

Continuous Method for Manufacturing Rubber Masterbatch and Rubber Masterbatch Prepared Thereby

TECHNICAL FIELD

[0001] The invention relates to the rubber field, especially to a continuous method for manufacturing a rubber masterbatch and a rubber masterbatch prepared thereby.

BACKGROUND

[0002] In the rubber/filler/additive/solvent system, the coagulation of the rubber/filler/additive from the solvent is a very important step in the manufacturing of the rubber/filler/additive masterbatch. As described in WO98/58985, the process is carried out in an apparatus comprising a large turbo-dryer with blade rotated at 400/1200 revolutions per minute, the speeds of coagulation and drying in this method are slow, the process is long and the energy consumption is high. The present invention relates to several high-speed mixing/coagulation methods, wherein the coagulation medium, including gas, especially high temperature gas and liquid, is mixed instantaneously with the rubber/filler/additive mixture in high-energy turbulence state, and due to the high temperature effect of the gas and difference in polarity between the liquid medium and the solvent, the rubber/filler/additive in the rubber/filler/additive/solvent mixture will occur a desolvation phenomenon in the solvent, so as to carry out coagulation. Due to the high-speed turbulence effect, the mixture and coagulation medium, i.e., the desolvation medium will be mixed in a very short period of time. Due to the greatly increased interface between the desolvation medium and the rubber/filler/additive/solvent, the coagulation speed of the rubber/filler/additive in the solvent is very fast, when the temperature of the desolvation medium is high, the solvent will quickly volatilized in the coagulation process, so that the coagulated rubber particles are small, therefore the solvent volatilization and drying effect of the coagulated rubber are further accelerated. Therefore, as compared with the prior art, the drying method designed in this present application has the characteristics of high efficiency, energy-saving and continuous operation.

SUMMARY

[0003] With respect to the problems present in the prior art, one purpose of the present invention is to provide a continuous method for manufacturing a rubber masterbatch and a rubber masterbatch prepared thereby. Another purpose of the present invention is to provide a rubber article prepared by using the rubber masterbatch of the present invention.

[0004] The continuous method for manufacturing a rubber masterbatch in the present invention has the following advantages:

[0005] 1) the process is continuous and highly efficient;

[0006] 2) the drying is uniform and rapid;

[0007] 3) the physical and mechanical properties of the vulcanized rubber and the quality of the rubber article are significantly improved;

[0008] 4) as compared with the coagulation technology in the prior wet compounding, the present invention has no special requirements on the rubber and the filler, thus having a wide application range with respect to the types and contents of the rubber, filler and additive;

[0009] 5) the production device and process are very simple, continuous, and highly efficient, and have low energy consumption, and less labour, thus the cost is low; and

[0010] 6) the masterbatch prepared by the method has excellent processability, physical and mechanical properties, and product quality.

[0011] The invention further relates to the following embodiments:

[0012] A continuous method for manufacturing a rubber masterbatch, comprises the following steps:

[0013] step 1): a filler is added into a rubber solution so as to form a rubber/filler/solvent mixture under stirring;

[0014] step 2): the rubber/filler/solvent mixture in step 1) is coagulated so as to obtain a mixture of rubber/filler complex and solvent; and

[0015] step 3): the solvent is removed and the mixture is dried so as to obtain a rubber/filler masterbatch;

[0016] wherein the drying in step 3) comprises the mixture obtained in step 2) is transferred to a heating conveyor belt dryer, and carried out heat drying in vacuum or inert gas, and the volatilized solvent and the unreacted monomer in rubber synthesis are sent into a condenser and a fractionation column for recovery; or the drying in step 3) comprises the mixture obtained in step 2) is spray dried or flashed, the heating medium used is an inert gas or water vapor, and the volatilized solvent and the unreacted monomer in rubber synthesis are sent into a condenser and a fractionation column for recovery.

[0017] Preferably, among them, the coagulating in step 2) can be one or more of a flocculant flocculation method, heating method, and desolvation method, or a combination thereof.

[0018] Preferably, among them, the solvent removed in step 3) is optionally recovered for recycling.

[0019] Preferably, among them, one or more additives selected from oil, anti-aging agent, coupling agent, active agent, antioxidant, flame retardant, heat stabilizer, light stabilizer, dye, pigment, vulcanizing agent and accelerator are optionally added in step 1) and/or step 2).

[0020] Preferably, among them, water vapor is used as the heating medium, and the solid mixture obtained after drying will contain water, then carried out vacuum drying, heat drying or extrusion heat drying, so as to obtain a rubber/filler masterbatch.

[0021] Preferably, among them, the inert gas is nitrogen.

[0022] More preferably, among them, the heat drying is oven drying or air drying.

[0023] More preferably, among them, the extrusion heat drying comprises first removing water by extrusion, then carrying out a further drying.

[0024] More preferably, among them, the further drying is air drying, oven drying, or mechanical drying.

[0025] More preferably, among them, the mechanical drying is drying by using an open mill, kneader, internal mixer, continuous internal mixer, single-screw extruder, and twin-screw extruder.

[0026] The present invention further provides a rubber masterbatch prepared by the abovementioned method.

[0027] Further, the present invention also provides a rubber article prepared by using the abovementioned masterbatch.

[0028] The continuous method for manufacturing a rubber masterbatch in the present invention comprises the following steps:

[0029] step 1): a filler is added into a rubber solution so as to form a rubber/filler/solvent mixture under stirring;

[0030] step 2): the rubber/filler/solvent mixture in step 1) is coagulated so as to obtain a mixture of rubber/filler complex and the solvent; and

[0031] step 3): the solvent is removed and the mixture is dried so as to obtain a rubber/filler masterbatch;

[0032] wherein the drying in step 3) comprises the mixture obtained in step 2) is transferred to a

heating conveyor belt dryer, and carried out heat drying in vacuum or inert gas, and the volatilized solvent and the unreacted monomer in rubber synthesis are sent into a condenser and a fractionation column for recovery; or the drying in step 3) comprises the mixture obtained in step 2) is spray dried or flashed, the heating medium used is an inert gas or water vapor, and the volatilized solvent and the unreacted monomer in rubber synthesis are sent into a condenser and a fractionation column for recovery.

[0033] Among them, the coagulation method in step 2) can use any method known in the art, such as one or more of a flocculant flocculation method, heating method, desolvation method, etc., or a combination thereof. The continuous method for manufacturing a rubber masterbatch in the present invention further optionally comprises a step of recovering the solvent removed in step 3) for recycling. In addition, one or more additives selected from oil, anti-aging agent, coupling agent, active agent, antioxidant, flame retardant, heat stabilizer, light stabilizer, dye, pigment, vulcanizing agent and accelerator are optionally added in step 1) and/or step 2).

[0034] Step 1) can be carried out by using the method known in the art. The stirring in step 1) may be carried out by using a common stirrer, including, but being not limited to, blade stirrer, tank stirrer, planetary stirrer, crank stirrer, and the like.

[0035] Step 1) can further comprise a step of fine dispersion, the fine dispersion can be carried out as follows: the mixture obtained after stirring is ejected through a nozzle under high pressure and high shear, so as to improve the dispersion of the filler and/or additive; the ejected material is passed through a multi-elbow pipe to make the mixed solution collided with the pipe wall in the pipe, thus increasing the dispersion of the filler and/or additive; or the ejected material is passed through a pipe, of which the inner diameter is changed in shrinkage and expansion for many times, to change shear stress, thus increasing the dispersion of the filler and/or additive. The used pressure range is from 0.1 MPa to 60 MPa, preferably 10 MPa to 40 MPa.

[0036] The mixture formed after the fine dispersion can also be carried out the following refine dispersion to further improve the dispersion of the filler and/or additive in the rubber solution:

[0037] i. the mixture obtained after the fine dispersion is added continuously into a ball mill and/or colloid mill for dispersion, so that the filler and/or additive are uniformly dispersed in the rubber solution;

[0038] ii. the mixture obtained after the fine dispersion is added continuously into a grinder for grinding, so that the filler and/or additive are dispersed adequately in the rubber solution, the grinder has one or more sets of the high speed rotating flat grinding discs and fixed pins or fixed discs fixed on the grinder sleeve and interleaved with the flat grinding discs.

[0039] iii. the mixture obtained after fine dispersion is added continuously into the grinder for grinding, the grinder has two blades rotating in the opposite directions, the blades have a pore gutter, the dispersion degree of the filler and/or additive in the rubber solution is improved by the rotating blade under high pressure. The used pressure range is from 0.1 MPa to 60 MPa, preferably 10 MPa to 40 MPa.

[0040] iv. the mixture obtained after the fine dispersion is continuously added into a multi-layer high-pressure slit disperser, and extruded from the slit between the two layers under high pressure, so that the produced strong shear force can improve the dispersion degree of the filler and/or additive in the rubber solution. The used pressure range is from 0.1 MPa to 60 MPa, preferably 10 MPa to 40 MPa.

[0041] v. the mixture obtained after the fine dispersion is continuously added to a power disperser for dispersion, the high-speed rotating rotors in the power disperser have many radially distributed slits or pores, the mixture is collided on the surface of the stator at a high speed to make the filler and/or additive uniformly dispersed in the rubber solution.

[0042] Two or more of the above five fine dispersion methods can be used in tandem.

[0043] The rubber solution can be directly obtained from the production line for preparation of solution-polymerized rubber, and also can be prepared by dissolving any type of dry rubber in the solution of the rubber. When preparing the rubber solution with dry rubber, the dry rubber may be any kind of rubber used in the art, such as natural polymer or synthetic polymer. The natural polymer includes, but is not limited to, natural rubber, gutta-percha, guayule, and the like; the synthetic polymer includes, but is not limited to, the material obtained by polymerizing a monomer in a solution (i.e., solution-polymerized rubber), the material obtained by polymerizing a monomer in an emulsion (i.e., emulsion-polymerized rubber), and the material obtained by polymerizing a monomer itself. When the rubber solution is directly obtained from the production line for preparation of solution-polymerized rubber, the solution-polymerized rubber is a homopolymer or copolymer of monomer of ethylene, propylene, butylene, pentene, hexene, heptene, diene having 4-7 carbon atoms or triene having 6-7 carbon atoms, or alkenes containing other atoms or functional groups, the other atoms or functional groups comprise silicon atom, fluorine atom, chlorine atom, nitrogen atom, oxygen atom, sulfur atom, ester group, amino ester group, and cyano group, and also comprise a homopolymer and copolymer containing the abovementioned monomers, including, but being not limited to, polybutadiene, polyisoprene, styrene butadiene rubber, ethylene-propylene rubber, butyl rubber, butadiene nitrile rubber, neoprene, silicone rubber, fluorine rubber, polyurethane rubber, chlorosulfonated polyethylene

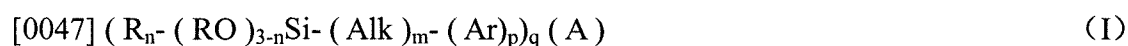
rubber, acrylate rubber, and the like. The rubber has a molecular weight of 1000 to 40 million, preferably 5000 to 30 million, and more preferably 10000 to 8 million.

[0044] The solvents in the rubber solution are good solvents for various kinds of rubbers. Specifically, the solvent can be aliphatic hydrocarbon solvent, aromatic hydrocarbon solvent, chlorinated hydrocarbon solvent, ketone solvent, ether solvent and ester solvent, the aliphatic hydrocarbon solvent comprises, but is not limited to, various kinds of solvent gasoline, cycloalkane, substituted cycloalkane, and n-alkane, the aromatic hydrocarbon solvent comprises, but is not limited to, benzene, toluene, xylene, and styrene, the chlorinated hydrocarbon solvent comprises, but is not limited to, methylene chloride, chloroform, carbon tetrachloride, dichloroethane, chlorobenzene, tetrachloroethylene, and chlorotoluene. The concentration range of the rubber in the solution is from 1% to 60% by weight, preferably 5% to 40% by weight, and more preferably from 10% to 30% by weight.

[0045] The filler comprises, but is not limited to, various kinds of solid powder reinforcing agents and fillers used in the rubber, such as various types of carbon black, silica, metal oxides, salts, various resins and nanoscale materials of the abovementioned fillers. Among them, the metal oxide comprises, but is not limited to, aluminum oxide, magnesium oxide, zinc oxide, and the like, the salt comprises, but is not limited to, calcium carbonate, pottery clay, and nanoscale materials of the abovementioned fillers. The specific surface area of the filler is 0.1 to 800 m²/g, preferably 1 to 500 m²/g, and more preferably 5 to 300 m²/g. With respect to carbon black, and silica (white carbon black), they have an oil absorption value of 20 to 250 ml/100 g, preferably 25 to 200 ml/100 g, and more preferably 30 to 150 ml/100 g, wherein the filler comprises a mixture thereof, such as multiphase filler, including, but being not limited to, biphasic or multiphasic filler composed of carbon black, silica, alumina, magnesium oxide, zinc oxide, calcium oxide, titanium oxide, boron oxide and the like. With respect to the biphasic or multiphasic filler, they have an oil absorption value of 20 to 250 ml/100 g, preferably 25 to 200 ml/100 g, and more preferably 30 to 150 ml/100 g. The used amount of filler is between 5 and 300 parts by weight (based on 100 parts by weight of the rubber), preferably 10 to 200 parts by weight, and more preferably 30 to 150 parts by weight. The filler also comprises a combination of two or more of the abovementioned fillers.

[0046] The filler also comprises the surface modified filler thereof. Among them, the surface modification can be made by a chemical reaction to attach some functional groups on the filler surface or by mixing or adsorption to physically combine the modifier on the filler surface. With respect to the modification, the modifier can be dissolved in the solvent, then mixed with the

filler to carry out a liquid phase modification, such as described in Wang W, Nanse G, Vidal, A, et al., K. G. K. [J], 1994, 47:493, and the modifier can also be mixed with the filler and heated to carry out a solid phase modification, such as described in Wang MJ, Wolff S. R.C.T [J], 1992, 65:715. The surface modification can also be carried out before adding the filler in the rubber solution, or during the period of adding the modifier to the mixture of the rubber solution and the filler. The modifier is a conventional modifier in the art, such as an organic silane coupling agent illustrated in the following general formula:



[0050] wherein, when $q = 1$, A is -SCN, -SH, -Cl, -NH₂;

[0051] when $q = 2$, A is -S_x-;

[0052] R and R' are branched or linear alkyl or phenol groups having 1 to 4 carbon atoms, R and R' can be the same or different;

[0053] n is 0, 1 or 2;

[0054] Alk is a linear or branched alkyl having 1 to 6 carbon atoms;

[0055] Alk_{enyl} is a linear or branched alkenyl having 1 to 6 carbon atoms;

[0056] m is 0 or 1;

[0057] Ar is an aryl having 6 to 12 carbon atoms;

[0058] p is 0 or 1, p and n cannot be 0 both;

[0059] x is 2 to 8;

[0060] wherein those most commonly used is bis(triethoxy propyl silane)tetrasulfide and disulfide, 3-sulfur cyano propyl-triethoxy silane, γ - mercapto-trimethoxysilane, zirconium acid ester coupling agent, titanate coupling agent, nitro coupling agent, and alcohol compound. The alcohol compound comprises, but is not limited to, monohydric alcohol, dihydric alcohol, and polyhydric alcohol. The alcohol compound comprises, but is not limited to, propyl alcohol, butyl alcohol, ethylene glycol, polyethylene glycol and their derivatives.

[0061] In step 1) of the present invention, the filler and/or additive can be directly added to the rubber solution, and the filler and/or additive can also be added firstly to a solvent which is the same or different from the rubber solution, and mixed, so as to form an uniform suspension, then

added, and mixed in the rubber solution under stirring. The additive can optionally comprise one or more additives selected from oil, anti-aging agent, coupling agent, active agent, antioxidant, heat stabilizer, light stabilizer, flame retardant, dye, pigment, vulcanizing agent or accelerator. The used amount of the additive is the conventional amount, or can be adjusted according to the requirement of the actual situation.

[0062] The coagulation in Step 2) can be one or more of a flocculant flocculation method, heating method, and desolvation method, or a combination thereof.

[0063] Preferably, in Step 2), the rubber/filler/solvent mixture in step 1) is transferred into the coagulator, and contacted and mixed with one or more fluids selected from nitrogen gas, water vapor, water, filler aqueous slurry and oil in the coagulator, then coagulated, so as to obtain a mixture of rubber/filler complex and solvent.

[0064] The coagulator used in step 2) can be a tubular coagulator having one or more feed inlets, wherein the feed direction of the feed inlets can be parallel with the axial direction of the tubular coagulator pipe, and the outlet is at the end of the pipe, and can also be at an angle of $1-180^{\circ}$ with respect to the axial direction of the tubular coagulator pipe, preferably $20-120^{\circ}$, more preferably $70-100^{\circ}$, and most preferably $85-95^{\circ}$. When there are a plurality of feed inlets, the feed direction of a part of the feed inlets is parallel with the axial direction of the tubular coagulator pipe; and the feed direction of the other feed inlets is at an angle of $1-180^{\circ}$ with respect to the axial direction of the cylinder of the tubular coagulator, preferably $20-120^{\circ}$, more preferably $70-100^{\circ}$, and most preferably $85-95^{\circ}$, and the projection of the feed direction of each feed inlet on a cross section perpendicular to the pipe axis is any direction between the radial direction of the cross section and the tangential direction of the cross section, preferably the radial direction, or the tangential direction. The feed inlets are all on the same planar surface perpendicular to the axial direction of the pipe or the feed inlets are on the different planar surfaces.

[0065] The coagulator used in step 2) can also be a coagulator composed of two or more concentric pipes, wherein each pipe has one or more feed inlets, the feed direction of the feed inlets is parallel with the axial direction of the pipe or at the tangential direction of the pipe, and the outlet is at the end of the pipe. The fluid can be directly introduced, or introduced in the tangential direction of the pipe wall. The end of the feed inlet of each pipe can be on the same planar surface, and the end of the feed inlet of each pipe can also be longer or shorter sequentially from inside to outside.

[0066] The coagulator used in step 2) can also be a cylinder coagulator, wherein the

cylinder coagulator has only one feed inlet, which is located on the upper end or wall of the cylinder coagulator, and the outlet is at the lower end of the cylinder. The fluid can be directly injected into the coagulator through the feed inlet, and can also be injected into coagulator in the tangential direction along the cylinder wall.

[0067] The coagulator used in step 2) can also be a cone type structure having a cylinder upper portion and a conical lower portion, and has one or more feed inlets. The feed direction of the feed inlets can be the tangential direction of the cylinder wall; each feed inlet can be on the same planar surface, and also can be on the different planar surfaces. The feed direction of the feed inlets can also be perpendicular to the axial direction of the cylinder or at an angle of 1-180° with respect to the axial direction of the cylinder, preferably 20-110°, more preferably 70-100°, and most preferably 85-95°. The projection of the feed direction of each feed inlet on a cross section perpendicular to the cylinder axis is any direction between the radial direction of the cross section and the tangential direction of the cross section, preferably the tangential direction of the cross section.

[0068] The one or more fluids selected from nitrogen gas, water vapor, water, filler aqueous slurry and oil in step 2) and the rubber/filler/solvent mixture obtained in step 1) are introduced into a coagulator through one or more feed inlets, wherein the temperature of nitrogen is 20-300°C, the temperature of water vapor is 100-300°C, the temperature of the liquid water is 20-100°C, the temperature of the oil is 20-300°C, and the temperature of the filler aqueous slurry is 20-100°C. The oil is the common one for manufacturing an oil-filled rubber in the rubber field. The oil optionally used in step 1) can be the same or different from the oil used in step 2). The fillers used in step 1) can also be the same or different from the fillers used in step 2).

[0069] The drying in step 3) comprises the mixture obtained in step 2) is transferred in a heating conveyor belt dryer, carried out heat drying in vacuum or inert gas (such as nitrogen), and the volatilized solvent and the unreacted monomer in rubber synthesis are sent into a condenser and a fractionation column for recovery; or the mixture obtained in step 2) is spray dried or flashed, the heating medium used is an inert gas (for example nitrogen) or water vapor, and the volatilized solvent and the unreacted monomer in rubber synthesis are sent into a condenser and a fractionation column for recovery.

[0070] Among them, when water vapor is used as a heating medium, the solid mixture obtained after drying will contain water, then carried out vacuum drying, heat drying or extrusion heat drying, so as to obtain a rubber/filler masterbatch. The vacuum drying comprises vacuum drying at ambient temperature, frozen vacuum drying and heat vacuum drying. The heat drying

can be a common drying mode, such as oven drying or air drying. The extrusion heat drying comprises first removing the heating medium by extrusion, then carrying out a further drying, wherein the further drying is air drying, oven drying or mechanical drying, the mechanical drying is drying by using an open mill, kneader, internal mixer, continuous internal mixer, single-screw extruder, and twin-screw extruder.

[0071] The method for recovering solvents can use any method known in the art, for example the gasified solvent is recovered by the surface condensation or direct contact condensation method. When using the direct contact condensation method, the coolant can be water.

[0072] The technical features of the present invention are listed as follows:

[0073] i. the technical features of the present invention are strong process adaptability: not only an rubber/filler/additive masterbatch can be prepared by generally mixing a rubber solution which have simple process and slightly lower filler dispersion and product performance, with fillers and additives, and using the direct heating method, but also a rubber/filler/additive masterbatch which have higher cost and better performance can be manufactured by using a specially designed dispersion device, mixing coagulator and a mechanical drying method; the masterbatches prepared by different processes can appropriately meet the requirements of different rubber articles.

[0074] ii. The technical features of the present invention are the use of a specially designed coagulator, which is one device composed of one or more inlets and one outlet. When a refinedly dispersed rubber/filler/additive/solvent mixture is injected into the coagulator in a high-speed and high turbulence state, due to the very high speed, and according to the principles of hydromechanics and turbulence hydromechanics, the internal pressure of the mixture is decreased sharply. Under the effect of high shear, the mixture will be formed into small droplets, in addition, the low boiling solvent in the liquid mixture can reach its boiling point under low pressure, so that the volatilization of the solvent is accelerated, thus separating the solvent from the mixture. Such separation process can also be realized by ejecting the mixture droplets containing a large amount of solvent vapor from the coagulator through a narrow outlet, due to the increased flow rate, the pressure is decreased greatly, so that the gasification speed and degree of the solvent are increased greatly. When the mixed fluid is injected into a drying device containing a high temperature gas such as nitrogen, the increased temperature makes the solvent quickly diffused from the mixture to the hot atmosphere, thus greatly increasing the drying efficiency.

[0075]iii. The abovementioned coagulation and desolvation mode in the present invention is that the rubber/filler/additive/solvent mixture is injected into the coagulator with a plurality of inlets through one or two of the coagulator, and nitrogen is injected through the other one or more inlets. When the introduced mixture and gas are both in a high-energy and high-speed turbulence state, the mixing of them can be completed within a few milliseconds to tens of milliseconds, and the mixture is formed into droplets during this time. The solvent in the droplets is rapidly expanded and gasified under the low pressure of the turbulence, so that the rubber/filler/additive components in the mixture are quickly coagulated so as to form a dispersed solid/liquid/gas three-phase mixture. In the process, when the temperature of the nitrogen injected into the coagulator is high, the expansion and gasification speed of the solvent and the coagulation speed of the solid will be greatly improved, and the liquid components will be reduced greatly. In the extreme situations, it becomes a gas-solid two-phases composed of only solid coagulation products and nitrogen gas and solvent vapor. When three-phase or two-phase mixture is passed through the narrow outlet of the coagulator, due to the increased flow rate, the pressure of the fluid is further reduced, so that the gasification degree and speed of the solvent are greatly increased and the liquid phase is reduced rapidly. When the mixed fluid is injected into a drying device containing a high temperature gas such as nitrogen atmosphere, due to the increased temperature, the solvent remained in the rubber/filler/additive coagulation product is further volatilized quickly and diffused into the hot gas phase, thus greatly increasing the drying efficiency.

[0076] iv. One mode of the abovementioned coagulation and desolvation in the present invention is when the oil is included in the additive, the rubber/filler/additive (which contains no or only the oil required in part of the rubber compounds)/solvent mixture is injected into a coagulator with a plurality of inlets through one or two inlets of the coagulator under high pressure and high speed, and the oil is injected through the other one or more inlets. The amount of oil is the difference between the amount required in the masterbatch formulation and the amount of the used oil in the rubber/filler/additive/solvent mixture. The mixture and the oil are rapidly mixed and coagulated under the condition of high-energy turbulence, and the low pressure of the high-speed turbulent fluid will make the solvent gasified quickly and separated from the rubber/filler/additive complex. When the temperature of the oil is increased, due to the high oil heat capacity, the gasification process of the solvent will be accelerated. When the formed foggy mixture of solid, liquid and gas is injected into a drying device containing a high temperature gas at a high speed through a narrow outlet, due to the reduced fluid pressure caused by ejecting, the foggy solid-liquid phase dispersion state further increases the contact area with

the gas phase, so that the gasification speed of the solvent is accelerated, and at the same time, the high temperature atmosphere will also greatly improve the efficiency of desolvation.

[0077] v. One mode of the abovementioned coagulation and desolvation in the present invention is the rubber/filler/additive/solvent mixture is injected into a coagulator with a plurality of inlets through one or two inlets of the coagulator under the high pressure and high speed, and high pressure water vapor is injected through the other one or more inlets. Under the desolvation effect of water and high temperature, the rubber/filler/additive is coagulated in the solvent in a few milliseconds to tens of milliseconds, and is in a foggy state under low pressure, and the solvent is volatilized greatly. Due to the latent heat of the vapor liquification, the gasification speed of the solvent is much faster than that of hot nitrogen. But the formed foggy three-phase mixture of solid, liquid and gas is also added with water. When the mixture is injected into a high temperature gas at a high speed through a narrow outlet of the coagulator under high pressure, due to the reduced pressure and further increased temperature, water and the solvent are gasified and separated from the solid-phase rubber/filler/additive complex, and gone into the gas phase, thus increasing the drying efficiency of the complex.

[0078] vi. One mode of the abovementioned coagulation and desolvation in the present invention is the rubber/filler/additive/solvent mixture is injected into a mixer/coagulator with a plurality of inlets through one or two inlets of the mixer/coagulator under high pressure and high speed, and at the same time water, especially the high temperature water, is injected into the coagulator through the other inlet under high pressure and high speed. Under high-energy turbulent state, and in combination with the desolvation effect of water on rubber solution, the rubber/filler/additive will be coagulated in a few milliseconds to tens of milliseconds. Due to the low pressure characteristics of the high-energy turbulent liquid, especially when the high temperature water is used, the solvent is rapidly reached to its boiling point and volatilized, and the water is also partially gasified. When a three-phase mixture of solid, liquid and gas in the coagulator is injected into the drying device containing a high temperature air or nitrogen through the narrow outlet under high pressure, due to the low pressure formed by the high speed, the fluid will be dispersed in high temperature air or nitrogen in foggy state. The huge specific surface area of the rubber/filler/additive solid/liquid phase coagulated in the fog and low pressure will make the water and solvent therein further volatilized, thus increasing the drying effect of the solid complex off water and solvent. If too much water is injected into the coagulator, the complex obtained after coagulating the rubber/filler/additive can be mixed in water. At this time, the complex containing water is separated from water by the general separation methods such as filtration, centrifugation, etc., then dried.

[0079] vii. One mode of the abovementioned coagulation and desolvation in the present invention is the rubber/filler/additive/solvent mixture is injected into a coagulator with plurality of inlets through one or more inlets of the coagulator under high pressure and high speed, and the filler aqueous slurry, preferably high temperature filler aqueous slurry, is injected into the coagulator from other inlets at the same time under high pressure and high speed. In high-energy turbulence state, and in combination with the desolvation effect of water on the rubber solution, the rubber/filler/additive/solvent is uniformly mixed with the filler aqueous slurry, and the coagulation of the rubber/filler/additive will be completed in a few milliseconds to tens of milliseconds. Due to the low pressure property of the high-energy turbulence, especially when the high temperature filler aqueous slurry is used, the solvent is rapidly reached its boiling point and volatilized, and water is also partially gasified. After the solid-liquid-gas three-phase mixture in the mixer/coagulator is sent into the collecting device through the narrow outlet under high pressure, due to the low pressure caused by high speed, the fluid will be dispersed in a foggy form in the high temperature air or nitrogen. On one hand, due to the decreased pressure, and on the other hand, due to the greatly increased contact surface between solid and liquid phase and gas, the solvent and the water therein are quickly diffused into the gas phase. If too much water is injected into the filler aqueous slurry in the coagulator and ejected, water can not be completely volatilized, the complex obtained after coagulating the rubber/filler/additive can be mixed in water, at this time, the complex containing water is separated from water by the common separation methods, such as filtration, centrifugation, etc., then dried.

[0080] viii. The technical features of the present invention are when a high temperature inert gas is injected into the coagulator, the solid masterbatch particles obtained after coagulating and desolventizing in the coagulator can be separated from solvent gas through a separator so as to obtain a masterbatch. The separator comprises, but is not limited to, cyclone separator. Such technology allows the entire masterbatch manufacturing process not contact with water.

[0081] ix. The technical features of the present invention are when the complex obtained after coagulating any rubber/filler/additive contains water, water can removed by filtrating and extrusion, then dried at high temperature by a mechanical method. The drying devices can be an open mill, a kneader, an internal mixer, a continuous internal mixer, a single-screw extruder, and a twin-screw extruder. This method can further improve the dispersion of the fillers and additives.

DETAILED DESCRIPTION

[0082] The present invention is further described by the examples below, but the scope of the

present invention is not limited thereto.

[0083] 1. The experimental data in the examples are determined by using the following instruments and measuring methods:

[0084] Table 1. The instruments for preparation of the rubber samples

[0085]

No.	Device Name	Model No.	Manufacturer
1	Internal Mixer	XSM-1/10-120	Shanghai Kechuang Rubber Plastic Mechanical Equipment Co., Ltd.
2	Open Mill	152.5*320	Guangdong Zhanjiang Machinery Factory
3	Flat Vulcanizer	XLB-D600*600	Zhejiang Huzhou Dongfang Machinery Co., Ltd.

[0086] Table 2. Methods and instruments for testing the physical properties of the vulcanized rubbers

[0087]

No.	Test items	Test standards	Device name	Model No.	Manufacturer
1	Dispersion of filler in rubber compound	--	Carbon Black Dispersion Tester	GT-505-CBD	Gotech Testing Machines Inc.
2	Hardness	GB/T 531.1-2008	Hardness Meter (Shore A)	LX-A	Shanghai Liuling Instrument Factory
3	Tensile Strength (MPa)	GB/T 528-2009	Servo Control Tensile Tester	A1-3000	Gotech Testing Machines Inc.
4	Elongation at break (%)	GB/T 528-2009	Servo Control Tensile Tester	A1-3000	Gotech Testing Machines Inc.
5	Rebound resilience (%)	GB/T 1681-2009	Resilience Elasticity Tester	GT-7042-RE	Gotech Testing Machines Inc.
6	Heat generated by fatigue	GB/T 1687-1993	Flexometer	RH-2000N	Gotech Testing Machines Inc.
7	Abrasion Tester	GB/T1689-1998	DIN Abrasion Tester	GT7012-A	Gotech Testing Machines Inc.

[0088] 2. Examples and comparative examples

[0089] Raw materials:

[0090] Synthetized polyisoprene rubber, IR-70, Qingdao Yikesi New Material Co., Ltd.;

[0091] White carbon black, NEWSIL1165-MP, Wuxi Quechen Silicon Chemical Co., Ltd.;

[0092] Zinc oxide, Dalian Zinc Oxide Co., Ltd.;

[0093] Stearic acid, PF1808, Malaysia Integrated Fortune Sdn. Bhd.;

[0094] Anti-aging agent 4020, Jiangsu Sinorgchem Technology Co., Ltd.;

[0095] Silane coupling agent Si69, Nanjing Shuguang Chemical Group Co., Ltd.;

[0096] Accelerator CZ, Shandong Sunsine Chemical Co., Ltd.;

[0097] Accelerator DPG, Shandong Shanxian County Chemical Co., Ltd.;

[0098] Sulfur, Wudi Jinsheng Chemical Co., Ltd.

[0099] Comparative Example 1

[0100] 56 parts of white carbon black and 5.6 parts of silane coupling agent Si69 were added to 100 parts of synthetized cis-polyisoprene in an internal mixer for compounding, after the fillers were mixed in the rubber, 3.5 parts of zinc oxide, 2 parts of stearic acid, and 2 parts of anti-aging agent 4020 were added, then compounded for 4 minutes, discharged from the internal mixer, then rolled and batched out in an open mill so as to obtain a pre-compounding rubber. After standing for 8 hours, 2 parts of accelerator CZ, 1 part of accelerator DPG and 1.8 parts of sulfur were added to the pre-compounding rubber in the open mill so as to prepare a compounding rubber. After the obtained rubber material was batched out in the open mill and stood for 8 hours, it was vulcanized in a Flat Vulcanizer at 150°C until reaching optimum cure point, so as to prepare a dry vulcanized rubber 1.

[0101] Example 1

[0102] 56 parts of white carbon black, 5.6 parts of silane coupling agent Si69, and 3.5 parts of zinc oxide were added to 100 parts of 12% cis-polyisoprene in n-hexane, the rubber/white carbon black/Si69/n-hexane mixture was preliminarily mixed in a blade stirrer, then the mixture was injected into a multi-elbow pipe through a nozzle so as to make the mixed solution collided with the pipe wall in the pipe, thus increasing the dispersion of filler. Then the mixture was continuously added into a grinder for a refine dispersion, so as to obtain a refinedly dispersed mixture. Then the mixture was continuously injected into a cone coagulator with four inlets

through two inlets of the cone coagulator under a pressure of 30 MPa, and at the same time nitrogen at a temperature of about 180°C was continuously injected into the cone coagulator through the other two inlets thereof. Then the obtained mixture was continuously injected into a drier filled with nitrogen at a temperature of about 150°C, the solvent is volatilized from the rubber/white carbon black/Si69/n-hexane expanded droplet in 1-10 seconds, so as to form desolventized rubber particles, and the mixture of nitrogen and solvent containing power rubber particles was separated from the rubber particles by a cyclone separator so as to obtain power masterbatch 1.

Example 2

56 parts of white carbon black, 5.6 parts of silane coupling agent Si69, and 3.5 parts of zinc oxide were added to 100 parts of 12% cis-polyisoprene in n-hexane, the rubber/white carbon black/Si69/n-hexane mixture was preliminarily mixed in a blade stirrer, then the mixture was injected in a multi-elbow pipe through a nozzle so as to make the mixed solution collided with pipe wall in the pipe, thus increasing the dispersion of filler. Then the mixture is continuously added into a grinder for a refine dispersion, so as to obtain a refinedly dispersed mixture. Then the mixture was continuously injected into a cone coagulator with four inlets through two inlets of the cone coagulator under a pressure of 30 MPa, and at the same time water at a temperature of about 95°C was continuously injected into the cone coagulator through the other two inlets thereof, so as to make the mixture coagulated. The coagulated and desolventized rubber particles are filtrated, then dried in a vacuum drier under vacuum of -0.08 MPa for 20 min, then collected, so as to obtain a masterbatch 2.

Example 3

56 parts of white carbon black, 5.6 parts of silane coupling agent Si69, and 3.5 parts of zinc oxide were added to 100 parts of 12% cis-polyisoprene in n-hexane, the rubber/white carbon black/Si69/n-hexane mixture was preliminarily mixed in a blade stirrer, then the mixture was injected in a multi-elbow pipe through a nozzle to make the mixed solution collided with the pipe wall in the pipe, thus increasing the dispersion of filler. Then the mixture was continuously added into a grinder for a refine dispersion, so as to obtain a refinedly dispersed mixture. Then the mixture was continuously injected into a cone coagulator with four inlets through two inlets of the cone coagulator under a pressure of 30 MPa, and at the same time water at a temperature of about 95°C was continuously injected into the cone coagulator through the other two inlets thereof to make the mixture coagulated. The coagulated and desolventized rubber particles were filtrated, then dried in a single screw extruder for 3 min, so as to obtain a masterbatch 3.

In the internal mixer, to the above obtained masterbatches 1-3, 2 parts of stearic acid and 2 parts of anti-aging agent 4020 were added, then compounded for 4 min, discharged from the internal mixer, then the rubber compound is rolled and batched out in an open mill. After compounding and standing for 8 hours, 2 parts of accelerator CZ, 1 part of accelerator D and 1.8 parts of sulfur were added in the internal mixer, then compounded for 1.5 min, and discharged from the internal mixer. The obtained rubber material was batched out in the open mill, and stood for 8 hours, then vulcanized in a Flat Vulcanizer at 150°C until reaching optimum cure point, so as to prepare wet vulcanized rubbers 1, 2 and 3 respectively.

Table 3. The physical properties of the vulcanized rubbers

	Dry vulcanized rubber	Wet vulcanized rubber 1	Wet vulcanized rubber 2	Wet vulcanized rubber 3
Dispersion degree of White Carbon Black	3.5	7.6	8.0	8.8
Hardness, RT, Shore A	69.5	64.7	62.5	63.5
Tensile Strength, MPa	28.4	28.5	29.0	30.4
Elongation at break, %	484	446	463	447
Rebound resilience 23°C, %,	53.2	56.2	56.3	57.8
Rebound resilience, 60°C, %,	63.2	66.0	66.5	67.8
Bottom Temperature Rise , °C	21.8	18.2	17.0	15.8

DIN Abrasion Index, %	100	108	107	121
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As shown in Table 3, under the same formulations, due to the different drying methods used in wet compounding rubber, the properties of the prepared vulcanized rubbers are also different. Compared the wet masterbatch with the dry masterbatch, the dispersion degree of the filler in the rubber is greatly improved, the tensile strength, rebound resilience and abrasion resistance of the vulcanized rubbers are significantly improved, and the heat generated by compression fatigue is reduced.

CLAIMS

1. A continuous method for manufacturing a rubber masterbatch, comprising:

step 1): a filler is added to a rubber solution so as to form a rubber/filler/solvent mixture under stirring;

step 2): the rubber/filler/solvent mixture in step 1) is coagulated so as to obtain a mixture of rubber/filler complex and solvent; and

step 3): the solvent is removed and the mixture is dried so as to obtain a rubber/filler masterbatch;

wherein the coagulating in step 2) includes one or more of a flocculant flocculation method, heating method, and desolvation method, or a combination thereof;

wherein the drying in step 3) comprises that the mixture obtained in step 2) is transferred to a heating conveyor belt dryer, carried out heat drying in vacuum or an inert gas, and the volatilized solvent and the unreacted monomer in rubber synthesis are sent into a condenser and a fractionation column for recovery; or the drying in step 3) comprises that the mixture obtained in step 2) is spray dried or flashed, the heating medium used is an inert gas or water vapor, and the volatilized solvent and the unreacted monomer in rubber synthesis are sent into a condenser and a fractionation column for recovery.
2. The method according to claim 1, wherein the solvent removed in step 3) is recovered for recycling.
3. The method according to claim 1, wherein one or more additives selected from oil, anti-aging agent, coupling agent, active agent, antioxidant, flame retardant, heat stabilizer, light stabilizer, dye, pigment, vulcanizing agent and accelerator are added in step 1) and/or step 2).
4. The method according to any one of claims 1-3, wherein water vapor is used as the heating medium, the solid mixture obtained after drying will contain water, and then carries out vacuum drying, heat drying or extrusion heat drying, so as to obtain a rubber/filler masterbatch.
5. The method according to any one of claims 1-3, wherein the inert gas is nitrogen.
6. The method according to claim 4, wherein the heat drying is oven drying or air drying.
7. The method according to claim 4, wherein the extrusion heat drying comprises first removing water by extrusion, then carrying out a further drying.
8. The method according to claim 7, wherein the further drying is air drying, oven drying,

or mechanical drying.

9. The method according to claim 8, wherein the mechanical drying is drying by selecting one or more of an open mill, kneader, internal mixer, continuous internal mixer, single-screw extruder, and twin-screw extruder.

10. A method for manufacturing a rubber article, the method comprising:
manufacturing a rubber masterbatch by a method according to any one of claims 1 to 9, and
processing the rubber masterbatch into a rubber article.