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(54) **Title**: ELASTOMER COMPOSITE REINFORCED WITH SILICA AND PRODUCTS CONTAINING SAME

(57) **Abstract**: A silica elastomer composite having superior mechanical properties.

ELASTOMER COMPOSITE REINFORCED WITH SILICA AND PRODUCTS CONTAINING SAME

[0001] The present invention relates to silica elastomer composites. More particularly, the present invention relates to a silica reinforced elastomer composite formed by a wet masterbatch method.

[0002] Numerous products of commercial significance are formed of elastomeric compositions wherein particulate reinforcing material is dispersed in any of various synthetic elastomers, natural rubber or elastomer blends. Carbon black and silica, for example, are widely used as reinforcing agents in natural rubber and other elastomers. It is common to produce a masterbatch, that is, a premixture of reinforcing material, elastomer, and various optional additives, such as extender oil. Numerous products of commercial significance are formed of such elastomeric compositions. Such products include, for example, vehicle tires wherein different elastomeric compositions may be used for the tread portion, sidewalls, wire skim and carcass. Other products include, for example, engine mount bushings, conveyor belts, windshield wipers, seals, liners, wheels, bumpers, and the like.

[0003] Good dispersion of particulate reinforcing agents in rubber compounds has been recognized for some time as one of the most important objectives for achieving good quality and consistent product performance, and considerable effort has been devoted to the development of methods to improve dispersion quality. Masterbatch and other mixing operations have a direct impact on mixing efficiency and on dispersion quality. In general, for instance, when carbon black is employed to reinforce rubber, acceptable carbon black macro-dispersions can often be achieved in a dry-mixed masterbatch. However, high quality, uniform dispersion of silica by dry-mix processes poses difficulties, and various solutions have been offered by the industry to address this problem, such as precipitated silica in the form of “highly dispersible silica” or “HDS” flowable granules. More intensive mixing can improve silica dispersion, but also can

degrade the elastomer into which the filler is being dispersed. This is especially problematic in the case of natural rubber, which is highly susceptible to mechanical/thermal degradation.

[0004] In addition to dry mixing techniques, it is known to feed elastomer latex or polymer solution and a carbon black or silica slurry to an agitated tank. Such "wet masterbatch" techniques can be used with natural rubber latex and emulsified synthetic elastomers, such as styrene butadiene rubber (SBR). However, while this wet technique has shown promise when the filler is carbon black, this wet technique, when the filler is silica, poses challenges to achieving acceptable elastomer composite. Specific techniques for producing wet masterbatch, such as the one disclosed in U.S. Patent No. 6,048,923, the contents of which are incorporated by reference herein, have not been effective for producing elastomer composites employing silica particles as the sole or principal reinforcing agent.

[0005] Accordingly, there is a need for elastomer composites and vulcanized elastomer composites produced with silica particles as the sole or principal reinforcing agent and exhibiting improved mechanical properties.

SUMMARY OF THE PRESENT INVENTION

[0006] A feature of the present invention is to produce elastomer composites using a liquid-based process which permits the use of silica, and yet achieves desirable silica elastomer composites. Uniform distribution of silica particles within an elastomer matrix is achieved using a continuous process employing a destabilized silica slurry and an elastomer latex. Coordinating the rates of liquid dispersion of silica in elastomer latex with formation of a rubber network results in a unique solid or semi-solid silica-containing continuous rubber phase, a coagulated mixture of silica uniformly dispersed in elastomer latex. Dewatering of the silica-containing continuous rubber phase produces a silica elastomer composite which, when compounded and processed to form a vulcanized elastomer composite, yields improved reinforcement properties.

[0007] In one embodiment, the present invention relates to an elastomer composite produced using a wet masterbatch process that includes, but is not limited to, the use of a fluid that includes an elastomer latex, and the use of an additional fluid that includes a destabilized dispersion of particulate silica. The two fluids are combined together under continuous flow conditions and selected velocities. The combining is such that the silica is dispersed within the elastomer latex and, in parallel (or almost parallel), the elastomer latex is transformed from a liquid to a solid or semi-solid elastomer composite, such as to a solid or semi-solid silica-containing continuous rubber phase. This can occur, for instance, in about two seconds or less such as a fraction of a second, due to the one fluid impacting the other fluid with sufficient energy to cause the uniform and intimate distribution of silica particles in the elastomer. The use of a destabilized dispersion of silica in this masterbatch process enables formation of an elastomer composite with desirable properties.

[0008] The present invention further relates to elastomer composites formed from any one or more of the wet masterbatch processes described herein. The present invention also relates to articles that are made from or include the elastomer composite(s) of the present invention.

[0009] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide a further explanation of the present invention as claimed.

[0010] The accompanying drawings, which are incorporated in and constitute a part of this application, illustrate various features of the present invention and, together with the description, serve to explain the principles of the present invention.

BRIEF DESCRIPTION OF DRAWINGS

[0011] FIG. 1(a), 1(b), and 1(c) are diagrams illustrating exemplary mixing apparatuses that can be used to prepare vulcanizable elastomer composite according to embodiments of the present invention, and which were used in some of the examples.

[0012] FIG 2 is a block diagram of various steps that can occur in the formation of the vulcanizable and vulcanized elastomer composite according to embodiments of the present invention and in making rubber compounds with such elastomer composites.

[0013] FIG. 3 is a series of graphs illustrating, with respect to silica loading (phr), the mechanical properties of various vulcanized silica elastomer composites (Figure 3A - modulus ratio T300/T100, Figure 3B – tensile strength (MPa), Figure 3C – tan delta 60, and Figure 3D – elongation at break (%) * tensile strength (MPa)); Stars: elastomer composite produced by dry mixing; triangles: elastomer composite produced by a batch liquid based process; diamonds: elastomer composites according to exemplary embodiments.

[0014] FIG. 4 plots the modulus ratio (T300/T100) of the Comparative Example 1 samples (stars), the vulcanized elastomer composites of Runs 1-4 of Comparative Example 8 (triangles), and vulcanized elastomer composites of Example 5 (diamonds) with respect to the tan delta 60 value.

[0015] FIG. 5 plots the modulus ratio (T300/T100; diamonds) and tan delta 60 (squares) of the vulcanized elastomer composites of Example 5 with respect to swell index.

[0016] FIG. 6 plots the modulus ratio (T300/T100) of the vulcanized elastomer composites of Example 10 (diamonds) and the Comparative Example 1 samples (stars) with respect to silica loading.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0017] In one embodiment, a vulcanizable elastomer composite comprises at least 40 phr of silica dispersed in natural rubber. The silica may comprise, consist essentially of, or consist of precipitated silica. When the vulcanizable elastomer composite is vulcanized, the resulting vulcanizate exhibits a ratio T300/T100 of at least -0.024s + b, wherein s is the amount of silica in the elastomer composite masterbatch expressed as parts per hundred weight of rubber (phr) and b is 6.3, and at least one additional property selected from a) a tan delta 60 of at most 0.0022s – c, wherein c is 0.05; b) a tensile strength in MPa of at least -0.21s + d, wherein d is 41; c) elongation at break (%) * tensile strength (MPa) of at least -211s +e, where e = 27543, and d) a silica loading of at least 55 phr, for example, at least 60 phr. Alternatively or in addition, b may be 6.4, 6.6, or 6.8, c may be 0.06, and/or d may be 41.4. For example, T300/T100 may be from -0.024s + b to 7, tan delta 60 may be from 0.02 to 0.0022s – c, the tensile strength may be from -0.21s + d to 35 or 40, and/or elongation at break (%) * tensile strength (MPa) may be from -211s +e to 21500.

[0018] Alternatively or in addition, a vulcanizable elastomer composite comprises silica, for example, at least 40 or 55 phr of silica, dispersed in natural rubber. The silica may comprise, consist essentially of, or consist of precipitated silica. When the vulcanizable elastomer composite is vulcanized, the resulting vulcanizate exhibits a ratio T300/T100 of at least 5.5 and a tan delta 60 of at most 0.05. In another embodiment, a vulcanizable elastomer composite comprises at least 55 phr of silica dispersed in natural rubber; when the vulcanizable elastomer composite is vulcanized, it exhibits a ratio T300/T100 of at least about 5. In another embodiment, a vulcanizable elastomer composite comprising silica dispersed in natural rubber has a modulus ratio T300/T100 of at least 6.3. In another embodiment, vulcanizable elastomer composite comprises at least 40 phr of silica, for example, at least 50 phr, dispersed in natural rubber. When the vulcanizable elastomer composite is vulcanized, it has a ratio

T300/T100 of at least -0.025s + 6.2, for example, at least -0.025s + 6.3 or 6.4. The vulcanizable elastomer composite may comprise a dewatered wet masterbatch of silica dispersed as a slurry in field latex, which may be stabilized, e.g. with ammonia, desludged, or chemically or enzymatically modified.

[0019] In another embodiment, a solid silica-containing continuous rubber phase article comprises at least 40 phr of silica, which may comprise, consist essentially of, or consist of precipitated silica dispersed in coagulated natural rubber latex. The solid silica-containing continuous rubber phase article exhibits an elongation at break of at least 100%.

[0020] In a preferred method for producing vulcanizable elastomer composite, silica is selectively and strategically introduced into an elastomer latex in a continuous, rapid, wet masterbatch process. This process can be carried out in a semi-confined reaction zone, such as a tubular mixing chamber or other mixing chamber of an apparatus suitable for carrying out such a process under controlled volumetric flow and velocity parameters, leading to beneficial properties that would not be achieved, but for this selective and strategic use of silica. As explained in further detail herein, by 'selective', the method uses a destabilized dispersion of silica. And, by 'strategic' introduction, the preferred method uses at least two separate fluids, one fluid that includes an elastomer latex, and another fluid that includes the destabilized dispersion of silica. The two fluids can be pumped or transferred into a reaction zone, such as a semi-confined reaction zone. The two fluids can be combined under continuous flow conditions, and under selected volumetric flow and velocity conditions. The combining under pressure with selected differential velocity conditions is sufficiently energetic that the silica can be distributed in two seconds or less, such as in milliseconds, within the elastomer latex, and the elastomer latex is transformed from a liquid to a solid phase, such as to a silica elastomer composite in the form of a solid or semi-solid silica-containing continuous rubber phase.

[0021] The preferred method of producing a vulcanizable silica elastomer composite may comprise, consist essentially of, consist of, or include:

(a) providing a continuous flow under pressure of at least a first fluid comprising a destabilized dispersion of silica and providing a continuous flow of a second fluid comprising elastomer latex;

(b) adjusting volumetric flows of the first fluid and the second fluid to yield an elastomer composite having a silica content of from about 15 phr to about 180 phr; and

(c) combining the first fluid flow and the second fluid flow (for instance in a semi-confined reaction zone) with sufficient impact to distribute the silica within the elastomer latex, to obtain a flow of a solid silica-containing continuous rubber phase or semi-solid silica-containing continuous rubber phase. The method transforms the elastomer latex from a liquid to a flow of a solid or semi-solid silica-containing continuous rubber phase. The silica-containing continuous rubber phase can be recovered as a substantially continuous flow of the solid or semi-solid silica-containing continuous rubber phase.

[0022] Additional improvement in mechanical properties is correlated with the use of latex concentrate, the destabilization of the silica slurry using a salt, with or without additional acid, and a swell index in the vulcanized elastomer composite from about 1.80 to about 2.20, for example, from about 1.90 to about 2.10 or from about 1.95 to about 2.05.

[0023] Further details and/or options for producing vulcanizable elastomer composite are described below.

[0024] As used herein, "silica" means particulate silicon dioxide, or a particle coated with silicon dioxide, and includes precipitated silica in any form, such as highly dispersible (HDS) granules, non-HDS granules, silica aggregates and silica particles; colloidal silica; fumed silica; and any combinations thereof. Such silicon dioxide or silicon dioxide coated particles may have been chemically treated to include functional groups bonded (attached (e.g.,

chemically attached) or adhered (e.g., adsorbed)) to the silica surface. Thus, "silica" includes any particle having a surface substantially consisting of silica or silica having functional groups bonded or attached to it.

[0025] As used herein, "dispersion" means a stable suspension of solid particles in aqueous fluid, wherein the charge at the surface of the particles prevents particle agglomeration and the dispersion is characterized by a zeta potential magnitude of greater than or equal to 30 mV.

[0026] Zeta potential is used to measure stability of charged particles, such as silica particles, dispersed in a fluid. Measurement of zeta potential can have a variance of, for instance +/-2 mV, and, as used herein, zeta potential magnitude refers to the absolute value of the number, e.g., a zeta potential value of minus 30 mV has a greater magnitude than a zeta potential value of minus 10 mV.

[0027] As used herein, "destabilized dispersion" means a suspension of solid particles in an aqueous fluid wherein the charge at the surface of the particles has been reduced by the presence of an agent, or by treatment of the solid particles, and is characterized by a zeta potential magnitude of less than 30 mV, or more preferably a zeta potential of less than 28 mV or less than 25 mV. The aqueous fluid can be water, a water miscible fluid (e.g., alcohol or ether), partially water miscible fluid, or a mixture of fluids that contains at least a water miscible or partially water miscible fluid.

[0028] As used herein, the terms "silica slurry" and "dispersion" mean a dispersion of silica in an aqueous fluid, wherein the charge at the surface of the silica prevents particle agglomeration and the dispersion is characterized by a zeta potential value with a magnitude of at least 30 mV. A silica slurry or dispersion may be destabilized by treatment with sufficient agent(s), or by treatment of the silica, to reduce the charge on the surface of the

silica and the resulting destabilized silica slurry (or destabilized silica dispersion) is characterized by a zeta potential magnitude of less than 30 mV.

[0029] As used herein, the terms "uniform" and "uniformly" are intended to mean, conventionally for those skilled in the art, that the concentration of a component, for example, particulate filler, in any given fraction or percentage (e.g., 5%) of a volume is the same (e.g., within 2%) as the concentration of that component in the total volume of the material in question, e.g., elastomer composite or dispersion. Those skilled in the art will be able to verify the statistical uniformity of the material, if required, by means of measurements of concentration of the component using several samples taken from various locations (for example near the surface or deeper in the bulk).

[0030] As used herein, a "silica elastomer composite" means a masterbatch (a premixture of reinforcing material, elastomer, and various optional additives, such as extender oil) of coherent rubber comprising a reinforcing amount (e.g., about 15 phr to about 180 phr) of dispersed silica. Silica elastomer composite can contain optional, further components such as acid, salt, antioxidant, antidegradants, coupling agents, minor amounts (e.g., 10 wt % or less of total particulates) of other particulates, processing aids, and/or extender oil, or any combinations thereof.

[0031] As used herein, a "solid silica-containing continuous rubber phase" means a composite having a continuous rubber phase and a uniformly dispersed phase of silica and, for instance, up to 90%, by weight, aqueous fluid. The solid silica-containing continuous rubber phase may be in the form of a continuous rope or worm. When compressed these articles release water. The solid silica-containing continuous rubber phase can contain optional, further components such as acid, salt, antioxidant, coupling agents, minor amounts of other particulates (e.g., 10 wt % or less of total particulates), and/or processing oil, or any combinations thereof.

[0032] As used herein, a "semi-solid silica-containing continuous rubber phase" means a composite with a paste-like consistency, having a silica-containing, continuous rubber phase. The semi-solid product has a continuous phase of rubber, with entrapped silica uniformly distributed throughout the rubber phase. The semi-solid silica-containing continuous rubber phase remains coherent and expels water, while retaining solids content, upon further handling in one or more subsequent operations selected to develop the paste-like or gel-like material into a solid silica-containing continuous rubber phase.

[0033] As used herein, a "coherent" material is material existing in a substantially unitary form that has been created by the adhesion of many smaller parts, such as an elastic, solid mass of rubber created by the adhesion of many small rubber particles to each other.

[0034] As used herein, a "continuous flow" is a steady or constant flow of a fluid without interruption from a supply source (e.g., tank). But, it is to be understood that temporary interruptions (e.g., a second or a few minutes) of flow would still be considered a continuous flow (e.g., for instance, when switching supply from various supply holding areas, such as tanks and the like, or interrupting flows to accommodate downstream unit processes or maintenance of the equipment).

[0035] In a preferred embodiment, vulcanizable elastomer composite can be produced in a continuous flow process involving a liquid mixture of elastomer latex and destabilized dispersion of silica. Any device, or apparatus or system can be used, provided the device, apparatus, or system can be operated such that a liquid mixture of elastomer latex and a destabilized silica dispersion can be combined under continuous flow conditions and under controlled volumetric flow, pressure, and velocity conditions, including, but not limited to, the apparatus shown in Figure 1(a), (b), or (c), or any type of eductor or ejector, or any other device arranged to combine a continuous flow of at least two flows of liquid under controlled volumetric flow, pressure, and velocity conditions into and through a reaction zone. The

apparatus described in US20110021664, US6048923, WO2011034589, WO2011034587, US20140316058, and WO2014110499 (each incorporated in their entirety by reference) can be used or adapted to the processes herein as well. Also, ejectors and eductors or syphons such as water jet eductors or steam jet syphons can be used (e.g, ones commercially available from Schutte & Koerting, Trevose, PA).

[0036] The apparatus can include various supply tanks, pipes, valves, meters and pumps to control volumetric flow, pressure, and velocity. Further, as indicated at inlet (3) in Figures 1(a), (b), and (c), various types and sizes of nozzles or other orifice size control elements (3a) can be employed to control the velocity of the silica slurry. The volumetric dimension of the reaction zone (13) can be selected to provide desired volumetric flows of the fluids and the elastomer composite. The inlet (11) supplying the elastomer latex to the reaction zone may be tapered to provide different volumetric flow rates and velocities. Devices may include an inlet (11) of uniform diameter, without any taper at the orifice leading to the reaction zone.

[0037] In the method, a fluid that includes an elastomer latex and an additional fluid that includes a destabilized dispersion of silica supplied, for instance, as a jet under pressure are combined together under continuous flow conditions and under selected volumetric flow rates, pressure, and velocities to rapidly and intimately mix the two fluids. The combining, for instance in a semi-confined space under pressure, is such that the silica is distributed throughout the elastomer latex and, in parallel, the elastomer latex is transformed from a liquid to a solid or semi-solid phase, i.e., a liquid to solid inversion, or coagulation, of the latex occurs, capturing the distributed silica and water in the rubber and forming a solid or semi-solid silica-containing continuous rubber phase in a continuous or semi-continuous flow out of the reaction zone (e.g., from opening at bottom (7) in the Figures 1 (a) – (c)). At this point, the product can be considered an elastomer composite of a continuous rubber phase containing silica particles, a silica-containing coherent rubber, or a silica elastomer composite. It is believed that the silica

particles first must be distributed in the elastomer latex to obtain the desired product, and the liquid to solid phase inversion follows immediately upon the silica distribution. However, with the continuous and extremely rapid rate of combining the fluids (i.e., less than 2 seconds, less than 1 second, less than 0.5 second, less than 0.25 second, less than 0.1 second, or on the order of milliseconds), and the energetic and intimate mixing of relatively small volumes of fluids in the reaction zone (e.g., fluid volumes on the order of 10 to 500 cc), the parallel steps of distribution of the silica particles and liquid to solid phase transformation of the elastomer latex can happen nearly simultaneously. The 'reaction zone' as used herein is the zone where the intimate mixing occurs along with coagulation of the mixture. The mixture moves through the reaction zone and to an outlet (7).

[0038] An exemplary method for preparing the vulcanizable elastomer composite involves simultaneously feeding a first fluid comprising a destabilized dispersion of silica and a second fluid comprising an elastomer latex (e.g. natural rubber latex) fluid to a reaction zone. The first fluid comprising the destabilized dispersion of silica can be fed at a flow rate based on its volume, and the second fluid comprising the elastomer latex can be fed at a flow rate based on its volume (i.e., volumetric flow rates). The volumetric flows of either the first fluid, the second fluid, or both the first and second fluid can be adjusted or provided so as to yield an elastomer composite having a silica content of from 15 to 180 parts per hundred weight rubber (phr) (e.g., from 35 to 180 phr, from 20 phr to 150 phr, from 25 phr to 125 phr, from 25 phr to 100 phr, from 35 to 115 phr, or from 40 phr to 115 phr, or from 40 phr to 90 phr and the like). The fluid that contains the destabilized dispersion of silica may be referred to as the first fluid in some embodiments herein. This fluid is a separate fluid from the fluid containing the elastomer latex. Either fluid can be introduced through one inlet or injection point or through more than one inlet or injection point.

[0039] The volumetric flow ratio of the first fluid (destabilized silica dispersion) to the second fluid (latex fluid) can be adjusted to permit the desired elastomer composite to form. Examples of such volumetric flow ratios include, but are not limited to, a volumetric ratio of from 0.4:1 (first fluid to second fluid) to 3.2:1; from 0.2:1 to 2:1 and the like. The volumetric flow ratio between the first fluid and second fluid can be adjusted by any means or technique. For instance, the volumetric flow rate of the first or second fluid or both can be adjusted by a) increasing the volumetric flow rate, b) decreasing the volumetric flow rate, and/or c) adjusting the flow rates of the fluids relative to each other. Pressure created by physical constraints applied to the flow of the first fluid causes formation of a high velocity jet that enables the combination of the destabilized silica dispersion with the elastomer latex to occur rapidly, e.g., in a fraction of a second. As an example, the time during which two fluids are mixed and a liquid to solid phase inversion occurs can be on the order of milliseconds (e.g., about 50 ms to about 1500 ms or about 100 ms to about 1000 ms). For a given selection of fluids, if the velocity of the first fluid is too slow to adequately mix the fluids, or the residence time is too short, then a solid rubber phase and solid product flow may not develop. If the duration of the process is too long, back pressure may develop in the reaction zone and the continuous flow of materials halted. Likewise, if the velocity of the first fluid is too fast, and the duration of the process is too short, a solid rubber phase and solid product flow may not develop.

[0040] As described earlier, the relative volumetric flows of the first fluid (destabilized silica slurry) and the second fluid (latex) can be adjusted, and when at least one salt is used as the destabilization agent, it is preferred to adjust the volumetric flow ratio of destabilized silica slurry to elastomer latex so as to be 0.4:1 to 3.2:1. Other flow ratios may be used.

[0041] When at least one acid is used as the destabilization agent, it is preferred to adjust the volumetric flow ratio of destabilized silica slurry to elastomer latex so as to be 0.2:1 to 2:1. Other flow ratios may be used.

[0042] The elastomer latex can contain at least one base (such as ammonia), and the destabilized dispersion of silica can be achieved with the addition of at least one acid, wherein the molar ratio of the acid in the first fluid (silica) and the base (e.g., ammonia) in the second fluid (latex) is at least 1.0, or at least 1.1, or at least 1.2, such as from 1 to 2 or 1.5 to 4.5. The base can be present in a variety of amounts in the elastomer latex, such as, but not limited to, 0.3 wt% to about 0.7 wt% (based on the total weight of the elastomer latex), or other amounts below or above this range.

[0043] The destabilized silica dispersion can be fed to the reaction zone preferably as a continuous, high velocity, e.g., about 6 m/s to about 250 m/s, or about 30 m/s to about 200 m/s, or about 10 m/s to about 150 m/s, or about 6 m/s to about 200 m/s, jet of injected fluid, and the fluid containing the elastomer latex can be fed at a relatively lower velocity, e.g., about 0.4 m/s to about 11 m/s, or about 0.4 m/s to about 5 m/s, or about 1.9 m/s to about 11 m/s, or about 1 m/s to about 10 m/s or about 1 m/s to about 5 m/s. The velocities of the fluids are chosen for optimizing mixing between fluids and fast coagulation of elastomer latex. The velocity of the elastomer latex fed into the reaction zone should be preferably high enough to generate turbulent flow for better mixing with destabilized silica slurry. Yet, the velocity of the elastomer latex should be kept low enough so that latex would not coagulate from shear before it is well mixed with the destabilized silica slurry. In addition, the velocity of the elastomer latex should be kept low enough before it enters into the reaction zone for preventing clogging of latex supply lines from coagulation of latex due to high shear. Similarly, there is also an optimized range of the velocity of destabilized silica dispersion . It is theorized that if the velocity of the destabilized silica slurry is too high, the rate of shear induced agglomeration of silica particles could be too high to allow adequate, uniform mixing between silica particles and elastomer latex particles.

[0044] Shear thickening from agglomeration and networking of silica particles also could reduce turbulence of the destabilized silica slurry and adversely affect the mixing between silica and latex. On the other hand, if the velocity of the destabilized silica slurry is too low, there may not be sufficient mixing between silica particles and elastomer latex particles. Preferably, at least one of the fluids entering into the reaction zone has a turbulent flow. In general, due to much higher viscosity of a typical destabilized silica dispersion relative to a typical elastomer latex, a much higher velocity of the destabilized silica dispersion is needed for generating good fluid dynamics for mixing with the elastomer latex and fast coagulation of the latex. Such high velocity flow of the destabilized silica dispersion may induce cavitation in the reaction zone to enhance rapid mixing of fluids and distribution of silica particles in the elastomer latex. The velocity of the destabilized silica dispersion can be altered by using different volumetric flow rates, or a different nozzle or tip (wider or narrower in diameter) at the inlet (3a) that feeds the first fluid comprising destabilized silica dispersion. With use of a nozzle to increase the velocity of the destabilized silica dispersion, it can be provided under pressure ranging from about 30 psi to about 3,000 psi, or about 30 psi to about 200 psi, or about 200 psi to about 3,000 psi, or about 500 psi to about 2,000 psi or a relative pressure at least 2 times higher than the pressure applied to the fluid containing the elastomer latex, or 2 to 100 times higher. The second fluid of elastomer latex can be provided, as an example, at a pressure ranging from about 20 psi to about 30 psi. The pressure in the first fluid supply system may be up to about 500 psi.

[0045] Based on the production variables described herein, such as the velocity of the destabilized silica slurry fluid, the velocity of the latex fluid, the relative flow rates of the destabilized silica slurry and latex fluids, the concentration of the destabilizing agent such as a salt and/or acid, the silica concentration in the destabilized slurry, the rubber weight percent in the latex, the ammonia concentration in the latex, and/or the acid (if present) to ammonia

ratio, it is possible to control, obtain, and/or predict formation of a solid or semi-solid silica-containing continuous rubber phase over a range of desired silica contents. Thus, the process can be operated over an optimized range of variables. Thus, the a) velocity of one or both fluids, b) the volumetric flow ratio of the fluids, c) the destabilized nature of the silica, d) particulate silica concentration, e.g., 6 to 35 weight percent, of the destabilized silica dispersion, and e) the dry rubber content, e.g., 10 to 70 weight percent, of the latex, can permit mixing under high impact conditions so as to cause a liquid to solid inversion of the elastomer latex and uniformly disperse the silica in the latex at a selected silica to rubber ratio, and thus form a flow of a solid or semi-solid silica-containing continuous rubber phase. The recovery of the flow of solid or semi-solid silica-containing continuous rubber phase can be achieved in any conventional technique for recovery of a solid or semi-solid flow of material. The recovery can permit the solid or semi-solid flow to enter into a container or tank or other holding device. Such container or holding tank may contain a solution of salt or acid or both to effect further coagulation of the product to a more elastic state. For example, the recovering can be transporting or pumping the solid flow to other processing areas or devices for further processing, of which some options are described herein. The recovering can be continuous, semi-continuous, or by batch. The outflow end of the reaction zone preferably is semi-confined and open to the atmosphere, and the flow of solid or semi-solid elastomer composite is preferably recovered at ambient pressure to allow continuous operation of the process.

[0046] The flow of a solid silica-containing continuous rubber phase can be in the form of more or less elastic, rope-like "worms" or globules. In one embodiment, the solid silica-containing continuous rubber phase has, or is an article having, an elongation at break of at least about 100%, for example, about 100% to about 600%, about 120% to about 200%, about 130% to about 150%, about 130% to about 250%, about 150% to about 200%, about

200% to about 300%, about 300% to about 600%, about 300% to about 500%, or about 300% to about 400%. In other cases, a semi-solid silica-containing continuous rubber phase can be in the form of non-elastic, viscous paste or gel-like material that can develop elastic properties. In each case, the output is a coherent, flowing solid whose consistency can be highly elastic or slightly elastic and viscous. The output from the reaction zone can be a substantially constant flow concurrent with the on-going feeding of the elastomer latex and the destabilized dispersion of silica fluids into the reaction zone. Steps in the process, such as the preparation of the fluids, may be done as continuous, semi-continuous, or batch operations. The resulting solid or semi-solid silica-containing continuous rubber phase can be subjected to subsequent further processing steps, including continuous, semi-continuous, or batch operations.

[0047] The solid or semi-solid silica-containing continuous rubber phase created in the process contains water, or other aqueous fluid, and solutes from the original fluids, and, for instance, can contain from about 40 wt% to about 95 wt% water, or 40 wt% to about 90 wt% water, or from about 45 wt% to about 90 wt% water, or from about 50 to about 85 wt% water content, or from about 60 to about 80 wt% water, based on the total weight of the flow of silica elastomer composite. As an option, after forming the solid or semi-solid silica-containing rubber phase comprising such water contents, this product can be subjected to suitable de-watering and masticating steps and compounding steps to develop desired rubber properties and fabricate rubber compounds. Further details of the process and other post-processing steps are set forth below and can be used to produce vulcanizable elastomer composites according to any embodiment of the present invention.

[0048] A semi-solid silica-containing continuous rubber phase may be converted to a solid silica-containing continuous rubber phase. This for instance can be done by subjecting the semi-solid silica-containing continuous rubber phase to mechanical steps that remove water

from the composite and/or having the semi-solid material sit for a time (e.g., after recovery from the reaction zone in an offline location) for instance, 10 minutes to 24 hours or more; and/or heating the semi-solid silica-containing continuous rubber phase to remove water content (e.g., a temperature of from about 50 ^{o}C to about 200 ^{o}C); and/or subjecting the semi-solid material to acid or additional acid such as in an acid bath, or to salt or additional salt, or a salt bath, or to a combination of acid and salt, and the like. One or more or all of these steps can be used. In fact, one or more or all of steps can be used as a further processing step(s) even when a solid silica-containing continuous rubber phase is initially or subsequently recovered. The elongation at break of the resulting solid silica-containing continuous rubber phase or solid silica-containing continuous rubber phase article may be at least about 100%, for example, about 100% to about 600%, about 130% to about 150%, about 120% to about 200%, about 200% to about 500%, about 300% to about 400%, about 150% to about 200%, or about 130% to about 250%.

[0049] The degree of destabilization of the silica slurry, at least in part, determines the amount of silica that can be present in the silica elastomer composite (e.g., captured and distributed uniformly within the composite) for a given silica concentration in the silica slurry and a given dry rubber content of the latex. At lower selected target silica to rubber ratios (e.g., 15 phr to 45 phr), the concentration of destabilizing agent may not be high enough in the silica slurry and ultimately the silica/latex mixture to rapidly coagulate and form a solid or semi-solid silica-containing continuous rubber phase. In addition, selecting appropriate silica and rubber concentrations and appropriate relative fluid flow rates as described herein are considerations for forming the solid or semi-solid product. For example, at relatively low volumetric flow ratios of destabilized slurry to latex, the amount of the destabilizing agent in the destabilized silica slurry may not be sufficient to facilitate rapid coagulation of elastomer latex in the reaction zone. Generally, for a given elastomer latex, lower silica loadings can be

achieved by increasing the destabilization of the silica slurry and/or reducing the weight percentage of silica in the destabilized slurry.

[0050] When a dispersion of silica is destabilized, the silica particles tend to flocculate. When a dispersion of silica is too highly destabilized, the silica can 'fall out' of solution and become unsuited for use in preferred embodiments.

[0051] When destabilization occurs, the surface charges on the silica are typically not completely removed. However, sometimes when the silica particle, or the silica dispersion, is treated to destabilize, the isoelectric point (IEP) may be crossed over from a negative zeta potential to a positive zeta potential value. Generally for silica, the net charge on the surface of the silica particles is reduced and the magnitude of the zeta potential is decreased during destabilization.

[0052] For higher silica to rubber ratios in the silica elastomer composite, one may select higher silica concentrations in the destabilized slurry and/or a higher silica fluid to latex fluid volumetric flow ratio. Once the silica slurry is destabilized and initially combined with the latex fluid, if the mixture does not coagulate, the volume flow ratio of the first fluid and second fluid can be adjusted, such as by decreasing the volume flow of latex, which effectively provides a higher silica to rubber ratio in the elastomer composite. In this step of adjusting the amount of latex present, the amount of latex is, or becomes, an amount that does not cause excessive dilution of the concentration of the destabilizing agent in the overall mixture such that the desired product can be formed within the residence time in the reaction zone. To obtain a desired silica to rubber ratio in the elastomer composite, various options are available. As an option, the level of destabilization of the silica slurry can be increased, such as by reducing the magnitude of the zeta potential of the destabilized silica slurry (e.g., by adding more salt and/or acid). Or, as an option, the silica concentration in the destabilized silica slurry can be adjusted, for instance, by lowering or increasing the silica concentration in the destabilized silica slurry. Or,

as an option, a latex can be used that has a higher rubber content, or a latex can be diluted to a lower rubber content, or the relative flow rate of the latex can be increased. Or, as an option, the flow rate and orifice size (where each can control or affect velocity of the fluid(s)) or relative orientation of the two fluid flows can be modified to shorten or lengthen the residence time of the combined fluids in the reaction zone, and/or alter the amount and type of turbulence at the point of impact of the first fluid on the second fluid. Any one or two or more of these options can be used to adjust the process parameters and obtain a target or desired silica to rubber ratio in the elastomer composite.

[0053] The amount or level of destabilization of the silica slurry is a major factor in determining what silica to rubber ratio can be achieved in the silica elastomer composite. A destabilizing agent used to destabilize silica in the slurry may play a role in accelerating coagulation of elastomer latex particles when the destabilized silica slurry is mixed with elastomer latex in the reaction zone. It is theorized that the rate of latex coagulation in the reaction zone may depend on the concentration of the destabilizing agent in the combined fluids. It has been observed that by running the process for producing silica elastomer composite under various conditions, one may determine a threshold concentration of a destabilizing agent present in the combined mixture of fluids at the time of mixing that is effective to produce solid or semi-solid silica-containing continuous rubber phase. An example of selecting and adjusting process conditions to achieve the threshold concentration to yield solid or semi-solid silica-containing continuous rubber phase, is described in the Examples below. If the threshold concentration for a given selection and composition of fluids, volumetric flows, and velocities is not equaled or exceeded, a solid or semi-solid silica-containing continuous rubber phase will generally not be produced.

[0054] The minimum amount of destabilization of the silica slurry is indicated by a zeta potential magnitude of less than 30 mV (e.g. with zeta potentials such as -29.9 mV to about 29.9

mV, about -28 mV to about 20 mV, about -27 mV to about 10 mV, about -27 mV to about 0 mV, about -25 mV to about 0 mV, about -20 mV to about 0 mV, about -15 mV to about 0 mV, about -10 mV to about 0 mV and the like). If the silica slurry has been destabilized to within this zeta potential range, then the silica in the destabilized slurry can be incorporated into a solid or semi-solid silica-containing continuous rubber phase when combined with the elastomer latex.

[0055] While it may be desirable to destabilize the latex before combining it with the silica slurry, under shear conditions such as those present while continuously pumping the latex into the reaction zone, it is difficult to destabilize the latex fluid beforehand without causing premature coagulation of the latex. However, the destabilization agent used in the destabilized silica slurry may be present in a surplus amount to enhance destabilization of the latex, and/or mitigate dilution of the agent once the destabilized silica slurry and latex fluid are combined. As a further option, at especially high silica concentrations (e.g., >25 wt% silica in the silica slurry), some added destabilization agent can be added separately to the mixture of the destabilized silica slurry and elastomer latex in the reaction zone to enhance coagulation of the latex.

[0056] Without wishing to be bound to any theory, the process for producing silica elastomer composite is believed to form interpenetrated coherent networks of both rubber particles and silica aggregates in about two seconds or less, such as a fraction of a second, as the two fluids combine and the phase inversion occurs, resulting in a solid or semi-solid material comprising these networks with encapsulated water. Such fast network formation allows the continuous production of a solid or semi-solid silica-containing continuous rubber phase. It is theorized that shear induced agglomeration of silica particles as the destabilized silica slurry passes through an inlet nozzle to be combined with the elastomer latex may be useful for creating unique, uniform particle arrangement in rubber masterbatches and capturing silica particles within rubber through hetero-coagulation between silica and rubber

particles. It is further theorized that without such an interpenetrated network, there may not be a composite of a solid or semi-sold, continuous rubber phase containing dispersed silica particles, in the shape of a worm, or solid pieces, for instance, that encapsulates 40-95 wt% water and retains all or most of the silica in subsequent dewatering processes including squeezing and high energy mechanical working.

[0057] It is theorized that the formation of a silica network arises, at least in part, from shear induced silica particle agglomeration as the destabilized silica slurry passes through a pressurized nozzle (3a) at high velocity through the first inlet (3) into the reaction zone (13), as shown in Figure 1. This process is facilitated by reduction of stability of silica in the destabilized slurry when the silica slurry has been destabilized (e.g., by treating the silica slurry with salt or acid or both).

[0058] It is theorized that the liquid to solid phase inversion of the latex may result from various factors, including shear induced coagulation from mixing with the high velocity jet of destabilized silica slurry, interaction of the silica surface with the latex components, ionic or chemical coagulation from contact with the silica slurry containing destabilizing agent, and a combination of these factors. In order to form composite material comprising the interpenetrated silica network and rubber network, the rates of each network formation as well as the rate of mixing should be balanced. For example, for highly destabilized silica slurries at a high salt concentration in the slurry, agglomeration and network formation of silica particles occurs rapidly under shear conditions. In this case, volumetric flows and velocities are set so the latex has a rapid rate of coagulation for formation of the interpenetrated silica/rubber networks. Rates of formation are slower with more lightly destabilized silica slurries.

[0059] One exemplary process to produce a silica elastomer composite includes feeding a continuous flow of a fluid that contains at least elastomer latex (sometimes referred to as the

second fluid) through inlet 11 (Figure 1 (a), (b), and/or (c)), to a reaction zone 13 at a volumetric flow rate of about 20 L/hr to about 1900 L/hr. The method further includes feeding a continuous flow of a further fluid containing a destabilized dispersion of silica through inlet 3 (sometimes referred to as the first fluid) under pressure that can be accomplished by way of nozzle tips (in Figure 1, at 3a) at a volumetric flow rate of 30 L/hr to 1700 L/hr. The destabilized state of the silica dispersion and the impacting of the two fluid flows (introduced at inlets 3 and 11) under high energy conditions created by introducing the first fluid as a high velocity jet (e.g., about 6 m/s to about 250 m/s) that impacts the lower velocity latex flow (e.g., 0.4-11 m/s) entering the reaction zone at an angle approximately perpendicular to the high speed jet of the first fluid is effective to intimately mix the silica with the latex flow, promoting a uniform distribution of silica in the flow of solid silica-containing continuous rubber phase from the outlet of the reaction zone.

[0060] As an option, the elastomer latex introduced, for instance, through inlet 11 can be a blend of two or more latexes, such as a blend of two or more synthetic latexes. As an option, the devices in Figures 1(a), (b) and/or (c) can be modified to have one or more additional inlets so as to introduce other components to the reaction zone, such as one or more additional latexes. For instance, in Figure 1(c), inlet 14 can be used to introduce a further latex besides using inlet 11. The one or more additional inlets can be sequential to each other, or be adjacent to each other or set forth in any orientation as long as the material (e.g. latex) being introduced through the inlet(s) has sufficient time to disperse or be incorporated into the resulting flow. In WO 2011/034587, incorporated in its entirety by reference herein, Figures 1, 2A, and 2B provide examples of additional inlets and their orientations which can be adopted here for production of vulcanizable elastomer composites according to embodiments of the present invention. As a particular example, one inlet can introduce a flow that includes natural rubber latex and an additional inlet can introduce a synthetic elastomer latex, and these latex flows are combined

with the flow of the destabilized dispersion of silica to result in the flow of a solid or semi-solid silica-containing continuous rubber phase. When more than one inlet is utilized for elastomer latex introduction, the flow rates can be the same or different from each other.

[0061] Figure 2 sets forth an example, using a block diagram of various steps that can occur in the formation of the elastomer composite . As shown in Figure 2, the destabilized dispersion of silica (first fluid) 100 is introduced into the reaction zone 103 and the fluid containing the elastomer latex (second fluid) 105 is introduced also into the reaction zone 103. As an option, a flow of solid or semi-solid silica-containing continuous rubber phase exits the reaction zone 103 and can optionally enter a holding zone 116 (e.g., a holding tank, with or without the addition of a salt or acid solution to further enhance coagulation of rubber and formation of silica/rubber networks); and can optionally enter, directly, or after diversion to a holding zone 116, a dewatering zone 105; can optionally enter a continuous mixer/compounder 107; can optionally enter a mill (e.g., open mill, also called a roll mill) 109; can be subjected to additional extra milling 111 (same or different conditions as mill 109) (such as same or different energy input); can be subjected to optional mixing by mixer 115, and/or can be granulated using a granulator 117, and then can optionally be baled, using a baler 119, and can optionally be broken down by use of an additional mixer 121.

[0062] With regard to the silica, one or more types of silica, or any combination of silica(s), can be used in any embodiment of the present invention. The silica suitable for reinforcing elastomer composites can be characterized by a surface area (BET) of about 20 m^2/g to about 450 m^2/g; about 120 to about 225 m^2/g; about 30 m^2/g to about 450 m^2/g; about 30 m^2/g to about 400 m^2/g; or about 60 m^2/g to about 250 m^2/g; and for heavy vehicle tire treads a BET surface area of about 60 m^2/g to about 250 m^2/g or for example from about 80 m^2/g to about 200 m^2/g. Highly dispersible precipitated silica can be used as the filler in the present methods. Highly dispersible precipitated silica ("HDS") is understood to mean any

silica having a substantial ability to dis-agglomerate and disperse in an elastomeric matrix. Such determinations may be observed in known manner by electron or optical microscopy on thin sections of elastomer composite. Examples of commercial grades of HDS include, Perkasil® GT 3000GRAN silica from WR Grace & Co, Ultrasil® 7000 silica from Evonik Industries, Zeosil® 1165 MP and 1115 MP silica from Solvay S.A., Hi-Sil® EZ 160G silica from PPG Industries, Inc., and Zeopol® 8741 or 8745 silica from JM Huber Corporation. Conventional non-HDS precipitated silica may be used as well. Examples of commercial grades of conventional precipitated silica include, Perkasil® KS 408 silica from WR Grace & Co, Zeosil® 175GR silica from Solvay S.A., Ultrasil® VN3 silica from Evonik Industries, Hi-Sil® 243 silica from PPG Industries, Inc. and the Hubersil® 161 silica from JM Huber Corporation. Hydrophobic precipitated silica with surface attached silane coupling agents may also be used. Examples of commercial grades of hydrophobic precipitated silica include Agilon®400, 454, or 458 silica from PPG Industries, Inc. and Coupsil silicas from Evonik Industries, for example Coupsil 6109 silica.

[0063] Typically the silica (e.g., silica particles) have a silica content of at least 20 wt%, at least 25 wt%, at least 30 wt%, at least 35 wt%, at least 40 wt%, at least 50 wt%, at least 60 wt%, at least 70 wt%, at least 80 wt%, at least 90 wt%, or almost 100 wt% or 100 wt%, or from about 20 wt% to about 100 wt%, all based on the total weight of the particle. Any of the silica(s) can be chemically functionalized, such as to have attached or adsorbed chemical groups, such as attached or adsorbed organic groups. Any combination of silica(s) can be used. The silica that forms the silica slurry and/or destabilized silica slurry can be in part or entirely a silica having a hydrophobic surface, which can be a silica that is hydrophobic or a silica that becomes hydrophobic by rendering the surface of the silica hydrophobic by treatment (e.g., chemical treatment). The hydrophobic surface may be obtained by chemically modifying the silica particle with hydrophobizing silanes without ionic groups,

e.g., bis-triethoxysilylpropyltetrasulfide. Such a surface reaction on silica may be carried out in a separate process step before dispersion, or performed in-situ in a silica dispersion. The surface reaction reduces silanol density on the silica surface, thus reducing ionic charge density of the silica particle in the slurry. Suitable hydrophobic surface-treated silica particles for use in dispersions may be obtained from commercial sources, such as Agilon® 454 silica and Agilon® 400 silica, from PPG Industries. Silica dispersions and destabilized silica dispersions may be made using silica particles having low surface silanol density. Such silica may be obtained through dehydroxylation at temperatures over 150°C via, for example, a calcination process.

[0064] Further, the silica slurry and/or destabilized silica slurry can contain, as an option, a minor amount (10 wt% or less, based on a total weight of particulate material) of any non-silica particles, such as carbon black(s) or zinc oxide, or calcium carbonate, or other particulate materials useful in rubber compositions (e.g., 95 wt% precipitated silica and 5 wt% carbon black). Any reinforcing or non-reinforcing grade of carbon black may be selected to yield the desired property in the final rubber composition.

[0065] Silica may be dispersed in aqueous fluid according to any technique known to those of skill in the art. A dispersion of particulate silica can be subjected to mechanical processing, for instance, to reduce particle size. This can be done prior to or during or after destabilizing of the dispersion and can contribute in a minor way or major way to the destabilizing of the dispersion. The mechanical processing can comprise or include grinding, milling, comminution, bashing, or high shear fluid processing, or any combinations thereof.

[0066] For example, a silica slurry can be made by dispersing silica in a fluid by means of a grinding process. Such a grinding process reduces the size of most silica agglomerates (e.g. over 80% by volume) in the fluid to below 10 microns, and preferably below 1 micron, the typical size range of colloidal particles. The fluid may be water, an aqueous fluid, or a

non-aqueous polar fluid. The slurry, for instance, may comprise from about 6 wt% to about 35 wt% silica-containing particles, based on the weight of the slurry. The size of silica particles may be determined using a light scattering technique. Such a slurry when made in water using silica particles having low residual salt content at a pH of 6-8, typically has a zeta potential magnitude higher than, or equal to, 30 mV and shows good stability against aggregation, gelling, and settlement in a storage tank with slow stirring (e.g. stirring speed below 60 RPM). As well-ground silica particles are generally stable in water at a pH of around 7 due to high negative charges on silica, very high shear is generally needed to overcome the repulsive energy barrier between particles to induce particle agglomeration.

[0067] In an exemplary method employing silica, such as HDS granules, the silica can be combined with water, and the resulting mixture is passed through a colloid mill, pipeline grinder, or the like to form a dispersion fluid. This fluid is then passed to a homogenizer that more finely disperses the filler in the carrier liquid to form the slurry. Exemplary homogenizers include, but are not limited to, the Microfluidizer® system commercially available from Microfluidics International Corporation (Newton, Mass., USA). Also suitable are homogenizers such as models MS18, MS45 and MC120, and series homogenizers available from the APV Homogenizer Division of APV Gaulin, Inc. (Wilmington, Mass., USA). Other suitable homogenizers are commercially available and will be apparent to those skilled in the art given the benefit of the present disclosure. The optimal operating pressure across a homogenizer may depend on the actual apparatus, the silica type, and/or the silica content. As an example, a homogenizer may be operated at a pressure of from about 10 psi to about 5000 psi or higher, for example, from about 10 psi to about 1000 psi, about 1000 psi to about 1700 psi, about 1700 psi to about 2200 psi, about 2200 psi to about 2700 psi, about 2700 psi to about 3300 psi, about 3300 psi to about 3800 psi, about 3800 psi to about 4300 psi, or about 4300 psi to about 5000 psi. As indicated earlier, the dispersion of particulate

silica is destabilized before carrying out the masterbatch process, and the dispersion can be destabilized by following one of the techniques mentioned herein, before, during, or after any grinding or similar mechanical process.

[0068] Depending on the wet masterbatch method employed, a high silica concentration in slurry may be used to reduce the task of removing excess water or other carrier. For the destabilized dispersion of silica particles, the liquid used can be water or other aqueous fluid or other fluid. For the destabilized dispersion, from about 6 weight percent to about 35 weight percent filler may be employed, for example, from about 6 weight percent to about 9 weight percent, from about 9 weight percent to about 12 weight percent, from about 12 weight percent to about 16 weight percent, from about 10 weight percent to about 28 weight percent, from about 16 weight percent to about 20 weight percent, from about 20 weight percent to about 24 weight percent, from about 24 weight percent to about 28 weight percent, or from about 28 weight percent to about 30 weight percent, based on the weight of the destabilized dispersion. For the destabilized dispersion, a higher silica concentration can have benefits. For instance, silica concentration in the destabilized slurry can be at least 10 weight percent or at least 15 weight percent, based on the weight of the slurry (e.g., about 12 wt% to about 35 wt% or about 15.1 wt% to about 35 wt%, or about 20 wt% to about 35 wt%), which can provide benefits such as, but not limited to, reduced wastewater, increased production rates, and/or reduction of the equipment size needed for the process. Those skilled in the art will recognize, given the benefit of this disclosure, that the silica concentration (in weight percent) of the silica slurry (and in the destabilized silica slurry) should be coordinated with other process variables during the wet process to achieve a desired silica to rubber ratio (in phr) in the ultimate product.

[0069] Details of a dispersion of silica are further described below. In general, a dispersion can be a material comprising more than one phase where at least one of the phases

contains or includes or consists of finely divided phase domains, optionally in the colloidal size range, dispersed throughout a continuous phase. A dispersion or slurry of silica or silica dispersion can be prepared as a stable suspension of particulate silica in aqueous fluid, wherein the charge at the surface of the particles prevents particle agglomeration and the dispersion is characterized by a zeta potential magnitude of greater than or equal to 30 mV. In such dispersions, the silica particles remain in stable dispersion, and/or suspension, with respect to aggregation and coalescence, for instance, for at least 8 hours. A stable dispersion can be one where constant particle size is maintained, and wherein the particles do not settle or gel, or take a very long time to settle appreciably in the presence of slow or periodic stirring, for example, not settling appreciably after 8 hours, or 12 hours or 24 hours, or 48 hours. For instance, for colloidal silica particles well dispersed in aqueous fluid, stability can generally be observed from a pH of 8 to 10. Further, with slow stirring of the dispersion, the silica particles remain suspended in the fluid by means of particle surface charge, particle surface polarity, pH, selected particle concentration, particle surface treatment, and combinations thereof. The fluid may be or include water, an aqueous mixture, or a water miscible or partially miscible fluid, such as various alcohols, ethers, and other low molecular weight water-miscible solvents, preferably having C_1-C_5 organic groups (e.g., ethanol, methanol, propanol, ethyl ether, acetone, and the like). As indicated above, the dispersion, for instance, may comprise about 6 wt% to about 35 wt%, about 10 wt% to about 28 wt%, about 12 wt% to about 25 wt%, or about 15 wt% to about 30 wt% silica-containing particles, based on the weight of the dispersion.

[0070] A stable dispersion may be a colloidal dispersion. In general, a colloidal dispersion or colloid can be a substance where dispersed particles are suspended throughout another substance. The dispersed-phase particles have a diameter of from approximately about 1 nanometer to about 1000 nanometers, and typically about 100 nanometers to about

500 nanometers. In a stable colloidal dispersion, particle size, density, and concentration are such that gravity does not cause particles to settle out of dispersion easily. Colloids with the magnitude of zeta potential of 30 mV or over are generally regarded as stable colloidal systems. Reduction of particle stability (e.g., silica) in a colloid or dispersion due to charge stabilization can be measured by reduction of magnitude of zeta potential. Particle size may be measured by a light scattering method.

[0071] A destabilized silica dispersion can be understood to be a dispersion of silica in a fluid wherein weakened particle-to-particle repulsive forces allow clustering of particles and formation of a silica particle-to-particle network or gel once the destabilized dispersion is subjected to an effective amount of shear. In certain cases, mechanical shear may cause destabilization of silica dispersions and clustering of silica particles. The higher the degree of destabilization of silica slurry, the lower the shear needed for aggregation of particles, and the higher the rate of particle aggregation. For a destabilized dispersion, the dispersion can comprise from about 6 wt% to about 35 wt% particulate silica (based on the weight of the dispersion), e.g., from about 8 wt% to about 35 wt%, from about 10 wt% to about 28 wt%, from about 12 wt% to about 25 wt%, from about 15 wt% to about 30 wt%. The aqueous fluid in the destabilized dispersion of silica particles may be or include water, an aqueous mixture, or a water miscible or partially miscible fluid, such as various alcohols, ethers, and other low molecular weight water-miscible solvents, preferably having C_1-C_5 organic groups (e.g., ethanol, methanol, propanol, ethyl ether, acetone, and the like). To form silica elastomer composites, the stability of silica particles in a slurry or dispersion is reduced (i.e., destabilized) by lowering the electrostatic energy barrier between particles using an effective amount of a destabilizing agent such as acid or salt or both before the slurry is mixed with latex. A destabilizing agent may be selected for its capacity to reduce repulsive charge interaction among particle surfaces that prevent particles from agglomeration in the fluid.

[0072] A destabilized dispersion of silica may be obtained by lowering the pH of the dispersion of silica to close to the isoelectric point of the silica (around pH 2 for typical hydrophilic silicas). For example, destabilizing silica can be achieved by adding acid to lower a pH of the dispersion of particulate silica to 2 to 4, thus reducing the magnitude of the zeta potential of the dispersion to less than 30 mV, such as below about 28 mV (e.g., zeta potentials of magnitude of about 18 mV to about 6 mV for formic acid as the destabilization agent). The addition of acid and/or salt into silica slurry can effectively reduce the stability of silica particles dispersed in water. The acid or salt molar concentration is generally the dominant factor that determines the zeta potential of the destabilized silica slurry. In general, a sufficient amount of acid or salt or both can be used to reduce the magnitude of the zeta potential of the silica slurry to less than 30 mV, such as 28 mV or less, preferably 25 mV or less, for producing a semi-solid or solid silica-containing continuous rubber phase.

[0073] The amount of acid used to destabilize the silica dispersion can be an amount to obtain a zeta potential magnitude in the destabilized dispersion of less than 30 mV, such as 28 mV or less, or 25 mV or lower. The acid can be at least one organic or inorganic acid. The acid can be or include acetic acid, formic acid, citric acid, phosphoric acid, or sulfuric acid, or any combinations thereof. The acid can be or include a C_1 to C_4 alkyl containing acid. The acid can be or include one that has a molecular weight or a weight average molecular weight below 200, such as below 100 MW, or below 75 MW, or from about 25 MW to about 100 MW. The amount of acid can vary and depend on the silica dispersion being destabilized. The amount of acid can be, for instance, from about 0.8 wt% to about 7.5 wt%, for example, from about 1.5 wt% to about 7.5 wt% or more (based on the total weight of the fluid comprising the dispersion of silica). If an acid is the only destabilizing agent used, the amount of acid can be an amount that lowers the pH of the dispersion of silica by at least 2

pH units, or to at least a pH of 5 or lower, or the pKa range of the acid or acids in use, so as to reduce charge interactions among particles.

[0074] A destabilized dispersion may be obtained by treating a dispersion of silica with a destabilizing agent comprising one or more salts to alter slurry zeta potential to the range described above. The salt can be or include at least one metal salt (e.g., from Group 1, 2, or 13 metals). The salt can be or include a calcium salt, magnesium salt, or aluminum salt. Exemplary counterions include nitrate, acetate, sulfate, halogen ions such as chloride, bromide, iodine, and the like. The amount of salt can be, for instance, from about 0.2 wt% to about 2 wt% or more, for example, from about 0.5 or 1 wt% to about 1.6 wt% (based on the weight of the fluid comprising the destabilized dispersion of silica).

[0075] A combination of at least one salt and/or at least one acid can be used to destabilize the dispersion of the silica.

[0076] When the destabilized dispersion of silica is achieved with the addition of at least one salt, the salt concentration in the destabilized dispersion of silica can be from about 10 mM to about 160 mM, or other amounts above or below this range.

[0077] When the destabilized dispersion of silica is achieved with the addition of at least one acid, the acid concentration in the destabilized dispersion can be from about 200 mM to about 1000 mM, for example, about 340 mM to about 1000 mM, or other amounts above or below this range.

[0078] A destabilized silica dispersion may be made using silica particles treated to comprise an appropriate amount of surface functional groups carrying positive charges so that the net charges on the silica surface are reduced sufficiently to decrease the magnitude of zeta potential of the dispersion below 30 mV. The net charge on the silica surface can be positive, instead of negative, as a result of such surface treatment. The positively charged functional group may be introduced to silica surface through chemical attachment or physical

adsorption. For example, the silica surface may be treated with N-trimethoxylsilylpropyl-N,N,N-trimethylammonium chloride either before or after preparation of the silica dispersion. It is also possible to adsorb cationic coating agents, such as amine containing molecules and basic amino acids on the silica surface. It is theorized that a net positive charge on silica particle surfaces may enhance coagulation of the latex, which comprises negatively charged rubber particles, by means of heterocoagulation.

[0079] With regard to the "second fluid," which contains at least one elastomer latex, this fluid may contain one or more elastomer latices. An elastomer latex can be considered a stable colloidal dispersion of rubber and may contain, for example, from about 10 wt% to about 70 wt% rubber based on the total weight of the latex. The rubber can be dispersed in a fluid, such as water or other aqueous fluid, for example. The aqueous content of this fluid (or water content) can be 40 wt% or higher, such as 50 wt% or higher, or 60 wt% or higher, or 70 wt% or higher, for instance from about 40 wt% to 90 wt% based on the weight of the fluid comprising the at least one elastomer latex. Suitable elastomer latices include both natural and synthetic elastomer latices and latex blends. For example, elastomer latex may be made synthetically by polymerizing a monomer such as styrene that has been emulsified with surfactants. The latex should be appropriate for the wet masterbatch process selected and the intended purpose or application of the final rubber product. It will be within the ability of those skilled in the art to select suitable elastomer latex or a suitable blend of elastomer latices for use in the methods and apparatus disclosed here, given the benefit of this disclosure.

[0080] The elastomer latex can be or include natural rubber, such as an emulsion of natural rubber. Exemplary natural rubber latices include, but are not limited to, field latex, latex concentrate (produced, for example, by evaporation, centrifugation or creaming), skim latex (e.g., the supernatant remaining after production of latex concentrate by centrifugation) and

blends of any two or more of these in any proportion. Natural rubber latex typically is treated with ammonia to preserve it, and the pH of treated latex typically ranges from 9 to 11. The ammonia content of the natural rubber latex may be adjusted, and can be reduced, e.g., by bubbling nitrogen across or through the latex. Typically, latex suppliers desludge the latex by addition of diammonium phosphate. They may also stabilize the latex by addition of ammonium laurate. The natural rubber latex may be diluted to a desired dry rubber content (DRC). Thus, the latex that can be used here can be a desludged latex. A secondary preservative, a mixture of tetramethylthiuram disulfide and zinc oxide (TZ solution) may also be included. The latex should be appropriate for the wet masterbatch process selected and the intended purpose or application of the final rubber product. The latex is provided typically in an aqueous carrier liquid (e.g, water). The amount of the aqueous carrier liquid can vary, and for instance be from about 30 wt% to about 90 wt% based on the weight of the fluid. In other words, such natural rubber latices may contain, or may be adjusted to contain, e.g., about 10 wt% to about 70 wt % rubber. Selection of a suitable latex or blend of latices will be well within the ability of those skilled in the art given the benefit of the present disclosure and the knowledge of selection criteria generally well recognized in the industry.

[0081] The natural rubber latex may also be chemically modified in some manner. For example, it may be treated to chemically or enzymatically modify or reduce various non-rubber components, or the rubber molecules themselves may be modified with various monomers or other chemical groups such as chlorine. Epoxidized natural rubber latex may be especially beneficial because the epoxidized rubber is believed to interact with the silica surface (Martin, et al., Rubber Chemistry and Technology, May 2015, doi:10.5254/rct15.85940). Exemplary methods of chemically modifying natural rubber latex are described in European Patent Publications Nos. 1489102, 1816144, and 1834980, Japanese Patent Publications Nos. 2006152211, 2006152212, 2006169483, 2006183036,

2006213878, 2006213879, 2007154089, and 2007154095, Great Britain Patent No. GB2113692, U.S. Pat. Nos. 6,841,606 and 7,312,271, and U.S. Patent Publication No. 2005-0148723. Other methods known to those of skill in the art may be employed as well.

[0082] Other exemplary elastomers include, but are not limited to, rubbers, polymers (e.g., homopolymers, copolymers and/or terpolymers) of 1,3-butadiene, styrene, isoprene, isobutylene, 2,3-dialkyl-1,3-butadiene, where alkyl may be methyl, ethyl, propyl, etc., acrylonitrile, ethylene, propylene and the like. The elastomer may have a glass transition temperature (Tg), as measured by differential scanning calorimetry (DSC), ranging from about -120°C. to about 0°C. Examples include, but are not limited to, styrene-butadiene rubber (SBR), natural rubber and its derivatives such as chlorinated rubber, polybutadiene, polyisoprene, poly(styrene-co-butadiene) and the oil extended derivatives of any of them. Blends of any of the foregoing may also be used. The latex may be in an aqueous carrier liquid. Particular suitable synthetic rubbers include: copolymers of styrene and butadiene comprising from about 10 percent by weight to about 70 percent by weight of styrene and from about 90 to about 30 percent by weight of butadiene such as a copolymer of 19 parts styrene and 81 parts butadiene, a copolymer of 30 parts styrene and 70 parts butadiene, a copolymer of 43 parts styrene and 57 parts butadiene and a copolymer of 50 parts styrene and 50 parts butadiene; polymers and copolymers of conjugated dienes such as polybutadiene, polyisoprene, polychloroprene, and the like, and copolymers of such conjugated dienes with an ethylenic group-containing monomer copolymerizable therewith such as styrene, methyl styrene, chlorostyrene, acrylonitrile, 2-vinyl-pyridine, 5-methyl-2-vinylpyridine, 5-ethyl-2-vinylpyridine, 2-methyl-5-vinylpyridine, allyl-substituted acrylates, vinyl ketone, methyl isopropenyl ketone, methyl vinyl either, alpha-methylene carboxylic acids and the esters and amides thereof, such as acrylic acid and dialkylacrylic acid amide. Also suitable for use herein are copolymers of ethylene and other high alpha olefins such as propylene, 1-butene, and 1-pentene. Blends of two or more types of elastomer latex, including blends of synthetic and

natural rubber latex or with two or more types of synthetic or natural rubber, may be used as well.

[0083] The vulcanizable elastomer composite can contain, in addition to the elastomer and filler and coupling agent, various processing aids, oil extenders, antidegradants, antioxidants, and/or other additives.

[0084] The amount of silica (in parts per hundred of rubber, or phr) present in the elastomer composite can be from about 15 phr to about 180 phr, about 20 phr to about 150 phr, about 25 phr to about 80 phr, about 35 phr to about 115 phr, about 35 phr to about 100 phr, about 40 phr to about 100 phr, about 40 phr to about 90 phr, about 40 phr to about 80 phr, about 29 phr to about 175 phr, about 40 phr to about 110 phr, about 50 phr to about 175 phr, about 60 phr to about 175 phr, and the like. The silica-reinforced elastomer composite may optionally include a small amount of carbon black for color, conductivity, and/or UV stability and/or for other purposes. Small amounts of carbon black contained in the elastomer composite can range, for instance, from about 0.1 wt% to about 10 wt%, based on the weight of the total particles present in the elastomer composite. Any grade or type of carbon black(s) can be used, such as reinforcing, or semi-reinforcing tire-grade furnace carbon blacks and the like.

[0085] In any method of producing a vulcanizable elastomer composite, the method can further include one or more of the following steps, after formation of the solid or semi-solid silica-containing continuous rubber phase:

- one or more holding steps or further solidification or coagulation steps to develop further elasticity;
- one or more dewatering steps can be used to de-water the composite to obtain a de-watered composite;
- one or more extruding steps;

- one or more calendaring steps;
- one or more milling steps to obtain a milled composite;
- one or more granulating steps;
- one or more baling steps to obtain a bailed product or mixture;
- the baled mixture or product can be broken apart to form a granulated mixture;
- one or more mixing or compounding steps to obtain a compounded composite.

[0086] As a further example, the following sequence of steps can occur and each step can be repeated any number of times (with the same or different settings), after formation of the solid or semi-solid silica-containing continuous rubber phase:

- one or more holding steps or further coagulation steps to develop further elasticity
- dewatering the composite (e.g., the elastomer composite exiting the reaction zone) to obtain a dewatered composite;
- mixing or compounding the dewatered composite to obtain a compounded mixture;
- milling the compounded mixture to obtain a milled mixture (e.g., roll milling);
- granulating or mixing the milled mixture;
- optionally baling the mixture after the granulating or mixing to obtain a baled mixture;
- optionally breaking apart the baled mixture and mixing.

[0087] In any embodiment, a coupling agent can be introduced in any of the steps (or in multiple steps or locations) as long as the coupling agent has an opportunity to become dispersed in the elastomer composite.

[0088] As just one example, the solid or semi-solid silica-containing continuous rubber phase exiting the reaction zone or area can be transferred by a suitable apparatus (e.g., belt or

conveyor), to a dewatering extruder. Suitable dewatering extruders are well known and commercially available from, for example, the French Oil Mill Machinery Co. (Piqua, Ohio, USA). Alternatively or in addition, the solid or semi-solid silica-containing continuous rubber phase may be compressed, for example, between metallic plates, to expel at least a portion of the aqueous fluid phase, e.g., to expel aqueous fluid until the water content of such material is below 40 wt%.

[0089] In general, the post processing steps can comprise compressing the elastomer composite to remove from about 1 wt% to about 15 wt % or more, of an aqueous fluid phase, based on the total weight of the elastomer composite. The dewatering extruder may bring the silica elastomer composite from, e.g., approximately about 40% to about 95% water content to approximately about 5% to about 60% water content (for example, from about 5% to about 10% water content, from about 10% to about 20% water content, from about 15% to about 30% water content, or from about 30% to about 50% water content) with all weight percent based on total weight of composite. The dewatering extruder can be used to reduce the water content of the silica elastomer composite to about 35 wt% or other amounts. The optimal water content may vary with the elastomer employed, the amount, and/or type of filler, and the devices employed for mastication of the dewatered product. The elastomer composite may be dewatered to a desired water content, following which the resulting dewatered product can be further masticated while being dried to a desired moisture level (e.g., from about 0.5% to about 10%, for example, from about 0.5% to about 1%, from about 1% to about 3%, about 3% to about 5%, or from about 5% to about 10%, preferably below 1% all weight percent based on total weight of product). The mechanical energy imparted to the material can provide improvement in rubber properties. For example, the dewatered product may be mechanically worked with one or more of a continuous mixer, an internal mixer, a twin screw extruder, a single screw extruder, or a roll mill. This optional mixing step can

have the ability to masticate the mixture and/or generate surface area or expose surface which can permit removal of water (at least a portion thereof) that may be present in the mixture. Suitable masticating devices are well known and commercially available, including for example, a Unimix Continuous Mixer and MVX (Mixing, Venting, eXtruding) Machine from Farrel Corporation of Ansonia, CT, USA, a long continuous mixer from Pomini, Inc., a Pomini Continuous Mixer, twin rotor co-rotating intermeshing extruders, twin rotor counter-rotating non-intermeshing extruders, Banbury mixers, Brabender mixers, intermeshing-type internal mixers, kneading-type internal mixers, continuous compounding extruders, the biaxial milling extruder produced by Kobe Steel, Ltd., and a Kobe Continuous Mixer. Alternative masticating apparatus will be familiar to those of skill in the art and can be used.

[0090] As dewatered product is processed in a desired apparatus, the apparatus imparts energy to the material. Without being bound by any particular theory, it is believed that friction generated during mechanical mastication heats the dewatered product. Some of this heat is dissipated by heating and vaporizing the moisture in the dewatered product. A portion of the water may also be removed by squeezing the material in parallel with heating. The temperature should be sufficiently high to rapidly vaporize water to steam that is released to the atmosphere and/or is removed from the apparatus, but not so high as to scorch the rubber. The dewatered product can achieve a temperature from about 130°C to about 180°C, such as from about 140°C to about 160°C, especially when the coupling agent is added prior to or during mastication. The coupling agent can include a small amount of sulfur, and the temperature should be maintained at a sufficiently low level to prevent the rubber from cross-linking during mastication.

[0091] As an option, additives can be combined with the dewatered product in a mechanical mixer. Specifically, additives such as filler (which may be the same as, or different from, the filler used in the mixer; exemplary fillers include silica, carbon black,

and/or zinc oxide), other elastomers, other or additional masterbatch, antioxidants, coupling agents, plasticizers, processing aids (e.g., stearic acid, which can also be used as a curing agent, liquid polymers, oils, waxes, and the like), resins, flame-retardants, extender oils, and/or lubricants, and a mixture of any of them, can be added in a mechanical mixer. Additional elastomers can be combined with the dewatered product to produce elastomer blends. Suitable elastomers include any of the elastomers employed in latex form in the mixing process described above and elastomers such as EPDM that are not available in latex form and may be the same or different than the elastomer in the silica-containing elastomer composite. Exemplary elastomers include, but are not limited to, rubbers, polymers (e.g., homopolymers, copolymers and/or terpolymers) of 1,3-butadiene, styrene, isoprene, isobutylene, 2,3-dialkyl-1,3-butadiene, where alkyl may be methyl, ethyl, propyl, etc., acrylonitrile, ethylene, propylene, and the like. Methods of producing masterbatch blends are disclosed in commonly owned U.S. Patents Nos. 7,105,595, 6,365,663, and 6,075,084 and PCT Publication WO2014/189826. The antioxidant (an example of a degradation inhibitor) can be an amine type antioxidant, phenol type antioxidant, imidazole type antioxidant, metal salt of carbamate, para-phenylene diamine(s) and/or dihydrotrimethylquinoline(s), polymerized quinine antioxidant, and/or wax and/or other antioxidants used in elastomer formulations. Specific examples include, but are not limited to, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6-PPD, e.g., ANTIGENE 6C , available from Sumitomo Chemical Co., Ltd. and NOCLAC 6C, available from Ouchi Shinko Chemical Industrial Co., Ltd.), "Ozonon" 6C from Seiko Chemical Co., Ltd., polymerized 1,2-dihydro-2,2,4-trimethyl quinoline (TMQ, e.g., Agerite Resin D, available from R. T. Vanderbilt), 2,6-di-t-butyl-4-methylphenol (available as Vanox PC from Vanderbilt Chemicals LLC), butylhydroxytoluene (BHT), and butylhydroxyanisole (BHA), and the like. Other representative antioxidants may be, for example, diphenyl-p-phenylenediamine and others

such as, for example, those disclosed in The Vanderbilt Rubber Handbook (1978), pages 344-346.

[0092] The coupling agent can be or include one or more silane coupling agents, one or more zirconate coupling agents, one or more titanate coupling agents, one or more nitro coupling agents, or any combination thereof. The coupling agent can be or include bis(3-triethoxysilylpropyl)tetrasulfane (e.g., Si 69 from Evonik Industries, Struktol SCA98 from Struktol Company), bis(3-triethoxysilylpropyl)disulfane (e.g., Si 75 and Si 266 from Evonik Industries, Struktol SCA985 from Struktol Company), 3-thiocyanatopropyl-triethoxy silane (e.g., Si 264 from Evonik Industries), gamma-mercaptopropyl-trimethoxy silane (e.g., VP Si 163 from Evonik Industries, Struktol SCA989 from Struktol Company), gamma-mercaptopropyl-triethoxy silane (e.g., VP Si 263 from Evonik Industries), zirconium dineoalkanolatodi(3-mercapto) propionato-O, N,N'-bis(2-methyl-2-nitropropyl)-1,6-diaminohexane, S-(3-(triethoxysilyl)propyl) octanethioate (e.g., NXT coupling agent from Momentive, Friendly, WV), and/or coupling agents that are chemically similar or that have the one or more of the same chemical groups. Additional specific examples of coupling agents, by commercial names, include, but are not limited to, VP Si 363 from Evonik Industries. It is to be appreciated that any combination of elastomers, additives, and additional masterbatch may be added to the dewatered product, for instance in a compounder.

[0093] As an option, the dewatered product can be masticated using an internal mixer such as a Banbury or Brabender mixer. The dewatered product may first be brought to a moisture content of about 3 wt% to about 40 wt%, for example, about 5 wt% to about 20 wt%, or about 20 wt% to about 30 wt%. The moisture content may be achieved by dewatering to the desired level or by dewatering the dewatered product crumb to an intermediate moisture content as the first step and then further reducing moisture content by heating the resulting dewatered product, or by letting water evaporate from the dewatered product at room temperature, or by other

methods familiar to those of skill in the art. The dewatered product may then be masticated in an internal mixer until a desired moisture level or mechanical energy input is achieved. The dewatered product can be masticated until it reaches a predetermined temperature, allowed to cool, and then placed back into the internal mixer one or more times to impart additional energy to the material. Examples of temperatures include from about 140°C to about 180°C, for example, from about 145°C to about 160°C, or from about 150°C to about 155°C. The dewatered product may be sheeted in a roll mill after each mastication in the internal mixer. Alternatively or in addition, dewatered product that has been masticated in a Banbury or Brabender mixer may be further masticated in an open mill.

[0094] As an option, the masticated product can be further processed on an open mill. The masticated product can be discharged from the continuous compounder as a length of extrudate and may be cut into smaller lengths prior to entering the open mill. The masticated product may optionally be fed to the open mill via a conveyor. The conveyor may be a conveyor belt, conduit, pipe, or other suitable means for transporting the masticated product from a continuous compounder to an open mill. The open mill can include a pair of rollers that may optionally be heated or cooled to provide enhanced operation of the open mill. Other operating parameters of the open mill can include the gap distance between the rolls, the bank height, i.e., the reservoir of material in the gap between and on top of the rolls, and the speed of each roll. The speed of each roll and the temperature of the fluid used to cool each roll may be controlled independently for each roll. The gap distance may be from about 3 mm to about 10 mm or from about 6 mm to about 8 mm. The roll speed may be about 15 rpm to about 70 rpm, and the rollers may roll towards one another with respect to the inlet side of the mill. The friction ratio, the ratio of the speed of the collection roller, e.g., the roller on which the masticated product collects, to that of the back roller, may be from about 0.9 to about 1.1. The fluid employed to cool the rollers may be from about 35°C to about 90°C, for example, from about 45°C to about 60°C, from about

55°C to about 75°C, or from about 70°C to about 80°C. In addition to controlling the operation of the open mill to provide a desired level of mastication and desiccation to the masticated product, it is also desirable that the output of the open mill should collect on the collection roller as a smooth sheet. Without being bound by any particular theory, it is thought that cooler roller temperatures facilitate this goal. The open mill may reduce the temperature of the masticated product to approximately about 110 °C to about 140°C. The residence time of the masticated product in the mill can be determined in part by the roller speed, the gap distance and the amount of mastication and drying desired and may be about 10 minutes to about 20 minutes for material that has already been masticated, for example, in a twin-rotor continuous mixer.

[0095] One skilled in the art will recognize that different combinations of devices may be employed to provide mastication and desiccation to a solid silica-containing continuous rubber phase produced according to the various embodiments. Depending on which devices are used, it may be desirable to operate them under different conditions than those described above to impart varying amounts of work and desiccation to the material. In addition, it may be desirable to employ more than one particular kind of device, e.g., an open mill or internal mixer, in series or to pass masticated product through a given device more than one time. For example, the masticated product may be passed through an open mill two or three or more times or passed through two or three or more open mills in series. In the latter case, it may be desirable to operate each open mill under different operating conditions, e.g., speed, temperature, different (e.g. higher) energy input, etc. Masticated product can be passed through one, two, or three open mills after being masticated in an internal mixer.

[0096] The vulcanizable elastomer composite may be used to produce an elastomer or rubber containing product. As an option, the elastomer composite may be used in or produced for use in various parts of a tire, for example, tires, tire treads, tire sidewalls, wire-skim for tires, and cushion gum for retread tires. Alternatively or in addition, elastomer composite may be

used in or produced for use in hoses, seals, gaskets, anti-vibration articles, tracks, track pads for track-propelled equipment such as bulldozers, etc., engine mounts, earthquake stabilizers, mining equipment such as screens, mining equipment linings, conveyor belts, chute liners, slurry pump liners, mud pump components such as impellers, valve seats, valve bodies, piston hubs, piston rods, plungers, impellers for various applications such as mixing slurries and slurry pump impellers, grinding mill liners, cyclones and hydrocyclones, expansion joints, marine equipment such as linings for pumps (e.g., dredge pumps and outboard motor pumps), hoses (e.g., dredging hoses and outboard motor hoses), and other marine equipment, shaft seals for marine, oil, aerospace, and other applications, propeller shafts, linings for piping to convey, e.g., oil sands and/or tar sands, and other applications where abrasion resistance and/or enhanced dynamic properties are desired. Following vulcanization, the vulcanized elastomer composite may be used in rollers, cams, shafts, pipes, tread bushings for vehicles, or other applications where abrasion resistance and/or enhanced dynamic properties are desired.

[0097] Traditional compounding techniques may be used to combine vulcanization agents and other additives known in the art, including the additives discussed above in connection with the dewatered product, with the vulcanizable elastomer composite, depending on the desired use. Following such compounding, the material remains vulcanizable until any sulfur or other cross-linking agent incorporated into the elastomer composite forms a desired degree of cross-linking within the material, for example upon heating to a suitable temperature e.g.. 105°C, for a desired time, e.g., a time to achieve 90% vulcanization as measured by a conventional rubber rheometer. Preferably, the elastomer composite achieves a swell index of about 1.80 to about 2.20 during vulcanization, for example, from about 1.90 to about 2.10 or from about 1.95 to about 2.05. One of skill in the art will recognize that the swell index may be adjusted by the choice of accelerator, the amount of accelerator and sulfur, the vulcanization time, and the ratio of accelerator and sulfur. The ratio of accelerator and sulfur also influences the types of cross-links

present in the rubber. Suitable accelerators, along with information about reaction kinetics, include those listed in the Vanderbilt Rubber Handbook, published by the RT Vanderbilt Company, Inc. (14th ed, 2010) and the Bayer Manual for the Rubber Industry, Bender et al., Bayer AG, 1993.

[0098] The present invention further relates to a vulcanizable or vulcanized elastomer composite formed by any one or more methods described herein.

[0099] Unless otherwise specified, all material proportions described as a percent herein are in weight percent.

[0100] The present invention will be further clarified by the following examples which are intended to be only exemplary in nature.

EXAMPLES

[0101] In these examples, the "field latex" was field latex (Muhibbah Lateks Sdn Bhd, Malaysia) having a dry rubber content of about 30 wt%. The "latex concentrate" was latex concentrate (high ammonia grade, from Muhibbah Lateks Sdn Bhd, Malaysia, or from Chemionics Corporation, Tallmadge, Ohio) diluted by about 50% to a dry rubber content of about 30 wt% using either pure water or water with 0.6 wt% to 0.7 wt% ammonia. Unless noted otherwise, the "silica" was ZEOSIL® Z1165 MP precipitated silica from Solvay USA Inc., Cranbury, NJ (formerly Rhodia).

[0102] **Thermogravimetric Analysis.** The actual silica loading levels were determined by thermogravimetric analysis (TGA) following the ISO 6231 method.

[0103] **Water Content of Product.** The test material was cut into mm size pieces and loaded into the moisture balance (e.g., Model MB35 and Model MB45; Ohaus Corporation, Parsippany NJ) for measurement. The water content was measured at 130°C for 20 minutes to 30 minutes until the test sample achieved a consistent weight.

[0104] **Slurry Zeta Potential**. In these examples, the zeta potential of particulate slurries was measured using a ZetaProbe Analyzer™ from Colloidal Dynamics, LLC, Ponte Vedra Beach, Florida USA. With multi-frequency electroacoustic technology, the ZetaProbe measures zeta potential directly at particle concentrations as high as 60% by volume. The instrument was first calibrated using the KSiW calibration fluid provided by Colloidal Dynamics (2.5 mS/cm). A 40 g sample was then placed into a 30 mL Teflon cup (Part #A80031) with a stir bar, and the cup was placed on a stirring base (Part #A80051) with 250 rpm stirring speed. The measurement was performed using the dip probe 173 in a single-point mode with 5-point run at ambient temperature (approximately 25 °C). The data were analyzed using ZP version 2.14c Polar™ software provided by Colloidal Dynamics. The zeta potential values can be negative or positive depending on polarity of charge on the particles. The "magnitude" of zeta potential refers to the absolute value (e.g., a zeta potential value of -35 mV has a higher magnitude than a zeta potential value of -20 mV). The magnitude of the zeta potential reflects the degree of electrostatic repulsion between similarly charged particles in dispersion. The higher the magnitude of zeta potential, the more stable of particles in dispersion. Zeta potential measurements were carried out on particulate silica slurries prepared as described below.

[0105] Dry silica was weighed and combined with deionized water using a 5-gallon bucket and a high shear overhead laboratory mixer with a shrouded agitator (Silverson Model AX3, Silverson Machines, Inc., East Longmeadow, MA; operating at 5200-5400 rpm for 30 minutes to 45 minutes). Once the silica was roughly dispersed in water and able to be pumped, the silica slurry was transferred via a peristaltic pump (Masterflex 7592-20 system – drive and controller, 77601-10 pump head using I/P 73 tubing; Cole-Palmer, Vernon Hills, IL) into a mixing loop with an inline high shear rotor-stator mixer (Silverson Model 150LB located after the peristaltic pump, operated at 60 Hz) in a run tank (30 gal. convex bottom

port vessel) and was ground to further break down silica agglomerates and any remaining silica granules. The slurry in the run tank was then circulated at 2 L/min using the same peristaltic pump through the mixing loop for a time sufficient for turnover of at least 5-7 times of the total slurry volume (>45 minutes) to make sure any silica agglomerates were properly ground and distributed. An overhead mixer (Ika Eurostar power control visc-P7; IKA-Works, Inc., Wilmington, NC) with a low shear anchor blade rotating at about 60 rpm was used in the run tank to prevent gelling or sedimentation of silica particles. An acid (formic acid or acetic acid, reagent grade from Sigma Aldrich, St. Louis, MO) or salt (calcium nitrate, calcium chloride, calcium acetate or aluminum sulfate, reagent grade from Sigma Aldrich, St. Louis, MO) was added to the slurry in the run tank after grinding. The amount of silica in the slurry and the type and concentration of acid or salt are indicated in the specific Examples below.

[0106] Exemplary Process A. Where indicated in the examples below, a method was carried out utilizing Exemplary Process A. In Process A, dry precipitated silica and water (municipal water filtered to remove particulate matter) were metered and combined and then ground in a rotor-stator mill to form silica slurry, and the silica slurry was further ground in a feed tank using an agitator and another rotor-stator mill. The silica slurry was then transferred to a run tank equipped with two stirrers. The silica slurry was recirculated from the run tank through a homogenizer and back into the run tank. A solution of acid (formic acid or acetic acid, industrial grade obtained from Kong Long Huat Chemicals, Malaysia) or salt (calcium nitrate, industrial grade obtained from Mey Chern Chemicals, Malaysia) was then pumped into the run tank. The slurry was maintained in dispersed form through stirring and, optionally, by means of the recirculating loop in the run tank. After a suitable period, the silica slurry was fed to a confined reaction zone (13), such as the one shown in Figure 1a, by

means of the homogenizer. The concentration of silica in the slurry and the concentration of acid or calcium nitrate are indicated in the specific Examples below.

[0107] The latex was pumped with a peristaltic pump (at less than about 40 psig pressure) through the second inlet (11) into the reaction zone (13). The latex flow rate was adjusted between about 300-1600 kg latex/hr in order to obtain a desired production rate and silica loading levels in the resulting product. The homogenized slurry containing acid, or salt, or a combination of acid and salt, was pumped under pressure from the homogenizer to a nozzle (0.060"-0.130" inside diameter (ID)) (3a), represented by the first inlet (3) shown in Figure 1(a), such that the slurry was introduced as a high speed jet into the reaction zone. Upon contact with the latex in the reaction zone, the jet of silica slurry flowing at a velocity of 25 m/s to 120 m/s entrained the latex flowing at 1 m/s to 11 m/s. In Examples that successfully produced elastomer composite according to embodiments of the invention, the impact of the silica slurry on the latex caused an intimate mixing of silica particles with the rubber particles of the latex, and the rubber was coagulated, transforming the silica slurry and the latex into a material comprising a solid or semi-solid silica-containing continuous rubber phase containing 40 to 95 wt% water, based on total weight of the material, trapped within the material. Adjustments were made to the silica slurry flow rate (500-1800 kg/hr), or the latex flow rate (300-1800 kg/hr), or both, to modify the silica to rubber ratios (e.g., 15-180 phr silica) in the final product, and to achieve the desired production rate. The production rates (dry material basis) were 200-800 kg/hr. Specific silica contents (by TGA analysis) in the rubber following dewatering and drying of the material are listed in the Examples below.

[0108] **Process A Dewatering.** Material was discharged from the reaction zone at atmospheric pressure at a flow rate from 200 to 800 kg/hr (dry weight) into a dewatering extruder (The French Oil Machinery Company, Piqua, OH). The extruder (8.5 inch I.D.) was equipped with a die plate with various die-hole buttons configurations and operated at a

typical rotor speed of 90 to 123 RPM, die plate pressure 400 -1300 psig, and power of 80 kW to 125 kW. In the extruder, silica-containing rubber was compressed, and the water squeezed out of the silica-containing rubber was ejected through a slotted barrel of the extruder. Dewatered product typically containing 15 -60 wt% water was obtained at the outlet of the extruder. The dewatered product was then passed to the Process A Drying and Cooling Process or further dewatered using the Process B dewatering process and then to the Process B Drying and Cooling Process described further below, as indicated in Table 5.

[0109] Process A Drying and Cooling. Where indicated, the dewatered product was dropped into a continuous compounder (Farrel Continuous Mixer (FCM), Farrel Corporation, Ansonia, CT; with #7 and 15 rotors) where it was dried, masticated and mixed with 1-2 phr of antioxidant (e.g. 6PPD from Flexsys, St. Louis, MO) and optionally silane coupling agent (e.g. NXT silane, obtained from Momentive Performance Materials, Inc., Waterford, NY; 8 wt% silane on silica weight basis). The temperature of the FCM water jacket was set at 100°C, and the FCM temperature at the output orifice was 140°C to 180°C. The moisture content of the masticated, dewatered elastomer composite exiting the FCM was around 1 wt% to 5 wt%. The product was further masticated and cooled on an open mill. A rubber sheet of the elastomer composite was directly cut from the open mill, rolled and cooled in air.

[0110] Exemplary Process B. Where indicated in the examples below, an exemplary method was carried out utilizing Exemplary Process B. In Process B, dry silica was weighed and combined with deionized water using a 5-gallon bucket and a high shear overhead laboratory mixer with a shrouded agitator (Silverson Model AX3, Silverson Machines, Inc., East Longmeadow, MA; operating at 5200 rpm to 5400 rpm for 30 -45 minutes). Once the silica was roughly dispersed in water and able to be pumped, the silica slurry was transferred via a peristaltic pump (Masterflex 7592-20 system – drive and controller, 77601-10 pump head using I/P 73 tubing; Cole-Palmer, Vernon Hills, IL) into a mixing loop with an inline

high shear rotor-stator mixer (Silverson Model 150LB located after the peristaltic pump, operated at 60 Hz) in a run tank (30 gal convex bottom port vessel) and was ground to further break down silica agglomerates and any remaining granules. The slurry in the run tank was then circulated at 2 L/min through the mixing loop for a time sufficient for turnover of at least 5 -7 times of the total slurry volume (>45 minutes) to make sure any silica agglomerates were properly ground and dispersed. An overhead mixer (Ika Eurostar power control visc-P7; IKA-Works, Inc., Wilmington, NC) with a low shear anchor blade rotating at about 60 rpm was used in the run tank to prevent gelling or sedimentation of silica particles. An acid (formic acid or acetic acid, reagent grade from Sigma Aldrich, St. Louis, MO) or salt (calcium nitrate, calcium chloride, calcium acetate, or aluminum sulfate salt, reagent grade from Sigma Aldrich, St. Louis, MO) was added to the slurry in the run tank after grinding. The amount of silica in the slurry and the type and concentration of acid or salt are indicated in Table 5 for the specific Examples below.

[0111] The latex was pumped using a peristaltic pump (Masterflex 7592-20 system – drive and controller, 77601-10 pump head using I/P 73 tubing; Cole-Palmer, Vernon Hills, IL) through a second inlet (11) and into a reaction zone (13) configured similarly to that shown in Figure 1(b). The latex flow rate was adjusted between about 25 kg/h to about 250 kg/h in order to modify silica to rubber ratios of the elastomer composites.

[0112] When the silica was well dispersed in the water, the slurry was pumped from the run tank through a diaphragm metering pump (LEWA-Nikkiso America, Inc., Holliston, MA) through a pulsation dampener (to reduce pressure oscillation due to the diaphragm action) into either the reaction zone or the run tank via a recycle loop "T" connector. The direction of the slurry was controlled by two air actuated ball valves, one directing the slurry to the reaction zone and the other directing the slurry to the run tank. When ready to mix the silica slurry with latex, the line feeding the first inlet (3) to the reaction zone was pressurized to 100

psig to 150 psig by closing both valves. The ball valve directing the slurry to the reaction zone was then opened and pressurized silica slurry was fed to a nozzle (0.020' to 0.070" ID) (3a) shown in Figure 1(b), at an initial pressure of 100 psig to 150 psig, such that the slurry was introduced as a high speed jet into the reaction zone. Upon contact with the latex in the reaction zone, the jet of silica slurry flowing at a velocity of 15 m/s to 80 m/s entrained the latex flowing at 0.4 m/s to 5 m/s. In Examples that successfully produced elastomer composite according to embodiments of the invention, the impact of the silica slurry on the latex caused an intimate mixing of silica particles with the rubber particles of the latex, and the rubber was coagulated, transforming the silica slurry and the latex into an elastomer composite comprising the silica particles and 40 wt% to 95 wt% water trapped within a solid or semi-solid silica-containing, continuous rubber phase. Adjustments were made to the silica slurry flow rate (40 kg/hr to 80 kg/hr) or the latex flow rate (25 kg latex/hr to 300 kg latex/hr), or both, to modify silica to rubber ratios (e.g., 15 phr to 180 phr silica) in the resulting product and to achieve the desired continuous production rates (30 kg/hr to 200 kg/hr on dry material basis). Specific silica to rubber ratio (phr) contents following dewatering and drying are listed in the Examples below.

[0113] Process B Dewatering.

[0114] Material discharged from the reaction zone was recovered and sandwiched between two aluminum plates inside a catch pan. The "sandwich" was then inserted between two platens of a hydraulic press. With 2500 psig pressure exerted on the aluminum plates, water trapped inside the rubber product was squeezed out. If needed, the squeezed material was folded into a smaller piece and the squeezing process was repeated using the hydraulic press until the water content of the rubber product was below 40 wt%.

[0115] Process B Drying and Cooling. The dewatered product was put into a Brabender mixer (300 cc) for drying and mastication to form a masticated, dewatered elastomer

composite. Sufficient dewatered material was charged into the mixer to cover the rotors. The initial temperature of the mixer was set at 100°C and the rotor speed was generally at 60 rpm. The water remaining in the dewatered product was converted to steam and evaporated out of the mixer during the mixing process. As the material in the mixer expanded as result of evaporation, any overflowing material was removed as necessary. Either or both of a silane coupling agent (NXT silane, obtained from Momentive Performance Materials, Inc., Waterford, NY; 8 wt% silane on silica weight basis) and/or antioxidant (6-PPD, N-(1,3-dimethylbutyl)-N'-phenyl-*p*-phenylenediamine, Flexsys, St. Louis, MO) was optionally added to the mixer when the mixer temperature was above 140°C. When the temperature of the mixer reached 160°C, the material inside the mixer was held at 160°C to 170°C by varying the rotor speed for 2 minutes before the material was dumped. The masticated, dewatered elastomer composite was then processed on an open mill. The moisture content of the material being taken off of the mill typically was below 2 wt%.

[0116] Preparation of Rubber Compounds.

[0117] Dried elastomer composite obtained by any of the processes outlined above was compounded according to the formulation in Table A and the procedure outlined in Table B. For silica elastomer composites where either silane or antioxidant was added during drying, the final compound composition is as specified in Table A. The amount of silane coupling agent and/or antioxidant added during compounding was adjusted accordingly.

Table A

Ingredient	**phr**
NR in Composite	100
Silica in Composite	S
6PPD* (antioxidant)	2.0
Silane (NXT silane**)	0.08 x (phr silica)
ZnO	4
Stearic acid	2
DPG***	1.5
Cure Rite® BBTS****	1.5
Sulfur	1.5

*N-(1,3-dimethylbutyl)-N'-phenyl-*p*-phenylenediamine (Flexsys, St. Louis, MO)
**main active component: S-(3-(triethoxysilyl)propyl)octanethioate (Momentive, Friendly, WV)
*** DiphenylGuanidine (Akrochem, Akron, OH)
****N-tert-Butylbenzothiazole-2-sulphenamide (Emerald Performance Materials, Cuyahoga Falls, OH)
NR = natural rubber
S = as stated

Table B

	Time (min)	Operation
Stage 1		Brabender mixer (300 cc), 65% fill factor, 60 rpm, 100 °C
	0	Add rubber-silica composite
	1	Add silane coupling agent, if needed
		Hold for 2 minutes beginning at 150 °C
	2	Sweep and add 6PPD and mix for 1 additional minute at 150 °C
	3	Sweep
		Dump, 160 °C
		Pass through roll mill 6x
Stage 2		Brabender mixer (300 cc), 63% fill factor, 60 rpm, 100 °C
	0	Add stage 1 compound
	1	Add zinc oxide and stearic acid
	2	Sweep
	4	Dump, 150 °C
		Pass through roll mill 6x
Stage 3		Brabender mixer (300 cc), 63% fill factor, 60 rpm, 100 °C
	0	Add stage 2 compound, sulfur and accelerators
	0.5	Sweep
	1	Dump

		Roll mill for one minute with adequate band. Remove and perform 6 end rolls. Sheet off to required thickness.

[0118] Vulcanization was carried out in a heated press set at 150°C for a time determined by a conventional rubber rheometer (i.e., T90 + 10% of T90, where T90 is the time to achieve 90% vulcanization).

[0119] Properties of rubber/silica compounds.

[0120] The elongation at break of solid silica-containing continuous rubber phase was determined by manually stretching the material as recovered from the reaction zone with reference to a metered length scale until it fractured. The tensile properties of vulcanized samples (T300 and T100, elongation at break, tensile strength) were measured according to ASTM standard D-412. Tan delta 60^{o} was determined using a dynamic strain sweep in torsion between 0.01% and 60% at 10 Hz and 60 °C. Tan δ_{max} (listed as tan delta 60 in the tables below) was taken as the maximum value of tan δ within this range of strains.

Comparative Example 1.

[0121] Dry mixed silica elastomer compounds were prepared with SMR 20 natural rubber (Hokson Rubber) and Z1165 silica using the formulation in Table A, in which the NXT silane was used, and the compounding protocol in Table 1. Samples were vulcanized as described above. The mechanical properties of the resulting vulcanizates are listed in Table 2.

Table 1

	Time (min)	**Operation**
Stage 1		Brabender mixer (300 cc), 65% fill factor, 60 rpm, 80 °C
	0	Add NR

	0.5	Add silica and silane (preblended)
		Hold for 2 minutes at 160-170°C
		Add 6PPD and mix for 1 additional minute at 160-170 °C
		Sweep, mix for 1 additional minute at 160-170 °C
		Dump
		Roll mill using 6 end rolls
Stage 2		Brabender mixer (300 cc), 63% fill factor, 60 rpm, 80 °C
	0	Add stage 1 compound
	0.5	Add zinc oxide and stearic acid
	1.5	Sweep, mix for additional minute at 140-150 °C
	3	Dump
		Roll mill using 6 end rolls
Stage 3		Brabender mixer (300 cc), 60% fill factor, 60 rpm, 60 °C
	0	Add stage 2 compound, sulfur and accelerators
	0.5	Sweep
	1	Dump
		Roll mill for one minute with adequate band. Remove and perform 6 end rolls. Sheet off to required thickness.

Table 2

Example Number	Silica Loading (phr)	T300/T100	Tan delta 60	Tensile Strength (MPa)	Elongation @ Break (%) * Tensile Strength (MPa)
C1	33	5.27	0.038	33	17560
C2	38	4.53	0.079	37	21963

C3	47	4.79	0.089	32	17807
C4	51	4.38	0.099	34	20340
C5	56	4.58	0.106	31	16717
C6	61	4.23	0.121	31	16663
C7	65	4.40	0.134	29	15077
C8	70	4.05	0.153	28	14858
C9	74	4.13	0.162	26	13517

[0122] Example 2.

[0123] A silica slurry with 27.8 wt% Zeosil® 1165 silica was prepared as described above in connection with the Slurry Zeta Potential test method. The slurry was then diluted using either deionized water or a supernatant obtained from ultracentrifugation of the 27.8 wt% slurry to make a series of silica slurries at various silica concentrations. The zeta potential of various silica slurries was measured to show the relationship between the concentration of the silica in the slurry and the zeta potential of the slurry. The zeta potential of the silica slurry, as shown in Table 3A, appears to depend upon the silica concentration when the silica slurry is made using deionized water. However, as shown in Table 3B, when slurry was diluted using the supernatant obtained from ultracentrifugation of the 27.8 wt% slurry, the zeta potential stays roughly the same at different silica concentrations.

Table 3A

Zeta potential of slurry of silica made using deionized water.

Silica Concentration in slurry (w/w)	6%	10%	15%	20%	22%	25%
Zeta Potential (mV)	-46.4	-42.7	-39.6	-36.2	-34.7	-32.3
pH	5.19	5.04	4.92	4.86	4.83	4.77

Table 3B

Zeta potential of silica slurry made from dilution of a

27.8 wt% silica slurry using the supernatant of the 27.8 wt% silica slurry.

Silica Concentration in slurry (w/w)	6%	22%
Zeta Potential (mV)	-31.5	-31.4
pH	4.86	4.79

[0124] This result demonstrates that an increase of magnitude of zeta potential when such silica slurries are diluted with deionized water is mostly due to reduction of ionic strength of the slurry. The ions in the silica slurry are believed to be from residual salts present in the silica from the silica particle manufacturing process. The high magnitude of zeta potential of the silica slurries (all over 30 mV) indicated that the silica has high electrostatic stability in the slurry.

[0125] **Example 3.**

[0126] The effect of adding salt or acid at various concentrations to silica slurries on the zeta potential of these slurries is set forth in Table 4. Slurries were prepared in deionized water by the Slurry Zeta Potential test method described above. Data summarized in Table 4 illustrate the dependence of zeta potential of silica slurries and destabilized silica slurries on the silica concentration, salt concentration, and acid concentration. Adding salt or acid to silica slurry reduces the magnitude of zeta potential, thus the stability of the silica slurry. As shown in Table 4, the zeta potential depends mostly on the concentration of salt or acid in the slurry or destabilized slurry, and not on silica concentration.

Table 4

Zeta potential of slurry and destabilized of silica at various slurry concentrations, salt concentrations, and acid concentrations.

Silica Concentration in Slurry (wt%)	[$CaCl_2$] (mM)	[acetic acid] (mM)	[formic acid] (mM)	Zeta (mV)	pH
22.0	0	0	0	-34.4	4.80
6.0	0	0	0	-45.0	ND
22.0	10.6	0	0	-24.2	4.49
22.0	29.7	0	0	-17.0	4.27
22.0	51.1	0	0	-14.6	4.17
22.0	105	0	0	-9.2	ND
22.0	155	0	0	-6.4	ND
6.0	4.6	0	0	-29.9	ND
6.0	10.4	0	0	-23.4	ND
6.0	27.6	0	0	-18.5	ND
6.0	46.4	0	0	-15.4	ND
6.0	140	0	0	-7.7	ND
22.0	0	98	0	-23.6	3.72
22.0	0	192	0	-21.4	3.65
22.0	0	564	0	-17.1	3.26
22.0	0	1857	0	-12.7	ND
6.0	0	27	0	-33.6	3.84
6.0	0	45	0	-29.9	3.68
6.0	0	174	0	-22.1	3.38

Silica Concentration in Slurry (wt%)	[$CaCl_2$] (mM)	[acetic acid] (mM)	[formic acid] (mM)	Zeta (mV)	pH
6.0	0	431	0	-18.9	3.61
22.0	0	0	118	-15.3	3.17
22.0	0	0	197	-14.2	2.96
22.0	0	0	731	-10.7	2.46
22.0	0	0	1963	-6.5	2.04
6.0	0	0	36	-17.7	3.07
6.0	0	0	42	-17.4	3.04
6.0	0	0	168	-14.6	2.62
6.0	0	0	456	-11.4	2.29
22.0	10.7	0	130	-12.9	3.04
22.0	26.6	0	248	-9.0	2.78
22.0	101	0	978	-3.1	2.10
6.0	4.7	0	36	-15.9	3.12
6.0	46.4	0	224	-10.1	2.41

ND = not determined.

[0127] Results shown in Table 4 illustrate the dependence of zeta potential of silica slurries and destabilized silica slurries on acetic acid concentration and silica concentration. The data show that the zeta potential values are more dependent on the acid concentration than the silica concentration. A similar relationship between zeta potential to acid concentration and silica concentration is observed for formic acid. At a given concentration, formic acid reduces zeta potential magnitude more than acetic acid. As shown in Table 4, a combination of formic acid and calcium chloride was effective in reducing the zeta potential magnitude. The results in Table 4 show that the stability of silica particles in slurry can be

reduced effectively through addition of destabilization agents, such as acid or salt or a combination of acid and salt. Similar results were seen for calcium nitrate and calcium acetate.

[0128] Example 4.

[0129] In this example, the importance of destabilizing the dispersion of silica particles prior to contacting the silica dispersion with elastomer latex was established. Specifically, four experiments were run using the mixing apparatus (c) in Figure 1, equipped with three inlets (3, 11, 14) for introducing up to three fluids into a confined reaction zone (13), such that one fluid impacted the other fluids at a 90 degree angle as a high speed jet at a velocity of 15 m/s to 80 m/s (See Figure 1(c)). In three of the four experiments, the silica was ground as described above in Process B and acetic acid was optionally added as described in Examples 4-A to 4-D, below. The slurry or destabilized slurry was then pressurized to 100 psig to 150 psig and fed into the confined reaction zone through the inlet (3) at a volumetric flow rate of 60 liter per hour (L/hr) such that the slurry or destabilized slurry was introduced as a high speed jet at 80 m/s into the reaction zone. At the same time, natural rubber latex concentrate (60CX12021 latex, 31 wt% dry rubber content, from Chemionics Corporation, Tallmadge, Ohio, diluted with deionized water) was introduced into the second inlet (11) through a peristaltic pump at a volumetric flow rate of 106 L/hr and velocity of 1.8 m/s. These rates were selected and flows were adjusted to yield an elastomer composite product comprising 50 phr (parts per hundred weight dry rubber) silica. The silica slurry or destabilized silica slurry and latex were mixed by combining the low velocity latex flow and the high velocity jet of silica slurry or destabilized slurry through entraining the latex flow in the jet of silica slurry or destabilized silica slurry at the point of impact. The production rate (on a dry material basis) was set at 50 kg/hr. Specific actual silica to rubber ratios in rubber composites

produced by the process are listed in the Examples below. TGA was performed following drying according to the Process B method.

[0130] Example 4-A:

[0131] First Fluid: A destabilized aqueous dispersion of 25 wt% of silica with 6.2 wt% (or 1.18 M) acetic acid was prepared as described in Process B described above. The zeta potential of the destabilized slurry was -14 mV, indicating that the slurry was significantly destabilized by the acid. The destabilized silica slurry was pumped continuously under pressure into the first inlet (3).

[0132] Second Fluid: Elastomer latex was supplied to the reaction zone through the second inlet (11).

[0133] The first fluid impacted the second fluid in the reaction zone.

[0134] Results: A liquid to solid phase inversion occurred in the reaction zone when the destabilized silica slurry and latex were intimately mixed by entraining the low velocity latex flow into the high velocity jet of destabilized silica slurry. During the entrainment process, the silica was intimately distributed into the latex and the mixture coagulated into a solid phase which contained 70 wt% to 85 wt% of water. As a result, a flow of a solid silica-containing, continuous rubber phase in a worm or rope-like shape was obtained at the outlet of the reaction zone (15). The composite was elastic and could be stretched to 130% of the original length without breaking. TGA analysis on the dried product showed the elastomer composite contained 58 phr of silica.

[0135] Example 4-B:

[0136] First Fluid: A destabilized aqueous dispersion of 25 wt% of silica with 6.2 wt% acetic acid was prepared according to Process B described above. The zeta potential of the slurry was -14 mV, indicating the slurry was significantly destabilized by the acid. The destabilized silica slurry was pumped continuously under pressure into the first inlet (3).

[0137] Second Fluid: Elastomer latex was supplied to the reaction zone through the second inlet (11).

[0138] Third Fluid: Deionized water was also injected into the reaction zone through third inlet (14) at a volumetric flow rate of 60 L/hr and a velocity of 1.0 m/s.

[0139] The three fluids met and impacted each other in the reaction zone.

[0140] Results: A liquid to solid phase inversion occurred in the reaction zone and a solid or semi-solid silica containing continuous rubber phase in a rope or worm-like shape was obtained from the outlet of the reaction zone. A significant amount of cloudy liquid containing silica and/or latex flowed out of the exit (7) with the solid or semi-solid silica-containing continuous rubber phase. The silica-containing continuous rubber phase contained about 70 wt % to about 75 wt% water based on the weight of the composite. TGA analysis on the dried product showed the elastomer composite contained 44 phr of silica. Thus, the addition of water through the third inlet had a negative impact on the process, yielding a product with lower silica content (44 phr in contrast to 58 phr in Example 4-A) and significant waste product.

[0141] **Example 4-C:**

[0142] First Fluid: A 10 wt% acetic acid aqueous solution without silica was prepared. A continuous feed of the acid fluid was pumped using a peristaltic pump at a volumetric flow rate of 60 L/hr through the third inlet (14) into the reaction zone at a velocity of 1.0 m/s at the time of entry into the reaction zone.

[0143] Second Fluid: Elastomer latex was supplied to the reaction zone through the second inlet (11) by a peristaltic pump at a velocity of 1.8 m/s and a volumetric flow rate of 106 L/hr.

[0144] The two fluids met and impacted each other in the reaction zone.

[0145] Results: A solid worm-like, sticky rubber phase was formed. TGA analysis on the dried product showed the solid rubber phase contained no silica.

[0146] **Example 4-D:**

[0147] First Fluid: An aqueous dispersion of 25 wt% of silica without acetic acid was prepared according to Process B described above. The silica slurry was pumped under pressure continuously into the first inlet (3) at a volumetric flow rate of 60 L/hr and at a velocity of 80 m/s at the point of entry into the reaction zone. The zeta potential of the slurry was -32 mV, indicating that silica was stably dispersed in the slurry. Thus, in this Example 4-D, the silica slurry was not destabilized by addition of acid to the slurry prior to impacting the latex fluid.

[0148] Second Fluid: Elastomer latex was supplied to the reaction zone through the second inlet (11) by a peristaltic pump at a velocity of 1.8 m/s and a volumetric flow rate of 106 L/hr.

[0149] Third fluid: After an initial period of continuous flow of the first and second fluids, a 10 wt% acetic acid aqueous solution was injected through the third inlet (14) into the reaction zone at a volumetric flow rate that increased from 0 L/hr to 60 L/hr and a velocity that increased from 0 m/s to 1.0 m/s. All three fluids impacted each other and mixed in the reaction zone.

[0150] Results: Initially, prior to the injection of acid, no silica-containing continuous rubber phase formed and only cloudy liquid came out of the reaction zone exit (15). Upon the injection of acid into the reaction zone (13), a worm-like, semi-solid silica-containing continuous rubber phase started to form as the flow of acetic acid through the third inlet was increased from 0 L/hr to 60 L/hr. The materials flowing from the exit still contained a significant amount of cloudy liquid, indicating a significant amount of waste. TGA analysis of the dried product showed that the silica-containing continuous rubber phase formed in this

experimental run only contained 25 phr silica. Based on the production conditions selected and the amount of silica used, if the silica had been substantially incorporated into the silica-containing rubber phase as in Example 4-A, the silica would have yielded a silica-containing rubber phase comprising in excess of 50 phr silica.

[0151] These experiments show that the silica slurry must be destabilized prior to initial impact with the elastomer latex in order to achieve the desired silica-containing, continuous rubber phase. Example 4-A achieved what was considered efficient capture of the silica within the solid silica-containing, continuous rubber phase, whereas Example 4-D illustrates a comparative process utilizing an initially stable silica slurry and demonstrating less than half of the efficiency of Example 4-A utilizing an initially destabilized silica slurry. The observation of a cloudy liquid exiting the reaction zone exit point indicates insufficient mixing of the silica with the latex and a lower proportion of silica captured within the continuous rubber phase. It is theorized that in comparative processes 4B and 4D, there was insufficient destabilization of fluids during mixing. The results further show that poor capture of silica occurs when additional fluid is added while the first fluid and second fluid are being mixed together, and such process conditions generate unwanted amounts of waste.

[0152] **Example 5.**

[0153] In these examples, processes to produce elastomer composite according to various embodiments of the invention were run in the apparatus shown in Figure 1 (either (a) or (b)) under various conditions as described in Table 5, utilizing either Process A or Process B described above. Operating conditions were selected to yield a solid or semi-solid silica-containing, continuous rubber phase with the silica to rubber ratios set forth in Table 5.

Table 5

Example Number	Process A/B	Silica[a] in slurry (wt%)	Rubber in latex[b] (DRC, wt%)	NH_3 in latex (wt%).	Salt Type	Salt wt% in slurry	Acid Type	Acid wt% in slurry	Acid/ NH_3 molar ratio
1	B	25.0%	31.0%	0.27%	$CaCl_2$	1.00%	Acetic	3.8%	1.47
2	B	25.0%	31.0%	0.27%	$CaCl_2$	1.00%	Acetic	3.8%	1.47
3	B	25.0%	31.0%	0.27%	$CaCl_2$	1%	Acetic	1.8%	1.29
4	B	25.0%	31.0%	0.27%	$CaCl_2$	1%	Acetic	1.8%	1.29
5	B	25.0%	31.0%	0.27%	$CaCl_2$	1%	Acetic	1.8%	1.29
6	B	25.0%	31.0%	0.27%	N/A	0	Acetic	1.8%	1.29
7	B	25.0%	31.0%	0.27%	N/A	0	Acetic	1.8%	1.29
8	B	25.0%	31.0%	0.27%	N/A	0	Acetic	1.8%	1.29
9	B	25.0%	31.0%	0.27%	N/A	0	Formic	1.5%	2.20
10	B	25.0%	31.0%	0.27%	N/A	0	Formic	1.5%	2.20
11	B	25.0%	31.0%	0.27%	N/A	0	Formic	1.5%	2.20
12	B	25.0%	31.0%	0.27%	$CaCl_2$	1%	N/A	0	0.00
13	B	25.0%	31.0%	0.27%	$CaCl_2$	1%	N/A	0	0.00
14	B	25.0%	31.0%	0.27%	$CaCl_2$	1%	N/A	0	0.00
15	B	25.0%	31.0%	0.27%	$Ca(NO_3)_2$	0.35%	Acetic	1.8%	1.29
16	B	25.0%	31.0%	0.27%	$Ca(NO_3)_2$	0.35%	Acetic	1.8%	1.29
17	B	25.0%	31.0%	0.27%	$Ca(NO_3)_2$	0.35%	Acetic	1.8%	1.29
18	B	25.0%	31.0%	0.27%	$Ca(NO_3)_2$	0.35%	N/A	0	0.00
19	B	25.0%	31.0%	0.27%	$Ca(NO_3)_2$	0.35%	N/A	0	0.00
20	B	25.0%	31.0%	0.27%	$Ca(NO_3)_2$	0.35%	N/A	0	0.00
21	B	25.0%	31.0%	0.27%	$Ca(NO_3)_2$	0.35%	Formic	1.5%	1.40
22	B	25.0%	31.0%	0.27%	$Ca(NO_3)_2$	0.35%	Formic	1.5%	1.40
23	B	25.0%	31.0%	0.27%	$Ca(NO_3)_2$	0.35%	Formic	1.5%	1.40
24	B	25.0%	31.0%	0.27%	$Ca(NO_3)_2$	0.35%	Formic	1.5%	1.78
25	B	25.0%	31.0%	0.27%	$Ca(NO_3)_2$	0.35%	Formic	1.5%	1.78
26	B	25.0%	31.0%	0.27%	$Ca(NO_3)_2$	0.35%	Formic	1.5%	1.78
27	B	25.0%	30.5%	0.27%	$Ca(NO_3)_2$	0.75%	N/A	0	0.00
28	B	25.0%	30.5%	0.27%	$Ca(NO_3)_2$	0.75%	N/A	0	0.00
29	B	25.0%	30.5%	0.27%	$Ca(NO_3)_2$	0.75%	N/A	0	0.00
30	B	25.0%	30.5%	0.27%	$Ca(NO_3)_2$	0.75%	N/A	0	0.00
31	B	20.0%	30.5%	0.27%	$Ca(NO_3)_2$	0.50%	N/A		0.00
32	B	20.0%	30.5%	0.27%	$Ca(NO_3)_2$	1%	N/A		0.00
33	B	25.0%	33.0%	0.60%	$Ca(NO_3)_2$	0.75%	N/A		0.00
34	A	20.0%	31.9%	0.53%	$Ca(NO_3)_2$	1%	N/A	0	0.00
35	A	20.0%	31.9%	0.53%	$Ca(NO_3)_2$	1%	N/A	0	0.00
36	A	10.0%	31.9%	0.53%	$Ca(NO_3)_2$	0.5%	N/A	0	0.00
37	A	10.0%	31.9%	0.53%	$Ca(NO_3)_2$	0.5%	N/A	0	0.00
38	A	20.0%	32.7%	0.35%	$Ca(NO_3)_2$	1%	N/A		0.00
39	A	16.0%	31.9%	0.53%	$Ca(NO_3)_2$	1%	N/A		0.00
40	A	18.5%	30.6%	0.70%	$Ca(NO_3)_2$	0.75%	N/A	0	0.00

Example Number	Process A/B	Silica[a] in slurry (wt%)	Rubber in latex[b] (DRC, wt%)	NH_3 in latex (wt%).	Salt Type	Salt wt% in slurry	Acid Type	Acid wt% in slurry	Acid/ NH_3 molar ratio
41	A	18.5%	30.6%	0.70%	$Ca(NO_3)_2$	0.75%	N/A	0	0.00
42	A	18.5%	30.6%	0.70%	$Ca(NO_3)_2$	0.75%	N/A	0	0.00
43	A	16.5%	32.8%	0.66%	N/A		acetic	3.61%	2.46
44	A	16.5%	30.6%	0.68%	N/A		acetic	3.61%	2.23
45	A	28.0%	30.6%	0.68%	$Ca(NO_3)_2$	1%	N/A		0.00
46	A	28.0%	30.6%	0.68%	$Ca(NO_3)_2$	1%	N/A		0.00
47	A	28.0%	30.6%	0.68%	$Ca(NO_3)_2$	1%	N/A		0.00
48	B	25.0%	30.5%	0.27%	CaCl2	0.60%	N/A		0.00
49	B	25.0%	31.0%	0.27%	N/A		formic	2.50%	2.31
50	B	25.0%	31.0%	0.27%	N/A		formic	2.50%	2.93
51	B	25.0%	31.5%	0.67%	N/A		acetic	5.18%	1.78
52	B	25.0%	30.9%	0.30%	$CaCl_2$	1.00%	N/A		0.00
53	B	25.0%	30.9%	0.30%	$CaCl_2$	1.00%	N/A		0.00
54	B	25.0%	30.9%	0.30%	N/A		acetic	2.34%	2.17
55	B	25.0%	30.9%	0.30%	$CaCl_2$	1.45%	N/A		0.00
56	B	25.0%	30.9%	0.30%	N/A		Acetic	2.4%	1.53
57	B	25.0%	30.9%	0.30%	N/A		Acetic	2.4%	1.95

N/A = not applicable

a. Examples 32, 33, and 40 used Agilon 454 silica (precipitated silica treated with silane coupling agents, obtained from PPG Industries Inc.). Examples 50 and 51 used Zeosil® 175GR silica (conventional precipitated silica, obtained from Solvay S.A.). All other examples used ZEOSIL® Z1165 MP precipitated silica.

b. Examples 34, 39, 44, and 52 used field latex. All other examples used latex concentrate.

Table 5 (continued)

Example Number	Slurry to MB rate (L/hr)[c]	Latex to MB rate (L/hr)[c]	Inlet Nozzle Velocity (m/s)[d]	Zeta Potential estimated (mV)[e]	Slurry -to- latex ratio (v/v)	Actual SiO_2 Loading	Drying Method[f]	AO or Silane added during drying?	Tensile Strength (MPa)	T300/ T100	Average Tan delta 60C	Elongation @ Break (%) * Tensile Strength (MPa)
1	60	189	29	-4.7	0.317	36	B	No	34.4	6.46	0.031	18145
2	60	189	29	-4.7	0.317	36	B	No	33.9	5.81	0.037	19266
3	60	103	29	-7.4	0.581	51	B	No	30.5	5.93	0.050	16522
4	60	103	29	-7.4	0.581	50	B	AO and silane	33.3	5.65	0.057	19304
5	60	103	29	-7.4	0.581	50	B	silane	32.3	6.09	0.049	17313
6	60	103	29	-19.6	0.581	74	B	No	29.5	6.40	0.092	16349
7	60	103	29	-19.6	0.581	74	B	AO and silane	29.2	5.37	0.109	15752
8	60	103	29	-19.6	0.581	75	B	silane	28.6	5.11	0.081	13776
9	60	67	29	-11.9	0.894	71	B	No	30.7	6.35	0.084	16306
10	60	67	29	-11.9	0.894	75	B	AO and silane	29.2	4.73	0.120	15096
11	60	67	29	-11.9	0.894	86	B	silane	27.6	4.54	0.173	13321
12	60	103	29	-9.5	0.581	76	B	No	24.2	5.44	0.071	9575
13	60	103	29	-9.5	0.581	77	B	AO and silane	25.6	4.87	0.078	10286
14	60	103	29	-9.5	0.581	76	B	silane	28.0	5.39	0.069	12731
15	60	103	29	-7.8	0.581	42	B	No	31.9	6.16	0.033	17130
16	60	103	29	-7.8	0.581	43	B	AO and silane	34.0	5.36	0.041	19448
17	60	103	29	-7.8	0.581	43	B	silane	34.0	5.77	0.039	19176
18	60	103	29	-18.8	0.581	57	B	No	30.6	6.24	0.061	16497

Example Number	Slurry to MB rate (L/hr)[c]	Latex to MB rate (L/hr)[c]	Inlet Nozzle Velocity (m/s)[d]	Zeta Potential estimated (mV)[e]	Slurry -to-latex ratio (v/v)	Actual SiO_2 Loading	Drying Method[f]	AO or Silane added during drying?	Tensile Strength (MPa)	T300/ T100	Average Tan delta 60C	Elongation @ Break (%) * Tensile Strength (MPa)
19	60	103	29	-18.8	0.581	55	B	AO and silane	31.7	5.75	0.065	17387
20	60	103	29	-18.8	0.581	56	B	silane	30.9	6.08	0.065	16862
21	60	103	29	-10.8	0.581	41	B	No	31.4	6.34	0.053	16140
22	60	103	29	-10.8	0.581	42	B	No	33.0	5.65	0.053	18744
23	60	103	29	-10.8	0.581	42	B	No	33.9	5.78	0.051	19120
24	60	81	29	-10.8	0.740	42	B	No	33.8	5.95	0.056	20449
25	60	81	29	-10.8	0.740	44	B	No	34.8	5.79	0.065	20497
26	60	81	29	-10.8	0.740	48	B	No	33.8	6.16	0.075	19976
27	60	82	75	-13.9	0.728	72	B	No	27.2	5.68	0.093	13086
28	60	59	75	-13.9	1.009	86	B	No	25.4	6.04	0.124	11083
29	60	82	19	-13.9	0.728	62	B	No	29.7	6.01	0.091	15549
30	60	64	19	-13.9	0.936	74	B	No	25.8	5.34	0.113	12006
31	60	64	76	-3.1	0.936	73	B	No	27.4	6.02	0.097	14198
32	60	64	76	-1.8	0.936	49	B	No	33.1	5.91	0.072	19234
33	60	76	75	-13.9	0.786	68	B	No	27.6	5.27	0.148	14175
34	828	697	75	-12.2	1.187	55	C	No	27.4	5.26	0.068	14735
35	828	1078	75	-12.2	0.768	40	C	No	33.5	5.43	0.059	20208
36	950	379	78	-17.1	2.506	64	C	No	27.8	5.01	0.072	14186
37	1425	690	75	-17.1	2.064	50	C	No	30.1	5.32	0.060	16182
38	738	688	76	-12.2	1.073	52	C	No	27.7	5.13	0.059	13789
39	644	425	78	-1.8	1.517	68	C	No	28.9	4.82	0.105	16244
40	788	1541	50	-14.1	0.512	74	C	No	34.4	5.54	0.025	19367
41	1079	1342	68	-14.1	0.804	44	C	No	31.6	6.08	0.037	16527

Example Number	Slurry to MB rate (L/hr)[c]	Latex to MB rate (L/hr)[c]	Inlet Nozzle Velocity (m/s)[d]	Zeta Potential estimated (mV)[e]	Slurry -to- latex ratio (v/v)	Actual SiO_2 Loading	Drying Method[f]	AO or Silane added during drying?	Tensile Strength (MPa)	T300/ T100	Average Tan delta 60C	Elongation @ Break (%) * Tensile Strength (MPa)
42	1079	1342	68	-14.1	0.804	44	A through FCM (no open mill)	No	30.5	6.20	0.060	15403
43	800	564	41	-16.5	1.419	49	C	No	31.1	5.26	0.095	16084
44	800	603	41	-16.5	1.326	37	C	No	33.3	5.71	0.061	18387
45	950	1384	58	-12.0	0.687	47	C	No	30.4	6.02	0.054	14789
46	950	1384	58	-12.0	0.687	47	C, Dewatering repeated once	No	32.7	6.00	0.055	17418
47	950	1384	58	-12.0	0.687	47	C, Dewatering repeated twice	No	27.9	5.82	0.050	13178
48	60	68	75	-12.8	0.884	50	B	No	32.0	5.32	0.074	18583
49	60	103	75	-10.6	0.581	41	B	No	29.5	6.02	0.048	14114
50	60	81	75	-10.6	0.740	60	B	No	27.4	5.81	0.081	13283
51	60	87	19	-14.5	0.692	63	B	No	27.4	4.93	0.084	13399
52	60	78	29	-9.5	0.772	70	B	No	26.2	5.73	0.100	13833
53	60	78	29	-9.5	0.772	70	B	No	27.5	5.44	0.100	14733
54	60	72	29	-18.4	0.837	68	B	No	27.8	5.57	0.094	15080
55	60	104	75	-7.2	0.579	55	B	No	24.0	5.96	0.070	14538
56	60	104	75	-18.3	0.579	52	B	No	28.8	5.65	0.057	15114
57	60	81	75	-18.3	0.737	79	B	No	24.9	5.08	0.109	11965

c. Slurry and Latex Flow Rates are the volumetric flow rates in L/hour of the silica slurry and the latex fluid, respectively, as they are delivered to the reaction zone.

d. The inlet nozzle velocity is the velocity of the silica slurry as it passes through a nozzle (3a) at first inlet (3) to the reaction zone (13) prior to contacting the latex.

e. Zeta potential values were estimated by interpolation of experimentally determined curves of zeta potential dependence on concentration of the salt or the acid of the slurries of the same grade of silica.

f. A and B indicate Process A and B drying and dewatering as described above. "C" indicates dewatering according to Process A, followed by additional dewatering and drying according to Process B. Any repetition of dewatering indicates repetition of Process A dewatering method.

[0154] In all the examples, the selected operating conditions yielded a solid silica-containing, continuous rubber phase in a roughly cylindrical form. The product contained a major amount of water, was elastic and compressible, and expelled water and retained solids content when manually compressed. Silica particles were observed to be uniformly distributed throughout a continuous rubber phase and this product was substantially devoid of free silica particles and larger silica grains, both on exterior and interior surfaces. For the solid silica-containing, continuous rubber phase to form, not only did the silica need to be destabilized (e.g., by prior treatment with acids and/or salts), but the volumetric flow rates of destabilized silica slurry relative to the latex had to be adjusted not only for achieving a desired silica to rubber ratio (phr) in the elastomer composite, but also for balancing the degree of slurry destabilization to the rate of slurry and latex mixing and the rate of coagulation of latex rubber particles. By means of such

adjustments, as the silica slurry entrained the latex, intimately distributing silica particles into the rubber, the rubber in the latex became a solid continuous phase, all within a fraction of a second after combining the fluids in the confined volume of the reaction zone. Thus, the process formed unique silica elastomer composites by means of a continuous fluid impact step done with sufficient velocity, selected fluid solids concentrations and volumes, and adjusted fluid flow rates to uniformly and intimately distribute the fine particulate silica within the latex and, in parallel, as such distribution occurs, to cause a liquid to solid phase inversion of the rubber.

[0155] Comparative Example 6.

[0156] In these comparative examples, the same basic steps and apparatus as described for Example 5 were used, but the combination of process conditions selected for each of the comparative examples in Table 6 failed to create a solid or semi-solid continuous rubber phase, and a silica elastomer composite could not be produced. Table 6 below sets forth the concentration of silica in the slurry and the concentration of acetic acid or calcium nitrate, if any, and other details of these examples.

Table 6

Comparative Example	Process A/B	Silica concen-tration in Slurry (wt%)	Latex Type	Rubber content of Latex (DRC) (wt%)	Latex wt% NH_3 (wt%)	Salt Type	Salt concen tration in Slurry (wt%)	Acetic Acid concen tration in Slurry (wt%)	Acid/ NH_3 molar ratio
6-1	A	18.5	Conc.	30.6	0.70	$Ca(NO_3)_2$	0.22	N/A	0
6-2	A	18.5	Conc.	30.6	0.70	$Ca(NO_3)_2$	0.48	N/A	0
6-3	A	20.0	Field	32.7	0.35	$Ca(NO_3)_2$	1	N/A	0
6-4	A	20.0	Field	32.7	0.35	$Ca(NO_3)_2$	1.3	N/A	0
6-5	A	10.0	Field	32.7	0.35	$Ca(NO_3)_2$	0.65	N/A	0

Comparative Example	Process A/B	Silica concen-tration in Slurry (wt%)	Latex Type	Rubber content of Latex (DRC) (wt%)	Latex wt% NH_3 (wt%)	Salt Type	Salt concen tration in Slurry (wt%)	Acetic Acid concen tration in Slurry (wt%)	Acid/ NH_3 molar ratio
6-6	A	20.0	Conc.	31.9	0.53	N/A	0	4.70	0.66
6-7	A	20.0	Field	32.7	0.33	N/A	0	2.80	0.98
6-8	B	25	Conc.	31	0.27	N/A	0	0	0.00
6-9	A	18.5	Conc.	30.6	0.70	N/A	0	0	0.00
6-10	A	18.5	Conc.	30.6	0.70	N/A	0	0	0.00
6-11	B	20	Conc.	30.5	0.27	N/A	0	0	0.00
6-12	A	16.0	Conc.	31.9	0.53	N/A	0	0	0.00

Table 6 (continued)

Comparative Example	Zeta Potential (Est.)[a] (mV)	Inlet Nozzle velocity[b] (m/s)	Silica/Rubber ratio setting (phr)	Slurry Flow Rate[c] (L/hr)	Latex Flow Rate[c] (L/hr)	Slurry to Latex Flow Ratio (v/v)
6-1	-22.0	65	50	818	1118	0.73
6-2	-17.0	50	30	792	1807	0.44
6-3	-12.2	76	40	738	1289	0.57
6-4	-10.6	76	40	738	1289	0.57
6-5	-15.4	78	60	950	524	1.81
6-6	-15.1	76	20	630	2255	0.28
6-7	-17.6	76	25	630	1761	0.36
6-8	-32.0	75	50	60	114	0.53

Comparative Example	Zeta Potential (Est.)[a] (mV)	Inlet Nozzle velocity[b] (m/s)	Silica/Rubber ratio setting (phr)	Slurry Flow Rate[c] (L/hr)	Latex Flow Rate[c] (L/hr)	Slurry to Latex Flow Ratio (v/v)
6-9	-37	82	30	792	1807	0.44
6-10	-37	85	50	818	1118	0.73
6-11	-4.8	76	70	60	64	0.94
6-12	-7.9	67	50	552	619	0.89

N/A = not applicable.

a. Zeta potential values were estimated by interpolation of experimentally determined curves of zeta potential dependence on concentration of the salt or the acid of the slurries of the same grade of silica.

b. The inlet nozzle velocity is the velocity of the silica slurry as it passes through a nozzle (3a) at first inlet (3) to the reaction zone prior to contacting the latex.

c. Slurry and Latex Flow Rates are the volumetric flow rates in L/hour of the silica slurry and the latex fluid, respectively, as they are delivered to the reaction zone.

d. Examples 6-11 and 6-12 used Agilon® 454 silica.

[0157] Comparative Examples 6-8, 6-9, and 6-10 show that without pre-destabilization of silica in the slurry, no silica-containing continuous rubber phase was produced, even when using the remaining process steps according to preferred methods to produce elastomer composite according to embodiments of the present invention. Comparative Examples 6-1, 6-2, 6-3, 6-4, 6-5, 6-6 and 6-7 show that even with prior destabilization of silica in the slurry (zeta potential of silica below 25 mV), a silica-containing continuous rubber phase could not be made with the combination of relative volumetric flow rates and degree of dilution of the destabilization agent,

(e.g., $Ca(NO_3)_2$ or acetic acid) in the reaction zone when fluids were mixed. Without being bound to any theory, it is theorized that such a low concentration of the destabilization agent in the mixture of slurry and latex in the reaction zone may reduce the coagulation rate of latex rubber particles so that a continuous rubber phase could not be formed within the short residence time in the reaction zone. In the Comparative Example 6-1, with 18.5 wt% of destabilized silica slurry and 30.6 wt% DRC latex concentrate, a relative flow ratio of destabilized slurry to latex was set at 0.73 (V/V) to deliver a silica to rubber ratio of 50 phr to the reaction zone. It is theorized that latex rubber particles did not coagulate within the 0.48 second residence time of the mixture in the reaction zone at such relatively low volumetric flow ratio of destabilized slurry to latex, whereby the original concentration of $Ca(NO_3)_2$ of 14.8 mM in the destabilized silica slurry was diluted by 58% to 6.2 mM in the reaction zone. Thus, it was not possible under these conditions to produce a solid or semi-solid silica-containing, continuous rubber phase comprising 50 phr silica. However, when a higher salt concentration (e.g., 0.5 wt% for Invention Example 5-37 versus 0.22 wt% for Comparative Example 6-1) was used (zeta potential of -17.1 mV versus -22 mV), and the volumetric flow ratio of slurry to latex was set at 2.1 to produce 50 phr silica-containing rubber, suitable product was made. Comparative Example 6-3 shows that a solid silica-containing, continuous rubber phase could not be made at settings of 40 phr silica and a volumetric flow ratio of destabilized slurry to field latex of 0.57 (V/V). Higher slurry-to-latex volumetric flow ratios would lead to less dilution of the salt in the reaction zone than in the Comparative Example 6-3, thus producing a solid silica-containing, continuous rubber phase.

[0158] The salt concentration in the 18.5% destabilized silica slurry of Comparative Example 6-2 was 0.48%, with a zeta potential of -17 mV, indicating a degree of destabilization on par with those of Invention Examples 5-41 (-14.1 mV), but no solid silica-containing, continuous

rubber phase was formed at a production setting of 30 phr silica content with latex concentrate at the relatively low flow ratio of selected for Comparative Example 6-2. Without wishing to be bound by any theory, it is believed that too much dilution of the salt and/or destabilized silica slurry by latex concentrate in the reaction zone in the Comparative Example 6-2 reduced the coagulation rate of the rubber latex particles in the reaction zone so much that a coherent continuous rubber phase would not form in the residence time of 0.36 seconds within the reaction zone.

[0159] When mixing field latex with a 10 wt% silica slurry destabilized by 0.65% $Ca(NO_3)_2$ (zeta potential at -15.4 mV), Comparative Example 6-5 did not produce a solid silica-containing, continuous rubber phase at a silica to rubber ratio of 60 phr and slurry-to-latex volumetric flow ratio of 0.57. These conditions did not deliver sufficient salt and/or destabilized slurry to the reaction zone for rapid coagulation of the rubber latex particles within the reaction zone. In general, either the degree of silica slurry destabilization and/or slurry-to-latex flow ratio adequate to coagulate latex concentrate were not sufficient to coagulate field latex.

[0160] Similar results were obtained when acid was employed to destabilize the silica slurry of Comparative Examples 6-6 and 6-7. When acid was used as the sole agent to destabilize the silica slurry, there was a preferred threshold acid-to-ammonia molar ratio in the mixture of the slurry and latex in the reaction zone, below which solid or semi-solid silica-containing continuous rubber phase would not form in the reaction zone. In these experiments, the threshold acid-to-ammonia molar ratio that is desired was always higher than 1.0, with the result that the pH of the product exiting the reaction zone was acidic. In the case of Comparative Examples 6-6 and 6-7, for silica-to-rubber ratio production settings of 20 phr and 25 phr, relatively low slurry-to-latex volumetric flow ratios of 0.28 and 0.36 were used, respectively. At these low flow ratios,

the acidic slurry was not sufficiently acidic to neutralize the ammonia in the latex. The acid-to-ammonia molar ratios for Comparative Examples 6-6 and 6-7 were 0.66 and 0.98, respectively. In both cases, only cloudy liquid sprayed out of the reaction zone. Using a higher slurry-to-latex volumetric flow ratio would deliver sufficient acid from slurry into the reaction zone for neutralizing ammonia from latex.

[0161] Example 7.

[0162] To explore the process variables that enable formation of a solid or semi-solid silica-containing continuous rubber phase, a series of experiments were conducted under various combinations of process variables, including, but not limited to, concentration of silica in the destabilized slurry, concentration of acid or salts in the destabilized slurry, types of latex (e.g. field latex and latex concentrate), concentration of ammonia in latex, latex lots, flow rates of destabilized slurry and latex, velocities of destabilized slurry and latex in reaction zone, and acid or salt concentrations in reaction zone. This series of experiments was carried out according to Process A, and calcium nitrate was used as the salt. The solid contents of fluids and the inlet nozzle velocities for the experiments are listed in Tables 7A and 7B for a latex concentrate and field latex, respectively. At a low slurry to latex volumetric flow ratio (i.e., low silica to rubber ratio in the reaction zone), the destabilized slurry and salt were diluted by the latex, and no solid or semi-solid silica-containing continuous rubber phase was formed. The setting for silica to rubber ratio was then gradually increased by raising the slurry-to-latex volumetric flow ratio until a solid or semi-solid silica-containing, continuous rubber phase was observed exiting the reaction zone. In Tables 7A and 7B, the "Silica Loading Delivered to Reaction Zone" indicates the lowest silica-to-rubber ratio at which a solid or semi-solid silica-containing, continuous rubber phase was produced. The minimum salt concentration in the reaction zone (including both

destabilized slurry and latex) for formation of solid or semi-solid silica-containing, continuous rubber phase was calculated for each set of experimental conditions (e.g., silica concentration in slurry, salt concentration in slurry, slurry velocity). For the first six examples listed in Table 7A, the silica concentration in the destabilized slurry was the same, namely 18.5 wt%, but the salt concentration in the destabilized slurry was varied, and the silica loading lower threshold for formation of a solid or semi-solid silica-containing, continuous rubber phase was determined in each example by increasing the latex volumetric flow rate until coagulum was formed. Results in Table 7A show that, when the salt concentration in the destabilized silica slurry was increased from 0.22 wt% to 0.75 wt%, it was possible to reduce the slurry-to-latex volumetric flow ratio, so as to obtain a solid or semi-solid silica-containing, continuous rubber phase having a lower silica to rubber ratio. For instance, by increasing the salt concentration from 0.22 wt% to 0.65 wt% of a 18.5 wt% silica slurry, the minimum silica phr setting for creating a solid or semi-solid silica-containing continuous rubber phase decreased from 80 phr silica to 35 phr silica as the relative volumetric flow of latex was increased and the ratio of slurry-to-latex volumetric flow rates was decreased from 1.17 to 0.51. Similar results were observed for other silica slurry concentrations and when acid was used to destabilize the silica slurry.

[0163] Table 7A. Solid or semi-solid silica-containing continuous rubber phase formation thresholds: phr silica loading and calcium nitrate concentration under various conditions when destabilized silica slurry was mixed with 50% diluted latex concentrate (31 wt% dry rubber content; 0.70 wt% ammonia content except for last sample, for which ammonia content was 0.53 wt%) using Process A.

Table 7A

Silica Conc. In Slurry (wt%)	$Ca(NO_3)_2$ in Slurry (wt%)	$[Ca^{2+}]$ in slurry (mM)	Zeta Potential (Est.) (mV)	Inlet Nozzle Velocity (m/s)[a]	Silica Loading Delivered to Reaction Zone (phr)	Slurry to latex flow ratio (v/v)	$[Ca^{2+}]$ Conc in Reaction Zone (mM)
18.5	0.22	14.8	-22.0	87	80	1.17	7.9
18.5	0.39	26.2	-18.4	46	46.3	0.68	10.5
18.5	0.48	32.3	-17.0	67	40	0.59	11.9
18.5	0.52	34.9	-16.5	58	45	0.66	13.8
18.5	0.65	43.6	-15.1	58	35	0.51	14.7
18.5	0.75	50.4	-14.1	59	35	0.51	17.0
26	0.68	47.6	-14.5	54	55	0.55	16.8
26	0.99	69.3	-12.1	77	50	0.50	23.0
11	0.36	23.2	-19.1	80	35	0.90	10.9
20	1.00	67.8	-12.2	49	35	0.49	22.2

a. The inlet nozzle velocity is the velocity of the silica slurry as it passes through a nozzle (3a) at first inlet (3) to the reaction zone prior to contacting the latex.

[0164] Table 7B. Solid or semi-solid silica-containing continuous rubber phase formation thresholds: phr silica loading and calcium nitrate concentration under various conditions when silica slurry was mixed with field latex using Process A.

Table 7B

Silica Conc. In Slurry (wt%)	$Ca(NO_3)_2$ in Slurry (wt%)	$[Ca^{2+}]$ in slurry (mM)	Zeta Potential Slurry (mV)	Inlet Nozzle Velocity (m/s)[a]	Silica Loading Lower Threshold (phr)	Slurry to latex ratio (v/v)	$[Ca^{2+}]$ Conc in Reaction Zone (mM)
10	0.65	41.7	-15.4	78	65	1.96	27.6
19.6	0.90	60.8	-12.9	71	65	0.95	29.6
20	1.0	67.7	-12.2	76	65	0.93	32.6
20	1.3	88.0	-10.6	76	50	0.72	36.7

a. The inlet nozzle velocity is the velocity of the silica slurry as it passes through a nozzle (3a) at first inlet (3) to the reaction zone prior to contacting the latex.

[0165] In a batch mode coagulation experiment conducted by mixing silica slurry with latex in a bucket under relatively low shear mixing, the minimum amount of the salt or acid to coagulate the latex in the mixture is a constant, independent of original concentration of salt or acid in the silica slurry before mixing. However, in preferred processes to produce elastomer composite according to various embodiments of the invention, the threshold concentration of the salt in the reaction zone for formation of a solid or semi-solid silica-containing, continuous rubber phase increases with increases in the salt concentration in the destabilized silica slurry before mixing (i.e. the degree of destabilization of silica slurry). For example, in Table 7A, one can see that the threshold concentration of $Ca(NO_3)_2$ for coagulating the latex concentrate is independent of silica concentration in the destabilized slurry, but depends strongly on the original salt concentration in the destabilized silica slurry. When the salt concentration increased from 14.8 mM to 69.3 mM, the threshold salt concentration increased from 7.9 mM to 23.0 mM. For comparison, a series of batch coagulation experiments were conducted in a bucket using low

shear stirring and it was determined that the threshold concentration of $Ca(NO_3)_2$ for coagulating the same latex concentrate was a constant at 10.7 mM, independent of both the original salt concentration in the destabilized silica slurry as well as the silica concentration in the destabilized slurry. These results highlight the importance of balancing the degree of destabilization of the silica slurry, rate of mixing, rate of silica particle agglomeration, and rate of latex coagulation under high shear for efficiently producing a solid or semi-solid silica-containing, continuous rubber phase.

[0166] Likewise, the threshold acid-to-ammonia ratio for formation of a solid or semi-solid silica-containing, continuous rubber phase according to embodiments of the invention is not a constant, but increases with the degree of acid destabilization of the silica slurry.

[0167] Based on the production variables described herein, such as the velocity of the destabilized silica slurry, the velocity of the latex, the relative flow rates of the destabilized silica slurry and latex fluids, the degree of destabilization of the silica slurry, the silica concentration in the destabilized slurry, the dry rubber content of the latex, and the ammonia concentration of the latex (e.g., the ammonia concentration can be reduced by bubbling nitrogen through the latex or on top of the liquid surface), it was possible to obtain and/or predict formation of a solid or semi-solid silica-containing, continuous rubber phase over a range of desired silica loadings. Thus, this process to produce elastomer composite according to the invention can be operated over an optimized range of variables.

[0168] **Comparative Example 8.**

[0169] The following comparative experiments utilizing a multi-step batch process were conducted as a comparison to a continuous process that successfully produced elastomer composites according to embodiments of the invention.

[0170] In these comparative examples, a slurry of silica was combined with elastomer latex under batch mixing conditions, using either a silica slurry that had been ground (as in the process of Process B above), or a silica slurry prepared without grinding, each at two slurry concentrations: 25 wt% and 6 wt%, respectively (based on the total weight of the slurry). The silica used in these examples was ZEOSIL® 1165 MP. The elastomer latex used in all experiments was high ammonia latex concentrate (60CX12021, from Chemionics Corporation, Tallmadge, Ohio) diluted by 50% (by weight) with deionized water.

[0171] **Experiment 8-A:** Batch mixing with ground silica slurry.

[0172] The silica slurry prepared above was mixed with a desired amount of deionized water in a 5 gallon bucket to achieve the target silica concentration of slurry.

[0173] For each run described below, the indicated quantity of silica slurry was taken from the slurry run tank and mixed for fifteen minutes with the indicated quantity of elastomer latex in a 5 gallon bucket- using an overhead low shear stirrer (Model #1750, Arrow Engineering Co, Inc., Hillside, NJ). Except in Run 5, calcium chloride salt was then added to the mixture and mixing continued until coagulation appeared to be complete. Unless otherwise indicated, the salt was added as a 20 wt% salt solution in deionized water. The amount of salt used (dry amount) is indicated below. The "target phr silica" reflects the amount of silica in phr expected to be present in the rubber composite based on the starting amount of silica used, assuming all silica was incorporated into all of the rubber. Runs 1-4 were dewatered and dried according to the Process B methods described above.

[0174] **Run 1** – Target 55 phr silica rubber composite using 25 wt% silica slurry.

Conditions (for approx. 1.9 kg dried material):

2.7 kg of 25 wt% silica slurry, ground

4.0 kg of latex concentrate

0.060 kg (equivalent dry amount) of salt in solution.

[0175] Observations: Big pieces of wet rubber composite were formed around the mixing blade after coagulation was complete. However, coagulation did not incorporate all of the rubber and silica into the coagulum, as a milky liquid remained in the mixing bucket and a layer of wet silica was deposited on the bottom of the bucket. The dried coagulum weighed about 0.5 kg, which was much less than the 1.9 kg targeted yield. A significant amount of silica appeared on the surface of the rubber product indicating poor distribution of silica within the rubber composite. The silica appeared to be very poorly mixed with rubber in the coagulum, and undispersed grains of silica were felt and seen throughout the coagulum. Silica particles were observed falling off dried coagulum. When dry rubber product was cut using a pair of scissors, silica particles fell from the cut surface. Following drying, TGA analysis of the rubber product indicated loadings of silica averaged about 44 phr.

[0176] **Run 2** – Target 70 phr silica rubber composite using 25 wt% silica slurry.

Conditions (for approx. 1.9 kg dried material):

3.1 kg of 25 wt% silica slurry, ground

3.6 kg of latex concentrate

0.060 kg of salt, added dry.

[0177] Observations: Big pieces of wet rubber were formed around the mixing blade and the post coagulation liquid was cloudy or milky. A layer of silica remained on the bottom of the bucket. Approximately 1 kg of dried coagulum was produced. Similar to Run 1, very poor distribution of silica particles within the rubber coagulum was observed. Following drying, TGA analysis of the rubber product revealed silica loadings averaging about 53 phr.

[0178] **Run 3** – Target 55 phr silica rubber composite using 6 wt% silica slurry.

Conditions (for approx. 2 kg dried material):

2.6 kg of 25 wt% silica slurry, ground

8.4 kg deionized water

4.0 kg of latex concentrate

0.090 kg of salt in solution.

[0179] Observations: After adding the salt, the whole mixture of latex and slurry became a soft gel. About 0.9 kg dry composite was made. Similar to Run 1, very poor distribution of silica particles within the rubber coagulum was observed. Following drying, the silica loading in the coagulum measured by TGA was about 45 phr.

[0180] **Run 4** – Target 70 phr silica rubber composite using 6 wt% silica slurry.

Conditions (for approx. 2 kg dried material):

3.1 kg of 25 wt% silica slurry, ground

9.9 kg water

3.7 kg of latex concentrate

0.10 kg of salt in solution.

[0181] Observations: After adding the salt, small crumbs formed in milky liquid. A sieve was used to collect and compact the small crumbs. Similar to Run 1, very poor dispersion of silica particles within the rubber coagulum was observed. About 0.7 kg dry composite was collected with silica loading in the crumb measured by TGA at about 50 phr.

[0182] **Run 5** Target 55 phr silica rubber composite using 25 wt% silica slurry destabilized with 1% of $CaCl_2$.

Conditions (for approx. 1.9 kg dried material):

4.0 kg of 25 wt% slurry containing 1% $CaCl_2$, ground

2.7 kg latex concentrate.

[0183] Observations: The latex was put in a 5-gallon bucket with an overhead low shear stir. The ground 25% destabilized silica slurry containing 1% of $CaCl_2$ was poured into the bucket with stirring, and stirring continued until coagulation was complete. Visual and tactile observations of the rubber piece revealed many large pockets (mm to cm size) of silica slurry within the rubber piece and a large quantity of silica particles trapped but not distributed within the solid rubber phase. The average silica loading in the dried coagulum measured by TGA was about 58 phr. Sample-to-sample variations of silica loadings were greater than 10 phr.

[0184] **Experiment 8-B:** Batch mixing using silica slurry without grinding.

[0185] For preparing the silica slurry without grinding, the silica was slowly added to water using only an overhead stirrer (Model #1750, Arrow Engineering Co, Inc., Hillside, NJ). When the silica appeared to be completely dispersed, the latex was added and the liquid mixture stirred for 20 minutes. The $CaCl_2$ salt solution was then added to the liquid mixture and allowed to mix until coagulation appeared to be complete. Samples were dried in an oven prior to TGA analysis.

[0186] **Run 5B** – Target 65 phr silica rubber composition using 25 wt% silica slurry.

Conditions (for approx. 1.9 kg dried material):

3.0 kg of 25 wt% silica slurry

3.8 kg of latex concentrate

0.06 kg of salt in solution.

[0187] Observations: After adding the salt, very large pieces of rubber coagulum were formed around the blade of the stirrer. After coagulation, a thick layer of silica settled at the bottom of the bucket. The rubber piece felt gritty and slimy. Grains of silica could be felt and

seen on the surface of the rubber coagulum and visual observation revealed very poor distribution of silica in the rubber coagulum. The silica loading in the coagulum was determined as 25 phr using TGA.

[0188] **Run 6** – Target 80 phr silica rubber composite using 25 wt% silica slurry.

Conditions (for approx. 1.9 kg dried material):

3.3 kg of 25 wt% silica slurry

3.4 kg of latex concentrate

0.06 kg of salt in solution.

[0189] Observations: The loading of silica in the rubber was determined as 35 phr and visual observation revealed very poor distribution of silica in the rubber coagulum.

[0190] **Run 7** – Target 110 phr silica rubber composite using 6 wt% silica slurry.

Conditions (for approx. 1.9 kg dried material, done in two batches):

1.0 kg of 25 wt% silica slurry

15.6 kg of water

3.0 kg of latex concentrate

0.120 kg of salt in solution.

[0191] Observations: Small rubber crumbs were formed in the bucket and the liquid remaining after coagulation was mostly clear, with a layer of silica on the bottom of the bucket. TGA measured silica loading in the rubber product averaged about 30 phr. The coagulum was elastic, with silica grains on the surface. As it dried, silica could easily be brushed off the surface, and visual observation revealed very poor distribution of silica in the rubber coagulum.

[0192] **Run 8** – Target 140 phr silica rubber composite using 6 wt% silica slurry.

Conditions (for approx. 1.9 kg dried material, done in two batches):

1.0 kg of 25 wt% silica slurry

15.7 kg of water

2.4 kg of latex concentrate

0.110 kg of salt in solution.

[0193] Observations: Small rubber crumbs were formed in the bucket and the liquid remainder after coagulation was mostly clear, with a layer of silica on the bottom of the bucket. TGA measured silica loading in the rubber product averaged about 35 phr. Particles of silica were settled on the surface of the rubber product that could be brushed free as it dried, and visual observation revealed very poor distribution of silica in the rubber coagulum.

[0194] **Summary of Observations.** Compared with the continuous process of making elastomer composite, as for instance in Examples 5 and 7, batch latex mixing process of Comparative Example 8 were incapable of achieving the desired quality or quantity of silica dispersion in rubber. With ground silica slurries, the actual silica loading in rubber products produced with batch mixing was observed to be < 55 phr. After coagulation, a significant amount of silica settled at the bottom of the mixing bucket and appeared on the surface of the rubber product , indicating poor capture of silica particles within the rubber coagulum. With silica slurries that had not been ground, the actual silica loading in rubber produced with batch mixing was limited to 30 phr to 35 phr. After coagulation, a thick layer of silica settled at the bottom of the mixing bucket, the silica appeared to be very poorly mixed with rubber in the coagulum, and undispersed grains of silica were felt and seen throughout the coagulum. Compared to preferred processes for producing elastomer composite according to embodiments of the present invention, batch mixing processes yielded poor incorporation and distribution of silica particles within the rubber matrix of the coagulum. In the product of each of these batch mixing runs, silica particles

were observed falling off dried coagulum. When dry rubber composite was cut using a pair of scissors, silica particles fell from the cut surface. Such loss of silica particles was not observed in examining the solid or semi-solid silica-containing continuous rubber phase produced by preferred processes for producing elastomer composite according to embodiments of the invention.

[0195] Figure 3 plots the mechanical properties of the Comparative Example 1 samples (stars), and the vulcanized elastomer composites of Runs 1-4 of Comparative Example 8 (triangles) with respect to silica loading (Figure 3A - modulus ratio T300/T100, Figure 3B – tensile strength (MPa), Figure 3C – tan delta 60, and Figure 3D – elongation at break (%) * tensile strength (MPa)). In each graph, the Example 5 samples meeting the equations T300/T100 $\geq$ -0.024s + 6.3 (Figure 3A), tensile strength (MPa $\geq$ -0.21s + 41 (Figure 3B), tan delta 60 $\leq$ 0.0022s – 0.05 (Figure 3C), or elongation at break (%) * tensile strength (MPa) $\geq$ -211s +27543 (Figure 3D), where s is the silica loading in phr, are plotted as diamonds. The graphs show that that improved mechanical properties generally correlated with the use of one or more of latex concentrate and/or a salt in a continuous wet masterbatch method, whether or not acid was used as an additional destabilization agent. In contrast, the methods of Comparative Example 8 were unable to consistently produce high quality rubber meeting more than one of the criteria in the equations above.

[0196] Figure 4 plots the modulus ratio (T300/T100) of the Comparative Example 1 samples (stars), the vulcanized elastomer composites of Runs 1-4 of Comparative Example 8 (triangles), and vulcanized elastomer composites of Example 5 (diamonds) with respect to the tan delta 60 value. The graph demonstrates that only elastomer composites according to embodiments of the invention are able to achieve both high modulus ratio (greater than 5.5) and low tan delta (less

than 0.05) (box 301). As modulus ratio generally decreases with loading, more highly loaded silica elastomer composites may demonstrate desirable properties without meeting these criteria.

[0197] Figure 5 plots the modulus ratio (T300/T100; diamonds) and tan delta 60 (squares) of the vulcanized elastomer composites of Example 5 with respect to swell index. Swell index was measured by incubating a 0.5g sample in toluene (enough to cover the sample) for 120 hours, with the toluene changed after 48 hours. The sample is weighed to obtain a swollen weight, dried overnight at ambient temperature and pressure and then again overnight in a vacuum oven at 50 ^{0}C, after which the sample is weight to obtain a dried weight. The swell index is the difference between the swollen weight and the dried weight, divided by the dried weight. The graph shows that an optimum to provide a high modulus ratio of the vulcanized elastomer composite at a swell index from about 1.80 to about 2.20, especially from about 1.90 to about 2.10. Thus, the combination of mechanical properties of vulcanized elastomer composite may be optimized by adjusting the swell index, for example, by adjusting the type of accelerator. T

[0198] **Example 9**

[0199] In these examples, the process to produce silica elastomer composite was run on the apparatus shown in Figure 1 (either (a) or (b)) under various operating conditions as described in Table 8, using either Process A or Process B as described above. Operating conditions were selected to yield silica-containing continuous rubber phase with the silica to rubber ratios set forth in Table 8. In each example, the silica containing continuous rubber phase included at least 40 wt% aqueous fluid. The approximate elongation at break of the silica-containing continuous rubber phase emerging from the reaction zone is also given in Table 8.

Table 8

Example	Process A/B	Silica[a] concentration in Slurry (wt%)	Latex Type	Rubber concentration in Latex (DRC) (wt%)	Latex wt% NH_3 (wt%)	Salt Type	Salt wt% in Slurry (wt%)	Zeta Potential (Est.)[b] (mV)
9-1	B	25	Conc.	31	0.27	$CaCl_2$	0.75	-11.4
9-2	B	25	Conc.	31	0.27	$CaCl_2$	0.75	-11.4
9-3	B	25	Conc.	31	0.27	$CaCl_2$	1.0	-9.5
9-4	B	25	Conc.	31	0.27	N/A	0	-11.2
9-5	B	25	Conc.	31	0.27	N/A	0	-11.2
9-6	B	25	Conc.	31	0.27	N/A	0	-17.8
9-7	B	12.5	Conc.	31	0.27	$CaCl_2$	0.50	
9-8	A	20	Conc.	31.9	0.53	$Ca(NO_3)_2$	1.0	-12.2
9-9	A	20.0	Field	32.7	0.33	N/A	0	-17.6
9-10	A	20.0	Field	32.7	0.33	N/A	0	-17.6
9-11	A	20.0	Field	32.7	0.33	$Ca(NO_3)_2$	1	-6.1
9-12	A	20.0	Field	32.7	0.33	$Ca(NO_3)_2$	1	-6.1
9-13	A	20.0	Field	32.7	0.33	$Ca(NO_3)_2$	1	-6.1
9-14	B	25	Conc.	31.0	0.27	$CaCl_2$	1.50	-6.9
9-15	B	25	Conc.	31.0	0.27	$CaCl_2$	1.00	-9.5
9-16	A	16.5	Conc.	30.6	0.68	N/A	0.00	-16.5
9-17	B	25	Conc.	30.5	0.27	$Ca(NO_3)_2$	0.59	-3.0
9-18	B	25	Conc.	31	0.27	$Ca(NO_3)_2$	1.00	-12.1

Table 8 (continued)

Example	Acid Type	Acid wt% in Slurry (wt%)	Acid/ NH_3 molar ratio	Inlet Nozzle Velocity[c] (m/s)	Actual Silica loading (phr)	Slurry Flow Rate[d] (L/hr)	Latex Flow Rate[d] (L/hr)	Slurry-to-Latex Flow Ratio (v/v)	Elongation @ Break of Solid Rubber Phase (%)
9-1	N/A	0	0.00	19	95	60	67	0.898	300-400
9-2	N/A	0	0.00	19	101	60	53	1.141	300-600
9-3	N/A	0	0.00	19	92	60	67	0.898	200-250
9-4	Formic	2.0	1.36	19	45	60	142	0.423	200-400
9-5	Formic	2.0	1.87	19	47	60	103	0.581	150-250
9-6	Acetic	2.6	1.35	19	61	60	142	0.423	200-300
9-7	Acetic	1.3	1.86	37	33	60	48	1.245	300-400
9-8	N/A	0	0.00	49	38.4	540	703	0.77	130
9-9	Acetic	2.8	3.14	75	54.8	945	826	1.14	130-150
9-10	Acetic	2.8	3.93	75	67.2	945	660	1.43	120
9-11	Acetic	2.8	1.77	76	54.9	963	841	1.14	120
9-12	Acetic	2.8	2.36	76	43.3	630	734	0.86	150
9-13	Acetic	2.8	1.77	76	34.0	630	978	0.64	150-200
9-14	N/A	0	0	19	138	60	43	1.38	300-400
9-15	N/A	0	0	19	122	60	37	1.63	300-500
9-16	acetic	3.6	1.81	64	40.4	800	743	1.08	120-150
9-17	N/A	0	0	75	70.9	60	58	1.040	200-300
9-18	N/A	0	0	75	ND	60	142	0.422	130-150

N/A = not applicable ND = not determined

a. Example 9-17 used Agilon 400 silica (obtained from PPG Industries Inc.). All other examples used ZEOSIL® Z1165 MP precipitated silica.

b. Zeta potential values were estimated by interpolation of experimentally determined curves of zeta

potential dependence on concentration of the salt or the acid of the slurries of the same grade of silica.

c. The inlet nozzle velocity is the velocity of the silica slurry as it passes through a nozzle (3a) at first inlet (3) to the reaction zone (13) prior to contacting the latex.

d. Slurry and Latex Flow Rates are the volumetric flow rates in L/hour of the silica slurry and the latex fluid, respectively, as they are delivered to the reaction zone.

[0200] The results show that highly elastic silica-containing continuous rubber phase materials in the form of solid articles can be achieved at a variety of operating conditions. Higher elongation is correlated with the use of latex concentrate, lower production rates (rate of flow of material on a dry basis), increased residence time in the reaction zone, and/or lower flow rates of latex and/or destabilized silica slurry.

[0201] **Example 10.**

[0202] In these examples, processes to produce elastomer composite according to various embodiments of the invention were run in the apparatus shown in Figure 1(a) under various conditions as described in Table 9, utilizing Process A with field latex. Example 10-4 employed a 10 wt% silica slurry; all other samples were produced with a 20% silica slurry. All examples used ZEOSIL® Z1165 MP precipitated silica. Operating conditions were selected to yield a solid or semi-solid silica-containing, continuous rubber phase with the silica to rubber ratios set forth in Table 9. Samples were dewatered according to Process A, followed by additional dewatering and drying according to Process B without addition of coupling agent or antioxidant.

Table 9

Example Number	Rubber in latex (DRC, wt%)	NH_3 in latex (wt%).	Salt wt% in slurry[a]	Acid wt% in slurry[b]	Acid/ NH_3 molar ratio	Slurry to MB rate (L/hr)[c]	Latex to MB rate (L/hr)[c]

Example Number	Rubber in latex (DRC, wt%)	NH_3 in latex (wt%).	Salt wt% in slurry[a]	Acid wt% in slurry[b]	Acid/ NH_3 molar ratio	Slurry to MB rate (L/hr)[c]	Latex to MB rate (L/hr)[c]
1	32.7%	0.35%	1%	0	0.00	738	794
2	32.7%	0.35%	1%	0	0.00	738	688
3	32.7%	0.35%	1.3%	0	0.00	738	543
4	32.7%	0.35%	0.65%	0	0.00	950	484
5	32.7%	0.33%	0	2.80%	2.36	630	734
6	32.7%	0.33%	0	2.80%	3.14	945	826
7	32.7%	0.33%	0	2.80%	3.93	945	660
8	32.7%	0.33%	1%	2.80%	3.14	963	841
9	32.7%	0.33%	1%	2.80%	2.36	630	734
10	30.4%	0.37%	0	3.30%	2.69	738	791

a. All examples with salt employed calcium nitrate.

b. All examples with acid employed acetic acid

c. Slurry and Latex Flow Rates are the volumetric flow rates in L/hour of the silica slurry and the latex fluid, respectively, as they are delivered to the reaction zone.

Table 9 (continued)

Example Number	Inlet Nozzle Velocity (m/s)[d]	Zeta Potential estimated (mV)[e]	Slurry-to-latex ratio (v/v)	Actual SiO_2 Loading	T300/ T100
1	76	-12.2	0.930	45.4	5.61
2	76	-12.2	1.073	52.3	5.13
3	76	-10.6	1.359	57.0	4.84
4	78	-15.4	1.963	52	5.68
5	76	-17.6	0.858	41.8	5.39
6	75	-17.6	1.145	54.8	5.53
7	75	-17.6	1.431	67.2	5.40
8	76	-6.1	1.145	54.9	5.13
9	76	-6.1	0.858	43.3	5.27
10	89	-16.8	0.933	44.1	5.12

d. The inlet nozzle velocity is the velocity of the silica slurry as it passes through a nozzle (3a) at first inlet (3) to the reaction zone (13) prior to contacting the latex.

e. Zeta potential values were estimated by interpolation of experimentally determined curves of zeta potential dependence on concentration of the salt or the acid of the slurries of the same grade of silica.

[0203] In all the examples, the selected operating conditions yielded a solid or semi-solid silica-containing, continuous rubber phase in a roughly cylindrical form. The semi-solid material remained coherent, retaining solids content and expelling water, when pressed. The solid product contained a major amount of water, was elastic and compressible, and expelled water and retained solids content when manually compressed. Silica particles were observed to be uniformly distributed throughout a continuous rubber phase and this product was substantially devoid of free silica particles and larger silica grains, both on exterior and interior surfaces. As shown in Figure 6, the use of a process in which a stream of a destabilized silica slurry is combined with an elastomer latex provides an improvement in reinforcement in comparison to elastomer composite prepared by mixing dry silica with dry rubber (corresponding to stars in Figure 6). The inventive examples (diamonds) listed in Table 9 and shown in Figure 6 all have modulus ratios (T300/T100) equal to or greater than -0.025s +6.2, where s is the silica loading.

[0204] The present invention includes the following aspects/embodiments/features in any order and/or in any combination:

[0205] A vulcanizable elastomer composite comprising at least 40 phr of silica dispersed in natural rubber, wherein, when the vulcanizable elastomer composite is vulcanized, the resulting vulcanizate exhibits a ratio T300/T100 of at least -0.024s + b, wherein s is the amount of silica in the vulcanizable elastomer composite expressed as parts per hundred weight of rubber (phr) and b is 6.3, and at least one additional property selected from

a) a tan delta 60 of at most 0.0022s – c, wherein c is 0.05;

b) a tensile strength in MPa of at least -0.21s + d, wherein d is 41;

c) elongation at break (%) * tensile strength (MPa) of at least -211s +e, where e = 27543; and

d) a silica content of at least 55 phr, for example, at least 60 phr.

[0206] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizate exhibits a ratio T300/T100 of at least -0.024s + b, wherein b is 6.4, 6.6, or 6.8.

[0207] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizate exhibits tan delta 60 of at most 0.0022s – c, wherein c is 0.06.

[0208] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizate exhibits a tensile strength in MPa of at least -0.21s + d, wherein d is 41.4

[0209] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizate exhibits a ratio T300/T100 from -0.024s + b to at most 7.

[0210] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizable elastomer composite comprises up to about 180 phr or up to about 100 phr of silica.

[0211] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizable elastomer composite comprises up to 10% by weight of carbon black with respect to the total weight of reinforcing particles in the vulcanizable elastomer composite.

[0212] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizate exhibits a tan delta 60 from 0.02 to 0.0022s – c.

[0213] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizate exhibits a tensile strength of from -0.21s + d to 40 or 35 MPa.

[0214] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizate exhibits an elongation at break (%) * tensile strength (MPa) of from -211s +e to 21500.

[0215] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the silica comprises precipitated silica having a surface area from about 20 m^2/g to about 450 m^2/g as measured by nitrogen adsorption, for example, about 120 to about 225 m^2/g, 20 m^2/g to about 450 m^2/g; about 30 m^2/g to about 450 m^2/g; about 30 m^2/g to about 400 m^2/g; about 120 m^2/g to about 225 m^2/g; about 80 m^2/g to about 200 m^2/g; or about 60 m^2/g to about 250 m^2/g.

[0216] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizable elastomer composite comprises a dewatered wet masterbatch of silica dispersed as a slurry in natural rubber latex.

[0217] A vulcanized elastomer composite comprising a vulcanizate of the vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, optionally having a swell index of about 1.80 to about 2.20, for example, from about 1.90 to about 2.10 or from about 1.95 to about 2.05.

[0218] A vulcanizable elastomer composite comprising at least 55 phr of silica dispersed in natural rubber, wherein, when the vulcanizable elastomer composite is vulcanized, the resulting vulcanizate exhibits a ratio T300/T100 of at least 5.

[0219] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizable elastomer composite comprises at least 60 phr of silica.

[0220] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizate exhibits elongation at break (%) * tensile strength (MPa) of at least -211s +e, where e = 27543 and s is the silica loading in phr.

[0221] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizate exhibits a ratio T300/T100 of at most 7.

[0222] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizable elastomer composite comprises up to 180 phr or up to 100 phr of silica.

[0223] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizable elastomer composite comprises up to 10% by weight of carbon black with respect to the total weight of reinforcing particles in the vulcanizable elastomer composite.

[0224] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the silica comprises precipitated silica having a surface area from about 20 m^2/g to about 450 m^2/g as measured by nitrogen adsorption, for example, about 120 to about 225 m^2/g, 20 m^2/g to about 450 m^2/g; about 30 m^2/g to about 450 m^2/g; about 30

m^2/g to about 400 m^2/g; about 120 m^2/g to about 225 m^2/g; about 80 m^2/g to about 200 m^2/g; or about 60 m^2/g to about 250 m^2/g.

[0225] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizable elastomer composite comprises a dewatered wet masterbatch of silica dispersed as a slurry in natural rubber latex.

[0226] A vulcanized elastomer composite comprising a vulcanizate of the vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, optionally having a swell index of about 1.80 to about 2.20, for example, about 1.90 to about 2.10 or about 1.95 to 2.05.

[0227] A vulcanizable elastomer composite comprising silica, for example, at least 40 phr of silica, dispersed in natural rubber, wherein, when the vulcanizable elastomer composite is vulcanized, the resulting vulcanizate exhibits a ratio T300/T100 of at least 6.3.

[0228] A vulcanizable elastomer composite comprising at least 40 phr of silica, for example, at least 50 phr, dispersed in natural rubber, wherein when the vulcanizable elastomer composite is vulcanized, it has a ratio T300/T100 of at least -0.025s + 6.2, for example, at least -0.025s + 6.3 or 6.4. The vulcanizable elastomer composite may comprise a dewatered wet masterbatch of silica dispersed as a slurry in field latex, which may be stabilized, e.g., with ammonia, desludged, or chemically or enzymatically modified.

[0229] A vulcanizable elastomer composite comprising silica, for example, at least 40 or 55 phr of silica, dispersed in natural rubber, wherein, when the vulcanizable elastomer composite is vulcanized, the resulting vulcanizate exhibits a ratio T300/T100 of at least 5.5 and a tan delta 60 of at most 0.05.

[0230] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizable elastomer composite comprises at least 55 phr of silica.

[0231] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizate exhibits a tan delta 60 of at least 0.02.

[0232] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizate exhibits a ratio T300/T100 of at most 7.

[0233] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizable elastomer composite comprises up to 180 phr or up to 100 phr of silica.

[0234] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizable elastomer composite comprises up to 10% by weight of carbon black with respect to the total weight of reinforcing particles in the vulcanizable elastomer composite.

[0235] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the silica comprises precipitated silica having a surface area from about 20 m^2/g to about 450 m^2/g as measured by nitrogen adsorption, for example, about 120 to about 225 m^2/g, 20 m^2/g to about 450 m^2/g; about 30 m^2/g to about 450 m^2/g; about 30 m^2/g to about 400 m^2/g; about 120 m^2/g to about 225 m^2/g; about 80 m^2/g to about 200 m^2/g; or about 60 m^2/g to about 250 m^2/g.

[0236] The vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanizable elastomer composite comprises a dewatered wet masterbatch of silica dispersed as a slurry in natural rubber latex.

[0237] A vulcanized elastomer composite comprising a vulcanizate of the vulcanizable elastomer composite of any preceding or following embodiment/feature/aspect, optionally having a swell index of about 1.80 to about 2.20, for example, about 1.90 to 2.10 or about 1.95 to 2.05.

[0238] A vulcanized elastomer composite comprising at least 40 phr of silica dispersed in natural rubber, wherein the vulcanized elastomer composite exhibits one or more of the following:

a) a ratio T300/T100 of at least -0.024s + b, wherein s is the amount of silica in the vulcanized elastomer composite expressed as parts per hundred weight of rubber (phr) and b is 6.3, and a tan delta 60 of at most 0.0022s – c, wherein c is 0.05;

b) a ratio T300/T100 of at least 5 and a silica loading of at least 55 phr;

c) a ratio T300/T100 of at least 6.3; and

d) a ratio T300/T100 of at least -0.024s + b, wherein s is the amount of silica in the vulcanized elastomer composite expressed as parts per hundred weight of rubber (phr) and b is 6.3, and a tensile strength in MPa of at least -0.21s + d, wherein d is 41.

[0239] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanized elastomer composite exhibits a ratio T300/T100 of at least -0.024s + b, wherein b is 6.4, 6.6, or 6.8.

[0240] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanized elastomer composite exhibits a tan delta 60 of at most 0.0022s – c, wherein c is 0.06.

[0241] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanized elastomer composite exhibits a tensile strength in MPa of at least -0.21s + d, wherein d is 41.4.

[0242] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanized elastomer composite comprises up to 180 phr or up to 100 phr of silica.

[0243] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanized elastomer composite comprises at least 55 phr silica.

[0244] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanized elastomer composite comprises up to 10% by weight of carbon black with respect to the weight of particulate filler in the vulcanized elastomer composite.

[0245] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanized elastomer composite exhibits a ratio T300/T100 of at most 7.

[0246] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanized elastomer composite exhibits a tan delta 60 of at least 0.02.

[0247] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanized elastomer composite exhibits a tensile strength of at most 40 or 35 MPa.

[0248] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanized elastomer composite exhibits elongation at break (%) * tensile strength (MPa) of at least -211s +e, where e = 27543.

[0249] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanized elastomer composite exhibits elongation at break (%) * tensile strength (MPa) of at most 21500.

[0250] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the silica comprises precipitated silica having a surface area from about 20 m^2/g to about 450 m^2/g as measured by nitrogen adsorption, for example, about 120 to about 225 m^2/g, 20 m^2/g to about 450 m^2/g; about 30 m^2/g to about 450 m^2/g; about 30 m^2/g to about 400 m^2/g; about 120 m^2/g to about 225 m^2/g; about 80 m^2/g to about 200 m^2/g; or about 60 m^2/g to about 250 m^2/g.

[0251] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanized elastomer composite comprises a vulcanizate of a dewatered wet masterbatch of silica dispersed as a slurry in natural rubber latex.

[0252] The vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the vulcanized elastomer composite has a swell index of about 1.80 to about 2.20, for example, about 1.90 to about 2.10 or about 1.95 to about 2.00.

[0253] The vulcanizable elastomer composite or vulcanized elastomer composite of any preceding or following embodiment/feature/aspect, wherein the silica comprises precipitated silica.

[0254] A solid silica-containing continuous rubber phase article comprising at least 40 parts per hundred of rubber (phr) of silica dispersed in natural rubber and at least 40 wt%

aqueous fluid, wherein the solid silica-containing continuous rubber phase article exhibits an elongation at break of at least about 100%.

[0255] The solid silica-containing continuous rubber phase article of any preceding or following embodiment/feature/aspect, wherein the solid silica-containing continuous rubber phase article exhibits an elongation at break of about 100% to about 600%, for example, 100% to about 600%, for example, about 120% to about 200%, about 100% to about 150%, about 130% to about 250%, about 150% to about 200%, about 200% to about 300%, about 300% to about 600%, about 300% to about 500%, or about 300% to about 400%.

[0256] The solid silica-containing continuous rubber phase article of any preceding or following embodiment/feature/aspect, wherein the solid silica-containing continuous rubber phase article comprises from about 40 to about 180 phr or from about 40 to about 100 phr of silica, for example, from about 50 phr to about 150 phr.

[0257] The solid silica-containing continuous rubber phase article of any preceding or following embodiment/feature/aspect, wherein the silica comprises precipitated silica having a surface area from about 20 m^2/g to about 450 m^2/g as measured by nitrogen adsorption, for example, about 120 to about 225 m^2/g, 20 m^2/g to about 450 m^2/g; about 30 m^2/g to about 450 m^2/g; about 30 m^2/g to about 400 m^2/g; about 120 m^2/g to about 225 m^2/g; about 80 m^2/g to about 200 m^2/g; or about 60 m^2/g to about 250 m^2/g.

[0258] The solid silica-containing continuous rubber phase article of any preceding or following embodiment/feature/aspect, wherein the solid silica-containing continuous rubber phase article comprises up to 10% by weight of carbon black with respect to the total weight of reinforcing particles in the solid silica-containing continuous rubber phase article.

[0259] The solid silica-containing continuous rubber phase article of any preceding or following embodiment/feature/aspect, wherein the solid silica-containing continuous rubber phase article comprises from about 40% to about 90% by weight of water, for example, from about 50% to about 85% or from about 60% to about 80%.

[0260] The present invention can include any combination of these various features or embodiments above and/or below as set forth in any sentences and/or paragraphs herein. Any combination of disclosed features herein is considered part of the present invention and no limitation is intended with respect to combinable features.

[0261] Applicants specifically incorporate the entire contents of all cited references in this disclosure. Further, when an amount, concentration, or other value or parameter is given as either a range, preferred range, or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

[0262] Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the present specification and practice of the present invention disclosed herein. It is intended that the present specification and examples be considered as exemplary only with a true scope and spirit of the invention being indicated by the following claims and equivalents thereof.

WHAT IS CLAIMED IS:

1. A vulcanizable elastomer composite comprising at least 40 phr of silica dispersed in natural rubber, wherein, when the vulcanizable elastomer composite is vulcanized, the resulting vulcanizate exhibits a ratio T300/T100 of at least -0.024s + b, wherein s is the amount of silica in the vulcanizable elastomer composite expressed as parts per hundred weight of rubber (phr) and b is 6.3, and at least one additional property selected from
    a. a tan delta 60 of at most 0.0022s – c, wherein c is 0.05;
    b. a tensile strength in MPa of at least -0.21s + d, wherein d is 41;
    c. elongation at break (%) * tensile strength (MPa) of at least -211s +e, where e = 27543; and
    d. a silica content of at least 55 phr, for example, at least 60 phr.
2. The vulcanizable elastomer composite of claim 1, wherein the vulcanizate exhibits a ratio T300/T100 of at least -0.024s + b, wherein b is 6.8.
3. The vulcanizable elastomer composite of claim 1 or 2, wherein the vulcanizate exhibits tan delta 60 of at most 0.0022s – c, wherein c is 0.06.
4. The vulcanizable elastomer composite of any of claims 1-3, wherein the vulcanizate exhibits a tensile strength in MPa of at least -0.21s + d, wherein d is 41.4
5. The vulcanizable elastomer composite of any of claims 1-4, wherein the vulcanizate exhibits a ratio T300/T100 of at most 7.
6. The vulcanizable elastomer composite of any of claims 1-5, wherein the vulcanizable elastomer composite comprises up to about 180 phr of silica.
7. The vulcanizable elastomer composite of any of claims 1-6, wherein the vulcanizable elastomer composite comprises up to 10% by weight of carbon black with respect to the total weight of reinforcing particles in the vulcanizable elastomer composite.
8. The vulcanizable elastomer composite of any of claims 1-7, wherein the vulcanizate exhibits a tan delta 60 of at least 0.02.

9. The vulcanizable elastomer composite of any of claims 1-8, wherein the vulcanizate exhibits a tensile strength of at most 40 or 35 MPa.

10. The vulcanizable elastomer composite of any of claims 1-9, wherein the vulcanizate exhibits an elongation at break (%) * tensile strength (MPa) of at most 21500.

11. The vulcanizable elastomer composite of any of claims 1-10, wherein the silica comprises precipitated silica having a surface area from about 20 m^2/g to about 450 m^2/g as measured by nitrogen adsorption.

12. The vulcanizable elastomer composite of any of claims 1-11, wherein the vulcanizable elastomer composite comprises a dewatered wet masterbatch of silica dispersed as a slurry in natural rubber latex.

13. A vulcanized elastomer composite comprising a vulcanizate of the vulcanizable elastomer composite of any of claims 1-12, optionally having a swell index of about 1.80 to about 2.20.

14. A vulcanizable elastomer composite comprising silica dispersed in natural rubber, wherein, when the vulcanizable elastomer composite is vulcanized, the resulting vulcanizate exhibits a ratio T300/T100 of at least 6.3.

15. The vulcanizable elastomer composite of claim 14, comprising at least 40 phr of silica.

16. A vulcanizable elastomer composite comprising at least 55 phr of silica dispersed in natural rubber, wherein, when the vulcanizable elastomer composite is vulcanized, the resulting vulcanizate exhibits a ratio T300/T100 of at least 5.

17. The vulcanizable elastomer composite of any of claims 14-16, wherein the vulcanizable elastomer composite comprises a dewatered wet masterbatch of silica dispersed as a slurry in natural rubber latex.

18. A vulcanizable elastomer composite comprising at least 40 phr of silica dispersed in natural rubber, wherein when the vulcanizable elastomer composite is vulcanized, it has a ratio T300/T100 of at least -0.025s + 6.2.

19. The vulcanizable elastomer composite of claim 18, wherein the vulcanizable elastomer composite comprises a dewatered wet masterbatch of silica dispersed as a slurry in field latex.

20. The vulcanizable elastomer composite of any of claims 14-19, wherein the vulcanizable elastomer composite comprises at least 60 phr of silica.

21. The vulcanizable elastomer composite of any of claims 14 -20, wherein the vulcanizate exhibits elongation at break (%) * tensile strength (MPa) of at least -211s +e, where e = 27543 and s is the silica loading in phr.

22. The vulcanizable elastomer composite of any of claims 14 - 21, wherein the vulcanizate exhibits a ratio T300/T100 of at most 7.

23. The vulcanizable elastomer composite of any of claims 14-22, wherein the vulcanizable elastomer composite comprises up to 180 phr of silica.

24. The vulcanizable elastomer composite of any of claims 14-23, wherein the vulcanizable elastomer composite comprises up to 10% by weight of carbon black with respect to the total weight of reinforcing particles in the vulcanizable elastomer composite.

25. The vulcanizable elastomer composite of any of claims 14-24, wherein the silica comprises precipitated silica having a surface area from about 20 m^2/g to about 450 m^2/g as measured by nitrogen adsorption.

26. A vulcanized elastomer composite comprising a vulcanizate of the vulcanizable elastomer composite of any of claims 14-25, optionally having a swell index of about 1.80 to about 2.20.

27. A vulcanizable elastomer composite comprising silica dispersed in natural rubber, wherein, when the vulcanizable elastomer composite is vulcanized, the resulting vulcanizate exhibits a ratio T300/T100 of at least 5.5 and a tan delta 60 of at most 0.05.

28. The vulcanizable elastomer composite of claim 27, wherein the vulcanizable elastomer composite comprises at least 40 phr of silica.

29. The vulcanizable elastomer composite of claim 27 or 28, wherein the vulcanizate exhibits a tan delta 60 of at least 0.02.

30. The vulcanizable elastomer composite of any of claims 27 -29, wherein the vulcanizate exhibits a ratio T300/T100 of at most 7.

31. The vulcanizable elastomer composite of any of claims 27-30, wherein the vulcanizable elastomer composite comprises at least 55 phr of silica.

32. The vulcanizable elastomer composite of any of claims 27-31, wherein the vulcanizable elastomer composite comprises up to 10% by weight of carbon black with respect to the total weight of reinforcing particles in the vulcanizable elastomer composite.

33. The vulcanizable elastomer composite of any of claims 27-32, wherein the silica comprises precipitated silica having a surface area from about 20 m^2/g to about 450 m^2/g as measured by nitrogen adsorption.

34. The vulcanizable elastomer composite of any of claims 27-33, wherein the vulcanizable elastomer composite comprises a dewatered wet masterbatch of silica dispersed as a slurry in natural rubber latex.

35. A vulcanized elastomer composite comprising a vulcanizate of the vulcanizable elastomer composite of any of claims 27-34, optionally having a swell index of about 1.80 to about 2.20.

36. A vulcanized elastomer composite comprising at least 40 phr of silica dispersed in natural rubber, wherein the vulcanized elastomer composite exhibits one or more of the following:

    a. a ratio T300/T100 of at least -0.024s + b, wherein s is the amount of silica in the vulcanized elastomer composite expressed as parts per hundred weight of rubber (phr) and b is 6.3, and a tan delta 60 of at most 0.0022s – c, wherein c is 0.05;

    b. a ratio T300/T100 of at least 5 and a silica loading of at least 55 phr;

    c. a ratio T300/T100 of at least 6.3; and

    d. a ratio T300/T100 of at least -0.024s + b, wherein s is the amount of silica in the vulcanized elastomer composite expressed as parts per hundred weight of rubber (phr) and b is 6.3, and a tensile strength in MPa of at least -0.21s + d, wherein d is 41.

37. The vulcanized elastomer composite of claim 36, wherein the vulcanized elastomer composite exhibits a ratio T300/T100 of at least -0.024s + b, wherein b is 6.8.

38. The vulcanized elastomer composite of any of claims 36-37, wherein the vulcanized elastomer composite exhibits a tan delta 60 of at most 0.0022s – c, wherein c is 0.06.

39. The vulcanized elastomer composite any of claims 36-38, wherein the vulcanized elastomer composite exhibits a tensile strength in MPa of at least -0.21s + d, wherein d is 41.4.

40. The vulcanized elastomer composite of any of claims 36-39, wherein the vulcanized elastomer composite comprises up to 180 phr of silica.

41. The vulcanized elastomer composite of any of claims 36-40, wherein the vulcanized elastomer composite comprises at least 55 phr silica.

42. The vulcanized elastomer composite of any of claims 36-41, wherein the vulcanized elastomer composite comprises at least 60 phr silica

43. The vulcanized elastomer composite of any of claims 36-42, wherein the vulcanized elastomer composite comprises up to 10% by weight of carbon black with respect to the weight of particulate filler in the vulcanized elastomer composite.

44. The vulcanized elastomer composite of any of claims 36-43, wherein the vulcanized elastomer composite exhibits a ratio T300/T100 of at most 7.

45. The vulcanized elastomer composite of any of claims 36-44, wherein the vulcanized elastomer composite exhibits a tan delta 60 of at least 0.02.

46. The vulcanized elastomer composite of any of claims 36-45, wherein the vulcanized elastomer composite exhibits a tensile strength of at most 40 MPa.

47. The vulcanized elastomer composite of any of claims 36-46, wherein the vulcanized elastomer composite exhibits elongation at break (%) * tensile strength (MPa) of at least -211s +e, where e = 27543.

48. The vulcanized elastomer composite of claim 47, wherein the vulcanized elastomer composite exhibits elongation at break (%) * tensile strength (MPa) of at most 21500.

49. The vulcanized elastomer composite of any of claims 36-48, wherein the silica comprises precipitated silica having a surface area from about 20 m^2/g to about 450 m^2/g.

50. The vulcanized elastomer composite of any of claims 36-49, wherein the vulcanized elastomer composite comprises a vulcanizate of a dewatered wet masterbatch of silica dispersed as a slurry in natural rubber latex.

51. The vulcanized elastomer composite of any of claims 36-50, wherein the vulcanized elastomer composite has a swell index of about 1.80 to about 2.20.

52. The vulcanized elastomer composite of any of claims 36-51, wherein the silica comprises precipitated silica.

53. A solid silica-containing continuous rubber phase article comprising at least 40 parts per hundred of rubber (phr) of silica dispersed in natural rubber and at least 40 wt% aqueous fluid, wherein the solid silica-containing continuous rubber phase article exhibits an elongation at break of at least about 100%.

54. The solid silica-containing continuous rubber phase article of claim 53, wherein the solid silica-containing continuous rubber phase article exhibits an elongation at break of about 100% to about 600%.

55. The solid silica-containing continuous rubber phase article of claim 53 or 54, wherein the solid silica-containing continuous rubber phase article comprises from about 40 to about 180 phr.

56. The solid silica-containing continuous rubber phase article of any of claims 53-55, wherein the silica comprises precipitated silica having a surface area from about 20 m^2/g to about 450 m^2/g.

57. The solid silica-containing continuous rubber phase article of any of claims 53-56, wherein the solid silica-containing continuous rubber phase article comprises up to 10% by weight of carbon black with respect to the total weight of reinforcing particles in the solid silica-containing continuous rubber phase article.

58. The solid silica-containing continuous rubber phase article of any of claims 53-57, wherein the solid silica-containing continuous rubber phase article comprises from about 40% to about 90% by weight of water.

59. The vulcanizable elastomer composite of claim 19, wherein the field latex is desludged or chemically or enzymatically modified or comprises added ammonia.

60. The vulcanizable elastomer composite of any of claims 1-12, 14-25, and 27-34, wherein the silica is precipitated silica.

.

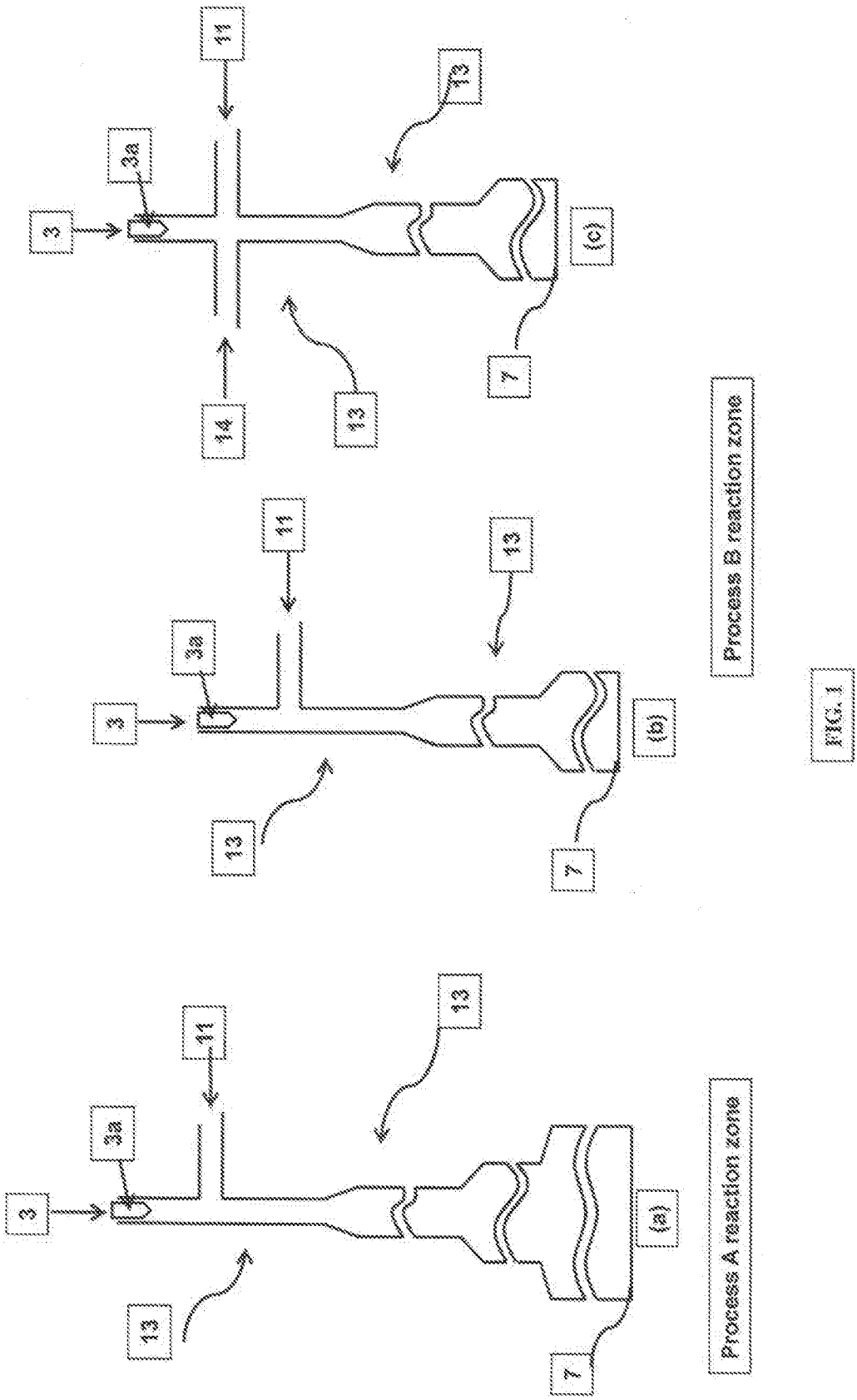
11
12
3a
3
(c)
7
14
13
Process B reaction zone
11
13
3a
3
(b)
13
7
11
13
3a
3
(a)
13
7
Process A reaction zone

FIG. 1

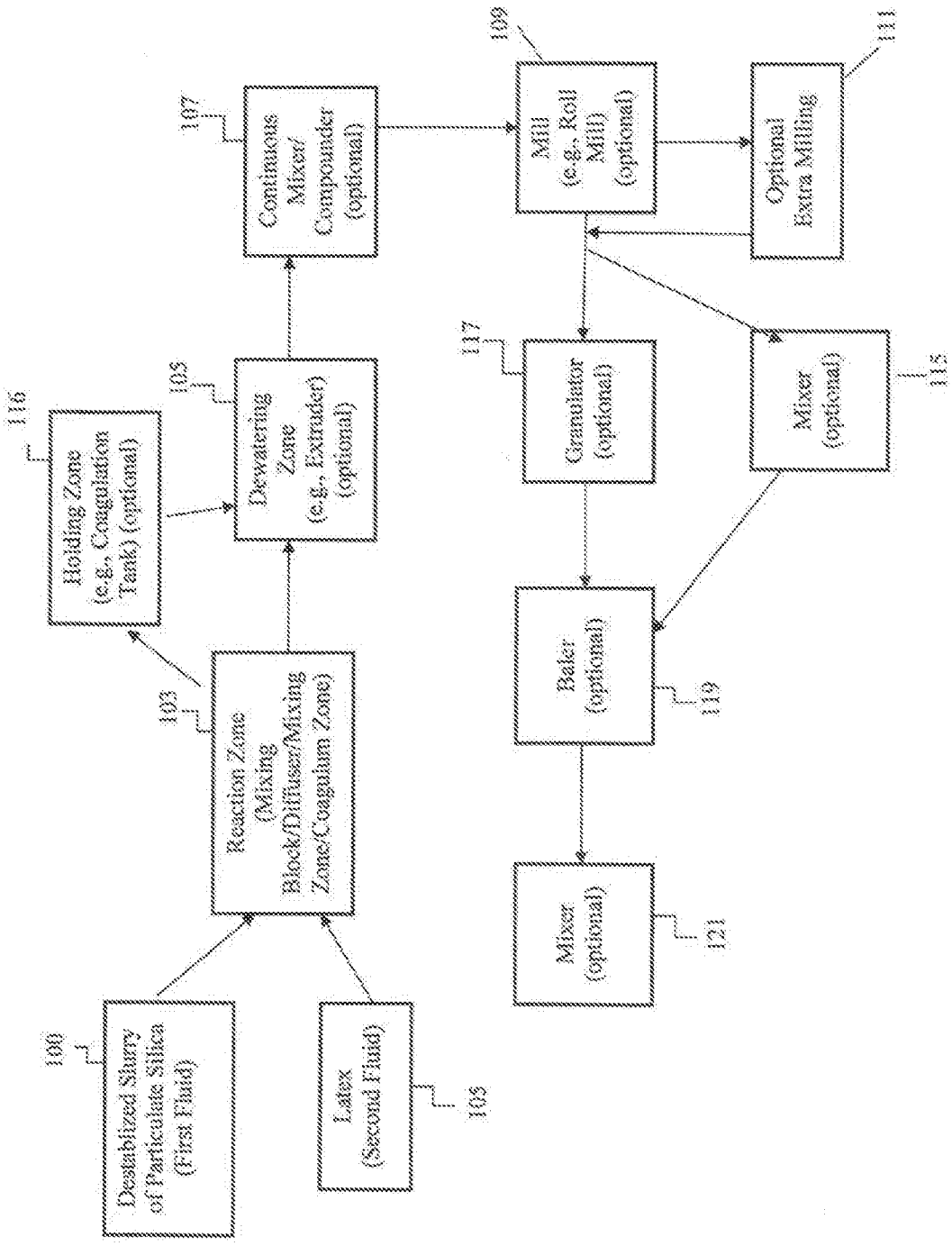
Destabilized Slurry of Particulate Silica (First Fluid)
100
Latex (Second Fluid)
105
Reaction Zone (Mixing Block/Diffuser/Mixing Zone/Coagulum Zone)
103
Holding Zone (e.g., Coagulation Tank) (optional)
116
Dewatering Zone (e.g., Extruder) (optional)
108
Continuous Mixer/ Compounder (optional)
107
Mill (e.g., Roll Mill) (optional)
109
Optional Extra Milling
111
Granulator (optional)
117
Mixer (optional)
115
Baker (optional)
119
Mixer (optional)
121

FIG. 2

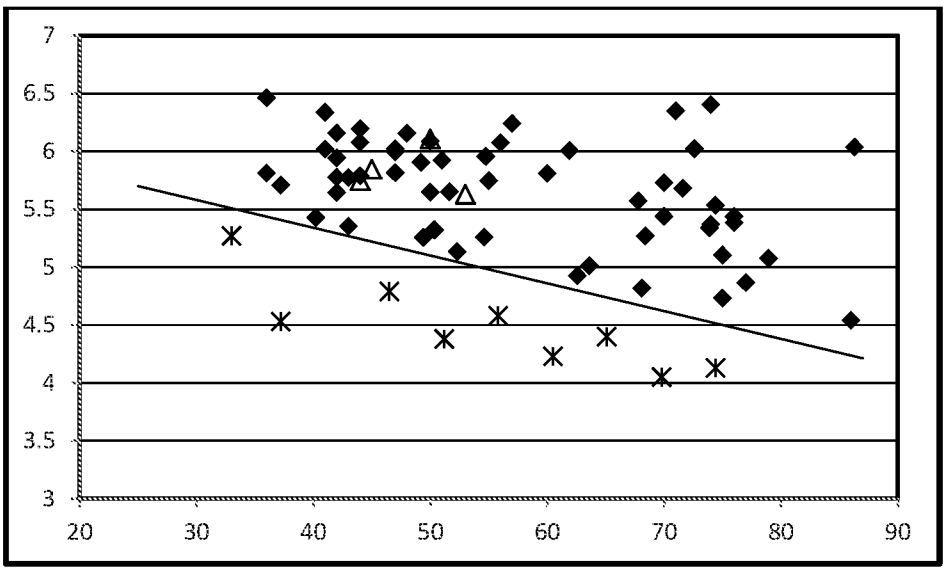

Figure 3A

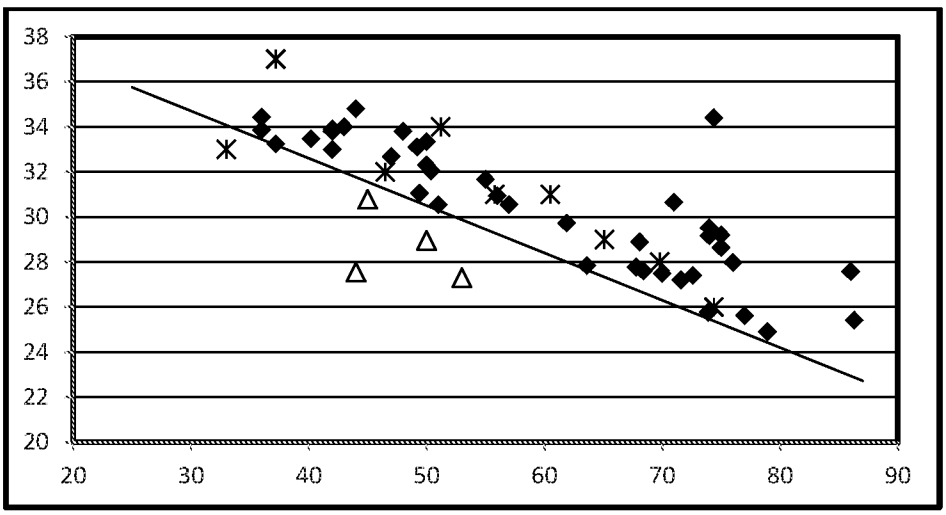

Figure 3B

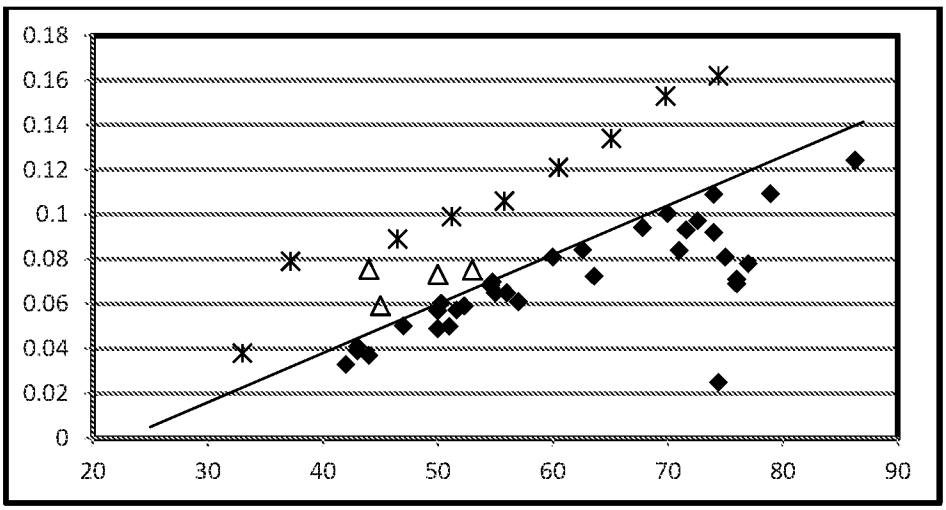

Figure 3C

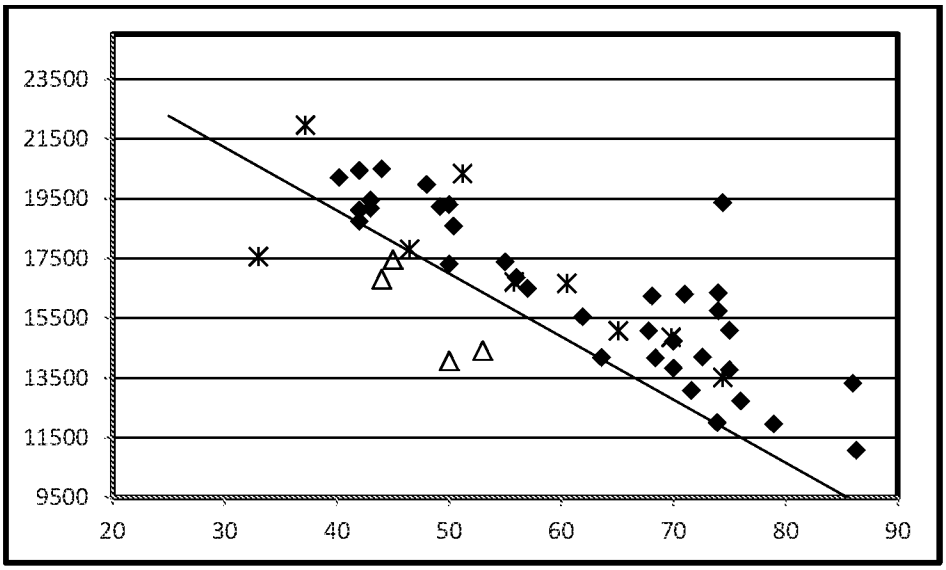

Figure 3D

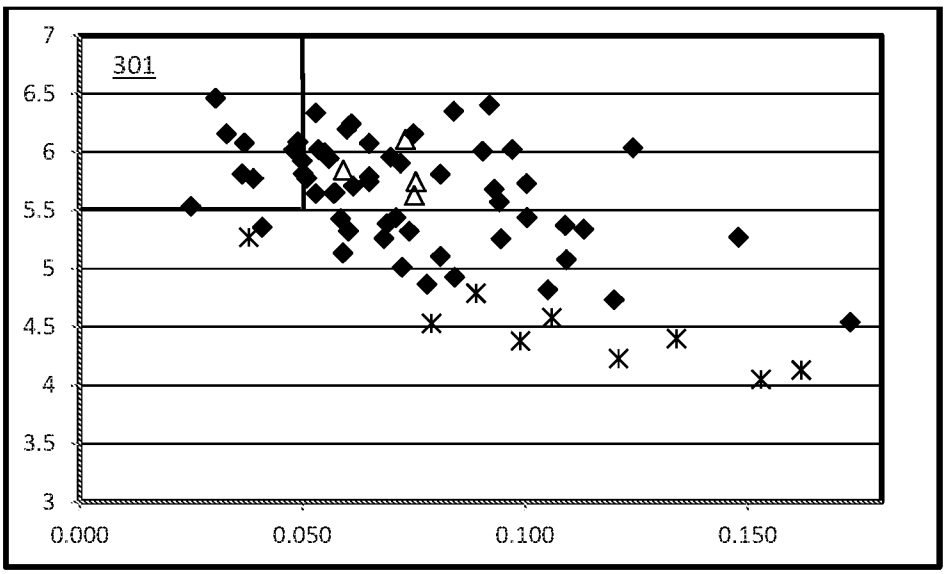

Figure 4

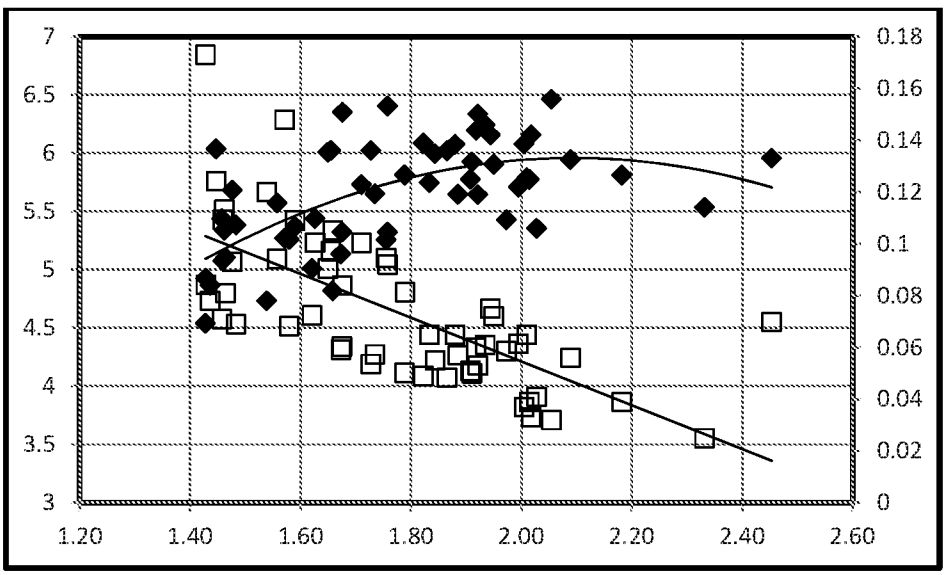

Figure 5

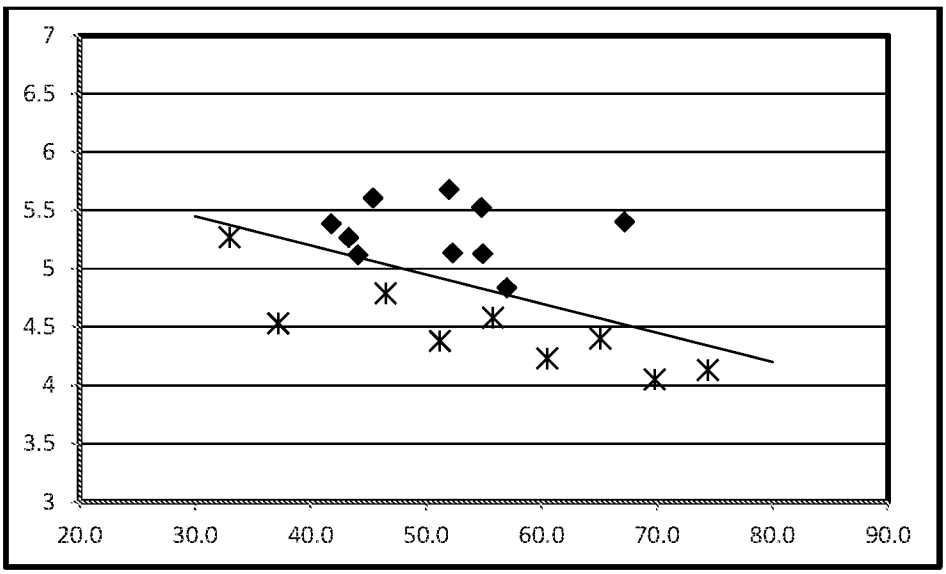

Figure 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/042120

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K3/36 C08L7/02 C08L9/10 C08L21/02 C08J3/16
ADD. C08K3/04

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)
C08K C08J C08L

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/111923 A1 (JIANG PING [US] ET AL) 30 April 2009 (2009-04-30) examples Comp. Ex 4-5, Ex. 4-5 tables 1, 3 claim 34	1,2, 4-19, 21-26, 36,37, 39-41, 43-60
X	WO 02/096914 A2 (CROMPTON CORP [US]) 5 December 2002 (2002-12-05) examples 3, 4; table 1	1-3, 5-18,20, 22-38, 40-46, 48-51,60

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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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

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"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

Date of the actual completion of the international search	Date of mailing of the international search report
15 September 2016	28/09/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Vandoolaeghe, P

1

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 674 932 A (AGOSTINI GIORGIO [LU] ET AL) 7 October 1997 (1997-10-07) examples 1-6; tables 1, 2, 4, 5 -----	1-3,5,6, 8-18,20, 22,23, 25-38, 40-42, 44-46, 48-52,60
X,P	WO 2016/014037 A1 (LI JUNJUAN [CN]; YOU LUJUN [CN]; TANG SOLOMON HSING-KUO [US]) 28 January 2016 (2016-01-28) paragraph [0014]; examples 3, C-3; tables 2, 3 claim 1 -----	1,2,5,6, 8-20,22, 23,25, 26,36, 37, 40-42, 44-46, 48-50, 52,60

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2016/042120

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		US 5674932 A	07-10-1997
WO 2016014037 A1	28-01-2016	NONE	