

SPECIFICATION

METHOD FOR PRODUCING MODIFIED SULFUR CONTAINING MATERIAL

5 FIELD OF ART

 The present invention relates to a method for preparing a material containing modified sulfur, which enables ready and efficient preparation of materials containing modified sulfur useful as materials for civil engineering
10 or construction, and which may employ wastes and industrial by-products as raw materials.

BACKGROUND ART

 Application of sulfur as civil engineering and construction materials has been under research, which
15 makes use of its properties to melt over 119 °C and be solid at ordinary temperatures. For example, there have been proposed to use sulfur as a material for paving roads (US Patent No. 4,290,816), a binding material for construction materials (JP-55-49024-B), and a binding material for
20 sealing waste (JP-62-15274-B). Sulfur is known to have an application as a binding material, and has been used by mixing with various aggregates to prepare molded products for civil engineering and construction materials.

25 Wastes and industrial by-products have generally been disposed of by landfilling or incineration, but sites for these treatment have been running short of. Thus it is

demanded to recycle as much of the wastes and industrial by-products as possible. For example, in order to make industrial by-products such as incinerated ash into landfilling materials for civil engineering or
5 construction materials, it is necessary for the materials to have sufficient mechanical strength such as compressive strength, bending strength, tensile strength, and impact resistance, sufficient water sealability for preventing elusion of heavy metal compounds contained in the
10 industrial by-products, and noncombustibility for preventing ignition by fire. In addition, for use in soil or the sea, resistance to sulfur-oxidizing bacteria that cause corrosion of sulfur on the product surfaces is also required.

15 In order to solve these problems, molded products have been proposed that are prepared by mixing a binding material composed solely of sulfur with industrial by-products. However, such molded products have various problems in their property, and have only limited use.
20 Thus improvement technique is required for preparing materials containing modified sulfur that are capable of completely sealing industrial by-products with sulfur, and that may be used as civil engineering or construction materials.

25 As one of such improvements, modification of sulfur by addition of dicyclopentadiene thereto has been under research. The reaction between dicyclopentadiene and

sulfur is said to be a kind of polymerization, wherein dicyclopentadiene first reacts with sulfur to ring-open the S8 rings, which allows binding of sulfur with cyclopentadiene to form modified sulfur. In this
5 reaction, sulfur is polymerized by radical chain reaction due to the exothermic reaction to form modified sulfur, so that the temperature suddenly rises and the viscosity increases sharply. Due to this sudden temperature rise and the viscosity increase, the uncontrollable reaction
10 between dicyclopentadiene and sulfur results in rapid solidification, and no shaping of the product into a desired shape is possible.

For addition of dicyclopentadiene to sulfur, sufficient studies have not been made in production
15 conditions, and the relationship between the reaction conditions, such as the dicyclopentadiene concentration and the temperature, and the desirable properties of the resulting material have not fully been established.

SUMMARY OF THE INVENTION

20 It is an object of the present invention to provide a method for preparing a material containing modified sulfur, which enables efficient preparation of a material containing modified sulfur in a molten state of which workability is improved, and a material containing
25 modified sulfur in a solid state of which surface conditions, mechanical strength, water sealability, ignitability, and resistance to sulfur-oxidizing bacteria

are improved, even when wastes and industrial by-products are used as aggregate, and in which the reactions during the preparation are easily controlled.

According to the present invention, there is provided
5 a method for preparing a material containing modified sulfur comprising the steps of:

(A) reacting in a molten state 100 parts by weight of sulfur and not less than 0.1 parts by weight and less than 2 parts by weight of a sulfur modifier under hermetically
10 sealed conditions, and

(B1) adding and mixing aggregate to a reaction system containing 5 to 45 wt% molten modified sulfur having a weight average molecular weight of 320 to 500 formed by the reaction in step (A).

15 According to the present invention, there is also provided a method for preparing a material containing modified sulfur comprising the steps of:

(A) reacting in a molten state 100 parts by weight of sulfur and not less than 0.1 parts by weight and less than
20 2 parts by weight of a sulfur modifier under hermetically sealed conditions, and

(B2) adding and mixing aggregate to a reaction system having a viscosity of 20 to 200 mPa·s at 140 °C and containing a molten modified sulfur having a weight average
25 molecular weight of 320 to 500 formed by the reaction in step (A).

PREFERRED EMBODIMENTS OF THE INVENTION

The raw materials to be used in the method of the present invention are mainly composed of sulfur, a sulfur modifier, and aggregate. The material containing modified sulfur to be obtained by the present invention is in a molten state or a solid state, and contains aggregate in addition to the modified sulfur, and may optionally contain a sulfur modifier and/or unreacted sulfur.

The sulfur used in the present invention is ordinary, elemental sulfur, and commercially available sulfur may be used. For example, the sulfur may be natural sulfur or sulfur generated by desulfurization of oil or natural gas. The amount of sulfur to be used is usually 10 to 50 wt%, preferably 15 to 40 wt% of the total amount of the resulting material containing modified sulfur.

The sulfur modifier used in the present invention may be dicyclopentadiene as a simple substance, or a mixture mainly composed of monomer to tetramer of cyclopentadiene. Such mixture contains usually not less than 70 wt%, preferably not less than 85 wt% dicyclopentadiene. Thus most of the commercially available products referred to as dicyclopentadiene may be used for the present method.

According to the present invention, the reaction in a molten state of the sulfur modifier and sulfur is performed under hermetically sealed conditions in a hermetically sealed internal mixer or the like apparatus, so that the evaporation loss of the sulfur modifier is

eliminated to improve the reaction efficiency. The amount of the sulfur modifier to be used is not less than 0.1 parts by weight and less than 2 parts by weight based on 100 parts by weight of sulfur. If the amount of the sulfur modifier is too small, the increase in viscosity due to the reaction between the sulfur modifier and sulfur is slow, whereas if the amount is too large, the increase in viscosity due to the reaction between the sulfur modifier and sulfur is sharp. Thus the amount of the sulfur modifier should be within the above range in view of the workability. With less than 0.1 parts by weight of the sulfur modifier, the resulting material containing modified sulfur in the solid state may not be given sufficient strength. Properties of the resulting material containing modified sulfur, such as noncombustibility, water sealability, resistance to sulfur-oxidizing bacteria, and mechanical strength, relate to the amount of the sulfur modifier to be used. Usually, the more sulfur modifier is used, the more these properties are improved. However, at about 2 parts by weight of the sulfur modifier based on 100 parts by weight of sulfur, the improvement in these properties by the modified sulfur reaches the maximum, and further increase in the amount will not result in much change. Thus the amount of the sulfur modifier is not less than 0.1 parts by weight and less than 2 parts by weight, preferably not less than 1 part by weight and less than 2 parts by weight

base on 100 parts by weight of sulfur.

The aggregate used in the present invention is not particularly limited as long as it does not impair the properties of the resulting material containing modified sulfur, and may preferably be inorganic materials such as industrial by-products.

Examples of the industrial by-products may include inorganic materials such as incinerated ash, incinerated fly ash, molten fly ash generated in a high temperature melting furnace for city waste, coal ash discharged from the electric power industry and general industry, fluidized sand used in fluidized bed incinerators, grinding waste, by-products of various metal productions, and mixtures thereof. Examples of the by-products of various metal productions may include steel slag, steel dust, ferronickel slag, aluminum dross, copper slag, and mixtures thereof.

The incinerated ash is waste from various combustion furnaces such as city waste incinerators and industrial waste incinerators, and is mainly composed of oxides such as silica, alumina, calcium oxide, and iron oxide, with high contents of toxic metals, such as lead, cadmium, and arsenic. The incinerated ash that has conventionally been disposed of at sanitary landfill sites where no waste water is discharged, may be used.

The coal ash is waste from various coal combustion furnaces for power generation, heating, and the like, and

those used for concrete or as an admixture for civil engineering materials may be used.

The steel slag may be a by-product of the iron industry, and may include blast furnace slag, open furnace slag, 5 converter furnace slag, and the like. The main components of the steel slag may be oxides such as silica, alumina, calcium oxide, and iron oxide, and also inorganic sulfides.

The aggregate used in the present invention may be aggregate other than those mentioned above, for example, 10 inorganic and organic materials free of hazardous substances, such as clay mineral, activated carbon, carbon fibers, glass fibers, vinylon fibers, aramid fibers, polyester fibers, polyethylene fibers, sand, and gravel. Further, aggregate wherein these other aggregate and the 15 inorganic material such as industrial by-products mentioned above are combined as desired, may also be used.

The amount of the aggregate to be used in the present invention is usually 50 to 90 wt%, preferably 60 to 85 wt% of the total amount of the material containing modified 20 sulfur to be obtained.

According to the present invention, other materials may also be used as raw materials in addition to sulfur, the sulfur modifier, and the aggregate, as long as the objects of the present invention are not impaired.

25 Examples of such other materials may include heavy metal sealing and stabilizing agents such as sodium silicate, sodium sulfide, and chelating agents, asphalt,

nickel sulfate, cobalt sulfate, silver sulfate, and various polymers. The amount of such other materials may preferably be not more than 30 wt% of the total amount of the material containing modified sulfur to be obtained.

5 In the method of the present invention, step (A) of reacting in a molten state the particular ratio of sulfur and a sulfur modifier under hermetically sealed conditions, is carried out, and then step (B1) of adding and mixing aggregate to the reaction system containing a particular
10 amount of molten modified sulfur having a weight average molecular weight of 320 to 500 formed by the reaction in step (A), or step (B2) of adding and mixing aggregate to the reaction system having a particular viscosity and containing molten modified sulfur having a weight average
15 molecular weight of 320 to 500 formed by the reaction in step (A), is carried out.

In step (A), sulfur and the sulfur modifier may be reacted in a molten state under hermetically sealed conditions by, for example, first melting sulfur by heating
20 to usually 120 to 155 °C, preferably 135 to 145 °C, using an apparatus, such as an internal mixer, that is capable of effecting a reaction under hermetically sealed conditions. After the sulfur is melted, the entire mass is maintained preferably at 135 to 150 °C, more preferably
25 135 to 145 °C, under stirring, while the viscosity of the mass is monitored with an appropriate viscometer, such as a Brookfield type viscometer. Then a predetermined

amount of sulfur modifier is added little by little and mixed.

In step (A), if the temperature of the reaction system is higher than 150 °C, addition reaction proceeds and, with
5 the heat of formation in the addition reaction, the temperature of the reaction system usually exceeds 160 °C to disadvantageously form gummy sulfur. On the other hand, if the temperature of the reaction system is 130 °C, addition reaction proceeds, and the temperature of the
10 reaction system reaches about 140 °C with the heat of formation. However, the formation of the objective molten modified sulfur is slow, and the production time cannot be shortened, thus not being preferred. Thus, it is preferred to maintain the molten sulfur at 135 to 150
15 °C upon adding the sulfur modifier to the molten sulfur. Here, when a higher ratio of the sulfur modifier is used, a larger amount of heat is generated in the addition reaction, so that the temperature at which the reaction system is maintained needs to be lowered. However, if the
20 temperature is less than 135 °C, the commencement of the addition reaction is disadvantageously delayed. On the other hand, if the temperature at which the reaction system is maintained exceeds 150 °C, the formation of the objective molten modified sulfur is too rapid to control,
25 which disadvantageously narrows the range of the production conditions.

In step (A), when the reaction is in a molten state between

sulfur and the sulfur modifier is started, the temperature of the reaction system increases. For example, when 0.2 parts by weight of the sulfur modifier is added to 100 parts by weight of sulfur, temperature increase by about 10 °C is observed in about 10 minutes from the addition of the sulfur modifier.

In steps (B1) and (B2), the molecular weight of the molten modified sulfur having a weight average molecular weight of 320 to 500 formed by the reaction in step (A) may be measured by gel permeation chromatography (GPC) using the modified sulfur dissolved in a carbon disulfide or toluene. For example, the molecular weight may be measured by GPC using a sample solution containing 1 mass/vol% carbon disulfide at a flow rate of 1 ml/min at room temperature, with chloroform as an eluent and a UV detector at 254 nm, and determined against a calibration curve obtained from polystyrene standard.

The molten modified sulfur having the particular molecular weight mentioned above is believed to be formed by addition reaction of the sulfur modifier to sulfur forming eight member rings. As the molten modified sulfur is formed, the temperature rises, and the viscosity of the reaction system becomes almost constant usually at 10 to 20 mPa·s, which is almost the same as the viscosity of sulfur per se. After that, when the temperature rise is completed in about 5 to 30 minutes, and the viscosity starts to increase, the formation of the molten modified sulfur

may be regarded as completed.

In step (B1), the aggregate is added to the reaction system in a state wherein the reaction system contains 5 to 45 wt%, preferably 10 to 40 wt% of the particular molten modified sulfur mentioned above formed in the reaction system. The conditions for achieving such state may be decided by actually confirming the conditions in a pretest for forming the particular molten modified sulfur in an amount within the above mentioned range. The state wherein the reaction system contains 5 to 45 wt% of the particular molten modified sulfur formed may be the state wherein the particular molten modified sulfur is present at the above ratio in unreacted molten sulfur and molten modified sulfur, the state wherein the particular molten modified sulfur is present at the above ratio in unreacted molten sulfur, unreacted molten sulfur modifier, and molten modified sulfur, or the state wherein the particular molten modified sulfur is present at the above ratio in molten modified sulfur. These reaction systems may optionally contain other components.

In step (B2), the aggregate is added to the reaction system at the time point when the viscosity of the reaction system falls in the range of 20 to 200 mPa·s, preferably 20 to 100 mPa·s, more preferably 20 to 90 mPa·s, at 140 °C. The viscosity of the reaction system may be confirmed to be within the above range by means of a Brookfield type viscometer or the like, so that the time point for adding

the aggregate may be determined easily. As in this step, it makes the actual operation easier to determine the time point for adding the aggregate by a phenomenal aspect, i.e., the melt viscosity of the reaction system, rather than the ratio of the particular molten modified sulfur formed in the system as in step (B1).

The melt viscosity mentioned above may fluctuate slightly depending on the temperature for melting, so that it may suitably be decided by experiments. For example, the particular viscosity range and the preferred viscosity range at 140 °C mentioned above correspond to the ranges of 15 to 200 mPa·s and 15 to 100 mPa·s, respectively, at 150 °C. Alternatively, at 135 °C, the lower limit would be slightly higher than 20 mPa·s but lower than 25 mPa·s, and the upper limit is 200 mPa·s. The viscosity at a temperature between these temperatures may easily be determined by calculation of proportion.

If the aggregate is added after the viscosity exceeds the upper limit of the above range, the polymerization of sulfur proceeds too much, which makes it difficult to mix with the aggregate. On the other hand, if the aggregate is added before the viscosity reaches the above range, the particular molten modified sulfur has not been formed in a sufficient amount, and the polymerization of sulfur may not proceed smoothly.

In steps (B1) and (B2), the aggregate may preferably be added after it is preheated to 130 to 160 °C to dry.

The mixing may be carried out in a mixer, which is not particularly limited as long as thorough mixing is provided, and may preferably be a solid-liquid mixer. For example, an internal mixer, roll mill, drum mixer, screw extruder, 5 pug mill, pony mixer, or ribbon mixer may be used.

In steps (B1) and (B2), the aggregate may be added and mixed to the reaction system preferably at 135 to 155 °C. After the addition, the reaction system is further mixed usually for about 5 to 60 minutes, preferably for 10 to 10 30 minutes. This mixing time may be prolonged, but longer time of mixing will impair the workability, though the strength of the resulting molded product is increased. If the aggregate is added and mixed to the system at a temperature higher than 155 °C, the viscosity increases 15 sharply, and the aggregate and sulfur do not mix thoroughly. On the other hand, if the aggregate is added and mixed to the system at a temperature lower than 135 °C, the reaction of sulfur upon mixing is slow, which disadvantageously prolongs the production time.

20 In steps (B1) and (B2), when to terminate the mixing after the addition of aggregate may suitably be decided taking the weight average molecular weight of the modified sulfur into consideration. For example, the molecular weight at which the mixing is terminated may be higher than 25 500 and not higher than 2000, preferably 600 to 1500, in weight average molecular weight measured by GPC. At a molecular weight of 500 or lower, the compressive strength

of the resulting material containing modified sulfur in a solid state may be too low. On the other hand, at a molecular weight of over 2000, the workability is impaired, air bubbles may be entrained upon molding the resulting material containing modified sulfur in a molten state, and the surface conditions of the resulting solid product are deteriorated. The molecular weight may be measured in the same way as for the particular molten modified sulfur mentioned above.

Incidentally, in a method for preparing a material containing modified sulfur from sulfur, a sulfur modifier, and aggregate, the aggregate may possibly be added by a method other than the present method, for example, (1) by reacting simultaneously a mixture of sulfur, the sulfur modifier, and the aggregate, or (2) by reacting the sulfur modifier with a mixture of sulfur and aggregate.

However, by the above method (1), the sulfur modifier is adsorbed to the aggregate, and does not react with sulfur quickly, so that the production time is disadvantageously prolonged. In addition, since the sulfur modifier is adsorbed to the aggregate, an excess amount of the sulfur modifier is required. On the other hand, by the above method (2), the sulfur modifier is adsorbed to the main ingredients of the aggregate such as silica and alumina, and the reaction between the sulfur modifier and sulfur is extremely delayed. In addition, contact between the preheated, dried aggregate and the sulfur modifier results

in formation of peroxides, which cause problems in safety.

Alternatively, another method of adding the aggregate is possible, wherein the two components, the sulfur modifier and sulfur, are reacted in advance to prepare a binder having a viscosity of usually 100 mPa·s, and then the binder is mixed with the aggregate. By this method, a material containing modified sulfur having a high compressive strength may be obtained. However, the binder has to be re-melted upon mixing with the aggregate, which complicates the operation, and prolongs the production time after the addition of the aggregate, compared to the present method.

According to the present invention, since the aggregate is added to the melt in which the particular amount of the molten modified sulfur has been formed, polymerization of sulfur proceeds along with the mixing of the aggregate. Thus, the desired material containing modified sulfur may be prepared in a short time.

According to the present method, after step (B1) or (B2), the material containing modified sulfur in a molten state may be molded into a desired shape to obtain the material containing modified sulfur in a solid state. The preparation of the solid material containing modified sulfur may be carried out, for example, by cooling the molten material in a granulating machine or a suitable mold. The shape of the solid material may be any desired shape, such as particles, plates, rectangular prisms, and cubes,

without being limited to these.

The material containing modified sulfur in a molten state may be made into particles by any method without limitation, for example, by granulating method wherein the melt is granulated into particles while it is cooled and solidified, or by cooling and solidifying the melt to obtain a molded product, and then crushing the molded product into particles. The granulating method may be a rolling granulating method or a vibration granulating method, wherein an ordinary rolling type or vibration type granulating machine having a drum, horizontal plate, or tilting plate is used.

In the rolling granulating method, the grain size of the particles may be adjusted by controlling the tilting angle or rotational speed of the turntable or drum. Here, the size of the turntable or drum does not matter, and the desired grain size may be achieved, for example, by changing the tilting angle of the same turntable. The tilting angle may be adjusted generally within the range of 0 to 70 °.

In the vibration granulating method, the grain size of the particles may be adjusted by suitably controlling the number of vibration, amplitude, and tilting angle. For example, suitable conditions may be selected from the number of vibration of about 3000 times per minute, the amplitude of not smaller than 0.3 mm, and the duration of vibration of 30 minutes to 3 hours, so as not to cause

splashing of the material containing modified sulfur in a molten state. The tilting angle may be adjusted in the range of usually 0 to 60 °. The vibration may be reciprocating, rotary, or a combination of these.

5 Alternatively, a rotating drum, which is substantially vibrated, may be used for granulating.

In the method of molding the molten material containing modified sulfur and then crushing the molded product, the adjustment of the grain size of the particles is difficult.
10 Thus, for obtaining particles of a desired grain size, the above granulating method is preferred. However, even if the particles are prepared by the above crushing method, a desired grain size distribution may be achieved by sieving or the like process.

15 Besides the above mentioned granulating methods, the material containing modified sulfur in a molten state may possibly be made into particles by dropping the molten material into water. However, this method is not preferred since heavy metals may be eluted into water, and
20 the surface of the particles may be rusted, resulting in insufficient covering of the aggregate.

The conditions for preparing the particles may suitably be decided depending on the kinds and mixing ratio of the raw materials, i.e., sulfur, the sulfur modifier,
25 and the aggregate, as well as the use of the resulting product. Further, the grain size of the particles may suitably be selected depending on the use. For example,

when the particles are to be given a grain size that is suitable for aggregate for concrete or mortar, a preferred grain size is usually 2 to 44.4 mm measured through a JIS standard sieve.

5 The material containing modified sulfur in the solid state obtained by the method of the present invention has a compressive strength of usually 10 to 100 MN/m², preferably 20 to 100 MN/m², more preferably 30 to 100 MN/m². The density of the solid material containing modified
10 sulfur affects the strength, especially the compressive strength. When the density is higher, less air bubbles are entrained in the material containing modified sulfur, and the modified sulfur and aggregate mix thoroughly to give a completely continuous phase with smooth surface.
15 Such a smooth surface of the material containing modified sulfur may prevent generation of cracks caused by fine surface irregularities. As a result, the resulting molded product exhibits excellent mechanical strength, superior sealability against elusion of hazardous
20 substances, and beautiful appearance.

 The density of the material containing modified sulfur in the solid state obtained by the present method is, when coal ash, for example, is used as the aggregate, usually 2.40 to 2.51 g/cm³, preferably 2.45 to 2.51 g/cm³. At a
25 density of lower than 2.40 g/cm³, air bubbles may be entrained to lower the compressive strength. At a higher density, less air bubbles are entrained.

The material containing modified sulfur obtained by the present method may be, for example, made into particles and used by mixing with cement, concrete, gypsum, or the like. Also, the material may preferably be used as civil
5 engineering or construction materials, such as panels, flooring materials, walls materials, roof tiles, or underwater structures by molding the material into a desired structure, or such as landfilling materials, roadbed materials, filling materials, and aggregate for
10 concrete by making the material into particles.

Examples

The present invention will now be explained in detail with reference to Examples and Comparative Examples, but the present invention is not limited to these.

15 Example 1

721.4 g of solid sulfur was introduced into a hermetically sealed internal mixer, melted at 120 °C, and maintained at 140 °C. The viscosity of the melt was 18 mPa·s, as measured with a Brookfield type viscometer.
20 Then 3.6 g of dicyclopentadiene (about 0.5 parts by weight based on 100 parts by weight of solid sulfur) melted by heating to about 90 °C was added slowly, and stirred at a rotational speed of 150 rpm. The reaction started and after 12 minutes the reaction temperature rose by 10 °C
25 due to the exothermic reaction, and the temperature of the reaction system reached 150 °C. When the temperature rise was confirmed to complete, the viscosity of the reaction

system was measured, and found to be 20 mPa·a. A portion of the reaction system was taken out and measured for the molecular weight by GPC. It was confirmed that modified sulfur having a weight average molecular weight of 390 was
5 obtained. Here, the content of the molten modified sulfur having a weight average molecular weight of 390 in the reaction system was about 20 wt%, and no molten modified sulfur having a weight average molecular weight of 320 to 500 were contained in the rest of the reaction system.

10 To the reaction system in the above state, aggregate heated and dried at 150 °C consisting of 2400 g of blast furnace slag and 480 g of coal ash was introduced, and mixed. The temperature of the mixture was controlled to be at 150 °C, and mixing was carried out for 20 minutes. After the
15 mixing was completed, the resulting molten material containing modified sulfur was poured into a mold and cooled to prepare a columnar molded product of 5 cm in diameter and 10 cm in height. Here, it took 32 minutes for the molded product to cure. The compressive strength
20 of the obtained molded product was 75.70 MN/m², and the density was 2.51 g/cm³. The surface of the molded product was smooth.

Alternatively, the molten material containing modified sulfur obtained above was hardened to prepare
25 particles. 10 g of the obtained particles were introduced into a Soxhlet extractor tube, and performed Soxhlet extraction over 6 hours using 100 ml of carbon disulfide.

The resulting extract was diluted with carbon disulfide to 1 mass/vol%, and the molecular weight of the modified sulfur containing the addition product of sulfur and cyclopentadiene, polymerized sulfur, and the like was determined by GPC. As a result, the weight average molecular weight was 790.

Comparative Example 1

995 g of solid sulfur was introduced into a hermetically sealed internal mixer, melted at 120 °C, and maintained at 140 °C. The viscosity of the melt was 18 mPa·s, as measured with a Brookfield type viscometer. Then 5 g of dicyclopentadiene melted by heating to about 90 °C was added slowly, stirred mildly for 5 minutes, and heated to 145 °C. The reaction started and the reaction temperature and the viscosity gradually increased. When the temperature rise was confirmed to complete, the reaction temperature was controlled to be 150 °C. The viscosity reached 100 mPa·s in about 1 hour. The melt was then cooled to obtain a sulfur binder modified with dicyclopentadiene. The weight average molecular weight of this binder as determined by GPC was 2050.

686 g of this binder was introduced into a DALTON kneader, and melted at 120 °C. The temperature of the DALTON kneader was raised to 150 °C, 2880 g of aggregate dried at 150 °C was added, and the mixture was kneaded for 20 minutes at a controlled temperature of 150 °C. After the kneading, a molded product was prepared in the same

way as in Example 1. The compressive strength of the molded product was 65.8 MN/m², and the density was 2.46 g/cm³. The surface of the molded product was observed to be rough, and the density of the molded product was lower than that of the molded product of Example 1. It took 1 hour and 20 minutes for the molded product to cure, which was longer than the time in Example 1.

Example 2

721.4 g of solid sulfur was introduced into a hermetically sealed internal mixer, melted at 120 °C, and maintained at 140 °C. The viscosity of the melt was 18 mPa·s, as measured with a Brookfield type viscometer. Then 3.6 g of dicyclopentadiene melted by heating to about 90 °C was added slowly, and stirred at a rotational speed of 150 rpm. The reaction started and after 12 minutes the reaction temperature rose by 10 °C due to the exothermic reaction, and the temperature of the reaction system reached 150 °C. Then the melt was stirred for additional 3 minutes. The viscosity of the melt was 25 mPa·s, as measured with a Brookfield type viscometer. A portion of the reaction system was taken out and measured for the molecular weight by GPC. It was confirmed that modified sulfur having a weight average molecular weight of 412 was obtained. Here, the content of the molten modified sulfur having a weight average molecular weight of 422 in the reaction system was about 27 wt%, and no molten modified sulfur having a weight average molecular weight of 320 to

500 were contained in the rest of the reaction system.

To this reaction system, aggregate heated and dried at 160 °C consisting of 2500 g of blast furnace slag and 480 g of coal ash was introduced, and mixed. The

5 temperature of the mixture was controlled to be at 155 °C, and mixing was carried out for 20 minutes. After the mixing was completed, the resulting molten material was made into the molded product and the particles in the same way as in Example 1. The compressive strength of the
10 obtained molded product was 64.4 MN/m², and the density was 2.48 g/cm³. The weight average molecular weight of the particles was measured through Soxhlet extraction in the same way as in Example 1, and found to be 1100.

Example 3

15 The molded product and the particles were prepared in the same way as in Example 1, except that the amount of the solid sulfur used was 360 g. The compressive strength of the resulting molded product was 60.3 MN/m², and the density was 2.47 g/cm³. The weight average molecular
20 weight of the resulting particles was measured through Soxhlet extraction in the same way as in Example 1, and found to be 780.

CLAIMS

1. A method for preparing a material containing modified sulfur comprising the steps of:

5 (A) reacting in a molten state 100 parts by weight of sulfur and not less than 0.1 parts by weight and less than 2 parts by weight of a sulfur modifier under hermetically sealed conditions, and

10 (B1) adding and mixing aggregate to a reaction system containing 5 to 45 wt% molten modified sulfur having a weight average molecular weight of 320 to 500 formed by the reaction in step (A).

15 2. The method of claim 1, wherein said step (A) of reacting in a molten state was performed by adding and mixing the sulfur modifier to molten sulfur at 135 to 150 °C to prepare a mixture, and maintaining the mixture at 135 to 150 °C.

20 3. The method of claim 1, further comprising, after step (B1), the step of cooling and solidifying a resulting mixture into a desired shape.

4. A method for preparing a material containing modified sulfur comprising the steps of:

25 (A) reacting in a molten state 100 parts by weight of sulfur and not less than 0.1 parts by weight and less than 2 parts by weight of a sulfur modifier under hermetically sealed conditions, and

(B2) adding and mixing aggregate to a reaction system having a viscosity of 20 to 200 mPa·s at 140 °C and containing a molten modified sulfur having a weight average molecular weight of 320 to 500 formed by the reaction in
5 step (A).

5. The method of claim 4, wherein said step (A) of reacting in a molten state was performed by adding and mixing the sulfur modifier to molten sulfur at 135 to 150 °C to prepare
10 a mixture, and maintaining the mixture at 135 to 150 °C.

6. The method of claim 4, further comprising, after step (B2), the step of cooling and solidifying a resulting mixture into a desired shape.
15