo-polypropylene accounts for 13 parts. In the step 1, the molar ratio of monomer butene of the random propylene-butene copolymer polypropylene is 5%, the melting point is 145 °C, the melt index is 7.2 g/10 min, and the bending modulus is 1050 MPa. The melting point of the homo-polypropylene is 162 °C, the melt index is 6.5 g/10 min, and the bending modulus is 1500 MPa.

According to a preferred embodiment of the present invention, the blowing promoter in the step 1 is montmorillonite, and the special porous auxiliary agent is porous silicon dioxide.

Step 2, throwing the modified polypropylene microparticles into a reaction kettle, adding a

dispersion medium, and then performing heating pressurization, so that the polypropylene microparticles generate an outwardly expanding internal pressure under high temperature and high pressure and release the same to the atmospheric pressure instantly, thereby obtaining a high-expansibility foamed polypropylene material, wherein the finally formed pore size is 410 μm .

According to a preferred embodiment of the present invention, in the step 2, the temperature of the reaction kettle is 156.8 ° C, and the pressure is 2.2 MPa.

According to a preferred embodiment of the present invention, in the step 2, a foaming tube is connected in the reaction kettle, the foaming tube is 3 meters, and the temperature of the foaming tube is controlled at 98 °C.

After the foamed bead produced according to the present embodiment is formed, the bead has a smooth surface, and less pinholes and pits. Table 1 shows comprehensive performance measurement results of the foamed polypropylene bead produced according to the present embodiment. As can be seen, the foamed polypropylene bead produced according to the present invention has good performance on various respects. The prepressing time in the present embodiment is 5 hours, and the drying time is 5 hours. Compared with the prior art, the production time of the foamed polypropylene is greatly shortened, the energy consumption is reduced, and the production efficiency of the foamed polypropylene is improved.

Table 1 comprehensive performance measurement results of a product of the embodiment 1

Comprehensive performance measurement results of the product		
Serial number	Measurement item	Measurement result
1	Stacking density	49g/l
2	High temperature enthalpy	20J/g

3	Pore size	410 μ m
4	Forming prepresssing	1Mpa
5	Prepresssing time	5h
6	Forming pressure	3.6bar
7	Drying time	5h
8	Bonding state	100%
9	Compressive strength at 50% strain	810Kpa

Embodiment 2

The present invention discloses a preparation method of a foamed polypropylene bead at the same time, including the following steps:

step 1, performing mixing, extrusion and wire drawing on random propylene-butene copolymer polypropylene, homo-polypropylene and auxiliary agents according to a proportion of parts by weight via an extruding machine, and performing grain cutting via a grain cutting device to form modified polypropylene microparticles, wherein the random propylene-butene copolymer polypropylene accounts for 95 parts and the homo-polypropylene accounts for 5 parts. In the step 1, the molar ratio of monomer butene of the random propylene-butene copolymer polypropylene is 5%, the melting point is 145 °C, the melt index is 7.2 g/10 min, and the bending modulus is 1050 MPa. The melting point of the homo-polypropylene is 162 °C, the melt index is 6.5 g/10 min, and the bending modulus is 1500 MPa.

According to a preferred embodiment of the present invention, the blowing promoter in the step 1 is talcum powder, and the special porous auxiliary agent is porous titanium dioxide.

Step 2, throwing the modified polypropylene microparticles into a reaction kettle, adding a dispersion medium, and then performing heating pressurization, so that the polypropylene

microparticles generate an outwardly expanding internal pressure under high temperature and high pressure and release the same to the atmospheric pressure instantly, thereby obtaining a high-expansibility foamed polypropylene material, wherein the finally formed pore size is 360 μm .

According to a preferred embodiment of the present invention, in the step 2, the temperature of the reaction kettle is 155.9 ° C, and the pressure is 1.8 MPa.

According to a preferred embodiment of the present invention, in the step 2, a foaming tube is connected in the reaction kettle, the foaming tube is 3 meters, and the temperature of the foaming tube is controlled at 100 °C.

After the foamed bead produced according to the present embodiment is formed, the bead has a smooth surface, and less pinholes and pits. Table 2 shows comprehensive performance measurement results of the foamed polypropylene bead produced according to the present embodiment. As can be seen, the foamed polypropylene bead produced according to the present invention has good performance on various respects. The prepressing time in the present embodiment is 5 hours, and the drying time is 5 hours. Compared with the prior art, the production time of the foamed polypropylene is greatly shortened, the energy consumption is reduced, and the production efficiency of the foamed polypropylene is improved

Table 2 comprehensive performance measurement results of a product of the embodiment 2

Comprehensive performance measurement results of the product		
Serial number	Measurement item	Measurement result
1	Stacking density	58g/l
2	High temperature enthalpy	24J/g

3	Pore size	360 μ m
4	Forming prepresssing	1Mpa
5	prepresssing time	5h
6	Forming pressure	3.5bar
7	Drying time	5h
9	Bonding state	100%
10	Compressive strength at 50% strain	790Kpa

Embodiment 3

The present invention discloses a preparation method of a foamed polypropylene bead at the same time, including the following steps:

step 1, performing mixing, extrusion and wire drawing on random propylene-butene copolymer polypropylene, homo-polypropylene and auxiliary agents according to a proportion of parts by weight via an extruding machine, and performing grain cutting via a grain cutting device to form modified polypropylene microparticles.

Step 2, throwing the modified polypropylene microparticles into a reaction kettle, adding a dispersion medium, and then performing heating pressurization, so that the polypropylene microparticles generate an outwardly expanding internal pressure under high temperature and high pressure and release the same to the atmospheric pressure instantly, thereby obtaining a high-expansibility foamed polypropylene material, and finally formng a certain pore size.

According to one embodiment of the present invention, the properties of the random propylene-butene copolymer polypropylene and the homo-polypropylene that can be selected in the step 1 are shown in table 3.

Table 3 polypropylene raw material of the embodiment 3

Category	Unit	Polypropylene		
Serial number	—	a1	a2	a3
Type	—	Propylene-butene random copolymerization	Propylene-butene random copolymerization	Homo-polypropylene
Catalytic system	—	ziegler-natta	ziegler-natta	ziegler-natta
Comonomer	—	Butene	Butene	—
Monomer content	—	5.50%	5%	—
Density	g/cm^3	0.9	0.9	0.9
Melting point	$^{\circ}\text{C}$	143	145	162
Melt index	g/10min	6.8	7.2	6.5
Bending modulus	MPa	900	1050	1500

According to one embodiment of the present invention, in the step 1, the random propylene-butene copolymer polypropylene, the homo-polypropylene and the auxiliary agents can be added according to the proportion of parts by weight listed in table 4 to form the modified polypropylene microparticles.

Table 4 ingredients of modified polypropylene microparticles of the embodiment 3

Microparticle embodiment	M1	M2	M3	M4	M5	M6
Resin1	a1	a1	a1	a2	a2	a2
Resin2	a3	a3	a3	a3	a3	a3
Resin1 : resin2	87:13	95:5	97:3	87:13	95:5	97:3
Pore nucleating agent	White carbon black	Zinc borate	Talcum powder	Montmorillonite	Talcum powder	Zinc borate
Auxiliary storage gas	Porous silicon dioxide	Porous silicon dioxide	Porous titanium dioxide	Porous silicon dioxide	Porous titanium dioxide	Porous silicon dioxide
$\Delta T_m/^\circ\text{C}$	19	19	19	17	17	17
T_m mixing/ $^\circ\text{C}$	145.3/162.4	145.1/162.1	146.1	147.6/162.5	147.5/162.4	148
Microparticle embodiment	M7	M8	M9	M10	M12	
Resin1	a1	a2	a1	a2	a2	
Resin2	a3	a3				
Resin1 : Resin2	95:5	95:5	1	1	1	
Pore nucleating agent	White carbon black	Zinc borate	Talcum powder	Montmorillonite	Zinc borate	
Auxiliary storage gas	—	—	Porous silicon dioxide	Porous titanium dioxide	—	
$\Delta T_m/^\circ\text{C}$	19	17	—	—	—	
T_m mixing/ $^\circ\text{C}$	145.3/162	147.8/162.4	145.7	148.1	147.8	

According to one embodiment of the present invention, the foaming working condition, the forming working condition and the corresponding comprehensive performance measurement results of the polypropylene bead are shown in table 5.

Table 5 comprehensive performance measurement result table of polypropylene bead of the embodiment 3

Foaming sequence	B1	B2	B3	B4	B5	B6	B7	B8
Microparticle code	M1	M2	M3	M4	M5	M6	M7	M8
Foaming temperature/°C	155.6	154.3	151.7	156.8	155.9	153	154.4	156.5
Foaming pressure/Mpa	2	2	2	2.2	1.8	1.9	2	2
Foaming tube temperature/°C	100	105	90	98	100	105	110	100
Foaming tube length/m	2.5	3	3	3	3	4	3	2
Stacking density/g/l	58	55	53	49	58	49	55	57
High temperature enthalpy/ J/g	23	22	25	20	24	22	21	24
Pore size/ μm	400	380	350	410	360	300	220	240
Forming prepressing/Mpa	1	1	1	1	1	1	1	1
prepressing time/h	5	5	5	5	5	5	5	5
Forming pressure/bar	3.6	3.5	3.4	3.6	3.5	3.5	3.6	3.8
Drying time/h	5	5	5	5	5	5	5	5
Surface state	✓✓	✓✓	✓	✓✓	✓✓	✓	✓	✓
Bonding state	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓	✓

50% compressive strength/Kpa	780	750	710	810	790	760	730	720
Foaming sequence	B9	B10	B14	B15	B16			
Microparticle code	M9	M10	M12	M2	M2			
Foaming temperature/°C	149	151.2	151.3	154.6	152.7			
Foaming pressure/Mpa	1.95	2.3	1.8	2.2	2			
Foaming tube temperature/°C	104	95	105	—	110			
Foaming tube length/m	2	3	3	—	3			
Stacking density/g/l	53	57	47	52	54			
High temperature enthalpy/ J/g	26	22	21	20	24			
Pore size/μm	260	280	240	180	260			
Forming prepressing/Mpa	1	1	1	1	1			
prepressing time/h	5	5	5	5	5			
Forming pressure/bar	3.2	3.4	3.4	3.5	3.4			
Drying time/h	5	5	5	5	5			
Surface state	✓	✓	✓	✗	✓			
Bonding state	✓	✓	✓	✓	✓			
50% compressive strength/Kpa	640	680	630	730	730			

Wherein, surface state represents whether the bead surface is smooth and whether has pinholes and pits, ✓✓represents there is no pinhole or pit on the surface, ✓represents there are few pinholes and pits on the surface, and ✗ represents there are a large number of

pinholes and pits on the surface; and in the bonding state, ✓✓represents 100% bonding, ✓represents 70% bonding, and ✕represents no bonding.

It can be seen from the above tables that the foamed polypropylene particles formed by the material ratio and the process of the present invention have the technical characteristics of short prepressing time and short drying time under the premise that the performance is the same or higher, and compared with the prior art, the energy consumption is reduced, the production efficiency of foamed polypropylene is improved.

CLAIMS

1. A foamed polypropylene bead, wherein the raw material comprises the following ingredients in parts by weight: 87-100 parts of random propylene-butene copolymer polypropylene, 0-13 parts of homo-polypropylene, 1-5 parts of blowing promoter, 0.01-2 parts of special porous auxiliary agent, and 5-14 parts of other auxiliary agent, wherein the random propylene-butene copolymer polypropylene contains comonomer butene in a molar ratio of 3-5%, has a melting point of 140-147 °C, a melt index of 6- 8 g/10 min, and a bending modulus of greater than 900 MPa; the melting point of the homo-polypropylene is 160-165 °C; and the special porous auxiliary agent is one or two of porous silicon dioxide and porous titanium dioxide.

2. The foamed polypropylene bead according to claim 1, wherein the porous silicon dioxide or the porous titanium dioxide has an aperture of 70-80 nm and a porosity of 65-86%.

3. The foamed polypropylene bead according to claim 1, wherein the blowing promoter is one or more of zinc borate, kaolin, montmorillonite, calcium carbonate, barium sulfate, white carbon black, carbon nanotube, graphene, talcum powder, citric acid and metal powder.

4. The foamed polypropylene bead according to claim 1, wherein the other auxiliary agent is one or more of fire retardant, color master batch, dispersing agent, antioxidant, lubricant, antistatic agent, coupling agent, stabilizer and ultraviolet light absorber.

5. The foamed polypropylene bead according to claim 1, wherein the other auxiliary agent comprises 500-2000ppm of fire retardant, 6%-10% of color master batch, 1%-3% of antistatic agent, 200-1000 ppm of stabilizer, and 500-1000 ppm of antioxidant.

6. A preparation method of the foamed polypropylene bead according to any one of claims 1-5, comprising the following steps:

step 1, performing mixing, extrusion and wire drawing on random propylene-butene copolymer polypropylene, homo-polypropylene and auxiliary agents according to a

proportion of parts by weight via an extruding machine, and performing grain cutting via a grain cutting device to form modified polypropylene microparticles, wherein the random propylene-butene copolymer polypropylene accounts for 87-100 parts, the homo-polypropylene accounts for 0-13 parts, a blowing promoter accounts for 1-5 parts, a special porous auxiliary agent accounts for 0.01-2 parts, and other auxiliary agent accounts for 5-14 parts; in the step 1, the random propylene-butene copolymer polypropylene contains comonomer butene in a molar ratio of 3-5%, has a melting point of 140-147 °C, a melt index of 6- 8 g/10 min, and a bending modulus of greater than 900 MPa; the melting point of the homo-polypropylene is 160-165 °C; and the special porous auxiliary agent is one or two of porous silicon dioxide and porous titanium dioxide; and

step 2, throwing the modified polypropylene microparticles into a reaction kettle, adding a dispersion medium, and then performing heating pressurization, so that the polypropylene microparticles generate an outwardly expanding internal pressure under high temperature and high pressure and release the same to the atmospheric pressure instantly, and obtaining a high-expansibility foamed polypropylene material by treating the foamed particles in a constant temperature environment at a certain temperature for a certain time, wherein the finally formed pore size is 250-450 μm .

7. The preparation method of the foamed polypropylene bead according to claim 6, wherein in the step 1, the wire drawing diameter is 1 mm, the grain cutting length is 1.8-2.5 mm, and the single grain mass is 0.5-2 mg.

8. The preparation method of the foamed polypropylene bead according to claim 6, wherein in the step 2, the temperature of the reaction kettle is 145-160 °C, the pressure is 1.5-2.4 MPa, and the heating time is 60-100 minutes.

9. The preparation method of the foamed polypropylene bead according to claim 6, wherein the temperature of the reaction kettle is 149-157 °C, the pressure is 1.8-2.3 MPa, and the heating time is 65-97 minutes.

10. The preparation method of the foamed polypropylene bead according to any one of claims 6-9, wherein in the step 2, the dispersion medium is one or two of kaolin and butter.

11. The preparation method of the foamed polypropylene bead according to claim 6, wherein in the step 2, the selected pressurization gas is one or more of air, nitrogen, water vapor and carbon dioxide.

12. The preparation method of the foamed polypropylene bead according to claim 6, wherein a foaming tube is connected in the reaction kettle in the step, and the foaming tube is 2-4 meters.

13. The preparation method of the foamed polypropylene bead according to claim 6, wherein a foaming tube is connected in the reaction kettle in the step, and the temperature of the foaming tube is controlled at 90-110 °C.