

A Modified Polypropylene-based Cooling Tower Filler and Its Production Process**Technical Field**

The present invention relates to a modified polypropylene modification method, in particular to a preparation and production method of a functional polypropylene cooling tower filler.

Background

Currently, PVC-based cooling tower packing is the mainstream in the market. Due to the characteristics of PVC, its performance is poor in heat aging, high temperature resistance, etc., and water cannot spread on its surface. As the cooling tower packing material, PVC is used to cool water with maximum temperature of 65 °C. The material also releases chlorine-containing gas under reheating during processing and production, polluting the environment. Moreover, the waste PVC molecular chain is severely degraded and strongly impacts its performance; a large number of dioxins (strong carcinogens) are produced during recycling or waste disposal. These shortcomings seriously limit the application of PVC-based cooling tower packing; its extensive use has created serious environmental pressures.

As the second largest resin after polyethylene, polypropylene has excellent mechanical properties, good heat resistance, excellent insulation and low cost. All those qualities make polypropylene a strong candidate for cooling tower packing materials. However, since there is no polar group in the molecular chain of polypropylene, water cannot spread on its surface, and the thermal conductivity (0.25) of pure polypropylene is low, polypropylene should be modified or treated beforehand.

Polypropylene is modified by APEG, HPEG and TPEG containing carbon-carbon double bonds. Under the influence of an initiator, the double bond is opened to bind the HPEG or TPEG to the polypropylene macromolecular chain. The addition of carbon material will also improve the performance of polypropylene on rigidity and thermal conductivity. Carbon material will enhance the rigidity of polypropylene with its own rigidity when blended together. Since the thermal conductivity of carbon materials is higher, when the content of carbon materials reaches a certain value, the thermal conductivity of polypropylene can be greatly increased by forming a thermal conductivity network. The addition of fibers can improve the mechanical properties or polypropylene. Therefore, the cooling efficiency of the cooling tower packing can be greatly improved by the modification of the polypropylene molecular chain with modifier, the introduction of carbon materials and the addition of fibers. At the same time, the maximum

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heat-dissipating water temperature is increased to 85 °C, expanding the usefulness of polypropylene in a wider range of different environments.

Summary of the Invention

The purpose of the present invention is to overcome the disadvantages of the prior art and provide a modified polypropylene-based cooling tower filler as well as its preparation/production method thereof. The modified polypropylene-based cooling tower fillers have a highly efficient heat dissipation function. The modified cooling tower fillers of the present invention enable water to spread on the surface to form a uniform film, greatly improving the cooling efficiency per unit area. The present invention also presents good high-temperature resistance; it can be used to cool water with higher temperature, thereby improving the efficiency of heat dissipation.

To solve the above technical problems, the present invention provides a modified polypropylene-based cooling tower filler comprising the following components:

polypropylene: 100 parts, ethylene-propylene copolymer (EAA): 10 parts, polypropylene grafted maleic anhydride (PP-g-MAH): 10 parts, initiator: 0.05-2 Parts, modifier: 2-20 parts, antioxidant: 0.1-2 parts, carbon material: 5-15 parts, fiber: 5-20 parts, filler: 10-30 parts.

The technical solution further defined by the present invention is:

In the modified polypropylene-based cooling tower filler, the polypropylene is comprised of a mixture of homopolymer polypropylene and copolymerized polypropylene with a mass ratio of between 1:3 and 3:1.

In the modified polypropylene-based cooling tower filler mentioned in this document, the modifiers are selected from at least one of the following three: methyl allyl polyoxyethylene ether, allyl alcohol polyoxyether or (and) allyl polyoxyethylene ether; the carbon materials are selected from at least one of the following materials after surface modification: carbon fibers, multi-walled carbon nanotubes, single-arm carbon nanotubes and graphene; the initiator of is either dicumyl peroxide or benzoyl peroxide.

In the modified polypropylene-based cooling tower filler, the methallyl polyoxyethylene or allyl polyoxyethylene ether has a molecular weight of from 1,000 to 4,000.

In the modified polypropylene-based cooling tower filler, the antioxidant is a mixture of the main antioxidant 1010 and the secondary antioxidant 168, with the mass ratio of 3:1.

In the modified polypropylene-based cooling tower filler, the fibers are selected from at least one of the following fibers with length of 2-8 mm.: glass fibers, basalt fibers, boron fibers, ceramic fibers and modified aramid fibers.

In the modified polypropylene-based cooling tower filler, the filler is a polypropylene-based calcium carbonate masterbatch, of which 60% is calcium carbonate.

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The invention also provides a preparation method of the above polypropylene-based cooling tower filler; the specific steps are as follows:

- (1). The raw materials are weighed according to the ratio stated previously.
- (2). The modifier and initiator are dissolved in absolute ethanol to form a solution or a turbid liquid.
- (3). Polypropylene, ethylene propylene copolymer, polypropylene grafted maleic anhydride, antioxidant, carbon materials, fibers and fillers are mixed evenly and then calendered in an open mill.
- (4). After the materials in (3) are completely plasticized, the solution or turbid liquid disposed in (2) is sprayed onto the surface of the plasticized materials by a spray device to carry out a graft reaction;
Mixing and calendering of the triangle pack continues for another 5-15 minutes after the spraying is complete, to ensure a thorough grafting reaction. The synthetic material of polypropylene-based cooling tower filler can then be obtained.
- (5). The synthetic material in (4) is extruded into a sheet, and then compression-molded to obtain a flat sheet of the polypropylene-based cooling tower filler.

The technical solution further defined by the present invention is:

In the preparation and production process of the above modified polypropylene-based cooling tower filler, the reaction temperature of the grafting reaction in step (4) is from 175 to 210 °C.

In the preparation and production process of the above modified polypropylene-based cooling tower filler, the duration between the beginning of plasticization and the end of mixing and calendering process is between 20 and 40 minutes.

Benefits of the present invention are as follows:

The present invention adopts solid-phase grafting in an open mill and is environmentally friendly without any chemical solvent involved in the preparation process.

The process of graft copolymerization in an open mill is simple in operation and low in its requirement of graft reaction conditions. The addition of antioxidants ensures that the molecular chains of polypropylene do not decompose under high temperature and high shear stress for a long time. During mixing and calendring, the plasticized materials are under high temperature and high shear as well as the action of the “triangle pack”, so the materials are heated and mixed evenly. The process of spraying the modifier while mixing and calendering in the open mill ensures more contact between the modifier and the polypropylene. This process also ensures the reactants mix more uniformly and makes the grafting reaction more complete.

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The invention uses allyl polyoxyethylene ether (HPEG) or methylallyl polyoxyethylene ether (TPEG) as modifiers. The modifiers have a carbon-carbon double bond, which can easily initiate self-polymerization, which lengthens the graft chain, increases the size of the molecular group, promotes water to spread on the surface, and improves the heat dissipation efficiency of cooling tower packing.

The invention uses fibers and carbon materials to enhance polypropylene materials. On one hand, the rigidity of carbon materials improves the mechanical properties of polypropylene materials; on the other hand, carbon materials have good thermal conductivity. The introduction of carbon materials can optimize the thermal conductivity of polypropylene and improve the heat dissipation efficiency of cooling tower packing.

Description of the Figures

Fig. 1 is the equation of grafting reaction between allyl polyoxyethylene ether (HPEG) and polypropylene in the present invention.

Fig. 2 is the equation of grafting reaction between methylallyl polyoxyethylene ether (TPEG) and polypropylene in the present invention.

Detailed Implementation Methods

The present invention will be further described below in order to make the technical means, innovative features, achievement of purpose and effect achieved by the present invention easy to understand.

the present invention provides a modified polypropylene-based cooling tower filler comprising the following components:

polypropylene: 100 parts, ethylene-propylene copolymer (EAA): 10 parts, polypropylene grafted maleic anhydride (PP-g-MAH): 10 parts, initiator: 0.05-2 Parts, modifier: 2-20 parts, antioxidant: 0.1-2 parts, carbon material: 5-15 parts, fiber: 5-20 parts, filler: 10-30 parts.

The polypropylene stated above is a mixture of homopolymer polypropylene and copolymerized polypropylene with a mass ratio of 1:3 to 3:1. Preferably, the mass ratio of homopolymer polypropylene and copolymerized polypropylene is 1:2; more preferably, the mass ratio of homopolymer polypropylene and copolymerized polypropylene is 1:1.

The modifier is at least one of the following: methylallyl polyoxyethylene ether, allyl alcohol polyoxyethylene ether or allyl polyoxyethylene ether. Preferably, the modifier is methylallyl polyoxyl Vinyl ether and allyl polyoxyethylene ether.

The above methylallyl polyoxyethylene or allyl polyoxyethylene ether has a molecular weight of from 1,000 to 4,000, preferably a molecular weight of between 1,500 and 2,500.

The carbon materials mentioned above are selected from at least one of the

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surface-modified carbon fibers: multi-walled carbon nanotubes, single-arm carbon nanotubes and graphene. Preferably, the carbon material is surface-treated with a coupling agent for good compatibility with polypropylene.

5 The above antioxidant is a mixture of the primary antioxidant 1010 and the secondary antioxidant 168, with mass ratio of 3:1.

The above initiator is dicumyl peroxide or dibenzoyl peroxide.

10 The fiber is at least one of the following: glass fiber, basalt fiber, boron fiber, ceramic fiber, and modified aramid fiber. Preferably, the fiber is made of surface-treated glass fiber, basalt fiber. More preferably, the fibers are surface-chemically treated glass fibers which are compatible with polypropylene.

The length of fibers mentioned ranges from 2 to 8 mm, preferably between 3 and 6 mm.

The filler mentioned above is polypropylene-based calcium carbonate masterbatch, of which 60% mass is calcium carbonate.

15 The invention also provides a preparation method of the above polypropylene-based cooling tower filler, the specific steps are as follows:

1. The raw materials are weighed according to the ratio stated previously.
2. The modifier and initiator are dissolved in absolute ethanol to form a solution or a turbid liquid.
3. Polypropylene, ethylene propylene copolymer, polypropylene grafted maleic anhydride, antioxidant, carbon materials, fibers and fillers are mixed evenly and then calendered in an open mill.
4. After the materials in (3) are completely plasticized, the solution or turbid liquid disposed in (2) is sprayed onto the surface of the plasticized materials by a spray device to carry out a graft reaction at 175-210°C;
5. The synthetic material in (4) is extruded into a sheet, and then compression-molded to obtain a flat sheet of the polypropylene-based cooling tower filler.

25 30 The technical solution further defined by the present invention is:

Preferably, the spray in step (4) should be completed within 10 minutes.

Preferably, continue canlendering for another 10-12 minutes after the spraying in step (4) is complete, to ensure a thorough grafting reaction.

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In the preparation and production process of the above modified polypropylene-based cooling tower filler, the duration between the beginning of plasticization and the end of mixing and calendering process is between 20 and 40 minutes, preferably, between 30 and 40 minutes.

To further illustrate the present invention, a modified polypropylene-based cooling tower
5 filler and its preparation method thereof will be described in detail below with reference to embodiments. The embodiments described herein are specific embodiments of the present invention and are interpretative and illustrative in explaining the concepts of the present invention. They should not be construed as restrictions on the embodiments of the present invention and the scope of the present invention. In addition to the implementations described
10 herein, those skilled in the art will be able to devise other obvious technical solutions based on the disclosure of the present application and the specification. These technical solutions include the use of any obvious alternatives and modifications to the embodiments described herein.

Embodiments 1-10

A preferred embodiment of the present invention provides a modified polypropylene-based
15 cooling tower filler comprising the following components in parts by mass:

polypropylene: 100 parts, ethylene-propylene copolymer (EAA): 10 parts, polypropylene grafted maleic anhydride (PP-g-MAH): 10 parts, initiator: 0.05-2 Parts, modifier: 2-20 parts, antioxidant: 0.1-2 parts, carbon material: 5-15 parts, fiber: 5-20 parts, filler: 10-30 parts.

In Embodiments 1-10, the polypropylene is a mixture of homopolypropylene and
20 copolymerized polypropylene with mass ratio of 1:1.

In Embodiments 1-10, the modifier is a mixture of methallyl polyoxyethylene ether and allyl polyoxyethylene ether.

In Embodiments 1-10, the methylallyl polyoxyethylene or allyl polyoxyethylene ether has a molecular weight of between 1,000 and 4,000.

25 In Embodiments 1-10, the carbon material is a multi-walled carbon nanotube after surface treatment with a coupling agent.

In Embodiments 1-10, the antioxidant is a mixture of the primary antioxidant 1010 and the secondary antioxidant 168 with mass ratio of 3:1.

In Embodiments 1-10, the initiator is dicumyl peroxide or dibenzoyl peroxide.

30 In Embodiments 1-10, the fibers are 3–6mm long glass fibers that are surface treated.

In Embodiments 1-10, the filler was a polypropylene-based calcium carbonate masterbatch in which calcium carbonate accounted for 60% of the mass.

The specific steps to prepare and produce the above polypropylene-based cooling tower filler are as follows:

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1. The raw materials are weighed according to the ratio stated previously.
2. The modifier and initiator are dissolved in absolute ethanol to form a solution or a turbid liquid.
3. Polypropylene, ethylene propylene copolymer, polypropylene grafted maleic anhydride, antioxidant, carbon materials, fibers and fillers are mixed evenly and then calendered in an open mill.
4. After the materials in (3) are completely plasticized, the solution or turbid liquid disposed in (2) is sprayed onto the surface of the plasticized materials by a spray device to carry out a graft reaction at 175-210°C;
5. mixing and calendering of the triangle pack continues for another 5-15 minutes after the spraying is complete, to ensure a thorough grafting reaction. The synthetic material of polypropylene-based cooling tower filler can then be obtained.
5. The synthetic material in (4) is extruded into a sheet, and then compression-molded to obtain a flat sheet of the polypropylene-based cooling tower filler.

In Embodiments 1-10, the duration between the beginning of plasticization and the end of mixing and calendering process is between 20 and 40 minutes.

The specific components and the amount of each in embodiments 1-10 are shown in Table 1

Table 1 Filler Components and Amounts in Embodiment 1-10

Embodiments	1	2	3	4	5	6	7	8	9	10
Z30S	50	50	50	50	50	50	50	50	50	50
T1701	50	50	50	50	50	50	50	50	50	50
EAA	10	10	10	10	10	10	10	10	10	10
PP-g-MAH	10	10	10	10	10	10	10	10	10	10
DCP	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
HPEG	1	2	4	5	6	8	9	10	12	0
TPEG	1	2	2	2	4	4	6	7	8	0
Antioxidant	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MWCNTs	5	6	7	8	9	10	12	14	15	0
Glass Fiber	15	15	15	15	15	15	15	15	15	15
Calcium Carbonate Masterbatch	20	20	20	20	20	20	20	20	20	20

Embodiment 10 is the comparative embodiment.

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The modified polypropylene-based cooling tower packing was treated at 80 ° C and 85% RH for 48 hours. Its water contact angle, thermal conductivity and tensile strength were measured afterwards. Table 2 shows the test results of each embodiment.

Table 2 Embodiments 1-10 Filler Testing Results

Embodiment	1	2	3	4	5	6	7	8	9	10
Water Contact Angle (°)	98	89	71	65	62	54	41	32	18	101
Thermal Conductivity (W/(m·K))	0.34	0.37	0.36	0.35	0.37	0.48	0.53	0.56	0.58	0.27
Tensile Strength (MPa)	36	38	35	33	31	30	31	28	24	32

5 Table 2 shows that the water contact angle of the filler prepared by the invention is obviously smaller than that of the comparative embodiment 10, providing better water affinity and improved heat exchange efficiency. The thermal conductivity is noticeably superior to the comparative embodiment 10. The tensile strength has also been significantly improved. The invention introduces modifiers with a carbon-carbon double bond. The addition of the modifiers
 10 can easily initiate self-polymerization, which lengthens the graft chain, increases the size of the molecular group, promotes water to spread on the surface, and improves the heat dissipation efficiency of cooling tower packing. The inventions also uses fibers and carbon materials to enhance polypropylene materials. The rigidity of carbon materials improves the mechanical properties of polypropylene materials; additionally, carbon materials have good thermal
 15 conductivity. The introduction of carbon materials can optimize the thermal conductivity of polypropylene and improve the heat dissipation efficiency of the cooling tower filler.

The present invention adopts the optimal technical solution to improve the cooling tower filler's thermal conductivity, mechanical properties, and contact angle-related properties.

20 The above embodiments are merely illustrative of preferred embodiments of the invention and are not intended to limit the scope of the invention. Without departing from the spirit of the design of the present invention, various modifications and improvements of the technical solutions of the present invention made by those of ordinary skill in the art should be within the scope of the invention as defined by the appended claims.

25 Other than the above-described embodiments, the present invention may have other embodiments. Any technical solution formed by equivalent replacement or equivalent transformation falls within the protection scope of the present invention.

CLAIMS

1. A modified polypropylene-based cooling tower filler, comprising the following components:
polypropylene: 100 parts, ethylene-propylene copolymer: 10 parts, polypropylene grafted maleic anhydride: 10 parts, initiator: 0.05-2 Parts, modifier: 2-20 parts, antioxidant: 0.1-2 parts, carbon material: 5-15 parts, fiber: 5-20 parts, filler: 10-30 parts.
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2. A modified polypropylene-based cooling tower filler stated in claim 1, wherein the polypropylene is comprised of a mixture of homopolymer polypropylene and copolymerized polypropylene at a ratio of between 1:3 and 3:1.
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3. A modified polypropylene-based cooling tower filler stated in claim 1, comprising modifiers selected from at least one of the following three: methyl allyl polyoxyethylene ether, allyl alcohol polyoxyether or (and) allyl polyoxyethylene ether; comprising the carbon materials selected from at least one of the following: carbon fibers, multi-walled carbon nanotubes, single-arm carbon nanotubes and graphene, after surface modification; comprising the initiator of dicumyl peroxide or benzoyl peroxide.
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4. A modified polypropylene-based cooling tower filler stated in claim 3, comprising the methallyl polyoxyethylene or allyl polyoxyethylene ether with a molecular weight of 1,000 to 4,000.
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5. A modified polypropylene-based cooling tower filler stated in claim 1, comprising the antioxidant of a mixture of the main antioxidant 1010 and the secondary antioxidant 168, with the mass ratio of 3:1.
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6. A modified polypropylene-based cooling tower filler stated in claim 1, comprising the fibers selected from at least one of the following fibers with a length of 2-8 mm.: glass fibers, basalt fibers, boron fibers, ceramic fibers and modified aramid fibers.
7. A modified polypropylene-based cooling tower filler stated in claim 1, comprising the filler of a polypropylene-based calcium carbonate masterbatch, of which 60% is calcium carbonate.
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CLAIMS

8. A process to produce the modified polypropylene-based cooling tower filler stated in claim 1, comprising the following steps:
- (1). The raw materials are weighed according to the ratio stated in claim 1.
 - (2). The modifier and initiator are dissolved in absolute ethanol to form a solution or a turbid liquid.
 - (3). Polypropylene, ethylene propylene copolymer, polypropylene grafted maleic anhydride, antioxidant, carbon materials, fibers and fillers are mixed evenly and then calendered in an open mill.
 - (4). After the materials in (3) are completely plasticized, the solution or turbid liquid disposed in (2) is sprayed onto the surface of the plasticized materials by a spray device to carry out a graft reaction;
Mixing and calendaring of the triangle pack continues for another 5-15 minutes after the spraying is complete, to ensure a thorough grafting reaction. The synthetic material of polypropylene-based cooling tower filler can then be obtained.
 - (5). The synthetic material in (4) is extruded into a sheet, and then compression-molded to obtain a flat sheet of the polypropylene-based cooling tower filler.
9. A process to produce the modified polypropylene-based cooling tower filler stated in claim 8, comprising step (4) with the grafting reaction at a reaction temperature of 175-210°C.
10. A process to produce the modified polypropylene-based cooling tower filler stated in claim 8, comprising the duration between the beginning of plasticization and the end of mixing and calendaring process being between 20 and 40 minutes.