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(54) Title: A METHOD FOR RECOVERING A SILICATE FROM POLYMERIC COMPOSITION COMPRISING SILICA

(57) Abstract: A method for recovering a silicate from a polymeric composition comprising silica using an alkali metal hydroxide or ammonium hydroxide base. Advantageously, the molar ratio of SiO_2 to A_2O (Rm), wherein A is alkali metal or ammonium, in the resulting silicate solution is at least 0.5.



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A method for recovering a silicate from polymeric composition comprising silica

TECHNICAL FIELD

The present disclosure relates to a method for recovering a silicate from a polymeric composition comprising silica.

BACKGROUND

The following discussion of the prior art is provided to place the disclosure in an appropriate technical context and enable the advantages of it to be more fully understood. It should be appreciated, however, that any discussion of the prior art throughout the specification should not be considered as an express or implied admission that such prior art is widely known or forms part of common general knowledge in the field.

The use of precipitated silica as a reinforcing filler in polymeric compositions is known. In particular it is known to use precipitated silica as reinforcing filler in elastomeric compositions. Such use is highly demanding: the filler has to readily and efficiently incorporate and disperse in the elastomeric composition and, typically in conjunction with a coupling agent, enter into a chemical bond with the elastomer(s) on one side and silica on the other side, to lead to a high and homogeneous reinforcement of the elastomeric composition. In general, precipitated silica is used in order to improve the mechanical properties of the elastomeric composition as well as handling and abrasion performance.

The polymeric compositions comprising silica, such as automobile tires, are the classic example of product derived from non-renewable petroleum resources. Nearly one billion end-of-life tires are generated worldwide annually. The treatment and disposal of waste tires has proven to be an as-yet insurmountable global challenge. Precipitated silica is used as filler in the tire to improve wet grip performance and reduce rolling resistance for lower fuel consumption.

Currently, thermal pyrolysis is considered as a beneficial industrial process to add value to the waste rubber compounds by the recovery of the material and energy. However, in general, the ways to utilize such non-renewable petroleum resources are inefficient. There is risk of contaminating the local environment when waste polymeric compositions are not properly disposed of and the residue is not easy to reuse. Silica is barely never recycled with such a process and is often considered as a “poison”. Its removal before or after any further treatment could be beneficial for revalorising other residues.

As such, there is a need for developing a method for recovering a silicate from the polymeric composition comprising silica, especially from scrapped tires that could be end-of-life or out of spec (performance, size...and so on) or even from scrapped process rubber formulations.

The inventors have developed an extraction method, which allows the recovery of silicate from a polymeric composition comprising silica, especially from scrapped tires or scrapped rubber formulations, by extraction using an inorganic base, in particular alkali metal and ammonium hydroxide bases, in the presence of a solvent. However, due to high base concentrations used in this method, the silicate solution recovered from this method contains a high amount of alkali metal oxide, which is undesirable because it makes precipitation of the silicate less efficient.

It is therefore the object of the present disclosure to provide a process for the recovery of silicate from a polymeric composition, which allows the provision of a silicate with higher quality, i.e. reduced amounts of alkali metal or ammonium in the recovered product.

SUMMARY

This aim is addressed by the disclosure of the present invention, which, in a first aspect, is directed to a process for recovering a silicate from a polymeric composition comprising silica, comprising the following steps:

- (i) contacting a polymeric composition comprising silica with a base in the presence of a solvent,
- (ii) allowing the base to react with the silica comprised in the polymeric composition to form a silicate, thereby obtaining a polymeric composition having lost at least part of the silica and a solution comprising the silicate, and
- (iii) separating the solution obtained at step (ii) from the polymeric composition obtained at step (ii),

wherein the molar ratio of base to silica used in step (i) is lower than 1.

In a second aspect, the present disclosure relates to a process for preparing an aqueous silicate solution, wherein said process comprises the process according to the first aspect of the present disclosure, wherein the solvent used in step (ii) is water or a mixture of water and an organic solvent, wherein the organic solvent is removed from the solution obtained in step (iii) of the process.

In a third aspect, the present disclosure relates to a process for preparing a silicate in solid form, wherein said process comprises the process according to the

second aspect of the present disclosure, further comprising the step of drying the aqueous solution obtained from said process to obtain a silicate in solid form.

In a fourth aspect, the present disclosure relates to a process for preparing precipitated silica or a precipitated silica suspension, comprising the steps of:

- (a) preparing a silicate solution, preferably an aqueous silicate solution, using the process according to the first or second aspect of the present invention; or preparing a silicate in solid form using the process according to the third aspect of the present invention and dispersing, preferably redissolving the silicate in solid form obtained from said process in a dispersing medium, preferably an aqueous dispersing medium,
- (b) adding an acidifying agent to the solution obtained in step (a) to achieve precipitation of silica.

Other subjects and characteristics, aspects and advantages of the present disclosure will emerge even more clearly on reading the detailed description and the examples that follow.

DEFINITIONS

In the present specification, the terms “silica” and “precipitated silica” are used as synonyms.

Throughout the description, including the claims, the term "comprising one" should be understood as being synonymous with the term "comprising at least one", unless otherwise specified, and "between" should be understood as being inclusive of the limits.

As used herein, the terminology " (C_n-C_m) " in reference to an organic group, wherein n and m are both integers, indicates that the group may contain from n carbon atoms to m carbon atoms per group.

The articles “a”, “an” and “the” are used to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article.

The term “and/or” includes the meanings “and”, “or” and also all the other possible combinations of the elements connected to this term.

It is specified that, in the continuation of the description, unless otherwise indicated, the values at the limits are included in the ranges of values which are given.

Ratios, concentrations, amounts, and other numerical data may be presented herein in a range format. It is to be understood that such a range format is used merely for convenience and brevity and should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range, but also

all the individual numerical values or sub-ranges encompassed within that range as if each numerical value or sub-range is explicitly recited.

DETAILS OF THE INVENTION

In a first aspect, the present disclosure provides a method for recovering a silicate from a polymeric composition comprising silica, comprising the following steps:

- (i) contacting a polymeric composition comprising silica with a base in the presence of a solvent,
- (ii) allowing the base to react with the silica comprised in the polymeric composition to form a silicate, thereby obtaining a polymeric composition having lost at least part of the silica and a solution comprising the silicate, and
- (iii) separating the solution obtained at step (ii) from the polymeric composition obtained at step (ii),

wherein the molar ratio of base to silica used in step (i) is lower than 1.

The expression "molar ratio of base to silica used in step (i)" of the process according to the first aspect of the present disclosure refers to the molar amount of base in relation to the molar amount of silica (SiO_2) comprised in the polymeric composition used in step (i) of the process. That is the molar ratio of base to silica refers to the initial molar amounts of base and silica used in the process. The amount of SiO_2 comprised in the polymeric composition used in the process can be quantified using the ICP (Inductively Coupled Plasma Spectrometry). For the skilled person, it is a routine matter to convert weight amounts into molar amounts.

The term "polymeric composition" is used herein to refer to a composition comprising at least one polymer. The phrase "at least one" when referring to the polymer in the composition is used herein to indicate that one or more than one polymer of each type can be present in the composition.

The expression "copolymer" is used herein to refer to polymers comprising recurring units deriving from at least two monomeric units of different nature.

The at least one polymer can be selected among the thermosetting polymers and the thermoplastic polymers, the latter being preferred.

Notable, non-limiting examples of suitable thermoplastic polymers include styrene-based polymers such as polystyrene, (meth)acrylic acid ester/styrene copolymers, acrylonitrile/styrene copolymers, styrene/maleic anhydride copolymers, ABS; acrylic polymers such as polymethylmethacrylate; polycarbonates; polyamides; polyesters, such as polyethylene terephthalate and

polybutylene terephthalate; polyphenylene ethers; polysulfones; polyaryletherketones; polyphenylene sulfides; thermoplastic polyurethanes; polyolefins such as polyethylene, polypropylene, polybutene, poly-4-methylpentene, ethylene/propylene copolymers, ethylene/ α -olefins copolymers; copolymers of α -olefins and various monomers, such as ethylene/vinyl acetate copolymers, ethylene/(meth)acrylic acid ester copolymers, ethylene/maleic anhydride copolymers, ethylene/acrylic acid copolymers; aliphatic polyesters such as polylactic acid, polycaprolactone, and aliphatic glycol/aliphatic dicarboxylic acid copolymers.

The silica may advantageously be present in elastomeric compositions as reinforcing filler. Notable non-limiting examples of suitable elastomers are diene elastomers. For example, use may be made of elastomers deriving from aliphatic or aromatic monomers, comprising at least one unsaturation such as, in particular, ethylene, propylene, butadiene, isoprene, styrene, acrylonitrile, isobutylene or vinyl acetate, polybutyl acrylate, or their mixtures. Mention may also be made of functionalized elastomers, that is elastomers functionalized by chemical groups positioned along the macromolecular chain and/or at one or more of its ends (for example by functional groups capable of reacting with the surface of the silica), and halogenated polymers. Mention may be made of polyamides, ethylene homo- and copolymer, propylene homo- and copolymer. Other suitable elastomers are those including chloro- or bromo- butyl monomers (like bromo-butylene for instance).

Among diene elastomers mention may be made, for example, of polybutadienes (BRs), polyisoprenes (IRs), butadiene copolymers, isoprene copolymers, or their mixtures, and in particular styrene/butadiene copolymers (SBRs, in particular ESBRs (emulsion) or sSBRs (solution)), isoprene/butadiene copolymers (BIRs), isoprene/styrene copolymers (SIRs), isoprene/butadiene/styrene copolymers (SBIRs), ethylene/propylene/diene terpolymers (EPDMs), and also the associated functionalized polymers (exhibiting, for example, pendant polar or reactive groups or polar groups at the chain end, which can interact or react with the silica).

Mention may also be made of natural rubber (NR) and epoxidized natural rubber (ENR).

The polymer compositions can be vulcanized with sulfur or crosslinked, in particular with peroxides or other crosslinking systems (for example diamines or phenolic resins).

The type of silica according to the disclosure is not particularly limited. It can be a conventional or a highly dispersible silica, such as Zeosil® Premium SW, Zeosil® Premium 200MP, Zeosil® 1165MP, Zeosil® 1115MP or Zeosil® 1085 GR (commercially available from Solvay).

The surface area of the mesoporous silica (cetyltrimethylammonium bromide (CTAB) as template) according to the present disclosure may be from 40 to 500 m²/g.

The BET surface area of the silica according to the present disclosure may be from 40 to 500 m²/g, possibly from 100 to 350 m²/g or from 125 to 275 m²/g.

The proportion by weight of silica in the polymer composition can vary within a fairly wide range. It normally represents from 0.01% to 40 %, in particular from 10 % to 40 %, especially from 20 % to 40 %, with relation to the amount of the polymer(s).

The % are sometimes referred to as phr or Per Hundred Rubber in case of elastomeric compositions. Preferably, silica in the polymer composition may be from 5 to 200 phr and more preferably from 5 to 150 phr.

In some embodiments, the polymer composition may additionally comprise other reinforcing inorganic filler, such as nanoclays, alumina, or an organic reinforcing filler, such as carbon black, carbon black nanotubes, graphene, starch, cellulose and the like.

Silica according to the present disclosure then preferably constitutes at least 5 % by weight, preferably at least 30 %, more preferably 60 %, indeed even at least 80 % by weight, of the total amount of the reinforcing filler.

In a preferred embodiment, the polymer composition comprises silica and carbon black. The proportion by weight of silica and carbon black can be from 1 % to 50 %, with relation to the amount of the polymer(s).

Preferably, the polymeric composition used in the process of the present invention is a tire, preferably a scrapped tire.

Advantageously, the polymeric composition comprising silica, especially scrapped tires, can be provided in the form of powder. The average particle size of the powder can be from 0.05 mm to 100 mm and preferably from 0.1 mm to 50 mm, which can be measured by scanning electron microscope (SEM), particle size distribution analyzer (PSD) using laser diffraction or vernier caliper. Preferably, the particle size is measured by a particle size distribution analyzer (PSD) using laser diffraction.

For SEM analysis, a ZEISS EVO-18 with tungsten Filament having a voltage of 20 kV equipped with backscattered electron detector (BSD) or secondary electrons detector was used. The magnification can achieve up to 50K ~ 100K. The SEM was used to detect the particle size between 200 nm-1000 μm . Particles were deposited on a layer of graphite tape, coated by Pt for 40 s and measured by SEM. The obtained results were analyzed using the SmartSEM software. For each sample, around ten pictures were taken and a total of 100 particles were analyzed for obtaining the described size distribution. From this size distribution, the average particle size of the particles was obtained. The software used to measure the size of the particles was ImageJ thereby approximating the particles to be irregular shapes with measuring the longest distance. After setting the scale, the longest diameter of the particles was manually measured one by one to a total number of particles measured of 100. Every particle had been measured 3 times to obtain an average size.

As for the particle size distribution analyzer (PSD), a Malvern Mastersizer 3000 with range lens of 300RF mm was used. The PSD was used to detect the particle size range from 10 nm to 3500 mm. Particles were dissolved in ethanol and the mixture was stirred for 10 mins. The dispersed sample passed through the measurement area of the optical bench, where a laser beam illuminated the particles. A series of detectors then accurately measured the intensity of light scattered by the particles within the sample for both red and blue light wavelengths and over a wide range of angles. Three parallel samples were prepared and measured to obtain an averaged particle size distribution.

For ruler analysis, a vernier caliper was used to measure the particle size more than 1000 μm . The longest diameter of each particle was manually measured. Ca. 100 particles were measured to obtain average of particle size distribution.

The method for preparing the powder is not particularly limited. For example, the skilled person can use mechanical forces like crushing (pulverizing, rolling, and jawing), grinding (with ball and rod) or even shredding to prepare the powder. In a preferred embodiment, the powder can be prepared by cryogenic grinding.

The polymeric composition comprising silica, especially scrapped tires, may need pretreatment. It can be understood by the skilled person that different parts of scrapped tires may need different pretreatment.

For example, tire tread, which is a silica rich part, can be removed from a tire by a machine having a blade system, and then shredded and grinded.

As another example, when pretreating a non-tread part of the scrapped tire or the whole scrapped tire, the skilled person can firstly powder the non-tread part or the whole tire and then remove the metallic part and fibrous part in the tire. For instance, the pretreatment can be a method disclosed by US 2017/0043351, which comprises steps of pre-grinding processing, cryogenic freezing, and grinding of infeed material and warming, ferrous metal and fiber removal, accumulation, screening, and storage of micronized powder. The pretreatment can also be a method comprising steps of shredding processing, metal removal, and fiber removal.

The term “base” is used herein to refer to one or more than one base. Any base may be used in the method as long as it can react with silica to form a silicate, but typically the base used in the process of the present disclosure is selected from alkali metal hydroxide bases and ammonium hydroxide. Preferably, the base is sodium hydroxide or potassium hydroxide, especially sodium hydroxide.

The base amount used in the process of the present disclosure depends on the amount of silica comprised in the polymeric composition used in the process. The amount of silica in the polymeric composition is determined as described above. Based on that, the amount of base used in step (i) of the process is chosen such that the molar ratio of base and silica is lower than 1.

The molar ratio of base to silica is preferably from 0.18 to 0.99, more preferably from 0.20 to 0.90, even more preferably from 0.30 to 0.80.

The solvent according to the present disclosure is not particularly limited, as long as it is capable of favouring the mass transfer of the base into the polymeric composition, e.g. a scrapped tire or a scrapped process rubber formulation. Advantageously, the solvent is stable under alkaline condition. It can be water, an organic solvent as described herein below, or a mixture thereof.

It is preferred that the solvent is water or a mixture of an organic solvent and water. In this case, the base can be advantageously dissolved in the water to form an aqueous solution before contacting the polymeric composition.

In some generally more preferred embodiments, the solvent is a mixture of water and an organic solvent.

The organic solvent has preferably a total Hansen solubility parameter of less than $33 \text{ MPa}^{1/2}$, more preferably between 15 to $29 \text{ MPa}^{1/2}$, still more preferably from 20 to $25 \text{ MPa}^{1/2}$.

Hansen solubility parameter values are broadly available to the skilled person in chemistry handbooks. They can notably be found in Charles M. Hansen,

"Hansen Solubility Parameters - A User's Handbook", Second edition, CRC Press Taylor & Francis Group, 2007.

Alternatively, the skilled person can easily calculate them from the SMILE of the organic solvent using Yamamoto Molecular Breaking Method with HSPiP software version 5.3.06.

The organic solvent is typically selected from the group consisting of alcohols, hydrocarbons, ketones, sulfones, amines, amides, ethers and esters, preferably having a Hansen solubility parameter as indicated above. Each of them can be aliphatic or aromatic.

Preferably, the organic solvent is selected from the group consisting of aliphatic or aromatic alcohols, aromatic hydrocarbons, aliphatic ketones, aliphatic sulfones, aliphatic amines, aliphatic amides, aliphatic ethers, and aliphatic esters.

More preferably, the organic solvent is an aliphatic alcohol.

Besides, the organic solvent, possibly an organic solvent selected from any one of the groups in the aforementioned three passages, has preferably no more than 8 carbon atoms, more preferably no more than 6 carbon atoms and still more preferably no more than 4 carbon atoms. On the other hand, it has preferably at least 2, more preferably at least 3 carbon atoms.

Examples for suitable organic solvents for use in the present invention, preferably in a mixture with water, can be selected from the group consisting of the following solvents:

Solvent	Boiling point (°C)	Hansen solubility parameter(*) (total)
Dimethyl sulfoxide (DMSO)	189	26.7
Acetone	56	19.9
Toluene	110.6	18.2
Ethylene glycol	197.3	32.9
t-Butyl alcohol	82	21.8
Methanol	64.7	29.6
Ethanol	78.4	26.1
1-Propanol	97	24.6

2-Propanol	82.6	23.6
1-Butanol	117.7	23.3
2-Butanol	98	22.2
Cyclopentanone	130.6	22.1

(*) As available from Charles M. Hansen, "Hansen Solubility Parameters - A User's Handbook", Second edition, CRC Press Taylor & Francis Group, 2007

Preferably, said organic solvent can be selected from the group consisting of DMSO, toluene, acetone, 1-propanol, 2-propanol, 1-butanol, 2-butanol and tert-butyl alcohol, more preferably from the group consisting of 1-propanol, 2-propanol, 1-butanol, 2-butanol and tert-butyl alcohol and most preferably from the group consisting of 1-propanol and 2-propanol. Especially preferably, said organic solvent is 2-propanol (IPA).

In a particular embodiment, when the solvent is a mixture of water and an organic solvent, the volume ratio of water to the organic solvent is from 0.1:1 to 10:1, preferably from 0.2:1 to 3:1, more preferably from 0.5:1 to 2:1, especially preferably from 1:1 to 1.5:1.

The concentration of the base in the solvent is advantageously from 0.5 to 3 mol/L, more preferably from 0.9 to 2.5 mol/L.

The reaction temperature in step (ii) is advantageously from 80 to 250 °C, such as e.g. 82 to 250 °C, more preferably from 100 to 180 °C, even more preferably from 140 to 180 °C. The reaction time in step (ii) is typically from 1 to 44 hrs and preferably from 1 to 22 hrs.

The reactor is preferably made of a material resistant to the above-mentioned organic solvent and base, such as Teflon and Hastelloy.

Preferably, step (ii) of the process is carried out in a pressure vessel, such as a Hastelloy reactor. This is particularly necessary if solvents with lower boiling points than the required temperature is used in the process. In case the process is carried out in a pressure vessel, pressures up to 50 bar can be applied. Preferably, pressures between 1 and 40 bar are applied, more preferably between 2 and 30 bar, even more preferably between 5 and 20 bar, such as e.g. 15 bar.

The method for separating the solution and the polymeric composition in step (iii) is not particularly limited. Said method can be filtration, centrifugation and/or decantation, depending on the particle size.

Advantageously, it is possible to recover silicates without degrading or depolymerizing the polymeric compositions by using the method according to the present disclosure.

Advantageously, when the base is an alkali metal hydroxide base and/or ammonium hydroxide, the molar ratio of SiO_2 to A_2O (R_m), wherein A is alkali metal or ammonium, in the silicate products is advantageously from 0.5 to 4.0, more preferably from 1.0 to 4.0, even more preferably from 1.5 to 3.75 in the solution obtained at step (iii). The higher this value is, the better is the quality of the silicate obtained in step (iii) of the inventive process, in particular in terms of its precipitation ability to obtain a solid form.

When the base is sodium hydroxide and/or a sodium salt, such as e.g. sodium triphosphate, the weight ratio of SiO_2 to Na_2O (R_p) in the silicate products is advantageously from 0.5 to 4.0, more preferably from 1.0 to 4.0, even more preferably from 1.5 to 3.6, even more preferably from 2.0 to 3.6, especially preferably from 2.5 to 3.6, calculated based on the silicon and sodium content in the solution obtained at step (iii). The preferred embodiments described above for the process according to the first aspect likewise apply to the processes according to the second to fourth aspect of the present disclosure, unless otherwise indicated.

In a second aspect, the present disclosure also provides a process for preparing an aqueous silicate solution. Said process comprises the process according to the first aspect, wherein the solvent used in step (ii) is water or a mixture of water and an organic solvent, wherein the organic solvent is removed from the solution obtained in step (iii) of the process.

An "aqueous solution" in the sense of the second aspect of the present disclosure means a solution, wherein the solvent comprises at least 90 wt% of water, based on the total weight of the solvent, preferably at least 95 wt% of water, based on the total weight of the solvent. More preferably, the solvent is essentially composed of or is composed of water.

The solvent used in the process according to the second aspect of the present invention is water or a mixture of water and an organic solvent. If a mixture of water and an organic solvent is used, similar considerations as discussed in connection with the first aspect apply, i.e. the same organic solvents can be used in the mixture, and the same ratios of water and organic solvent can be used in the mixture.

If the solvent used is a mixture of water and an organic solvent, the process according to the second aspect of the present disclosure further comprises a step of removing the organic solvent from the solution recovered by the process according to the first aspect of the present disclosure, which corresponds to the solution obtained in step (iii) of said process. Methods for removing the organic solvent are known to the skilled person and for example include, depending on the organic solvent used, distillation such as vacuum distillation and extractive distillation, fractional freezing, reverse osmosis.

If the solvent used is water, the process according to the second aspect of the present disclosure may consist of the process according to the first aspect of the present disclosure.

In a preferred embodiment, the silicate solution obtained from the process according to the first or second aspect of the present disclosure is doped with another silicate solution, preferably an aqueous silicate solution. Said silicate solution has preferably a R_m value greater than the one of the silicate solution obtained from the process according to the first or second aspect of the present disclosure; in that case, it is advantageously used to increase the weight amount of SiO_2 contained in the silicate solution obtained from the first or second aspect of the present disclosure. Said other silicate solution, preferably an aqueous silicate solution, that is used for doping can be a silicate solution prepared from sand through a furnace process (which typically comprises melting the sand in the presence of sodium carbonate in a furnace at a temperature of at least 1000°C) or a hydrothermal process (which typically comprises reacting the sand with sodium hydroxide in water at a temperature of at least 200°C). Said other silicate solution, preferably an aqueous silicate solution, is preferably a silicate solution obtained from a sustainable source of silica, more preferably a biosource of silica or a recycled source of silica, and more preferably from plant ash, such as rice husk ash and/or bagasse ash; in that case, said other silicate solution is typically obtained by a hydrothermal process which comprises reacting the sustainable source of silica with sodium hydroxide in water at a temperature of at least 100°C .

In a third aspect, the present disclosure provides a process for preparing a silicate in solid form. The process according to the third aspect comprises the process according to the second aspect of the present disclosure. The process according to the third aspect of the present invention then further comprises the

step of drying the aqueous solution obtained from the process according to the second aspect of the present disclosure.

"Drying" means that the water is removed from the aqueous solution to obtain a silicate in solid form. Drying methods suitable to remove the water from the aqueous solution are known to the skilled person and include distillation such as vacuum distillation.

The silicate obtained in the processes according to the present disclosure is preferably an alkali metal or ammonium silicate, more preferably a potassium or sodium silicate, especially preferably a sodium silicate.

In accordance therewith, the base used in these processes is preferably an alkali metal/ammonium hydroxide, preferably sodium or potassium hydroxide, especially preferably sodium hydroxide.

The silicate obtained by the processes according to the first, second and third aspect of the present disclosure can be advantageously converted to silica, especially to precipitated silica. In a fourth aspect, the present invention thus provides a process for preparing precipitated silica or a precipitated silica suspension, comprising the steps of:

- (a) preparing a silicate solution, preferably an aqueous silicate solution, using the process according to the first or second aspect of the present invention; or preparing a silicate in solid form using the process according to the third aspect of the present invention and dispersing, preferably redissolving the silicate in solid form obtained from said process in a dispersing medium, preferably an aqueous dispersing medium,
- (b) reacting the silicate solution obtained in step (a) and, optionally in addition a silicate solution other than the silicate solution obtained in step (a), with at least one acidifying agent in a liquid medium, preferably in an aqueous liquid medium, to obtain a suspension of precipitated silica in the liquid medium,
- (c) optionally, separating the precipitated silica from the liquid medium to provide wet precipitated silica, and
- (d) optionally, drying said wet precipitated silica.

The silicate solution other than the silicate solution obtained in step (a), if present, is preferably an alkali metal silicate solution, more preferably a sodium silicate solution.

The term “acidifying agent” is used herein to refer to one or more than one acid which can be added during the course of the process according to the fourth aspect of the present invention. Any acid may be used in the process. Use is generally made of a mineral acid, such as sulfuric acid, nitric acid, phosphoric acid or hydrochloric acid, or of an organic acid, such as carboxylic acids, e.g. acetic acid, formic acid or carbonic acid. Good results are obtained with sulfuric acid (H_2SO_4), which is accordingly preferably used.

The dispersing medium of step (a), which is preferably an aqueous dispersing medium, can be water or a mixture of water with an organic solvent, wherein the organic solvent is preferably an organic solvent as described in connection with the first aspect of the present disclosure. It is preferably water.

The liquid medium of step (b), which is preferably an aqueous liquid medium, can be water or a mixture of water with an organic solvent, wherein the organic solvent is preferably an organic solvent as described in connection with the first aspect of the present disclosure. It is preferably water.

The pH of the liquid medium of step (b), which is preferably an aqueous liquid medium, that is to say the pH at which the silicate solution(s) is reacted with the at least one acidifying agent, can vary to a large extent, as well known to the skilled person and apparent notably from the above cited patent references (namely US 11,241,370, WO 2023/118281, US 10,011,495, US 5,547,502, US 9,938,154, US 2009/0214449, US 10,259,715, US 9,359,215, US 8,007,751, US 2023/0391630, WO 2023/072666, US 11,208,331, and US 11,279,623). In some embodiments, the whole step (b) takes places at a pH of at least 7.0, typically from 7.0 to 10.0, especially from 7.5 to 9.5. In some other embodiments, a first part of the step (b) occurs at a pH below 7.0, typically from 2.0 to 5.5, especially from 3.0 to 4.5, and is followed by another part that takes place at a pH of at least 7.0, typically from 7.0 to 10.0, especially from 7.5 to 9.5.

The reaction between the silicate and the acidifying agent is preferably carried out at a temperature between 60 and 100°C, more preferably between 70 and 95°C.

The reaction between the silicate and the acidifying agent is preferably carried out for 30 to 240 minutes, preferably from 60 to 180 minutes.

If necessary, acidifying agent can be added to the reaction medium in order to complete the reaction.

The precipitated silica or precipitated silica suspension obtained after completion of step (b) can be separated from the reaction medium, e.g. by means of filtration, to obtain a filtration cake of solid silica.

The filtration cake can be disintegrated and/or further dried.

Certain carboxylic acids are capable of modifying the properties of the precipitated silica by having carboxylic acid molecules at its surface. In one embodiment, a carboxylic acid or a polycarboxylic acid or a mixture thereof is added to the reaction medium before or in the course of the reaction, or to the slurry (i.e. the precipitated silica suspension) obtained after completion of the reaction in step (b), or to the filtration cake obtained after filtration. The carboxylic acid or polycarboxylic acid is preferably selected from the group consisting of maleic acid, formic acid, octanoic acid, acetic acid, oxalic acid, propionic acid, succinic acid, adipic acid, glutaric acid, methylglutaric acid, and ethylsuccinic acid, more preferably from the group consisting of maleic acid, formic acid, octanoic acid, propionic acid and succinic acid.

The process according to the fourth aspect of the present disclosure can be supplemented in accordance with known procedures for the preparation of precipitated silica, such as those described in US 11,241,370, WO 2023/118281, US 10,011,495, US 5,547,502, US 9,938,154, US 2009/0214449, US 10,259,715, US 9,359,215, US 8,007,751, US 2023/0391630, WO 2023/072666, US 11,208,331, and US 11,279,623. The whole content of those documents in relation with the precipitation of silica is incorporated herein by reference for all purposes.

The following examples are included to illustrate embodiments of the disclosure. However, the present disclosure is not limited to the content of those examples.

EXPERIMENTAL PART

Materials

- Simplified tire tread formulation sheet (prepared by Solvay) containing 32 wt. % SiO₂ (as determined by ICP using the General Procedure described below)
- Sodium hydroxide (CAS: 1310-73-2, > 96 %, Sinopharm);
- 2-Propanol (IPA) (CAS: 67-63-0, ≥ 96 %, Sinopharm);
- Ethanol (CAS: 64-17-5, ≥ 95 %, Sinopharm).

General Procedure for the determination of the content of silicate (SiO₂) and sodium (Na) by Inductively Coupled Plasma (ICP)

The Si content in the polymeric composition, such as e.g. a solid tire, was quantified using alkali fusion method according to ASTM D4004-06 (2017). This method involves weighing a certain amount of the sample with sodium carbonate and boric acid into a platinum crucible, followed by roasting in a muffle furnace. After roasting, the sample is dissolved using dilute acid. The acid solution is collected and subsequently tested by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

The Si and Na content in an aqueous sample was quantified using a mixed acid method named EPA Method 3050B:1996. This method involves adding a certain amount of the sample into a Teflon digestion vessel, adding the appropriate amount of mixed acid, heating the digestion on a heating plate, waiting for the sample to be completely digested, clarifying the solution, and fixing the volume to a plastic volumetric flask, followed by ICP-OES testing.

Preparation of a tire powder

A simplified tire tread formulation sheet prepared by Solvay was shredded and cut into a powder.

Its SiO₂ content was determined by ICP using the General Procedure described above. In the present case, a SiO₂ content of 32 wt. %, based on the total weight of the simplified tire tread sheet, was determined.

The particle size distribution the powder was determined by a particle size distribution analyzer (PSD), namely a Malvern Mastersizer 3000.

Tire powder was dispersed in ethanol while stirring during about 10 minutes for the sample to disperse evenly. The tests were repeated for 6 times to ensure consistent results.

According to PSD, 90% of particles with diameter are below 338 μm, 50% of particles with diameter are below 190 μm and 10% of particles with diameter are below 94.5 μm.

Example 1 (Comparative)

Tire treated by aqueous NaOH solution and organic solvent at atmospheric Pressure.

In a typical procedure, tire powder (1.5 g), NaOH (4.8 g), H₂O (15 mL), and isopropanol (IPA, 10 mL) were sequentially added into the Teflon reactor equipped with a Teflon condenser. The mixture was heated at 85 °C and stirred for 22 hours. After the reaction, the mixture was transferred into centrifuge tube.

A mixture of H₂O and EtOH was used to wash the reactor in order to completely remove the solvent and residual tire from reactor into centrifuge tube. The mixture was centrifuged at 10,000 rpm for 5 mins to separate tire from liquid. The separated liquid was collected and stored in a round-bottomed flask, and then a mixture of H₂O and EtOH was added into centrifuge tube in order to remove the residual NaOH from tire. This procedure was repeated several times until that the pH of separated liquid is equal ~7. Finally, the wet tire was dried at 100 °C under vacuum. All the separated liquid in the container was concentrated into ~50 mL by evaporation under 40 °C and 50 mbar.

The silicon and sodium content in solution were quantified by ICP, and the weight ratio of SiO₂ to Na₂O (Rp) was calculated using the following equation.

$$Rp = \frac{60 * \text{Si content}}{28} * \frac{23 * 2}{62 * \text{Na content}} \quad (1)$$

Reaction conditions and Rp calculated for this example are summarized in Table 1.

Example 2 (Comparative)

The reaction protocol is similar as Example 1, except that 2.7 g NaOH were used instead of 4.8 g.

The silicon and sodium content in liquid were quantified by ICP, and the weight ratio of SiO₂ to Na₂O (Rp) was calculated using equation (1). Reaction conditions and Rp calculated for this example are summarized in Table 1.

Example 9

Tire treated by aqueous NaOH solution and organic solvent under pressure.

In a typical procedure, tire powder (20 g), NaOH (2.2 g), H₂O (30 mL), and IPA (20 mL) were sequentially added into the Hastelloy reactor. After purging several times with N₂, the pressure was raised to 15 bar with N₂. The mixture was heated at 180 °C and stirred for 22 hours. After the reaction, the treated tire was separated by filtration and then washed with a mixture of H₂O and EtOH. This washing step was repeated several times until the pH of the filtrate is equal ~7. The filtrates were collected and stored in a round-bottomed flask. Finally, all the

separated liquid in the flask was concentrated into ~100 ml by evaporation under 40 °C and 50 mbar. The wet tire was dried at 100 °C under vacuum.

The silicon and sodium content in liquid were quantified by ICP, and the weight ratio of SiO₂ to Na₂O (Rp) was calculated using equation (1). Reaction conditions and Rp calculated for this example are summarized in Table 1.

Example 4

Tire treated by aqueous NaOH solution in without the use of any organic solvent.

The experimental procedure is similar as in Example 9, except that 10 g of tire powder, 1.1 g of NaOH and 50 mL water were added in the Hastelloy reactor instead of 20 g of tire powder, 2.2 g of NaOH, 30 mL water, and 20 mL IPA respectively.

The silicon and sodium content in liquid were quantified by ICP, and the weight ratio of SiO₂ to Na₂O (Rp) was calculated using equation (1). Reaction conditions and Rp calculated for this example are summarized in Table 1.

Examples 3, 5-8, and 10

Same general procedure as for Examples 9 and 4, with tire powder, NaOH, H₂O, and IPA amounts, and with temperature, time as specified in Table 1.

The silicon and sodium content in liquid were quantified by ICP, and the weight ratio of SiO₂ to Na₂O (Rp) was calculated using equation (1). The calculated value Rp for these examples are shown in Table 1.

Conclusion:

Examples 1 and 2 are comparative examples. The Rp value in those examples is with 0.07 and 0.1 undesirably low.

The comparison of inventive Examples 3 to 5 shows that the Rp increases with increased reaction time (Example 3: 2 hrs, Rp = 0.6; Example 5: 44 hrs, Rp = 1.4).

The comparison of inventive Examples 3 and 7 shows that the Rp increases if a mixture of water and IPA is used compared to water alone (Example 3: solvent = 100% water, Rp = 0.6; Example 7: solvent = 60% water + 40% IPA, Rp = 1.7).

A similar conclusion can be drawn from the comparison of inventive Examples 4 and 6 (Example 4: solvent = 100% water, $R_p = 1.1$; Example 6: solvent = 60% water + 40% IPA, $R_p = 2.0$).

The comparison of inventive Examples 8 to 10 shows that the lower the molar ratio of base to SiO_2 used in the process is, the higher is the resulting R_p value (Example 8: molar ratio of $\text{NaOH} / \text{SiO}_2 = 0.34$, $R_p = 2.9$; Example 9: molar ratio of $\text{NaOH} / \text{SiO}_2 = 0.52$, $R_p = 2.7$; Example 10: molar ratio $\text{NaOH}/\text{SiO}_2 = 0.82$, $R_p = 1.9$).

Table 1. Reaction conditions and Rp of the obtained silicate

Exp. No.	Reactor	Tire (g)	SiO ₂ (g) / (mmol)	NaOH (g) / (mmol)	Molar ratio NaOH / SiO ₂	H ₂ O (mL)	IPA (mL)	Temp. (°C)	Time (h)	Rp
1	Teflon	1.5	0.48 / 7.99	4.8 / 120	15.02	15	10	85	22	0.07
2	Teflon	1.5	0.48 / 7.99	2.7 / 67.5	8.45	15	10	85	22	0.1
3	Hastelloy	10	3.2 / 53.26	1.1 / 27.5	0.52	50	-	180	2	0.6
4	Hastelloy	10	3.2 / 53.26	1.1 / 27.5	0.52	50	-	180	22	1.1
5	Hastelloy	10	3.2 / 53.26	1.1 / 27.5	0.52	50	-	180	44	1.4
6	Hastelloy	10	3.2 / 53.26	1.1 / 27.5	0.52	30	20	180	22	2.0
7	Hastelloy	10	3.2 / 53.26	1.1 / 27.5	0.52	30	20	180	2	1.7
8	Hastelloy	15	4.8 / 79.89	1.1 / 27.5	0.34	30	20	180	22	2.9
9	Hastelloy	20	6.4 / 106.52	2.2 / 55	0.52	30	20	180	22	2.7
10	Hastelloy	20	6.4 / 106.52	3.5 / 87.5	0.82	30	20	180	22	1.9

CLAIMS

1. A process for recovering a silicate from a polymeric composition comprising silica, said method comprising the following steps:
 - (i) contacting a polymeric composition comprising silica with a base in the presence of a solvent,
 - (ii) allowing the base to react with the silica comprised in the polymeric composition to form a silicate, thereby obtaining a polymeric composition having lost at least part of the silica and a solution comprising the silicate, and
 - (iii) separating the solution obtained at step (ii) from the polymeric composition obtained at step (ii),wherein the molar ratio of base to silica used in step (i) is lower than 1.
2. Process according to claim 1, wherein the polymeric composition is a tire, preferably a scrapped tire.
3. Process according to any one of claims 1 or 2, wherein the base is selected from the group consisting of alkali metal hydroxide and ammonium hydroxide.
4. Process according to any one of the preceding claims, wherein the base is sodium hydroxide or potassium hydroxide, preferably sodium hydroxide.
5. Process according to any one of the preceding claims, wherein step (ii) is carried out in a pressure vessel, preferably a Hastelloy reactor.
6. Process according to claim 5, wherein the pressure applied in step (ii) is up to 50 bar, preferably between 1 and 40 bar, more preferably between 2 and 30 bar.
7. Process according to any one of the preceding claims, wherein the temperature in step (ii) is from 80 to 250 °C, preferably from 100 to 180 °C, and more preferably 140 to 180 °C.

8. Process according to any one of the preceding claims, wherein the solvent is water, an organic solvent or mixture thereof, preferably a mixture of water and an organic solvent.
9. Process according to any one of the preceding claims, wherein the organic solvent has a total Hansen solubility parameter of less than $33 \text{ MPa}^{1/2}$, preferably between 15 to $29 \text{ MPa}^{1/2}$, more preferably from 20 to $25 \text{ MPa}^{1/2}$.
10. Process according to claim 8 or 9, wherein the organic solvent is selected from the group consisting of alcohols, hydrocarbons, ketones, sulfones, amines, amides, ethers and esters, preferably having at least 2 and no more than 8 carbon atoms.
11. Process according to any one of claims 8 to 10, wherein the organic solvent is selected from the group consisting of dimethyl sulfoxide (DMSO), acetone, toluene, ethylene glycol, t-butyl alcohol, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and cyclopentanone, preferably selected from the group consisting of DMSO, toluene, acetone, 1-propanol, 2-propanol, 1-butanol, 2-butanol and t-butyl alcohol, more preferably selected from the group consisting of 1-propanol, 2-propanol, 1-butanol, 2-butanol and tert-butyl alcohol, and most preferably from the group consisting of 1-propanol and 2-propanol.
12. Process according to any one of the preceding claims, wherein the molar ratio of the base to silica is from 0.18 to 0.99, preferably from 0.20 to 0.90, more preferably from 0.30 to 0.80.
13. Process according to any one of the preceding claims, wherein the weight ratio of SiO_2 to Na_2O (Rp) in the silicate solution obtained in step (iii) is from 1.5 to 3.6, preferably from 2.0 to 3.6 when sodium hydroxide is used as the base.
14. Process according to any one of the preceding claims, wherein the weight amount of silica comprised in the polymer composition is 0.1% to 40 %, in particular from 10 % to 40 %, especially from 20 % to 40 % based on the total weight amount of the polymer composition.
15. Process according to any one of proceeding claims, wherein the polymeric composition comprising silica is in the form of powder.

16. Process according to claim 15, wherein the average particle size of the powder is from 0.05 mm to 100 mm and preferably from 0.1 mm to 50 mm, measured by a particle size distribution analyzer (PSD) using laser diffraction.

17. A process for preparing an aqueous silicate solution, comprising the process according to any one of the preceding claims, wherein the solvent used in step (ii) is water or a mixture of water and an organic solvent, wherein the organic solvent is removed from the solution obtained in step (iii) of the process.

18. A process for preparing a silicate in solid form, wherein said process comprises the process according to claim 17, further comprising the step of drying the aqueous solution obtained from said process to obtain a silicate in solid form.

19. A process for preparing a precipitated silica or a precipitated silica suspension, said process comprising the steps of:

- (a) preparing a silicate solution, preferably an aqueous silicate solution, using the process according to any one of claims 1 to 16 or the process according to claim 17; or preparing a silicate in solid form using the process according to claim 18 and dispersing, preferably redissolving the silicate in solid form obtained from said process in a dispersing medium, preferably an aqueous dispersing medium,
- (b) reacting the silicate solution obtained in step (a) and, optionally in addition a silicate solution other than the silicate solution obtained in step (a), with at least one acidifying agent in a liquid medium, preferably in an aqueous liquid medium, to obtain a suspension of precipitated silica in the liquid medium,
- (c) optionally, separating the precipitated silica from the liquid medium to provide a wet precipitated silica, and
- (d) optionally, drying said wet precipitated silica.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2023/140898

A. CLASSIFICATION OF SUBJECT MATTER

C01B 33/32(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01B;

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNTXT,ENTXTC,WPABS,WPABSC,DWPL,JPTXT,ISI web of knowledge,CNKI: SiO₂,silica, silicon, silicic acid, silicat??. recycled, alkali, polymeric, tire, hydroxide, pyrolysis,rubber, silicon oxide**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 203530201 U (WANG,Jing) 09 April 2014 (2014-04-09) paragraphs [23]-[25],[28]-[29]	1-18
X	CN 107952260 A (ZHANG,Ruiqiu) 24 April 2018 (2018-04-24) claims1-9	1-18
X	WO 2022259044 A1 (UNIV. DE COIMBRA) 15 December 2022 (2022-12-15) claims1-14	1-18
Y	WO 2015121328 A1 (RHODIA OPERATIONS) 20 August 2015 (2015-08-20) claim1	19
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Y	CN 203530201 U (WANG,Jing) 09 April 2014 (2014-04-09) paragraphs 23-28	19
A	CN 102491350 A (UNIV. DALIAN POLYTECHNIC) 13 June 2012 (2012-06-13) paragraphs 1-44	1-19

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

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“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

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Name and mailing address of the ISA/CN

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2023/140898**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 102963897 A (SEMICONDUCTOR ENERGY LAB.) 13 March 2013 (2013-03-13) summary	1-19
A	US 6713549 B1 (GOODYEAR TIRE & RUBBER CO.) 30 March 2004 (2004-03-30) summary	1-19

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2023/140898

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