

LIQUID STYRENE-BUTADIENE RUBBER, AND PREPARATION METHOD THEREFOR AND USE THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

5 **[0001]** This application claims priority to Chinese patent application No. 202311382441.8, filed with the China National Intellectual Property Administration on October 24, 2023 and entitled “Liquid styrene-butadiene rubber, preparation method and application thereof”, the entire contents of which are hereby incorporated by reference into the present application.

TECHNICAL FIELD

10 **[0002]** The present invention relates to the field of liquid styrene-butadiene rubber, specifically, the present invention relates to a liquid styrene-butadiene rubber, preparation method therefor and use thereof.

BACKGROUND OF THE INVENTION

15 **[0003]** Liquid rubber is a viscous oligomer liquid with a relative molecular weight ranging from 500 to 50,000. It exhibits a certain degree of fluidity at room temperature, and its viscosity changes according to the molecular weight and molecular configuration. There are many types of liquid rubber, such as liquid styrene-butadiene rubber, liquid nitrile butadiene rubber, and liquid
20 ethylene propylene rubber. Liquid rubber has advantages such as excellent fluidity, ease of processing, and low energy consumption compared to solid rubber, and is thus widely used in sealing materials, adhesives, tires, and other fields.

[0004] Liquid styrene-butadiene rubber is a diene copolymer-based liquid rubber prepared by free radical or anionic polymerization of butadiene and styrene. Because of its operational
25 simplicity, ease of temperature control, and high polymerization rate, free radical emulsion polymerization is currently the most widely employed method for preparation. Compared to a natural rubber, a liquid styrene-butadiene rubber exhibits a certain level of adhesion, temperature resistance, abrasion resistance, and mechanical properties, as well as good compatibility with some general-purpose rubbers, and is therefore widely used in applications such as adhesives, fillers,
30 and tires. However, in some rather extreme environments, the performance of traditional liquid styrene-butadiene rubber can no longer meet the material performance requirements. Therefore, it is necessary to further develop liquid styrene-butadiene rubber with improved temperature resistance, abrasion resistance, corrosion resistance, and mechanical properties.

[0005] CN103539912A discloses a method for preparing high-performance liquid styrene-

butadiene rubber, in which a terpene resin is first dissolved at 80-110 °C and then grafted onto styrene-butadiene latex by emulsion polymerization, affording a terpene-resin-modified liquid styrene-butadiene rubber. Substantively, however, this approach is the modification of styrene-butadiene rubber, and does not involve the polymerization process of styrene-butadiene itself, thus, it falls into the category of post-polymerization modification of liquid styrene-butadiene rubber.

[0006] CN115124663A discloses a modified styrene-butadiene rubber comprising a styrene-butadiene rubber matrix and a modified polymer bonded to at least a portion of the surface of the styrene-butadiene rubber matrix. The modified polymer includes polymer chain segments of a first monomer and polymer chain segments of a second monomer; the first monomer is selected from acrylamide compounds, (methyl)acrylate compounds, polyene compounds, or combinations thereof; and the second monomer is selected from azo initiators containing olefinically unsaturated groups. The modified styrene-butadiene rubber according to this application exhibits a high grafting rate, and the polymer chain segments of the second monomer in the modified styrene-butadiene rubber can further promote the cross-linking reaction between the functional groups in monomer polymer chains of the first monomer and other modifiers containing olefinic unsaturated groups during the preparation process of asphalt waterproofing membranes, thereby imparting excellent aging resistance. In this technical solution, styrene-butadiene rubber is employed as the base. On this basis, a free-radical solution polymerization is carried out, in which ester-containing monomers and azo initiators are used to achieve ternary copolymerization. This process does not involve polymerization of styrene-butadiene rubber and thus is classified as a post-polymerization modification of the rubber.

[0007] CN1468877A discloses a method for synthesizing a hydroxyl-terminated liquid styrene-butadiene rubber. The method involves using butadiene and styrene as monomers and an organic peroxide as the initiator to obtain a hydroxyl-terminated liquid styrene-butadiene rubber via free-radical solution polymerization.

[0008] CN111560096A discloses a method for preparing styrene-butadiene rubber. The method involves conducting an emulsion polymerization reaction at a polymerization temperature of $\leq 5^{\circ}\text{C}$ under a nitrogen atmosphere. In this process, styrene, butadiene, water, an emulsifier, an electrolyte, a reducing agent, an environmentally friendly molecular-weight regulator, and an initiator are employed as raw materials to carry out polymerization, resulting in the production of styrene-butadiene rubber. However, this method merely replaces the conventional modifier for styrene-butadiene rubber without further enhancing its performance.

[0009] CN110527020A discloses a method for preparing styrene-butadiene rubber, comprising the following steps: (1) butadiene, styrene, an emulsifier, an electrolyte, a deoxygenating agent, an activator, an oxidant, a regulator, and demineralized water are mixed and

subjected to emulsion polymerization; upon completion of the reaction, the system is degassed and then an antioxidant is added to afford a latex, in which the oxidant is pinane hydroperoxide; (2) the latex is added to water containing a flocculant and a concentrated sulfuric acid and stirred; after the latex coagulates, it is filtered and dried to obtain raw styrene-butadiene rubber, wherein the concentrated sulfuric acid is a sulfuric acid solution with a weight fraction of greater than or equal to 70%; (3) the raw styrene-butadiene rubber is mixed with carbon black and sulfur and then vulcanized to obtain styrene-butadiene rubber. This preparation method can effectively shorten the polymerization time, reduce the amount of regulator used, and lower down energy consumption. Moreover, the use of the preparation method enables the preparation of various styrene-butadiene latexes and qualified styrene-butadiene rubber products.

[0010] CN108017743A discloses a modified carboxylated styrene-butadiene latex and the preparation method thereof. The preparation method for the modified carboxylated styrene-butadiene latex comprises the following steps: (1) in the presence of an initiator, a mixed system containing butadiene, styrene, acrylic acid, a retarder, a molecular weight regulator, water, a pH buffer, a chelating agent, and an emulsifier is polymerized sequentially at 55-60°C and 65-75°C; (2) the polymerization reaction product is mixed with an oil phase containing a nitrile-functional monomer, styrene, and butadiene, and with a water phase containing water, an initiator, an emulsifier, and a molecular weight regulator, and the resulting mixture is polymerized sequentially at 75-80°C and 85-90°C. The modified carboxylated styrene-butadiene latex prepared by the method provided in this application not only has a small particle size but also exhibits excellent stability and extremely high adhesive strength. This method involves the ternary copolymerization of carboxylated styrene-butadiene latex at 55-60°C and 65-75°C, followed by graft copolymerization with functional monomers containing cyano groups. The method results in a high number-average molecular weight but is quite complex.

SUMMARY OF THE INVENTION

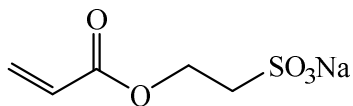
[0011] The purpose of the present invention is to provide a liquid styrene-butadiene rubber, a preparation method and use thereof.

[0012] In the present invention, sodium isethionate and acrylic acid are used as raw materials to prepare an ester-containing monomer, which is subsequently employed as a third monomer in the preparation of liquid styrene-butadiene rubber. By improving the feeding methods and raw material formulations, and introducing multi-stage addition of the emulsifier, ester-containing monomer, and molecular weight regulator in a low-temperature emulsion polymerization method, a liquid styrene-butadiene rubber with improved temperature resistance, abrasion resistance and corrosion resistance, and mechanical properties is produced.

[0013] To accomplish the above objectives, the present invention adopts a technical solution as follows.

[0014] The present invention provides a liquid styrene-butadiene rubber, of which the polymerizable monomers comprises butadiene, styrene, and a sulfonate group-containing ester monomer;

[0015] wherein the sulfonate group-containing ester monomer has a structural formula of:



[0016] The liquid styrene-butadiene rubber according to the present invention, preferably, 50-75 parts by weight of butadiene, 20-30 parts by weight of styrene, and 5-24 parts by weight of the sulfonate group-containing ester monomer are included, based on 100 parts of the total weight of the butadiene, the styrene, and the sulfonate group-containing ester monomer.

[0017] The liquid styrene-butadiene rubber according to the present invention, preferably, the liquid styrene-butadiene rubber is prepared by emulsion copolymerization of butadiene, styrene, and the sulfonate group-containing ester monomer.

[0018] The liquid styrene-butadiene rubber contains 3-18 wt% of the sulfonate group-containing ester monomer structure.

[0019] The liquid styrene-butadiene rubber according to the present invention, preferably, the liquid styrene-butadiene rubber has a Mooney viscosity of 40-60 Pa·s at 25°C and a number-average molecular weight (Mn) ranging from 3,000 to 5,000.

[0020] The present invention also provides a method for preparing a liquid styrene-butadiene rubber comprising the following steps:

[0021] introducing 160-220 parts of demineralized water, 4-8 parts of an emulsifier, 0.1-0.3 parts of a reducing agent, 0.1-0.4 parts of a dispersant, 0.4-0.8 parts of an electrolyte, 3-6 parts of a molecular weight regulator, 20-30 parts of styrene, 3-20 parts of the sulfonate group-containing ester monomer, and 0.01-0.1 parts of an oxygen scavenger to a reaction vessel, based on a total of 100 parts by weight of the butadiene, the styrene, and the sulfonate group-containing ester monomer; then introducing 50-75 parts of butadiene under a protective atmosphere, while stirring the mixture for pre-emulsification; and subsequently, introducing 0.1-0.2 parts of initiator to carry out a polymerization reaction;

[0022] introducing an additional amount of the emulsifier, the initiator, the molecular weight regulator, and the sulfonate group-containing ester monomer when the three monomers, i.e. the butadiene, the styrene, and the sulfonate group-containing ester monomer reach a pre-determined monomer conversion rate; and introducing 0.05-0.2 parts of a terminating agent to stop

the reaction when the monomer conversion rate reaches 82%-87%; and then subjecting the resultant to degassing, coagulation, washing, and drying to obtain the liquid styrene-butadiene rubber.

[0023] In the preparation method according to the present invention, preferably, the step of introducing an additional amount of the emulsifier, the initiator, the molecular weight regulator, and the sulfonate group-containing ester monomer when the three monomers, i.e. the butadiene, the styrene, and the sulfonate group-containing ester monomer reach a pre-determined monomer conversion rate specifically comprises:

[0024] introducing additionally 1-2 parts of the sulfonate group-containing ester monomer when the monomer conversion rate reaches 25-30%; introducing additionally 0.4-0.8 parts of the emulsifier, 0.002-0.004 parts of the initiator, and 0.5-0.8 parts of the molecular weight regulator when the monomer conversion reaches 50-55%; and introducing additionally 1-2 parts of the sulfonate group-containing ester monomer when the monomer conversion reaches 65-70%.

[0025] In the preparation method according to the present invention, preferably, the emulsifier is an anionic-anionic mixed surfactant or an anionic-nonionic mixed surfactant; wherein, the anionic-anionic mixed surfactant is a mixed surfactant of rosin soap and a fatty alkyl sulfonate in a weight ratio of (4-5):1; and the anionic-nonionic mixed surfactant is a mixed surfactant of rosin soap and a polyoxyethylene ether in a weight ratio of (3-4):1.

[0026] In the preparation method according to the present invention, preferably, the emulsifier is used in an amount of 5-6 parts.

[0027] In the preparation method according to the present invention, preferably, the reducing agent is at least one selected from, but is not limited to, sodium formaldehyde sulfoxylate, ferrous sulfate, cuprous sulfate, EDTA ferric sodium salt, and EDTA copper sodium salt, and the like.

[0028] In the preparation method according to the present invention, preferably, the reducing agent is used in an amount of 0.2-0.3 parts.

[0029] In the preparation method according to the present invention, preferably, the dispersant is a sodium naphthalenesulfonate-formaldehyde condensate, which is at least one selected from, but is not limited to, sodium β -naphthalenesulfonate-formaldehyde condensate, sodium methyl naphthalenesulfonate-formaldehyde condensate, benzyl naphthalenesulfonate-formaldehyde condensate, and the like; more preferably, sodium β -naphthalenesulfonate-formaldehyde condensate.

[0030] In the preparation method according to the present invention, preferably, the dispersant is used in an amount of 0.2-0.3 parts.

[0031] In the preparation method according to the present invention, preferably, the electrolyte is potassium phosphate or potassium chloride.

[0032] In the preparation method according to the present invention, preferably, the electrolyte is used in an amount of 0.5-0.6 parts.

[0033] In the preparation method according to the present invention, preferably, the molecular weight regulator is at least one selected from, but is not limited to, dodecyl mercaptan, tert-dodecyl mercaptan, and 2,4-diphenyl-4-methyl-1-pentene; more preferably, the molecular weight regulator is tert-dodecyl mercaptan or 2,4-diphenyl-4-methyl-1-pentene.

[0034] In the preparation method according to the present invention, preferably, the molecular weight regulator is used in an amount of 4-5 parts.

[0035] In the preparation method according to the present invention, preferably, the oxygen scavenger is at least one selected from, but is not limited to, sodium dithionite, dimethyl ketoxime, and isoascorbic acid, and the like; more preferably, sodium dithionite.

[0036] In the preparation method according to the present invention, preferably, the oxygen scavenger is used in an amount of 0.04-0.08 parts.

[0037] In the preparation method according to the present invention, the initiator is preferably an organic peroxide, including, but not limited to, cumene hydroperoxide, diisopropylbenzene hydroperoxide, and isopropyl tert-butyl peroxide, more preferably, diisopropylbenzene hydroperoxide.

[0038] In the preparation method according to the present invention, preferably, the initiator is used in an amount of 0.12-0.18 parts.

[0039] In the preparation method of the present invention, preferably, the polymerization reaction temperature is 5-25°C, preferably 10-15°C.

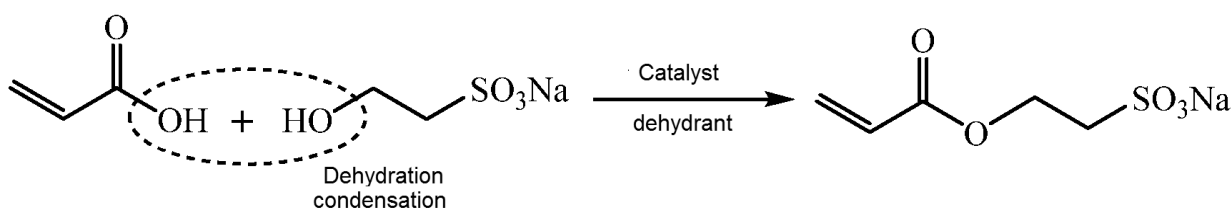
[0040] In the preparation method according to the present invention, preferably, the terminating agent is at least one selected from, but is not limited to, hydroxylamine sulfate, diethylhydroxylamine, isopropylhydroxylamine, and the like; more preferably, isopropylhydroxylamine or diethylhydroxylamine.

[0041] In the preparation method according to the present invention, preferably, the terminating agent is used in an amount of 0.05-0.1 parts.

[0042] In the preparation method of the present invention, the degassing is preferably carried out in a degassing tower; more preferably, it is carried out for 4 to 5 hours; after degassing, an ester-containing styrene-butadiene latex is obtained. Subsequently, the resultant is subjected to coagulation, washing, and drying to obtain the liquid styrene-butadiene rubber. The coagulation, washing, and drying processes are all conventional techniques in the preparation of liquid styrene-butadiene rubber, and they are not limited in the present invention. The “protective gas” is, for example, nitrogen or argon.

[0043] The preparation method for the high-performance modified liquid styrene-butadiene rubber in the present invention is simple and clear, and can be industrially carried out through ternary copolymerization using existing equipment. A sulfonate group-containing ester monomer containing both ester and sulfonate groups is introduced on the basis of conventional styrene-butadiene rubber. The introduction of ester groups can improve the heat resistance, ozone stability, and mechanical properties of liquid styrene-butadiene rubber, while the incorporation of sulfonate groups can alter the polarity of the liquid styrene-butadiene rubber, thereby further enhancing its abrasion resistance by modifying the surface polarity of the styrene-butadiene rubber. Meanwhile, the present invention employs a multi-stage process for introducing additionally the emulsifier, sulfonate group-containing ester monomer, initiator, and molecular weight regulator so as to control the molecular weight of the high-performance modified liquid styrene-butadiene rubber and to improve the uniformity of the distribution of ester groups in the liquid styrene-butadiene rubber.

[0044] According to the preparation method of the present invention, preferably, the sulfonate group-containing ester monomer is prepared by the following reaction scheme, including:



[0045] Adding acrylic acid, sodium isethionate, a dehydrant, and a catalyst to a reaction vessel, and heating the mixture to carry out an esterification reaction under a protective atmosphere, wherein during the reaction, the water formed and the dehydrant are continuously distilled off, and the dehydrant is separated and refluxed to the reaction vessel to participate in the reaction; terminating the reaction when the amount of separated water ceases to increase and reaches a theoretically calculated value; and then filtering the resultant to obtain a filter cake, which is subjected to distillation at a reduced pressure to obtain the sulfonate group-containing ester monomer.

[0046] In the preparation process of the sulfonate group-containing ester monomer of the present invention, preferably, the esterification reaction is carried out at a temperature of 110-120°C for a reaction time of 12-15 hours.

[0047] In the preparation process of the sulfonate group-containing ester monomer of the present invention, preferably, the molar ratio of sodium isethionate to acrylic acid is 1:(1-1.5), more preferably, 1:(1.2-1.3).

[0048] In the preparation process of the sulfonate group-containing ester monomer of the

present invention, preferably, the dehydrant is at least one selected from toluene, ethylbenzene, and p-xylene; more preferably, toluene or xylene.

[0049] In the preparation process of the sulfonate group-containing ester monomer of the present invention, preferably, the dehydrant is added in an amount of 4-6 times relative to the total weight of acrylic acid and sodium isethionate.

[0050] In the preparation process of the sulfonate group-containing ester monomer of the present invention, preferably, the catalyst is an organic sulfonic acid, and is at least one selected from, but is not limited to, methanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, and 2-naphthalenesulfonic acid; more preferably, benzenesulfonic acid or p-toluenesulfonic acid.

[0051] In the preparation process of the sulfonate group-containing ester monomer of the present invention, preferably, the catalyst is used in an amount of 0.2-0.8 wt%, more preferably, 0.4-0.6 wt%, based on the total weight of sodium isethionate and acrylic acid.

[0052] In another aspect of the present invention, a liquid styrene-butadiene rubber obtained by the above preparation methods is provided.

[0053] The liquid styrene-butadiene rubber according to the present invention, preferably, the liquid styrene-butadiene rubber contains 3-18 wt% of a sulfonate group-containing ester monomer structure; the liquid styrene-butadiene rubber has a Mooney viscosity of 40-60 Pa·s at 25°C and a number-average molecular weight (Mn) ranging from 3,000 to 5,000.

[0054] The method for preparing sulfonate group-containing ester functional monomers developed in this invention is highly suitable for industrial synthesis. Unlike current industrial practices that use concentrated sulfuric acid as a catalyst, the present invention uses sodium isethionate and acrylic acid as raw materials, an organic sulfonic acid as the catalyst, and a dehydrant as the solvent. By azeotropically removing the water produced during the esterification reaction, the efficiency of the esterification process is improved. This approach enables the industrial-scale production of a sulfonate group-containing ester monomer, achieving yields of 90% or more and ensuring a self-sufficient supply of sulfonate group-containing ester monomer raw materials for the production of high-performance modified liquid styrene-butadiene rubber. Subsequently, an emulsion copolymerization method was employed to conduct a ternary copolymerization of the sulfonate group-containing ester monomer with butadiene and styrene. By employing a multi-stage addition process for the emulsifier, sulfonate group-containing ester monomer, molecular weight regulator, and initiator, a high-performance modified liquid styrene-butadiene rubber is prepared. The high-performance modified liquid styrene-butadiene rubber incorporates sulfonate group-containing ester. It has a Mooney viscosity of 40-60 Pa·s at 25°C and a number-average molecular weight (Mn) ranging from 3,000 to 5,000, providing excellent fluidity and processability. The incorporation of an ester group structure improves the polymer's heat

resistance, and the introduction of a sulfonate group enhances its abrasion resistance. The high-performance modified liquid styrene-butadiene rubber can be used as a substitute for rubber processing oil, toughening agents, and tire tread rubber to improve tire performance.

5 **[0055]** In another aspect, the present invention provides the use of the above liquid styrene-butadiene rubber as a toughening agent for tires or epoxy resins.

BRIEF DESCRIPTION OF THE DRAWINGS

[0056] Fig. 1 is the nuclear magnetic resonance (NMR) spectrum of the sulfonate group-containing ester monomer prepared in Example 3.

10 **[0057]** Fig. 2 is the NMR spectrum of the high-performance modified liquid styrene-butadiene rubber prepared in Example 3.

[0058] Fig. 3 is a graph showing the effect of different amounts of high-performance modified liquid styrene-butadiene rubber on the abrasion resistance of a cured epoxy resin.

DESCRIPTION OF THE EMBODIMENTS

15 **[0059]** To further illustrate the present invention, the present invention will be described in detail with reference to the following preferred embodiments. It should be understood by those skilled in the art that the content described below is provided for purposes of illustration only and is not intended to limit the scope of the invention in any way.

20 **[0060]** All numerical values (such as temperature, time, concentration, weight, and the ranges of any of the foregoing) are to be understood as approximate and may vary by ± 0.1 or ± 1.0 units. All specified numerical values should be understood as being preceded by the term “about”.

[0061] Example 1

25 **[0062]** In this example, a high-performance modified liquid styrene-butadiene rubber was prepared by a process comprising the following steps:

[0063] S1: At room temperature, sodium isethionate (148 g, 1 mol), acrylic acid (72 g, 1 mol), and benzenesulfonic acid (0.44 g, 0.2 wt%) were introduced to a reaction vessel containing 880 g of toluene. The mixture was heated to 110°C under a nitrogen atmosphere and was allowed to react for 12 h to effect the esterification of acrylic acid with sodium isethionate. During the
30 reaction, the generated water and the dehydrant were continuously distilled. The dehydrant was separated and refluxed to the reaction vessel to continue the reaction. The volume of the water separated was measured, and once it reached the theoretical value, the reaction was terminated. The raw material solution was filtered to give a filter cake, which was returned to the reactor. The dehydrant, toluene, was removed by a distillation at a reduced pressure at 50°C and 0.2 MPa. The
35 resultant was then subjected to a distillation at a reduced pressure at 72°C and 0.4 MPa, giving

175.1 g of a sulfonate group-containing ester monomer in a yield of 86.7%.

[0064] S2: In a 10 L polymerization reactor, 160 parts of demineralized water, 4 parts of an emulsifier (rosin soap and fatty alkyl sulfonate with a mixing ratio of 4:1), 0.1 parts of sodium formaldehyde sulfoxylate, 0.1 parts of sodium β -naphthalenesulfonate-formaldehyde condensate, 0.4 parts of potassium phosphate, 3 parts of tert-dodecyl mercaptan, 20 parts of styrene, 3 parts of a sulfonate group-containing ester monomer, and 0.01 parts of sodium dithionite were introduced. After completion of the introduction, the reactor was purged three times with nitrogen. Then, 75 parts of butadiene were introduced. Subsequently, 0.1 parts of diisopropylbenzene hydroperoxide were added at 5°C to initiate the polymerization.

[0065] Once the three monomers, butadiene, styrene, and the sulfonate group-containing ester monomer reached a conversion rate of 25%, 1 part of the sulfonate group-containing ester monomer was additionally introduced; when the monomer conversion rate reached 50%, 0.4 parts of an emulsifier, 0.002 parts of diisopropylbenzene hydroperoxide, and 0.5 parts of tert-dodecyl mercaptan were additionally introduced; when the monomer conversion rate reached 65%, 1 part of the sulfonate group-containing ester monomer was additionally introduced. When the monomer conversion rate reached 82%, 0.05 parts of hydroxylamine sulfate were introduced to terminate the reaction, and the reaction mixture was discharged. The discharged material was degassed in a degassing tower for 4 h to obtain an ester-containing styrene-butadiene latex, which was then coagulated, washed, and dried to afford a high-performance liquid styrene-butadiene rubber containing sulfate and ester groups.

[0066] Example 2

[0067] In this example, a high-performance modified liquid styrene-butadiene rubber was prepared by a process comprising the following steps:

[0068] S1: At room temperature, sodium isethionate (148 g, 1 mol), acrylic acid (108 g, 1.5 mol), and benzenesulfonic acid (2.048 g, 0.8 wt%) were introduced to a reaction vessel containing 1536 g of toluene. The mixture was heated to 120°C under a nitrogen atmosphere and was allowed to react for 15 h to effect the esterification of acrylic acid with sodium isethionate. During the reaction, the generated water and the dehydrant were continuously distilled. The dehydrant was separated and refluxed to the reaction vessel to continue the reaction. The volume of the water separated was measured, and once it reached the theoretical value, the reaction was terminated. The raw material solution was filtered to give a filter cake, which was returned to the reactor. The dehydrant, toluene, was removed by a distillation at a reduced pressure at 50°C and 0.2 MPa. The resultant was then subjected to a distillation at a reduced pressure at 72°C and 0.4 MPa, giving 178.4 g of a sulfonate group-containing ester monomer in a yield of 88.3%.

[0069] S2: In a 10 L polymerization reactor, 220 parts of demineralized water, 8 parts of an

emulsifier (rosin soap and fatty alkyl sulfonate with a mixing ratio of 5:1), 0.3 parts of ferrous sulfate, 0.4 parts of sodium methyl naphthalenesulfonate-formaldehyde condensate, 0.8 parts of potassium chloride, 6 parts of dodecyl mercaptan, 21 parts of styrene, 5 parts of a sulfonate group-containing ester monomer, and 0.1 part of sodium dithionite were introduced. After completion of the introduction, the reactor was purged three times with nitrogen. Then, 70 parts of butadiene were introduced. Subsequently, 0.1 parts of cumene hydroperoxide were added at 25°C to initiate the polymerization.

[0070] Once the three monomers, butadiene, styrene, and the sulfonate group-containing ester monomer reach a conversion rate of 30%, 2 parts of the sulfonate group-containing ester monomer were additionally introduced; when the monomer conversion rate reached 55%, 0.8 parts of an emulsifier, 0.004 parts of cumene hydroperoxide, and 0.8 parts of dodecyl mercaptan were additionally introduced; when the monomer conversion rate reached 70%, 2 parts of the sulfonate group-containing ester monomer were additionally introduced. When the monomer conversion rate reaches 87%, 0.05 parts of diethylhydroxylamine were introduced to terminate the reaction, and the reaction mixture is discharged. The discharged material was degassed in a degassing tower for 5 h to obtain an ester-containing styrene-butadiene latex, which was then coagulated, washed, and dried to afford a high-performance liquid styrene-butadiene rubber containing sulfate and ester groups.

[0071] Example 3

[0072] In this example, a high-performance modified liquid styrene-butadiene rubber was prepared by a process comprising the following steps:

[0073] S1: At room temperature, sodium isethionate (148 g, 1 mol), acrylic acid (86.4 g, 1.2 mol), and benzenesulfonic acid (1.172 g, 0.5 wt%) were introduced to a reaction vessel containing 950 g of toluene. The mixture was heated to 120°C under a nitrogen atmosphere and was allowed to react for 15 h to effect the esterification of acrylic acid with sodium isethionate. During the reaction, the generated water and the dehydrant were continuously distilled. The dehydrant was separated and refluxed to the reaction vessel to continue the reaction. The volume of the water separated was measured, and once it reached the theoretical value, the reaction was terminated. The raw material solution was filtered to give a filter cake, which was returned to the reactor. The dehydrant, toluene, was removed by a distillation at a reduced pressure at 50°C and 0.2 MPa. The resultant was then subjected to a distillation at a reduced pressure at 72°C and 0.4 MPa, giving 186.6 g of a sulfonate group-containing ester monomer in a yield of 92.4%.

[0074] S2: In a 10 L polymerization reactor, 190 parts of demineralized water, 5 parts of an emulsifier (rosin soap and fatty alkyl sulfonate with a mixing ratio of 4:1), 0.2 parts of EDTA ferric sodium salt, 0.3 parts of benzyl naphthalenesulfonate-formaldehyde condensate, 0.5 parts of

potassium phosphate, 4 parts of 2,4-diphenyl-4-methyl-1-pentene, 26 parts of styrene, 12 parts of a sulfonate group-containing ester monomer, and 0.05 parts of isoascorbic acid were introduced. After completion of the introduction, the reactor was purged three times with nitrogen. Then, 60 parts of butadiene were introduced. Subsequently, 0.15 parts of isopropyl tert-butyl peroxide were added at 15°C to initiate the polymerization.

[0075] Once the three monomers, butadiene, styrene, and the sulfonate group-containing ester monomer reached a conversion rate of 25%, 1 part of the sulfonate group-containing ester monomer was additionally introduced; when the monomer conversion rate reached 50%, 0.5 parts of an emulsifier, 0.003 parts of isopropyl tert-butyl peroxide, and 0.6 parts of 2,4-diphenyl-4-methyl-1-pentene were additionally introduced; when the monomer conversion rate reaches 65%, 1 part of the sulfonate group-containing ester monomer was additionally introduced. When the monomer conversion rate reached 85%, 0.05 parts of isopropylhydroxylamine were introduced to terminate the reaction, and the reaction mixture was discharged. The discharged material was degassed in a degassing tower for 5 h to obtain an ester-containing styrene-butadiene latex, which was then coagulated, washed, and dried to afford a high-performance liquid styrene-butadiene rubber containing sulfate and ester groups.

[0076] Example 4

[0077] In this example, a high-performance modified liquid styrene-butadiene rubber was prepared by a process comprising the following steps:

[0078] S1: At room temperature, sodium isethionate (148 g, 1 mol), acrylic acid (93.6 g, 1.3 mol), and benzenesulfonic acid (0.9664 g, 0.4 wt%) were introduced to a reaction vessel containing 1208 g of toluene. The mixture was heated to 115°C under a nitrogen atmosphere and was allowed to react for 14 h to effect the esterification of acrylic acid with sodium isethionate. During the reaction, the generated water and the dehydrant were continuously distilled. The dehydrant was separated and refluxed to the reaction vessel to continue the reaction. The volume of the water separated was measured, and once it reached the theoretical value, the reaction was terminated. The raw material solution was filtered to give a filter cake, which was returned to the reactor. The dehydrant, toluene, was removed by a distillation at a reduced pressure at 50°C and 0.2 MPa. The resultant was then subjected to a distillation at a reduced pressure at 72°C and 0.4 MPa, giving 181.3 g of a sulfonate group-containing ester monomer in a yield of 89.8%.

[0079] S2: In a 10 L polymerization reactor, 200 parts of demineralized water, 6 parts of an emulsifier (rosin soap and polyoxyethylene ether with a mixing ratio of 3:1), 0.1 parts of EDTA copper disodium salt, 0.2 parts of sodium β -naphthalenesulfonate-formaldehyde condensate, 0.4 parts of potassium chloride, 5 parts of 2,4-diphenyl-4-methyl-1-pentene, 23 parts of styrene, 15 parts of a sulfonate group-containing ester monomer, and 0.06 parts of dimethyl ketoxime were

introduced. After completion of the introduction, the reactor was purged three times with nitrogen. Then, 60 parts of butadiene were introduced. Subsequently, 0.12 parts of diisopropylbenzene hydroperoxide were added at 10°C to initiate the polymerization.

[0080] Once the three monomers, butadiene, styrene, and the sulfonate group-containing ester monomer reached a conversion rate of 25%, 1 part of the sulfonate group-containing ester monomer was additionally introduced; when the monomer conversion rate reached 55%, 0.8 parts of an emulsifier, 0.002 parts of cumene hydroperoxide, and 0.5 parts of 2,4-diphenyl-4-methyl-1-pentene were additionally introduced; when the monomer conversion rate reached 65%, 1 part of the sulfonate group-containing ester monomer was additionally introduced. When the monomer conversion rate reached 83%, 0.05 parts of hydroxylamine sulfate were introduced to terminate the reaction, and the reaction mixture was discharged. The discharged material was degassed in a degassing tower for 4 h to obtain an ester-containing styrene-butadiene latex, which was then coagulated, washed, and dried to afford a high-performance liquid styrene-butadiene rubber containing sulfate and ester groups.

[0081] Example 5

[0082] In this example, a high-performance modified liquid styrene-butadiene rubber was prepared by a process comprising the following steps:

[0083] S1: At room temperature, sodium isethionate (148 g, 1 mol), acrylic acid (86.4 g, 1.2 mol), and benzenesulfonic acid (1.4064 g, 0.6 wt%) were introduced to a reaction vessel containing 1200 g of toluene. The mixture was heated to 110°C under a nitrogen atmosphere and was allowed to react for 13 h to effect the esterification of acrylic acid with sodium isethionate. During the reaction, the generated water and the dehydrant were continuously distilled. The dehydrant was separated and refluxed to the reaction vessel to continue the reaction. The volume of the water separated was measured, and once it reached the theoretical value, the reaction was terminated. The raw material solution was filtered to give a filter cake, which was returned to the reactor. The dehydrant, toluene, was removed by a distillation at a reduced pressure at 50°C and 0.2 MPa. The resultant was then subjected to a distillation at a reduced pressure at 72°C and 0.4 MPa, giving 185.2 g of a sulfonate group-containing ester monomer in a yield of 91.7%.

[0084] S2: In a 10 L polymerization reactor, 180 parts of demineralized water, 7 parts of an emulsifier (rosin soap and polyoxyethylene ether with a mixing ratio of 4:1), 0.3 parts of sodium formaldehyde sulfoxylate, 0.3 parts of benzyl naphthalenesulfonate-formaldehyde condensate, 0.6 parts of potassium phosphate, 4 parts of tert-dodecyl mercaptan, 25 parts of styrene, 8 parts of a sulfonate group-containing ester monomer, and 0.04 parts of isoascorbic acid were introduced. After completion of the introduction, the reactor was purged three times with nitrogen. Then, 63 parts of butadiene were introduced. Subsequently, 0.18 parts of diisopropylbenzene hydroperoxide

were added at 10°C to initiate the polymerization.

[0085] Once the three monomers, butadiene, styrene, and the sulfonate group-containing ester monomer reached a conversion rate of 30%, 2 parts of the sulfonate group-containing ester monomer were additionally introduced; when the monomer conversion rate reached 55%, 0.4 parts of an emulsifier, 0.002 parts of diisopropylbenzene hydroperoxide, and 0.6 parts of tert-dodecyl mercaptan were additionally introduced; when the monomer conversion rate reached 70%, 2 parts of the sulfonate group-containing ester monomer were additionally introduced. When the monomer conversion rate reached 86%, 0.15 parts of isopropylhydroxylamine were introduced to terminate the reaction, and the reaction mixture was discharged. The discharged material was degassed in a degassing tower for 5 h to obtain an ester-containing styrene-butadiene latex, which was then coagulated, washed, and dried to afford a high-performance liquid styrene-butadiene rubber containing sulfate and ester groups.

[0086] Example 6

[0087] The example provides a method for preparing a high-performance modified liquid styrene-butadiene rubber and the use thereof. The rubber was prepared by a process comprising the following specific steps:

[0088] S1: At room temperature, sodium isethionate (148 g, 1 mol), acrylic acid (108 g, 1.5 mol), and benzenesulfonic acid (0.512 g, 0.2 wt%) were introduced to a reaction vessel containing 1350 g of toluene. The mixture was heated to 115°C under a nitrogen atmosphere and was allowed to react for 12 h to effect the esterification of acrylic acid with sodium isethionate. During the reaction, the generated water and the dehydrant were continuously distilled. The dehydrant was separated and refluxed to the reaction vessel to continue the reaction. The volume of the water separated was measured, and once it reached the theoretical value, the reaction was terminated. The raw material solution was filtered to give a filter cake, which was returned to the reactor. The dehydrant, toluene, was removed by a distillation at a reduced pressure at 50°C and 0.2 MPa. The resultant was then subjected to a distillation at a reduced pressure at 72°C and 0.4 MPa, giving 172.1 g of a sulfonate group-containing ester monomer in a yield of 85.2%.

[0089] S2: In a 10 L polymerization reactor, 210 parts of demineralized water, 5 parts of an emulsifier (rosin soap and fatty alkyl sulfonate with a mixing ratio of 4:1), 0.2 parts of ferrous sulfate, 0.3 parts of sodium β -naphthalenesulfonate-formaldehyde condensate, 0.5 parts of potassium phosphate, 5 parts of tert-dodecyl mercaptan, 29 parts of styrene, 18 parts of a sulfonate group-containing ester monomer, and 0.08 parts of dimethyl ketoxime were introduced. After completion of the introduction, the reactor was purged three times with nitrogen. Then, 50 parts of butadiene were introduced. Subsequently, 0.16 parts of diisopropylbenzene hydroperoxide were added at 10°C to initiate the polymerization.

[0090] Once the three monomers, butadiene, styrene, and the sulfonate group-containing ester monomer reached a conversion rate of 25%, 2 parts of the sulfonate group-containing ester monomer were additionally introduced; when the monomer conversion rate reached 50%, 0.5 parts of an emulsifier, 0.004 parts of diisopropylbenzene hydroperoxide, and 0.5 parts of tert-dodecyl mercaptan were additionally introduced; when the monomer conversion rate reaches 65%, 1 part of the sulfonate group-containing ester monomer was additionally introduced. When the monomer conversion rate reached 85%, 0.15 parts of diethylhydroxylamine were introduced to terminate the reaction, and the reaction mixture was discharged. The discharged material was degassed in a degassing tower for 4 h to obtain an ester-containing styrene-butadiene latex, which was then coagulated, washed, and dried to afford a high-performance liquid styrene-butadiene rubber containing sulfate and ester groups.

[0091] Structural Characterization and Performance Testing:

[0092] To characterize the structural features of the high-performance liquid styrene-butadiene rubber, NMR measurements were carried out on the sulfonate group-containing ester monomer and on the liquid styrene-butadiene rubber obtained in Example 3. The test results are shown in Figs. 1 and 2, respectively.

[0093] From the ^1H NMR spectrum of the sulfonate group-containing ester monomer in Fig. 1, it can be seen that: ^1H NMR (400 MHz, CDCl_3), δ 6.48 - 6.41 (m, $\text{CH}_2=\text{CH}-$, 1H), 6.22-6.12 (m, $\text{CH}_2=\text{CH}-$, 1H), 5.83-5.62 (m, $\text{CH}_2=\text{CH}-$, 1H), 4.59-4.52(t, $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2-$, 2H), 2.78-2.71 (m, $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{Na}$, 2H). The characteristic peaks match those of the sulfonate group-containing monomer, indicating that the sulfonate group-containing monomer was successfully prepared. The results for other examples are not listed here. In Examples 1-6, the yield of the sulfonate group-containing ester monomer is maintained at approximately 85%. Furthermore, unlike laboratory synthesis, the method is suitable for scaling up to industrial production.

[0094] From the ^1H NMR spectrum of the liquid styrene-butadiene rubber in Fig. 2, it can be seen that: ^1H NMR (400 MHz, CDCl_3), wherein the peak at δ 4.66 (a) corresponds to the ester moiety $-\text{COO}-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{Na}$, the peak at δ 2.74 (b) corresponds to the sulfonic acid moiety $-\text{CH}_2-\text{SO}_3\text{Na}$, the peak at δ 2.56 (c) corresponds to the benzene ring moiety $\text{C}_6\text{H}_5-\text{CH}-$, and the peak at δ 2.26 (d) corresponds to the ester moiety $-\text{CH}-\text{COO}-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{Na}$. This proves that the high-performance liquid styrene-butadiene rubber modified with the sulfonate group-containing ester monomer was successfully prepared.

[0095] In order to characterize the basic properties of the obtained liquid styrene-butadiene rubber, performance tests were conducted on the liquid styrene-butadiene rubber containing sulfate and ester groups prepared in Examples 1-6. Among them, the bound styrene content was

determined by the refractive index method according to GB/T 8658-1998; the content of the sulfonate group-containing ester monomer was obtained from the integration of the NMR peak areas; the molecular weight was measured by gel permeation chromatography according to SH/T 1759-2007; and the Mooney viscosity was determined with a Mooney viscometer (GT-7082S2) in accordance with GB/T 1232.1-2016. The test results are shown in Table 1.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Content (Bound Styrene), wt%	19.3	20.4	24.7	21.2	23.1	28.3
Content (Sulfonate group-containing Ester), wt%	3.4	8.1	12.7	14.6	10.3	17.8
Molecular Weight, Mn	4584	3169	3956	3768	4327	3862
Mooney Viscosity, Pa·s@25°C	56.1	44.3	49.8	47.2	54.7	50.2
Glass Transition Temperature, °C	-46	-49	-56	-58	-51	-54

[0096] It can be seen from Table 1 that, the sulfonate group-containing ester were incorporated in all of the high-performance modified liquid styrene-butadiene rubbers prepared in Examples 1-6, which have a Mooney viscosity of 40-60 Pa·s and a number-average molecular weight (Mn) ranging from 3,000 to 5,000, providing excellent fluidity and processability.

[0097] In order to verify the effects of the multi-stage introduction of an emulsifier, a sulfonate group-containing ester monomer, an initiator, and a molecular weight regulator during the preparation process on the performance of the high-performance modified liquid styrene-butadiene rubber, Example 3 was used as a reference. It was compared with a series of comparative examples prepared under various conditions. The comparative examples were prepared as follows:

[0098] Comparative Example 1

[0099] A same procedure as Example 3 was carried out in comparative Example 1, except that the monomers are introduced in a one-time manner without any additional introduction. The specific step S2 is as follows:

[00100] In a 10 L polymerization reactor, 190 parts of demineralized water, 5 parts of an emulsifier (rosin soap and fatty alkyl sulfonate with a mixing ratio of 4:1), 0.2 parts of EDTA ferric sodium salt, 0.3 parts of benzyl naphthalenesulfonate-formaldehyde condensate, 0.5 parts of potassium phosphate, 4 parts of 2,4-diphenyl-4-methyl-1-pentene, 26 parts of styrene, 14 parts of a sulfonate group-containing ester monomer, and 0.05 parts of isoascorbic acid were introduced. After completion of the introduction, the reactor was purged three times with nitrogen. Then, 60 parts of butadiene were introduced. Subsequently, 0.15 parts of isopropyl tert-butyl peroxide were

added at 15°C to initiate the polymerization.

[00101] When the monomer conversion rate reaches 50%, 0.5 parts of an emulsifier, 0.003 parts of isopropyl tert-butyl peroxide, and 0.6 parts of 2,4-diphenyl-4-methyl-1-pentene are additionally introduced. When the monomer conversion rate reaches 85%, 0.05 parts of isopropylhydroxylamine are introduced to terminate the reaction, and the reaction mixture is discharged. The discharged material is degassed in a degassing tower for 5 h to obtain an ester-containing styrene-butadiene latex, which is then coagulated, washed, and dried to afford a liquid styrene-butadiene rubber.

[00102] Comparative Example 2

[00103] A same procedure as Example 3 was carried out in comparative Example 2, except that the initiator is introduced in a one-time manner. The specific step S2 is as follows:

[00104] In a 10 L polymerization reactor, 190 parts of demineralized water, 5 parts of an emulsifier (rosin soap and fatty alkyl sulfonate with a mixing ratio of 4:1), 0.2 parts of EDTA ferric sodium salt, 0.3 parts of benzyl naphthalenesulfonate-formaldehyde condensate, 0.5 parts of potassium phosphate, 4 parts of 2,4-diphenyl-4-methyl-1-pentene, 26 parts of styrene, 12 parts of a sulfonate group-containing ester monomer, and 0.05 parts of isoascorbic acid were introduced. After completion of the introduction, the reactor was purged three times with nitrogen. Then, 60 parts of butadiene were introduced. Subsequently, 0.153 parts of isopropyl tert-butyl peroxide were added at 15°C to initiate the polymerization.

[00105] Once the three monomers, butadiene, styrene, and the sulfonate group-containing ester monomer reach a conversion rate of 25%, 1 part of the sulfonate group-containing ester monomer is additionally introduced; when the monomer conversion rate reaches 50%, 0.5 parts of an emulsifier and 0.6 parts of 2,4-diphenyl-4-methyl-1-pentene are additionally introduced; when the monomer conversion rate reaches 65%, 1 part of the sulfonate group-containing ester monomer is additionally introduced. When the monomer conversion rate reaches 85%, 0.05 parts of isopropylhydroxylamine are introduced to terminate the reaction, and the reaction mixture is discharged. The discharged material is degassed in a degassing tower for 5 h to obtain an ester-containing styrene-butadiene latex, which is then coagulated, washed, and dried to afford a high-performance liquid styrene-butadiene rubber containing sulfate and ester groups.

[00106] Comparative Example 3

[00107] A same procedure as Example 3 was carried out in comparative Example 3, except that the sulfonate group-containing ester monomer is introduced in a one-time manner. The specific step S2 is as follows:

[00108] In a 10 L polymerization reactor, 190 parts of demineralized water, 5 parts of an emulsifier (rosin soap and fatty alkyl sulfonate with a mixing ratio of 4:1), 0.2 parts of EDTA ferric

sodium salt, 0.3 parts of benzyl naphthalenesulfonate-formaldehyde condensate, 0.5 parts of potassium phosphate, 4 parts of 2,4-diphenyl-4-methyl-1-pentene, 26 parts of styrene, 14 parts of a sulfonate group-containing ester monomer, and 0.05 parts of isoascorbic acid were introduced. After completion of the introduction, the reactor was purged three times with nitrogen. Then, 60 parts of butadiene were introduced. Subsequently, 0.15 parts of isopropyl tert-butyl peroxide were added at 15°C to initiate the polymerization.

[00109] Once the three monomers, butadiene, styrene, and the sulfonate group-containing ester monomer reach a conversion rate of 50%, 0.5 parts of an emulsifier, 0.003 parts of isopropyl tert-butyl peroxide, and 0.6 parts of 2,4-diphenyl-4-methyl-1-pentene are additionally introduced; When the monomer conversion rate reaches 85%, 0.05 parts of isopropylhydroxylamine are introduced to terminate the reaction, and the reaction mixture is discharged. The discharged material is degassed in a degassing tower for 5 h to obtain an ester-containing styrene-butadiene latex, which is then coagulated, washed, and dried to afford a high-performance liquid styrene-butadiene rubber containing sulfate and ester groups.

[00110] A comparison of the properties of the liquid styrene-butadiene rubbers prepared in Comparative Examples 1-3 and Example 3 is presented in Table 2.

Table 2

	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
Content (Bound Styrene), wt%	24.7	21.6	23.2	24.3
Content (Sulfonate group-containing Ester), wt%	12.7	7.4	9.6	8.3
Molecular Weight, Mn	3956	5138	3864	4016
Mooney viscosity, Pa·s@25 °C	49.8	61.3	48.6	50.2

[00111] By comparing Comparative Example 1 with Example 3, it can be observed that both the content of the bound styrene and the content of the sulfonate group-containing ester monomer are correspondingly reduced, while the molecular weight and Mooney viscosity are correspondingly increased. This is due to the use of the introduction in a one-time manner, which leads to an accelerated polymerization of styrene at the beginning of the reaction, resulting in an uneven distribution of styrene along the polymer chain and a reduced incorporation rate of the sulfonate group-containing ester monomer. In addition, the introduction of the molecular weight regulator and emulsifier in a one-time manner results in poor control over the molecular weight.

[00112] By comparing Comparative Example 2 with Example 3, it can be found that both the content of the bound styrene and the content of the sulfonate group-containing ester monomer

are correspondingly reduced. This is due to the introduction of the initiator in a one-time manner, which causes an accelerated polymerization at the beginning of the reaction and low polymerization in the later stage. As confirmed by on-site experiments, the reaction time required for Comparative Example 2 is much longer than that for Example 3.

5 **[00113]** By comparing Comparative Example 3 with Example 3, it can be observed that the content of the bound styrene does not show a significant decrease, whereas the content of the sulfonate group-containing ester monomer is markedly reduced. This is because the reactivity ratio of the sulfonate group-containing ester is lower than that of styrene and butadiene. Therefore, when the sulfonate group-containing ester is added in a one-time manner, the units of sulfonate group-
10 containing ester become unevenly distributed along the polymer chain, reducing the incorporation rate and leading to a lower content.

[00114] To further characterize the application performance of the obtained liquid styrene-butadiene rubber, the present invention further provides its use as a toughening agent for an epoxy resin, but not limited to the toughening agent. The high-performance modified liquid
15 styrene-butadiene rubber prepared in Example 3 was used for a toughening test for an epoxy resin, with a conventional liquid styrene-butadiene rubber (Comparative Example 4) without the sulfonate-containing ester monomer, as a control. The liquid styrene-butadiene rubber was added in an amount of 5 wt%. The thermal decomposition temperature and erosion-wear resistance of the cured epoxy resin after toughening were evaluated, and the test results are shown in Table 3
20 and Fig. 3.

[00115] Comparative Example 4

[00116] A same procedure as Example 3 was carried out in comparative Example 4, except that the sulfonate group-containing ester monomer is not introduced. The specific step S2 is as follows:

25 **[00117]** In a 10 L polymerization reactor, 190 parts of demineralized water, 5 parts of an emulsifier (rosin soap and fatty alkyl sulfonate with a mixing ratio of 4:1), 0.2 parts of EDTA ferric sodium salt, 0.3 parts of benzyl naphthalenesulfonate-formaldehyde condensate, 0.5 parts of potassium phosphate, 4 parts of 2,4-diphenyl-4-methyl-1-pentene, 26 parts of styrene, and 0.05 parts of isoascorbic acid were introduced. After completion of the introduction, the reactor was
30 purged three times with nitrogen. Then, 74 parts of butadiene were introduced. Subsequently, 0.15 parts of isopropyl tert-butyl peroxide were added at 15°C to initiate the polymerization.

[00118] Once butadiene and styrene reach a conversion rate of 50%, 0.5 parts of an emulsifier, 0.003 parts of isopropyl tert-butyl peroxide, and 0.6 parts of 2,4-diphenyl-4-methyl-1-pentene are additionally introduced. When the monomer conversion rate reaches 85%, 0.05 parts
35 of isopropylhydroxylamine are introduced to terminate the reaction, and the reaction mixture is

discharged. The discharged material is degassed in a degassing tower for 5 h to obtain an ester-containing styrene-butadiene latex, which is then coagulated, washed, and dried to afford the conventional liquid styrene-butadiene rubber.

Table 3

	Thermal Decomposition temperature, T _{max} , °C
Epoxy Resin Cured Product	373
Modified Epoxy Resin Cured Product of Comparative Example 4	365
Modified Epoxy Resin Cured Product of Example 3	387

[00119] From the comparison data in Table 3, it can be seen that the thermal decomposition temperature of the neat epoxy resin cured product is 373°C, while that of the epoxy resin cured product modified with the conventional liquid styrene-butadiene rubber of Comparative Example 4 is 365°C. This is because a crosslinking reaction occurs between the conventional liquid styrene-butadiene rubber and the epoxy resin, forming an incompletely crosslinked network structure. Additionally, since the thermal stability of the liquid styrene-butadiene rubber is relatively lower than that of the epoxy resin, the thermal decomposition temperature of the modified epoxy resin cured product modified with the conventional liquid styrene-butadiene rubber is reduced. However, the thermal decomposition temperature of the modified cured epoxy resin in Example 3 is 387°C, which is higher than that of the neat epoxy resin cured product (373°C). This is attributed to the introduction of ester groups into the polymer, which improves thermal resistance of the polymer.

[00120] As shown in Fig. 3, as the added amount of liquid styrene-butadiene rubber prepared in Comparative Example 4 and Example 3 increases, the erosion-wear rate decreases while abrasion resistance gradually improves. However, the epoxy resin modified with the high-performance modified liquid styrene-butadiene rubber in Example 3 exhibits superior abrasion resistance, owing to the fact that the addition of sulfonate groups further enhances the mechanical properties of the material. It was also found that when the added amount exceeds a certain level, the abrasion resistance diminishes. This is because the abrasion resistance of the cured product is influenced not only by the modifier but also by the adhesive properties. Therefore, when the added amount exceeds a certain level, the abrasion resistance of the cured product is weakened.

[00121] In order to further characterize the application performance of the obtained high-performance modified liquid styrene-butadiene rubber, the high-performance modified liquid styrene-butadiene rubber prepared in Example 3 is used to replace the rubber processing oil in the preparation of tire rubber compounds, employing the compounding formulation of Table 4.

Table 4

Components	Formulation 1, g	Formulation 2, g
Solution-polymerized Styrene-butadiene Rubber	60	60
Cis Polybutadiene Rubber	40	40
8# Carbon Black	7.5	7.5
Sulfur	0.5	0.5
Accelerator TMTD	3.0	3.0
Processing Oil	20.0	0.0
Example 3	0.0	20.0
Stearic Acid	1.0	1.0
Zinc Oxide	5.0	5.0

[00122] The properties of the vulcanized rubber produced according to Table 4 are shown in Table 5.

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Table 5

Item	Formulation 1	Formulation 2
Tensile strength, MPa	14.54	16.32
Tear Strength, MPa	43.15	45.76
Shore A Hardness	73	74
DIN wear volume, cm ³	0.173	0.064

[00123] As seen from Table 5, when the rubber processing oil is replaced with the high-performance modified liquid styrene-butadiene rubber, the tensile strength and tear strength of the vulcanized tire rubber are increased, and its abrasion resistance is also improved. Therefore, the high-performance modified liquid styrene-butadiene rubber can be used as a substitute for rubber processing oil to enhance the physical and mechanical properties of the tread rubber.

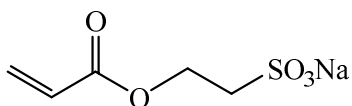
[00124] Evidently, the above embodiments of the present invention are provided merely to clearly illustrate the invention and are not intended to limit its scope. For those skilled in the art, various modifications and changes can be made based on the aforementioned description. It is impossible to enumerate every possible embodiment here, and any obvious variations or alterations derived from the technical solution of the present invention are still within the protection scope of the present invention.

CLAIMS

WHAT IS CLAIMED IS:

- 5 1. A liquid styrene-butadiene rubber, of which the polymerizable monomers comprises butadiene, styrene, and a sulfonate group-containing ester monomer;

wherein the sulfonate group-containing ester monomer has a structural formula of:



- 10 2. The liquid styrene-butadiene rubber according to claim 1, wherein 50-75 parts by weight of butadiene, 20-30 parts by weight of styrene, and 5-24 parts by weight of the sulfonate group-containing ester monomer are included, based on 100 parts of the total weight of the butadiene, the styrene, and the sulfonate group-containing ester monomer.

- 15 3. The liquid styrene-butadiene rubber according to claim 1, wherein the liquid styrene-butadiene rubber is prepared by emulsion copolymerization of butadiene, styrene, and the sulfonate group-containing ester monomer.

- 20 4. The liquid styrene-butadiene rubber according to claim 1, wherein the liquid styrene-butadiene rubber contains 3-18 wt% of the sulfonate group-containing ester monomer structure.

- 25 5. The liquid styrene-butadiene rubber according to claim 1, wherein the liquid styrene-butadiene rubber has a Mooney viscosity of 40-60 Pa·s and a number-average molecular weight (Mn) ranging from 3,000 to 5,000.

6. A method for preparing the liquid styrene-butadiene rubber according to any one of claims 1 to 5, comprising the following steps:

- 30 introducing 160-220 parts of demineralized water, 4-8 parts of an emulsifier, 0.1-0.3 parts of a reducing agent, 0.1-0.4 parts of a dispersant, 0.4-0.8 parts of an electrolyte, 3-6 parts of a molecular weight regulator, 20-30 parts of styrene, 3-20 parts of the sulfonate group-containing ester monomer, and 0.01-0.1 parts of an oxygen scavenger to a reaction vessel, based on a total of 100 parts by weight of the butadiene, the styrene, and the sulfonate group-containing ester monomer; then introducing 50-75 parts of butadiene under a protective atmosphere, while stirring the mixture for pre-emulsification; and subsequently, introducing 0.1-0.2 parts of initiator

to carry out a polymerization reaction;

introducing an additional amount of the emulsifier, the initiator, the molecular weight regulator, and the sulfonate group-containing ester monomer when the three monomers, i.e. the butadiene, the styrene, and the sulfonate group-containing ester monomer reach a pre-determined monomer conversion rate; and introducing 0.05-0.2 parts of a terminating agent to stop the reaction when the monomer conversion rate reaches 82%-87%; and then subjecting the resultant to degassing, coagulation, washing, and drying to obtain the liquid styrene-butadiene rubber.

7. The method according to claim 6, wherein, the step of introducing an additional amount of the emulsifier, the initiator, the molecular weight regulator, and the sulfonate group-containing ester monomer when the three monomers i.e. the butadiene, the styrene, and the sulfonate group-containing ester monomer reach a pre-determined monomer conversion rate specifically comprises:

introducing additionally 1-2 parts of the sulfonate group-containing ester monomer when the monomer conversion rate reaches 25%-30%; introducing additionally 0.4-0.8 parts of the emulsifier, 0.002-0.004 parts of the initiator, and 0.5-0.8 parts of the molecular weight regulator when the monomer conversion reaches 50%-55%; and introducing additionally 1-2 parts of the sulfonate group-containing ester monomer when the monomer conversion reaches 65%-70%.

8. The method according to claim 6 or 7, wherein the emulsifier is an anionic-anionic mixed surfactant or an anionic-nonionic mixed surfactant;

wherein, the anionic-anionic mixed surfactant is a mixed surfactant of rosin soap and a fatty alkyl sulfonate in a weight ratio of (4-5):1; and

the anionic-nonionic compound surfactant is a mixed surfactant of rosin soap and a polyoxyethylene ether in a weight ratio of (3-4):1.

9. The method according to claim 6 or 7, wherein the reducing agent is at least one selected from sodium formaldehyde sulfoxylate, ferrous sulfate, cuprous sulfate, EDTA ferric sodium salt, and EDTA copper sodium salt.

10. The method according to claim 6 or 7, wherein the dispersant is at least one selected from sodium β -naphthalenesulfonate-formaldehyde condensate, sodium methyl naphthalenesulfonate-formaldehyde condensate, and benzyl naphthalenesulfonate-formaldehyde condensate.

11. The method according to claim 6 or 7, wherein the electrolyte is potassium phosphate or potassium chloride.

12. The method according to claim 6 or 7, wherein the molecular weight regulator is at least one selected from dodecyl mercaptan, tert-dodecyl mercaptan, and 2,4-diphenyl-4-methyl-1-pentene.

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13. The method according to claim 6 or 7, wherein the oxygen scavenger is at least one selected from sodium dithionite, dimethyl ketoxime, and isoascorbic acid.

14. The method according to claim 6 or 7, wherein the initiator is selected from at least one of cumene hydroperoxide, diisopropylbenzene hydroperoxide, and isopropyl tert-butyl peroxide.

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15. The method according to claim 6 or 7, wherein the terminating agent is at least one selected from hydroxylamine sulfate, diethylhydroxylamine, isopropylhydroxylamine.

15 16. The method according to claim 6, wherein the sulfonate group-containing ester monomer is prepared by the following steps:

adding acrylic acid, sodium isethionate, a dehydrant, and a catalyst to a reaction vessel, and heating the mixture to carry out an esterification reaction under a protective atmosphere, wherein during the reaction, the water formed and the dehydrant are continuously distilled off, and the dehydrant is separated and refluxed to the reaction vessel to participate in the reaction;

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terminating the reaction when the amount of separated water ceases to increase and reaches a theoretically calculated value; and

then filtering the resultant to obtain a filter cake, which is subjected to distillation at a reduced pressure to obtain the sulfonate group-containing ester monomer.

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17. The method according to claim 16, wherein, the molar ratio of sodium isethionate to acrylic acid is 1:(1-1.5).

18. The method according to claim 16, wherein the dehydrant is at least one selected from toluene, ethylbenzene, and p-xylene; and

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the catalyst is at least one selected from methanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, and 2-naphthalenesulfonic acid.

19. Use of the liquid styrene-butadiene rubber according to any one of claims 1 to 5 in a toughening agent for tires or epoxy resins.

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