CORE-FIRST NANOPARTICLE FORMATION PROCESS, NANOPARTICLE, AND COMPOSITION

BACKGROUND AND SUMMARY

[0001] Polymer nanoparticles have attracted increased attention over the past several years in a variety of fields including catalysis, combinatorial chemistry, protein supports, magnets, and photonic crystals. Similarly, vinyl aromatic (e.g. polystyrene) microparticles have been prepared for uses as a reference standard in the calibration of various instruments, in medical research and in medical diagnostic tests. Such polystyrene microparticles have been prepared by anionic dispersion polymerization and emulsion polymerization.

[0002] One benefit of using nanoparticles as an additive in other materials is that they can be discrete particles conducive to uniform dispersion throughout a host composition. For certain applications nanoparticles are preferably monodisperse in size and uniform in shape. However, controlling the size of nanoparticles during polymerization and the surface characteristics of such nanoparticles, or both, can be difficult. Accordingly, achieving better control over the surface composition of such polymer nanoparticles is also desirable.

[0003] Development of nanoparticles having a surface layer or shell that can include a variety of functional groups or heteroatomic monomers that would be compatible with a wide variety of matrix materials is desirable. However, the development of a process capable of reliably producing acceptable nanoparticles with a variety of functional groups or heteroatomic monomers has been a challenging endeavor. For example, the solubility of various monomers in traditional alkane solvents has made solution polymerization a difficult process by which to achieve nanoparticles having a tailored variety of shell layers. Emulsion synthesis requires the use of aqueous solutions to synthesize the nanoparticles and many functional monomers and initiators are not suitable to be used in aqueous solutions. In addition, emulsion synthesis also requires a large amount of surfactants, which may be

undesirable for several reasons. Furthermore, functionalizing nanoparticles with certain functional groups can be difficult, if not impossible, because the functional group must be stable enough to survive the nanoparticle formation steps. In addition, post-nanoparticle formation functionalization may cause nanoparticles to bond together, leading to loss of their discrete nature.

[0004] Herein, a method is provided for synthesizing a core-shell nanoparticle that includes the following steps: providing a polymeric seed (in a solvent) that includes a mono-vinyl monomer cross-linked with a cross-linking agent to form the core of the nanoparticle, the core has an average diameter of about 5 nanometers to about 10,000 nanometers, and the core has polymer chains with living ends; adding a stabilizer to stabilize the seed and prevent the seed from precipitating out of solution; and grafting and/or polymerizing a shell species onto the living ends of the core to form the shell of the nanoparticle.

[0005] In addition, a method for making a rubber composition is provided. The method includes the steps of: making a core-shell nanoparticle(s) as described in the preceding paragraph and adding the core-shell nanoparticle(s) to a vulcanizable rubber matrix to form a rubber composition.

[0006] A method for making a tire is also provided. The method includes the steps of making core-shell nanoparticles as described above; adding the core-shell nanoparticles to a rubber composition; molding the rubber composition into a tire tread; and constructing a tire using the tire tread.

[0007] Furthermore, a core-shell nanoparticle is also provided. The core-shell nanoparticle includes a core formed from a polymeric seed that includes a mono-vinyl monomer cross-linked with a cross-linking agent, the core having an average diameter of about 5 nanometers to about 10,000 nanometers. A shell comprising a shell species is grafted and/or polymerized to the core, the shell being substantially uncrosslinked.

[0010] Herein throughout, unless specifically stated otherwise: "vinyl-substituted aromatic hydrocarbon" and "alkenylbenzene" are used interchangeably; and "rubber" refers to rubber compounds, including natural rubber, and synthetic elastomers including styrene-butadiene rubber and ethylene propylene rubber, which are known in the art. Furthermore, the terms "a" and "the," as used herein, mean "one or more."

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figure 1 is an SEM photo with a 100 nm scale depicting nanoparticles formed with the core-first process.

[0012] Figure 2 is an SEM photo with a 500 nm scale depicting nanoparticles formed with the core-first process.

[0013] Figure 3 is a third SEM photo with a 2 micrometer scale depicting nanoparticles formed with the core-first process.

DETAILED DESCRIPTION

[0014] A highly versatile method for forming core-shell nanoparticles of various shell species is described herein. This method forms the nanoparticle core prior to the formation shell by synthesizing a relatively large cross-linked seed and using living dispersion polymerization to stabilize the seed to keep it in solution. The shell may then be grafted and/or polymerized to the seed, allowing for the potential use of many different types of shell species, such as heteroatomic polymers, hydrocarbon polymers, oligomers, macrocyclic molecules, and monomers. In an embodiment the method may be performed in a single batch, and there is no requirement to isolate and dry the core before grafting and/or polymerizing the shell. This example method enables production of functional nanoparticles with different sizes, well-defined internal and surface structures, and carefully tailored interfaces. Nanoparticles synthesized by this method are demonstrated to be useful as reinforcing agents and performance enhancing additives in rubber compounds. The

nanoparticles having an uncrosslinked shell demonstrated surprisingly low compound viscosity properties and improved wet and possible snow traction when incorporated into a rubber composition.

[0015] In an embodiment a polymeric seed is provided in a solvent. The seed comprises a polymerized mono-vinyl monomer that is cross-linked with a cross-linking agent. The polymerized mono-vinyl polymeric chains are held together by the cross-linking agent in a relatively dense, stable core thereby enhancing the uniformity and permanence of shape and size of the resultant nanoparticle.

[0016] The polymerization is conducted by living dispersion polymerization, such as living anionic dispersion polymerization or living free radical dispersion polymerization. Living anionic dispersion polymerization may be favorable over free radical dispersion polymerization for some applications. In dispersion polymerization, the reaction is effected by polymerizing a monomer(s) in an organic liquid in which the resulting polymer is insoluble, using a steric stabilizer to stabilize the resulting particles of insoluble polymer in the organic liquid. Dispersion polymerization is used to prevent the seed from precipitating out of solution. This technique allows for a sizable seed to be formed into a core in a range of about 5 nanometers up to about 10,000 nanometers while remaining in solution. Consequently, a wide range of solvents may be used in which the polymeric seed would be otherwise insoluble.

[0017] In a generalized example seed-formation step, a reactor is provided with a hydrocarbon solvent, into which a mono-vinyl monomer species and a steric stabilizer, such as polystyrene-polybutadiene diblocks, are added. A polymerization initiator is added to the reactor along with a crosslinking agent. The cross-linking agent and initiator may be added in one charge to the reactor. A randomizing agent may also be added to the reactor. A polymeric mono-vinyl core cross-linked with a cross-linking agent is thus formed, wherein

the mono-vinyl polymer chains have living ends at the surface. The living ends are at the surface of the core due to their higher affinity to the solvent than the mono-vinyl species. The surface of the core is stabilized by the steric stabilizer, which is adsorbed on the surface of the core.

[0018] Specific examples of the mono-vinyl monomer species include mono-vinyl aromatic species, such as styrene, α-methylstyrene, 1-vinyl naphthalene, 2-vinyl naphthalene, 1-α-methyl vinyl naphthalene, 2-α-methyl vinyl naphthalene, vinyl toluene, methoxystyrene, t-butoxystyrene, as well as alkyl, cycloalkyl, aryl, alkaryl, and aralkyl derivatives thereof, in which the total number of carbon atoms in the combined hydrocarbon is generally not greater than 18, as well as any di- or tri-vinyl substituted aromatic hydrocarbons, and mixtures thereof. Further examples of mono-vinyl monomer species include non-aromatic mono-vinyl monomer species, such as vinyl acetate, vinyl-methacrylate, and vinyl-alcohols.

[0019] Crosslinking agents that are at least bifunctional, wherein the two functional groups are capable of reacting with the mono-vinyl species of the core are acceptable. Examples of suitable cross-linking agents include multiple-vinyl monomers and multiple-vinyl aromatic monomers in general. Specific examples of cross-linking agents include di- or tri-vinyl-substituted aromatic hydrocarbons, such as diisopropenylbenzene, divinylbenzene, divinyl ether, divinyl sulphone, diallyl phthalate, triallyl cyanurate, triallyl isocyanurate, 1,2-polybutadiene, N,N'-m-phenylenedimaleimide, N,N'-(4-methyl-m-phenylene)dimaleimide, triallyl trimellitate acrylates, methacrylates of polyhydric C_2-C_{10} alcohols, acrylates and methacrylates of polyethylene glycol having from 2 to 20 oxyethylene units, polyesters composed of aliphatic di- and/or polyols, or maleic acid, fumaric acid, and itaconic acid.

[0020] Specific examples of suitable steric stabilizers include styrene-butadiene diblock copolymer, polystyrene-b-polyisoprene, and polystyrene-b-polydimethylsiloxane.

[0021] As mentioned above, the dispersion polymerization technique allows for a variety of solvents. Polar solvents, including water, and non-polar solvents may be used; however, hydrocarbon solvents are beneficial for some applications. Specific example solvents include aliphatic hydrocarbons, such as pentane, hexane, heptane, octane, nonane, and decane, as well as alicyclic hydrocarbons, such as cyclohexane, methyl cyclopentane, cyclooctane, cyclopentane, cycloheptane, cyclononane, and cyclodecane. These hydrocarbons may be used individually or in combination. However, as more fully described herein below, selection of a solvent in which one polymer forming the nanoparticles is more soluble than another polymer forming the nanoparticles is important in micelle formation.

[0022] A 1,2-microstructure controlling agent or randomizing modifier is optionally used to control the 1,2-microstructure in the mono-vinyl monomer units of the core. Suitable modifiers include 2,2-bis(2'-tetrahydrofuryl)propane, hexamethylphosphoric acid triamide, N,N,N',N'-tetramethylethylene diamine, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, tetrahydrofuran, 1,4-diazabicyclo [2.2.2] octane, diethyl ether, triethylamine, tri-n-butylamine, tri-n-butylphosphine, p-dioxane, 1,2-dimethoxy ethane, dimethyl ether, methyl ethyl ether, ethyl propyl ether, di-n-propyl ether, di-n-octyl ether, anisole, dibenzyl ether, diphenyl ether, dimethylethylamine, bis-oxalanyl propane, tri-n-propyl amine, trimethyl amine, triethyl amine, N,N-dimethyl aniline, N-ethylpiperidine, N-methyl-N-ethyl aniline, N-methylmorpholine, tetramethylenediamine, oligomeric oxolanyl propanes (OOPs), 2,2-bis-(4-methyl dioxane), and bistetrahydrofuryl propane. A mixture of one or more randomizing modifiers also can be used. The ratio of the modifier to the monomers can vary from a minimum as low as about 0 to a maximum as great as about 4000 millimoles, for example about 0.01 to about 3000 millimoles of modifier per hundred grams of monomer currently being charged into the reactor. As the modifier charge increases, the percentage of 1,2-

microstructure (vinyl content) increases in the conjugated diene contributed monomer units in the surface layer of the polymer nanoparticle. The 1,2-microstructure content of the conjugated diene units is, for example, within a range of about 5% and about 95%, such as less than about 35%.

[0023] Suitable initiators for the core formation process include anionic initiators that are known in the art as useful in the polymerization of mono and multiple-vinyl monomers. Exemplary organo-lithium initiators include lithium compounds having the formula $R(Li)_x$, wherein R represents a C_1-C_{20} hydrocarbyl radical, such as a C_2-C_8 hydrocarbyl radical, and x is an integer from 1 to 4. Typical R groups include aliphatic radicals and cycloaliphatic radicals. Specific examples of R groups include primary, secondary, and tertiary groups, such as n-propyl, isopropyl, n-butyl, isobutyl, and t-butyl.

[0024] Specific examples of initiators include ethyllithium, propyllithium, n-butyllithium, sec-butyllithium, and tert-butyllithium; aryllithiums, such as phenyllithium and tolyllithium; alkenyllithiums such as vinyllithium, propenyllithium; alkylene lithium such as tetramethylene lithium, and pentamethylene lithium. Among these, n-butyllithium, sec-butyllithium, tert-butyllithium, tetramethylene lithium, and mixtures thereof are specific examples. Other suitable lithium inititators include one or more of: *p*-tolyllithium, 4-phenylbutyl lithium, 4-butylcyclohexyl lithium, 4-cyclohexylbutyl lithium, lithium dialkyl amines, lithium dialkyl phosphines, lithium alkyl aryl phosphine, and lithium diaryl phosphines.

[0025] Free radical initiators may also be used in conjunction with a free radical polymerization process. Examples of free-radical initiators include: 2,2'-azo-bis(isobutyronitril, 1,1'-azobis(cyclohexanecarbonitrile), 2,2'-azobis(2-methylpropionamidine) dihydrochloride, 2,2'-azobis(2-methylpropionitrile), 4,4'-azobis(4-cyanovaleric acid) , 1,1-bis(tert-amylperoxy)cyclohexane, 1,1-bis(tert-butylperoxy)-3,3,5-

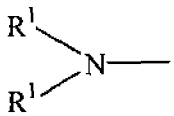
trimethylcyclohexane, 1,1-bis(tert-butylperoxy)cyclohexane, 2,2-bis(tert-butylperoxy)butane, 2,4-pentanedione peroxide, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, 2-butanone peroxide, 2-butanone peroxide, 2-butanone peroxide, benzoyl peroxide, cumene hydroperoxide, di-tert-amyl peroxide, dicumyl peroxide, lauroyl peroxide, tert-butyl hydroperoxide, ammonium persulfate, hydroxymethanesulfinic acid monosodium salt dehydrate, potassium persulfate, and reagent grade sodium persulfate .

[0026] Functionalized lithium initiators are also contemplated as useful in the polymerization of the core species. A functionalized initiator would serve to functionalize the core, and the functional groups would likely be distributed throughout the surface and interior of the core. Example functional groups include amines, formyl, carboxylic acids, alcohols, tin, silica, and mixtures thereof.

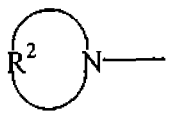
[0027] Amine-functionalized initiators, include those that are the reaction product of an amine, an organo lithium, and a solubilizing component. The initiator has the general formula:

$$(A)Li(SOL)_y$$

where y is from 1 to 3; SOL is a solubilizing component selected from the group consisting of hydrocarbons, ethers, amines or mixtures thereof; and, A is selected from the group consisting of alkyl, dialkyl and cycloalkyl amine radicals having the general formula:



and cyclic amines having the general formula:



where R^1 is selected from the group consisting of alkyls, cycloalkyls or aralkyls having from 1 to 12 carbon atoms, and R^2 is selected from the group consisting of an alkylene, substituted alkylene, oxy- or N-alkylamino-alkylene group having from 3 to 16 methylene groups. A specific example of a functionalized lithium initiator is hexamethylene imine propyllithium.

[0028] Tin functionalized lithium initiators may also be useful in synthesizing the nanoparticles. Suitable tin functionalized lithium initiators include tributyl tin lithium, trioctyl tin lithium, and mixtures thereof.

[0029] Anionic initiators generally are useful in amounts ranging from about 0.01 to about 60 millimoles per hundred grams of monomer charge. Free radical initiators are useful in amounts ranging from about 6-100 millimoles per hundred grams of monomer charge.

[0030] The core may range in size from about 5 nanometers to about 10,000 nanometers, for example about 25 to about 1,000 nanometers, about 40 to about 150 nanometers, or about 50 to about 125 nanometers.

[0031] The shell of the example nanoparticles is formed by grafting and/or polymerizing a shell species onto the living ends of the cross-linked core. The nanoparticle is thus formed with polymers or copolymers extending from the cross-linked core into uncrosslinked shell. The shell species can be selected from a variety of oligomers, polymers, monomers, or macromolecules and functionalized versions of all of these.

[0032] Because the shell is formed last, the shell species does not need to be as stable as it would if it were formed first and had to survive the core formation and cross-linking process. Thus, the core-first process can produce many new nanoparticles that were difficult or impossible to make with the shell first process. In addition, the example core-first process provides an easier and more reliable method to make functionalized nanoparticles in general.

[0033] In one example, the shell species is a polymer that has already been polymerized in a separate reactor and then added to the reactor that holds the core with living ends. An addition of the preformed polymer to the reactor containing the core would result in the polymer chains being grafted to the cross-linked core, thereby forming a shell with polymer brushes. The term "polymer brushes" or "brush-like surface" as used herein, is used to mean the uncrosslinked polymers that extend into the shell of the nanoparticles. The term "brushes" denotes the uncrosslinked nature of the polymer chains in the shell. A "brush-like surface" is a surface wherein most of the polymer chains have a free chain end. Alternatively, the preformed polymer may be functionalized with a functional initiator, a functional terminator, or both in the separate reactor and then grafted onto the living ends of the core, thereby forming functionalized polymer brushes in the shell of the nanoparticle.

[0034] In another example, the shell species is added as a monomer to the reactor containing the core and polymerized with initiator in the same reactor. The shell would thus comprise polymer brushes of the shell species. Optionally, functional terminators could be used to functionalize the polymer brushes of the shell.

[0035] In another example, the shell species is a monomer containing a heteroatom. The heteroatomic monomer is polymerized as described above to form the shell.

[0036] In another example, the shell species is a single monomer unit. The unit may be a hydrocarbon or contain one or more heteroatoms, and it may be functionalized. The monomer is added and polymerizes via the living ends of the core.

[0037] In another example the shell species is a macromolecule having a molecular weight up to about 10,000 g/mol or an oligomer. The shell species is added to the reactor containing the core. The macromolecule or oligomer is thus grafted onto the living ends of the core. Various functional groups may be present in the macromolecule or oligomer.

[0038] In another example the shell species is itself a functional terminator. When added to the reactor containing the core, the functional terminator terminates the living ends of the core. In this example, the functional group(s) is considered the shell.

[0039] The weight percent of the shell species may range from about 1 x 10^{-5}% to about 75% of the entire nanoparticle weight, such as about 1 x 10^{-5}% to about 5% when the shell species is a functional terminator for the living ends of the core, or about 1% to about 75%, such as 3% to 50%, or 5% to 25% when the shell species is macromolecule or has more than one "mer" unit.

[0040] Example shell species generally include hydrocarbons, heteroatomic species, polar functionalized species, water-soluble species, and thermoplastic and plastic elastomers.

[0041] Hydrocarbon shell species include C_4 to C_8 conjugated dienes, such as, 1,3-butadiene, isoprene, and 1,3-pentadiene. Olefinic species such as ethylene, propylene, isobutylene, and cyclohexene may also be used.

[0042] Heteroatomic shell species include species containing O, N, S, P, Cl, Ti, and Si atoms, such as, epoxides, urethanes, esters, ethers, imides, amines, carbonates, siloxanes, halogens, metals, synthetic oils, and vegetable oils. Specific examples include, polydimethylsiloxane (PDMS), polyethylene oxide (PEO), halogenated butyl rubber, polyethylene teraphthalate (PET), polyethylene glycol (PEG), polyphenylene oxide (PPO), poly(propylene glycol) diglycidyl ether (PPO-EO2), polyvinyl alcohol, pyridine, carbazole, imidazole, diethylamino-styrene, and pyrrolidone. Example macromolecules or oligomers include polyethylene glycol, polyphenylene oxide, and polydimethylsiloxane.

[0043] In a particular embodiment, the shell species is a fatty acid ester, triglyceride, or vegetable oil. Such oil-brushed nanoparticles synergistically enhance the capability of the nanoparticles as reinforcing agents and processing additives in rubber compounds. For example, in the non-limiting Examples disclosed herein, a castor oil-brushed nanoparticle is

shown to enhance tensile strength and wet traction without an increase of compound Mooney, and in addition, reduced hysteresis and Payne effect without trading off other properties are also displayed.

[0044] Functional terminators for use with or as the shell species include $SnCl_4$, R_3SnCl, R_2SnCl_2, $RSnCl_3$, carbodiimides, N-methylpyrrolidine, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino) benzophenone, N,N'-dimethylethyleneurea, and mixtures thereof, wherein R is selected from the group consisting of alkyls having from about 1 to about 20 carbon atoms, cycloalkyls having from about 3 to about 20 carbon atoms, aryls having from about 6 to about 20 carbon atoms, aralkyls having from about 7 to about 20 carbon atoms, and mixtures thereof.

[0045] The size of the entire core-shell nanoparticles, including both core and shell - expressed as a mean number average diameter – are, for example, between about 5 and about 20,000 nanometers, such as about 50 to about 5,000 nanometers, about 75 to about 300 nanometers, or about 75 to about 150 nanometers.

[0046] For some applications the nanoparticles are preferably substantially monodisperse and uniform in shape. The dispersity is represented by the ratio of M_w to M_n, with a ratio of 1 being substantially monodisperse. The nanoparticles may, for example, have a dispersity less than about 1.3, such as less than about 1.2, or less than about 1.1. Moreover, the nanoparticles may be spherical, though shape defects are acceptable, provided the nanoparticles generally retain their discrete nature with little or no polymerization between particles.

[0047] With respect to the monomers and solvents identified herein, nanoparticles are formed by maintaining a temperature that is favorable to polymerization of the selected monomers in the selected solvent(s). Reaction temperatures are, for example, in the range of about -40 to about 250 °C, such as a temperature in the range of about 0 to about 150 °C.

[0048] Additionally, the shell species may include copolymers, including random and block copolymers. These other blocks may include the hydrocarbon and heteroatomic monomers listed above. The copolymer shell species may be synthesized prior to introducing the species into the reactor with the core, or it may be polymerized after introduction into the reactor as described above.

[0049] Pre-formed multi-block polymers, are believed to aggregate to form micelle-like structures around the core, with the block that is the least soluble in the solvent directed toward the centers of the core and all other blocks as tails or brushes extending therefrom. For example, in a hydrocarbon solvent, vinyl-substituted aromatic blocks are directed toward the centers of the core and other blocks extend as tails therefrom. It is noted that a further hydrocarbon solvent charge or a decrease in polymerization mixture temperature may also be used, and may in fact be required, to obtain formation of the micelles. Moreover, these steps may be used to take advantage of the general insolubility of a vinyl-aromatic block. An exemplary temperature range for this step is between about -80 and about 100°C, such as between about 20°C and about 80°C.

[0050] After the formation of the nanoparticle core and shell, and prior to the termination of the living end, additional monomer charge(s), such as conjugated diene monomer and/or vinyl-substituted aromatic hydrocarbon monomer, can be added to the polymerization mixture as desired. The sequential addition of various monomers allows growth of particle size and formation of the shell with different internal structure.

[0051] The embodiments of nanoparticles described herein are substantially discrete, for example the nanoparticles have less than 20% cross-linking between nanoparticles, such as less than 15% or less than 10% cross-linking between nanoparticles.

[0052] The number average molecular weight (Mn) of the entire nanoparticle may be controlled within the range of from about 10,000 to about 200,000,000, within the range of

from about 50,000 to about 1,000,000, or within the range of from about 100,000 to about 500,000. The polydispersity (the ratio of the weight average molecular weight to the number average molecular weight) of the polymer nanoparticle may be controlled within the range of from about 1 to about 2.0, within the range of from about 1 to about 1.5, or within the range of from about 1 to about 1.2.

[0053] The Mn may be determined by using Gel Permeation Chromatography (GPC) calibrated with polystyrene standards and adjusted for the Mark-Houwink constants for the polymer in question. The Mn values used in the examples below were measured by GPC methods calibrated with linear polymers.

[0054] In one example, the core of the synthesized nanoparticles is relatively hard; that is, the core has a Tg of about 60°C or higher. In another example, the nanoparticles have a core that is relatively harder than the shell, for example, at least about 60°C higher than the Tg of the shell layer, or at least about 1°C higher than the Tg of the shell layer. In one example, the shell layer is soft; that is, the shell layer has a Tg lower than about 0°C. In one embodiment, the Tg of the shell layer is between about 0°C and about -100°C. Nanoparticles with hard cores and soft shells are particularly useful for reinforcing rubber compounds used for tire treads.

[0055] The Tg of the polymers in the nanoparticles can be controlled by the selection of monomers and their molecular weight, styrene content, and vinyl content.

[0056] POLYMER NANOPARTICLE APPLICATIONS

[0057] A variety of applications are contemplated for use in conjunction with the example nanoparticles. Furthermore, the several mechanisms described herein for modifying the nanoparticles render them more suitable for different applications. All forms of the example nanoparticles are, of course, contemplated for use in each of the exemplary applications and all other applications envisioned by the skilled artisan.

[0058] GENERAL RUBBER

[0059] After the nanoparticles have been formed, they may be blended with a rubber to improve the physical characteristics of the rubber composition. Nanoparticles are useful modifying agents for rubbers because they are discrete particles which are capable of dispersing uniformly throughout the rubber composition, resulting in uniformity of physical characteristics.

[0060] The present polymer nanoparticles are suitable for modifying a variety of rubbers including, but not limited to, random styrene/butadiene copolymers, butadiene rubber, poly(isoprene), natural rubber, ethylene-propylene, nitrile rubber, polyurethane, butyl rubber, EPDM, and silicone rubber.

[0061] Furthermore, nanoparticles with hydrogenated layers may demonstrate improved compatibility with specific rubbers. For example, nanoparticles including a hydrogenated polyisoprene layer may demonstrate superior bonding with and improved dispersion in an EPDM rubber matrix due to the compatibility of hydrogenated isoprene with EPDM rubber. U.S. Patent No. 6,689,469 to Wang describes methods for hydrogenating nanoparticles and is herein incorporated by reference.

[0062] Additionally, nanoparticles with copolymer layers may demonstrate improved compatibility with rubbers. The copolymer tails within a layer of the nanoparticles may form a brush-like surface. The host composition is then able to diffuse between the tails allowing improved interaction between the host and the nanoparticles.

[0063] Nanoparticles with a shell species that includes siloxane groups may exhibit improved interaction in silica filled rubber compositions. Nanoparticles with shell species that include vegetable or synthetic oils may enhance the processability of the rubber matrix.

[0064] Nanoparticles with shell species that include pyridine, carbazole, imidazole, diethylamino-styrene, pyrrolidone, polyethylene glycol (PEG), polydimethylsiloxane

(PDMS), polyphenylene oxide (PPO), and poly(propylene glycol) that are mixed with silica and carbon black filled rubbers have been shown to give improved properties such as G' with no significant increase in Mooney viscosity.

[0065] HARD DISK TECHNOLOGY

[0066] Hydrogenated nanoparticles may also find application in hard disk technology.

[0067] Disk drive assemblies for computers traditionally include a magnetic storage disk coaxially mounted about a spindle apparatus that rotates at speeds in excess of several thousand revolutions per minute (RPM). The disk drive assemblies also include a magnetic head that writes and reads information to and from the magnetic storage disk while the magnetic disk is rotating. The magnetic head is usually disposed at the end of an actuator arm and is positioned in a space above the magnetic disk. The actuator arm can move relative to the magnetic disk. The disk drive assembly is mounted on a disk base (support) plate and sealed with a cover plate to form a housing that protects the disk drive assembly from the environmental contaminant outside of the housing.

[0068] Serious damage to the magnetic disks, including loss of valuable information, can result by introducing gaseous and particulate contaminates into the disk drive assembly housing. To substantially prevent or reduce the introduction of gaseous and particulate contaminants into the disk drive housing, a flexible sealing gasket is disposed between the disk drive mounting base (support) plate and the disk drive assembly housing or cover plate. A sealing gasket is usually prepared by punching out a ring-shaped gasket from a sheet of cured elastomer. The elastomeric gasket obtained is usually attached to the base plate of the disk drive assembly mechanically, such as affixing the gasket with screws, or adhesives.

[0069] THERMOPLASTIC GELS

[0070] Nanoparticles prepared in accord with the present disclosure, whether hydrogenated or non-hydrogenated may also be blended with a variety of thermoplastic elastomers, such as

SEPS, SEBS, EEBS, EEPE, polypropylene, polyethylene, polystyrene, and mixtures thereof. For example, nanoparticles with hydrogenated isoprene layers may be blended with an SEPS thermoplastic to improve tensile strength and thermostability. These blends of thermoplastic elastomer and nanoparticles would typically be extended as known in the art. For example, suitable extenders include extender oils and low molecular weight compounds or components. Suitable extender oils include those well known in the art such as naphthenic, aromatic and paraffinic petroleum oils and silicone oils.

[0071] Examples of low molecular weight organic compounds or components useful as extenders in compositions containing nanoparticles are low molecular weight organic materials having a number-average molecular weight of less than about 20,000, for example less than about 10,000, or less than about 5000. Although there is no limitation to the material which may be employed, the following is a list of examples of appropriate materials:

[0072] (1) Softening agents, namely aromatic naphthenic and araffinic softening agents for rubbers or resins;

[0073] (2) Plasticizers, namely plasticizers composed of esters including phthalic, mixed pthalic, aliphatic dibasic acid, glycol, fatty acid, phosphoric and stearic esters, epoxy plasticizers, other plasticizers for plastics, and phthalate, adipate, scbacate, phosphate, polyether and polyester plasticizers for NBR;

[0074] (3) Tackifiers, namely coumarone resins, coumaroneindene resins, terpene phenol resins, petroleum hydrocarbons and rosin derivative;

[0075] (4) Oligomers, namely crown ether, fluorine-containing oligomers, polybutenes, xylene resins, chlorinated rubber, polyethylene wax, petroleum resins, rosin ester rubber, polyalkylene glycol diacrylate, liquid rubber (polybutadiene, styrene/butadiene rubber, butadiene-acrylonitrile rubber, and polychloroprene), silicone oligomers, and poly-a-olefins;

[0076] (5) Lubricants, namely hydrocarbon lubricants such as paraffin and wax, fatty acid lubricants such as higher fatty acid and hydroxyl-fatty acid, fatty acid amide lubricants such as fatty acid amide and alkylene-bisfatty acid amide, ester lubricants such as fatty acid-lower alcohol ester, fatty acid-polyhydrie alcohol ester and fatty acid-polyglycol ester, alcoholic lubricants such as fatty alcohol, polyhydric alcohol, polyglycol and polyglycerol, metallic soaps, and mixed lubricants; and,

[0077] (6) Petroleum hydrocarbons, namely synthetic terpene resins, aromatic hydrocarbon resins, aliphatic hydrocarbon resins, aliphatic or alicyclic petroleum resins, polymers of unsaturated hydrocarbons, and hydrogenated hydrocarbon resins.

[0078] Other appropriate low-molecular weight organic materials include latexes, emulsions, liquid crystals, bituminous compositions, and phosphazenes. One or more of these materials may be used as extenders.

[0079] Surface functionalized nanoparticles prepared in accordance with the present disclosure, whether hydrogenated or non-hydrogenated, may also be compounded with silica containing rubber compositions. Including surface functionalized nanoparticles in silica containing rubber compositions has been shown to decrease the shrinkage rates of such silica containing rubber compositions. Functionalized nanoparticles may be compounded in silica compositions in concentrations up to about 50 wt% of the total composition, such as up to about 40 wt%, or up to about 30 wt%.

[0080] **TIRE RUBBER**

[0081] One application for rubber compounds with nanoparticles is in tire rubber formulations.

[0082] Vulcanizable elastomeric compositions containing nanoparticles are prepared by mixing a rubber and a nanoparticle composition, with reinforcing filler(s) comprising silica,

or a carbon black, or a mixture of the two, a processing aid and/or a coupling agent, a cure agent and an effective amount of sulfur to achieve a satisfactory cure of the composition.

[0083] Example rubbers useful with the nanoparticles described above are conjugated diene polymers, copolymers or terpolymers of conjugated diene monomers and monovinyl aromatic monomers. These can be utilized as 100 parts of the rubber in the tread stock compound, or they can be blended with any conventionally employed treadstock rubber which includes natural rubber, synthetic rubber and blends thereof. Such rubbers are well known to those skilled in the art and include synthetic polyisoprene rubber, styrene-butadiene rubber (SBR), styrene-isoprene rubber, styrene-isoprene-butadiene rubber, butadiene-isoprene rubber, polybutadiene, butyl rubber, neoprene, acrylonitrile-butadiene rubber (NBR), silicone rubber, the fluoroelastomers, ethylene acrylic rubber, ethylene-propylene rubber, ethylene-propylene terpolymer (EPDM), ethylene vinyl acetate copolymer, epicholrohydrin rubber, chlorinated polyethylene-propylene rubbers, chlorosulfonated polyethylene rubber, hydrogenated nitrile rubber, and terafluoroethylene-propylene rubber.

[0084] Examples of reinforcing silica fillers which can be used in the vulcanizable elastomeric composition include wet silica (hydrated silicic acid), dry silica (anhydrous silicic acid), and calcium silicate. Other suitable fillers include aluminum silicate, and magnesium silicate. Among these, precipitated amorphous wet-process, hydrated silicas are specific examples. Silica can be employed in the amount of one to about 100 parts per hundred parts of the elastomer (phr), for example in an amount of about 5 to about 80 phr, or in an amount of about 30 to about 80 phrs. The useful upper range is limited by the high viscosity imparted by fillers of this type. Some of the commercially available silica which can be used include, but are not limited to, HiSil® 190, HiSil® 210, HiSil® 215, HiSil® 233, and HiSil® 243, produced by PPG Industries (Pittsburgh, PA). A number of useful commercial grades of

different silicas are also available from DeGussa Corporation (e.g., VN2, VN3), Rhone Poulenc (e.g., Zeosil® 1165MP0, and J.M. Huber Corporation.

[0085] Including surface functionalized nanoparticles in silica containing rubber compositions has been shown to decrease the shrinkage rates of such silica containing rubber compositions. Functionalized nanoparticles may be compounded in silica compositions in concentrations up to 30 wt% of the total composition, such as up to about 40 wt%, or up to about 50 wt%.

[0086] The rubber can be compounded with all forms of carbon black and optionally additionally with silica. The carbon black can be present in amounts ranging from one to 100 phr. The carbon black can include any of the commonly available, commercially-produced carbon blacks, such as those having a surface area of at least 20 m^2/g or at least $35m^2/g$ up to $200m^2/g$ or higher. Among useful carbon blacks are furnace black, channel blacks, and lamp blacks. A mixture of two or more of the above blacks can be used in preparing the carbon black compositions. Typical suitable carbon black are N-110, N-220, N-339, N-330, N-352, N-550, N-660, as designated by ASTM D-1765-82a.

[0087] Certain additional fillers can be utilized including mineral fillers, such as clay, talc, aluminum hydrate, aluminum hydroxide and mica. The foregoing additional fillers are optional and can be utilized in the amount of about 0.5 phr to about 100.

[0088] Numerous coupling agents and compatibilizing agents are known for use in combining silica and rubber. Among the silica-based coupling and compatibilizing agents include silane coupling agents containing polysulfide components, or structures such as, for example, trialkoxyorganosilane polysulfides, containing from 2 to 8 sulfur atoms in a polysulfide bridge such as, for example, bis-(3-triethoxysilylpropyl) tetrasulfide (Si69), bis-(3-triethoxysilylpropyl) disulfide (Si75), and those alkyl alkoxysilanes of the such as octyltriethoxy silane, and hexyltrimethoxy silane.

[0089] It is readily understood by those having skill in the art that the rubber composition would be compounded by methods generally known in the rubber compounding art, such as mixing the various vulcanizable polymer(s) with various commonly used additive materials such as, for example, curing agents, activators, retarders and accelerators processing additives, such as oils, resins, including tackifying resins, plasticizers, pigments, additional filers, fatty acid, zinc oxide, waxes, antioxidants, anti-ozonants, and peptizing agents. As known to those skilled in the art, depending on the intended use of the sulfur vulcanizable and sulfur vulcanized material (rubbers), the additives mentioned above are selected and commonly used in the conventional amounts.

[0090] **ENGINEERING PLASTIC AND OTHERS**

[0091] Similarly, the nanoparticles can be added into typical plastic materials, including polyethylene, polypropylene, polystyrene, polycarbonate, nylon, and polyimides, to for example, enhance impact strength, tensile strength and damping properties.

[0092] Of course, the present inventive nanoparticles are also suited to other presently existing applications for nanoparticles, including the medical field, e.g. drug delivery and blood applications, information technology, e.g. quantum computers and dots, aeronautical and space research, energy, e.g., oil refining, and lubricants.

[0093] **ENGINE MOUNT**

[0094] Another application for such rubbers is in situations requiring superior damping properties, such as engine mounts and hoses (e.g. air conditioning hoses). Rubber compounds of high mechanical strength, super damping properties, and strong resistance to creep are demanded in engine mount manufacturers. In engine mounts, a rubber, because it sits most of its life in a packed and hot position, requires very good characteristics. Utilizing the nanoparticles within selected rubber formulations can improve the characteristics of the rubber compounds.

[0095] The present invention now will be described with reference to non-limiting working examples. The following examples and tables are presented for purposes of illustration only and are not to be construed in a limiting sense.

[0096] **EXAMPLES**

[0097] A 0.8 liter nitrogen-purged glass bottle sealed with a septum liner and perforated crown cap was used as the reactor vessel for the examples below. 1,3-butadiene (22 wt% in hexane), styrene (33 wt% in hexane), hexane, n-butyllithium (1.60 M in hexane), 2,2-bis(2'-tetrahydrofuryl)propane (1.60 M in hexane, stored over calcium hydride) and BHT solution in hexane were also used. Commercially available reagents were obtained from Aldrich and Gelest Inc. (Morrisville, PA) and dried over molecular sieves (3Å).

[0098] Example 1: Nanoparticles Functionalized with 4-[2-Trichlorosilyl]ethylpyridine

[0099] 49 g of hexane, 62 g of 34 wt% styrene and 9 ml of 5% Stereon 730AC (polystyrene-b-polybutadiene: styrene 30.6%, vinyl 8.8%, Mn 134 kg/mol) were added to the reactor. The reactor was then charged with 1.6 ml of 1.4 M sec-butyl lithium at room temperature. After approximately 1 hour, 0.1 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane and 111 g of 22 wt% 1,3-butadiene were added to the charge. After 1 day, 39 g of 33 wt% styrene was added to the charge and stirred overnight. 2 ml of divinylbenzene (DVB) was added to the reactor. After approximately 3 hours, 1.5 ml of 17.5% 4-[2-trichlorosilyl]ethylpyridine was added to the polymer in solution (cement) and stirred overnight. The cement was coagulated in isopropanol and vacuum dried.

[0100] The particle size was determined by a number average method by viewing an SEM as shown in Figure 1. The particle size was about 50 nm. The styrene/DVB/BD particles had a weight distribution of 58.4/3.1/38.5, respectively, based on the unfunctionalized particle weight. The weight percent of the 4-[2-trichlorosilyl]ethylpyridine functional group was about 0.43% based on the total nanoparticle composition.

[0101] Example 2: Nanoparticles Functionalized with 9-Vinylcarbazole

[0102] 49 g of hexane, 62 g of 34 wt% styrene and 9 ml of 5% Stereon 730AC (polystyrene-b-polybutadiene: styrene 30.6%, vinyl 8.8%, Mn 134 kg/mol) were added to the reactor. The reactor was then charged with 1.6 ml of 1.4 M sec-butyl lithium at room temperature. After approximately 1 hour, 0.1 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane and 111 g of 22 wt% 1,3-butadiene were added to the charge. After 1 day, 40 g of 33 wt% styrene was added to the charge. After approximately 6 hours, 2 ml of divinylbenzene (DVB) was added to the reactor and stirred overnight. 30 ml of 0.1M 9-vinylcarbazole was added to the polymer in solution (cement) and stirred for 2 days. The cement was coagulated in isopropanol and vacuum dried. The particle size was about 50 nm. The styrene/DVB/BD particles had a weight distribution of 58.4/3.1/38.5, respectively, based on the unfunctionalized particle weight. The weight percent of the 9-Vinylcarbazole functional group was less than 0.95% based on the total nanoparticle composition.

[0103] Example 3: Nanoparticles Functionalized with 1-Vinylimidazole

[0104] 49 g of hexane, 72 g of 34 wt% styrene and 9 ml of 5% Stereon 730AC (polystyrene-b-polybutadiene: styrene 30.6%, vinyl 8.8%, Mn 134 kg/mol) were added to the reactor. The reactor was then charged with 1.6 ml of 1.4 M sec-butyl lithium at room temperature. After approximately 1 hour, 0.1 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane and 111 g of 22 wt% 1,3-butadiene were added to the charge. After 1 day, 38 g of 33 wt% styrene was added to the charge. After approximately 6 hours, 2 ml of divinylbenzene (DVB) was added to the reactor and stirred overnight. 30 ml of 0.1M 1-vinylimidazole was added to the polymer in solution (cement) and stirred for 2 days. The cement was coagulated in isopropanol and vacuum dried. The particle size was about 50 nm. The styrene/DVB/BD particles had a weight distribution of 60/3/37, respectively, based on the unfunctionalized particle weight. The

weight percent of the 1-vinylimidazole functional group was less than 0.43%, based on the total nanoparticle composition.

[0105] Example 4: Nanoparticles Functionalized with p-Diethylaminostyrene

[0106] 49 g of hexane, 62 g of 34 wt% styrene and 9 ml of 5% Stereon 730AC (polystyrene-b-polybutadiene: styrene 30.6%, vinyl 8.8%, Mn 134 kg/mol) were added to the reactor. The reactor was then charged with 1.6 ml of 1.4 M sec-butyl lithium at room temperature. After approximately 1 hour, 0.1 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane and 111 g of 22 wt% 1,3-butadiene were added to the charge. After 1 day, 30 g of 33 wt% styrene was added to the charge. After approximately 3 hours, 2 ml of divinylbenzene (DVB) was added to the reactor and stirred overnight. 2 ml of p-diethylaminostyrene was added to the polymer in solution (cement) and stirred for 1 day. The cement was coagulated in isopropanol and vacuum dried. The particle size was about 50 nm. The styrene/DVB/BD particles had a weight distribution of 56/4/40, respectively, based on the unfunctionalized particle weight. The weight percent of the p-diethylaminostyrene functional group was about 3% based on the total nanoparticle composition.

[0107] Example 5: Nanoparticles Functionalized with Tetrakis[(N-(1-ethyl)-2-pyrrolidone)-dimethylsiloxy)

[0108] 49 g of hexane, 62 g of 34 wt% styrene and 9 ml of 5% Stereon 730AC (polystyrene-b-polybutadiene: styrene 30.6%, vinyl 8.8%, Mn 134 kg/mol) were added to the reactor. The reactor was then charged with 1.6 ml of 1.4 M sec-butyl lithium at room temperature. After approximately 1 hour, 0.1 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane and 111 g of 22 wt% 1,3-butadiene were added to the charge. After 1 day, 40 g of 33 wt% styrene was added to the charge. After approximately 3 hours, 2 ml of divinylbenzene (DVB) was added to the reactor and stirred overnight. 16 ml of 0.1M tetrakis[(N-(1-ethyl)-2-pyrrolidone)-dimethylsiloxy) was added to the polymer in solution (cement) and stirred overnight. The

cement was coagulated in isopropanol and vacuum dried. The particle size was about 50 nm. The styrene/DVB/BD particles had a weight distribution of 58.4/3.1/38.5, respectively, based on the unfunctionalized particle weight. The weight percent of the tetrakis[(N-(1-ethyl)-2-pyrrolidone)-dimethylsiloxy) functional group was about 1.95%, based on the total nanoparticle composition.

[0109] Example 6: Nanoparticles Functionalized with N-Vinylcarbazole

[0110] 45 g of hexane, 68 g of 34 wt% styrene and 2.5 ml of 5% Stereon 730AC (polystyrene-b-polybutadiene: styrene 30.6%, vinyl 8.8%, Mn 134 kg/mol) were added to the reactor. The reactor was then charged with 1.4 ml of 1.4 M sec-butyl lithium at room temperature. After approximately 2 hour, 0.1 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane and 111 g of 22 wt% 1,3-butadiene were added to the charge and stirred overnight. 40 g of 33 wt% styrene was then added to the charge. After approximately 2 hours, 2 ml of divinylbenzene (DVB) was added to the reactor and stirred for 3 hours. 40 ml of 0.1M N-vinylcarbazole was added to the polymer in solution (cement) and stirred for 2 days. The cement was coagulated in isopropanol and vacuum dried. The particle size was about 50 nm. The styrene/DVB/BD particles had a weight distribution of 60/3/37, respectively, based on the unfunctionalized particle weight. The weight percent of the N-vinylcarbazole functional group was about 0.95%, based on the total nanoparticle composition.

[0111] Example 7: Nanoparticles Functionalized with Tetrakis[(N-(1-ethyl)-2-pyrrolidone)-dimethylsiloxy)

[0112] 49 g of hexane, 60 g of 34 wt% styrene and 9 ml of 5% Stereon 730AC (polystyrene-b-polybutadiene: styrene 30.6%, vinyl 8.8%, Mn 134 kg/mol) were added to the reactor. The reactor was then charged with 1.6 ml of 1.4 M sec-butyl lithium at room temperature. After approximately 12 hours, 0.1 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane, 14 g of 34 wt% styrene and 24 g of 22 wt% 1,3-butadiene were added to the charge. Two additions of 17 g

of 33 wt% styrene and 44 g of 22 wt% 1,3-butadiene were incrementally charged after approximately 2 hours. After sti rring for 1 day, 15 ml of 0.1M tetrakis[(N-(1-ethyl)-2-pyrrolidone)-dimethylsiloxy) was added to the polymer in solution (cement) and stirred overnight. The cement was coagulated in isopropanol and vacuum dried.

[0113] The particle size was determined by a number average method by viewing an SEM as shown in Figure 2. The particle size was about 100 nm. The styrene/BD particles had a weight distribution of 74/26, respectively, based on the unfunctionalized particle weight. The weight percent of the tetrakis[(N-(1-ethyl)-2-pyrrolidone)-dimethylsiloxy) functional group was about 2% based on the total nanoparticle composition.

[0114] Example 1A: Non-Functional Core First Nanoparticles

[0115] 300 g of hexane, 20 g of 33 wt% styrene and 5 ml of 10% polystyrene-polybutadiene diblock (styrene content 24.2%, vinyl 9.2%, and Mn 67 kg/mol) were added to a reactor. Then the reactor was charged with 1 ml of DVB, 2 ml of 1.6 M butyl lithium and 1 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane. After approximately 10 minutes, 30 g of 22 wt% 1,3-butadiene and 2 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane were added to the charge. After 4 hours at room temperature, the polymer in solution (cement) was terminated with isopropanol and coagulated in isopropanol and vacuum dried.

[0116] The particle size was determined by a number average method by viewing an SEM photo as shown in Figure 3. The particle size was about 0.6-0.8 μm. The styrene/DVB/BD particles had a weight distribution of 46.8/6.4/46.8, respectively.

[0117] Example 2A. Synthesis of Particles with a PEG Functionalized Shell.

[0118] 300 g of hexane, 20 g of 33 wt% styrene and 5 ml of 10% polystyrene-polybutadiene diblock (styrene content 24.2%, vinyl 9.2%, and Mn 67 kg/mol) were added to a reactor. Then the reactor was charged with 1 ml of DVB, 2 ml of 1.6 M butyl lithium and 1 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane. After approximately 10 minutes, 30 g of 22 wt% 1,3-

butadiene and 2 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane were added to the charge. After about 4 hours at room temperature, 5 ml of stock solution of poly(ethylene glycol) diglycidyl ether (PEG-EO2, Mn=526 g/mol) was added to the cements for 30 min. The stock solution of PEG-EO2 (1M) was prepared in toluene and treated with a molecular sieve. After the color of the solution bleached, the particles were coagulated with isopropanol and dried under the vacuum. The product weight was increased about 15% compared to non-functional particles synthesized in Example 1A. The particle size was about 0.6-0.8 μm. The styrene/DVB/BD/PEG particles had a weight distribution of 39.5/5.3/39.5/15.7, respectively.

[0119] Example 3A. Synthesis of Particles with a PDMS Functionalized Shell.

[0120] 300 g of hexane, 20 g of 33 wt% styrene and 5 ml of 10% polystyrene-polybutadiene diblock (styrene content 24.2%, vinyl 9.2%, and Mn 67 kg/mol) were added to a reactor. Then the reactor was charged with 1 ml DVB, 2 ml of 1.6 M butyl lithium and 1 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane. After approximately 10 minutes, 30 g of 22 wt% 1,3-butadiene and 2 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane were added to the charge. After about 4 hours at room temperature, 5 ml stock solution of hexamethylcyclotrisiloxane (D3) was added to the cements for about 1 hour. The particles were coagulated with isopropanol and dried under the vacuum. The stock D3 solution (2M) was prepared in hexane and treated with a molecular sieve. The product weight was increased about 6.7% compared to non-functional particles synthesized in Example 1A. The particle size was about 0.6-0.8 μm. The styrene/DVB/BD/D3 particles had a weight distribution of 34.6/4.7/34.6/26.1, respectively.

[0121] Example 4A. Synthesis of Particles with a PPO Functionalized Shell.

[0122] 300 g hexane, 20 g of 33 wt% styrene and 5 ml of 10% polystyrene-polybutadiene diblock were added to a reactor. Then the reactor was charged with 1 ml DVB, 2 ml of 1.6 M butyl lithium and 1 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane. After approximately 10 minutes, 30 g of 22 wt% 1,3-butadiene and 2 ml of 1.6 M 2,2'-di(tetrahydrofuryl)propane

were added to the charge. After about 4 hours at room temperature, 5 ml stock solution of poly(propylene oxide) diglycidyl ether (PPO-EO2, Mn=640 g/mol) was added to the cements for about 40 min. The stock solution of PPO-EO2 (1M) was prepared in toluene and treated with a molecular sieve. The particles were coagulated with isopropanol and dried under the vacuum. The product weight was increased about 20% compared to non-functional particles synthesized in Example 1A. The particle size was about 0.6-0.8 μm. The styrene/DVB/BD/PPO particles had a weight distribution of 38.2/5.2/38.2/18.4, respectively.

[0123] Example 1B: Synthesis of Non-Functional Core First Nanoparticles

[0124] To a 0.8 liter nitrogen-purged glass bottle was added 300 g of hexane, 20 ml of THF, 20 g of 33 wt% styrene, 10 ml of 10% PS-PB diblock (S730AC), and 0.6 ml of 50 wt% DVB. The reactor was charged with 0.5 ml of 1.6 M butyl lithium. Within 5 minutes, 5.5 ml of 50 wt% DVB was added to the charge and stirred at room temperature. After 30 minutes, 20 g of 22 wt% 1,3-butadiene and 1 ml of 1 M N,N,N',N'-tetramethylethylenediamine (TMEDA) were added to the charge. After stirring at room temperature for one day, the cements were coagulated in isopropanol (IPA) and vacuum dried.

[0125] The styrene/DVB/BD particles had a weight distribution of 49/18/33, respectively.

[0126] Example 2B. Synthesis of SBR Nanoparticles with Castor Oil Brushes (Shell).

[0127] To a 0.8 liter nitrogen-purged glass bottle was added 300 g of hexane, 20 ml of THF, 20 g of 33 wt% styrene, 10 ml of 10% PS-PB diblock (S730AC) and 0.6 ml of 50 wt% DVB. The reactor was charged with 0.5 ml of 1.6 M butyl lithium. Within 5 minutes, 5.5 ml of 50 wt% DVB was added to the charge and stirred at room temperature for 30 minutes. Then, 20 g of 22 wt% 1,3-butadiene and 1 ml of 1 M N,N,N',N'-tetramethylethylenediamine (TMEDA) were added to the charge. After stirring at room temperature for one day, 6 ml of castor oil glycidyl ether (10 wt% in hexane) was added to the charge. After 4 hours, the cements were coagulated in IPA and vacuum dried.

[0128] The styrene/DVB/BD/COGE particles had a weight distribution of 48/17/32/3, respectively.

[0129] **Rubber Compounding Examples 9-24**

[0130] Tables 1 and 2 show the general carbon black and silica composition formulation. Example 8 was a control example, compounded according to the formulation of Table 1. Examples 9-15 were compounded according to the formulation of Table 1, except the nanoparticles of Examples 1-7 were used to replace 10 phr (per hundred rubber) of the SBR polymer. Example 16 was a control example, compounded according to the formulation of Table 2. Examples 17-23 were compounded according to the formulation of Table 2, except the nanoparticles of Examples 1-7 were used to replace 10 phr (per hundred rubber) of the SBR polymer in Examples 17-23. The 10 phr of nanoparticles accounted for 5.7% by weight of the carbon black-filled compositions and 4.7% by weight of the silica-filled compositions. Tables 3 and 4 summarize the characterization of the functionalized nanoparticles and their compound properties.

Table 1. Carbon Black-Filled Formulation

	Composition	phr	Mixing Conditions
Master Batches	SBR[1]	100	Mixer: 300g Brabender
	Carbon Black (N343)	50	Agitation Speed: 60 rpm
	Aromatic Oil	15	
	Zinc Oxide	3.0	Initial Temperature 110°C
	Hydrocarbon Resin (tackifiers)	2.0	0 min charging polymers
	Santoflex 13 (antioxidants)	0.95	0.5 min charging oil and Carbon Black
	Stearic Acid	2.0	5.0 min drop sample for analysis
	Wax	1.0	
Final Batch	Sulfur	1.3	Initial Temperature 75°C
	Cyclohexyl-benzothiazole	1.4	0 sec charging master stock
	Diphenylguanidine (accelerator)	0.20	30 sec charging curing agent and accelerators
			1.25 min drop sample for analysis

[1] Trade Name HX263 from Firestone Polymers [styrene 23.8%, vinyl 13%, cis 35%, trans 52%, and Mw 261 kg/mol, Mw/Mn 2.30]

Table 2. Silica-Filled Formulation

	Composition	phr	Mixing Conditions
Master Batch	SBR[1]	100	Mixer: 300g Brabender
	Precipitated silica filler (HISIL 190G)	70	Agitation Speed: 60 rpm
	Aromatic Oil	30	
	Wax	1.5	Initial Temperature 110°C
	Stearic Acid	2.0	0 min charging polymers
	Santoflex 13 (antioxidants)	0.95	0.5 min charging oil and Silica
	Si 69 (Silane Coupling Agent)	8	5.0 min drop
Remill Stage			Initial Temperature 110°C 0 min charging stocks 5.0 min drop
Final Batch	N-(cyclohexylthio) phthalimide (retarder)	0.25	Initial Temperature 75°C 0 sec charging master stock 30 sec charging curing agent and accelerators 75 sec drop
	Sulfur	1.7	
	Zinc Oxide	2.5	
	Cyclohexyl-benzothiazole sulfenamide (accelerator)	1.50	
	Diphenylguanidine (accelerator)	0.5	

[1]Trade Name HX263 from Firestone Polymers [styrene 23.8%, vinyl 13%, cis 35%, trans 52%, and Mw 261 kg/mol, Mw/Mn 2.30]

Table 3. Properties Carbon Black-Filled Rubber Compositions with Nanoparticles

	Example	9	10	11	12	13	14	15	16
Functionality		Control	Pyridine(1)	Carbazole(2)	Imidazole(3)	Diethylamino-styrene(4)	Pyrrolidone(5)	Carbazole(6)	Pyrrolidone(7)
DYNASTAT (0°C)	K'* (lbf/in):	273.554	469.583	424.529	469.981	428.610	419.288	451.645	689.207
	K"* (lbf/in):	75.921	131.896	118.751	129.382	120.846	114.539	122.879	163.698
	tanδ:	0.278	0.281	0.280	0.275	0.282	0.273	0.272	0.238
DYNASTAT (50°C)	K' (lbf/in):	143.397	182.920	174.747	177.977	174.218	169.874	181.227	244.313
	K" (lbf/in):	28.826	42.837	40.853	41.659	41.383	38.811	41.032	63.537
	tanδ:	0.201	0.234	0.234	0.234	0.238	0.228	0.226	0.260
MOONEY (130°C)	ML1+4 (MU)	42.1	40.6	40.6	39.7	40.1	38.5	41.2	38.9
RING TENSILE (100°C)	M50 (MPa)	0.9	0.94	0.95	0.96	0.96	0.98	0.99	0.94
	M300 (MPa)	6.11	6.45	6.68	6.54	6.44	6.66	6.68	6.07
	Max Stress (MPa)	8.4	8.91	9.31	9.68	8.93	8.5	9.23	8.98
	Max Strain (%)	380.5	387.8	390.0	412.0	392.6	365.5	389.4	413.3
RING TENSILE (23°C)	M50 (MPa)	1.26	1.58	1.57	1.5	1.5	1.54	1.6	1.79
	M300 (MPa)	8.3	9.09	9.32	8.91	8.69	9.11	9.19	8.82
	Max Stress (MPa)	19.6	19.28	19.55	19.29	18.54	19.28	20.12	18.3
	Max Strain (%)	569.9	569.3	561.5	576.9	565.5	562.7	582.5	569.2
STRAIN SWEEP (25°C)	G' (MPa) @5%, 5 Hz:	2.259	3.050	2.887	2.934	2.872	2.777	2.860	3.966
	G" (MPa) @ 5%, 5 Hz:	0.533	0.788	0.743	0.764	0.757	0.721	0.726	1.022
	tanδ @ 5%, 5 Hz:	0.236	0.258	0.257	0.260	0.264	0.260	0.254	0.258
	ΔG' (MPa) [0.25-14%]	2.146	3.800	3.407	3.590	3.545	3.271	3.257	5.561

*K' and K'' are the dynamic compression modulus

Table 4. Properties of Silica-Filled Rubber Compositions with Nanoparticles

	Example	17	18	19	20	21	22	23	24
Functionality		Control	Pyridine(1)	Carbazole(2)	Imidazole(3)	Diethylamino-styrene(4)	Pyrrolidone(5)	Carbazole(6)	Pyrrolidone(7)
DYNASTAT (0°C)	K' (lbf/in):	549.765	1100.815	847.814	846.947	870.433	888.472	883.497	1059.119
	K" (lbf/in):	119.826	214.393	176.802	179.159	180.841	182.438	180.149	198.185
	tanδ:	0.218	0.195	0.209	0.211	0.208	0.205	0.204	0.187
DYNASTAT (50°C)	K' (lbf/in):	269.790	342.708	325.480	310.518	321.890	331.227	331.882	377.295
	K" (lbf/in):	46.188	76.988	64.532	61.547	65.136	64.834	65.529	79.203
	tanδ:	0.171	0.225	0.198	0.198	0.202	0.196	0.197	0.210
MOONEY (130°C)	MLI+4 (MU)	45.3	44.7	45.4	44.5	44.8	43.4	45.4	45.2
RING TENSILE (100°C)	M50 (MPa)	1.0	1.11	1.17	1.14	1.13	1.14	1.17	1.14
	M300(MPa)	5.85	6.09	6.83	6.71	6.50	6.53	6.89	6.56
	Max Stress (MPa)	9.33	9.44	11.62	11.04	10.39	11.92	12.06	11.95
	Max Strain (%)	422.6	423.2	450.4	440.5	430.4	470.6	460.4	473.1
RING TENSILE (23°C)	M50 (MPa)	1.21	1.51	1.38	1.37	1.38	1.39	1.41	1.46
	M300 MPa)	6.96	7.60	7.78	7.60	7.52	7.42	7.87	8.03
	Max Stress (MPa)	18.99	18.13	19.19	18.88	18.01	18.14	18.65	19.04
	Max Strain (%)	602.7	574.9	577.3	582.1	569.2	577.82	567.8	580.5
STRAIN SWEEP (25°C)	G' (MPa) @5%, 5 Hz:	4.329	5.567	4.980	5.069	4.884	5.224	5.369	5.614
	G" (MPa) @ 5%,5Hz:	0.888	1.466	1.202	1.234	1.234	1.282	1.262	1.415
	tanδ @ 5%, 5 Hz:	0.205	0.263	0.241	0.243	0.253	0.245	0.235	0.252
	ΔG' (MPa) [0.25-14%]	4.865	8.875	7.079	7.346	7.389	7.841	7.867	9.230

Rubber Compounding Examples 5A-9A

[0131] Table 1A shows the general silica composition formulation. Example 9A below is a control example that uses the silica formulation listed in Table 1A. Examples 5A-8A are

compounded according to the formulation of Table 1A except the nanoparticles of Examples 1A-4A were used to replace 15 phr of the SBR polymer. The 15 phr of nanoparticles accounted for 7% by weight of the silica-filled compositions. Table 2A summarizes the compound properties.

Table 1A. Silica Compound Formulation

	Composition	phr	Mixing Conditions
Master Batch	SBR/Nanoparticles[1]	100	Mixer: 300g Brabender Agitation Speed: 60 rpm Initial Temperature 110°C 0 min charging polymers 0.5 min charging oil and silica 5.0 min drop
	Precipitated silica filler	70	
	Aromatic Oil	30	
	Wax	1.5	
	Stearic Acid	2.0	
	Santoflex 13 (antioxidants)	0.95	
	Si 69 (Silane Coupling Agent)	8	
Remill Stage			Initial Temperature 110°C 0 min charging stocks 5.0 min drop
Final Batch	Zinc Oxide	2.5	Initial Temperature 75°C 0 sec charging master stock 30 sec charging curing agent and accelerators 75 sec drop
	N-(cyclohexylthio) phthalimide (retarder)	0.25	
	Sulfur	1.7	
	Cyclohexyl-benzothiazole sulfenamide (accelerator)	1.50	
	Diphenylguanidine (accelerator)	0.5	

[1]SBR rade Name HX263 from Firestone Polymers [styrene 23.8%, vinyl 13%, cis 35%, trans 52%, and Mw 261 kg/mol, Mw/Mn 2.30]

Table 2A: Properties of Silica Filled Rubber Compositions with Nanoparticles

Example		5A	6A	7A	8A	9A
Functionality		PEG (2A)	PDMS (3A)	PPO (4A)	none (1A)	Control
MOONEY (130°C)	ML1+4 (MU):	54	53.5	53.7	51.7	52
	t5 (min):	46.27	49.92	44.28	50.13	48.77
R-TENSILE (100°C)	M50	1.19	1.15	1.2	1.08	0.98
	M300	8.3	7.54	8.09	6.57	6.08
	Tb(MPa)	7.83	8.31	8.7	7.37	8.35
	Eb(%)	293	335	324	335	385
R-TENSILE (23°C)	M50	1.67	1.56	1.72	1.62	1.22
	M300	10.49	9.48	10.41	8.88	7.29
	Tb(MPa)	17.99	15.92	17.69	16.08	18.3
	Eb(%)	495	474	489	495	573
STRAIN SWP (25°C) 5%, 5Hz	G' (MPa)	5.04	4.72	4.91	5.16	3.93
	G" (MPa)	1.14	1.09	1.14	1.22	0.81
	tanδ	0.23	0.23	0.23	0.24	0.21
5Hz, [0.14-15%]	ΔG' (MPa)	6.35	5.86	6.36	7.06	4.04
TEMP SWP	T_g (°C)	-42	-42	-41	-42	-43
WET TRACTION	STANLEY LONDON	66	64	66	66	64

[0132] Example 3B-5B: Rubber Compounding

[0133] Nanoparticles with castor oil brushes were synthesized as discussed in Example 2B and compounded in an SBR rubber matrix with silica filler. Examples with no nanoparticles and unfunctionalized nanoparticles were also compounded.

[0134] In Example 3B, a 100 phr matrix of HX263 SBR was used as a control. In Example 4B, the unfunctionalized nanoparticles synthesized in Example 1B replaced 15 parts of the SBR matrix polymer (7 wt.% based on the total compound). In Example 5B the nanoparticles with a castor oil shell (brushes) replaced 15 parts of the SBR matrix polymer (7 wt.% based on the total compound).

[0135] Table 1B shows the rubber and silica compound formulation. Table 2B summarizes the compound properties.

Table 1B. Silica Compound Formulation

	Composition	phr	Mixing Conditions
Master Batch	SBR/nanoparticles[1]	100	Mixer: 300g Brabender Agitation Speed: 60 rpm Initial Temperature 110°C 0 min charging polymers 0.5 min charging oil and silica 5.0 min drop
	Precipitated silica filler	70	
	Aromatic Oil	30	
	Wax	1.5	
	Stearic Acid	2.0	
	Santoflex 13 (antioxidants)	0.95	
	Si 69 (Silane Coupling Agent)	8	
Remill Stage			Initial Temperature 110°C 0 min charging stocks 5.0 min drop
Final Batch	Sulfur	1.7	Initial Temperature 75°C 0 sec charging master stock 30 sec charging curing agent and accelerators 75 sec drop
	N-(cyclohexylthio) phthalimide (retarder)	0.25	
	Zinc Oxide	2.5	
	Cyclohexyl-benzothiazole sulfenamide (accelerator)	1.50	
	Diphenylguanidine (accelerator)	0.5	

[1]SBR Trade Name HX263 from Firestone Polymers [styrene 23.8%, vinyl 13%, cis 35%, trans 52%, and Mw 261 kg/mol, Mw/Mn 2.30]

Table 2B. Properties of Silica Filled Rubber Compositions with Nanoparticles

EXAMPLE:	3B	4B	5B
Nanoparticles (15 phr)	0	1B	2B
Brushes		none	castor oil
MOONEY (130°C)			
ML1+4 (MU):	44.6	50.9	51
RING TENSILE (100°C)			
M50 (MPa)	0.97	0.93	1.08
M300 (MPa)	5.78	5.76	6.79
Max Stress (MPa)	7.52	7.49	8.68
Max Strain (%)	365.0	369.0	364.0
RING TENSILE (23°C)			
M50 (MPa)	1.16	1.26	1.35
M300 (MPa)	6.84	7.06	7.89
Max Stress (MPa)	17.5	15.8	16.3
Max Strain (%)	569.0	530.0	501.0
SHORE A HARDNESS			
Shore A at 25C:	57.3	57.8	55.8
Shore A at 100C:	52.6	52.6	52.6
STRAIN SWEEP (25°C)			
G' (MPa) @ 5%, 5 Hz:	4.239	4.874	4.356

G'' (MPa) @ 5%, 5 Hz:	0.839	1.315	1.124
tanδ @ 5%, 5 Hz:	0.198	0.270	0.258
ΔG' (MPa) [0.25-14%]	4.395	5.576	4.184
DYNASTAT (0'°C, FINAL)			
% Displacement:	1.641	0.957	0.940
K' (lbf/in):	538.595	922.927	935.560
K'' (lbf/in):	116.288	198.960	218.603
tanδ:	0.216	0.216	0.234
DYNASTAT (50'°C, FINAL)			
% Displacement:	3.235	3.592	3.518
K' (lbf/in):	275.349	246.581	253.019
K'' (lbf/in):	46.569	50.568	44.122
tanδ:	0.169	0.205	0.174

[0136] This written description sets forth the best mode of the invention, and describes the invention so as to enable a person skilled in the art to make and use the invention by presenting certain embodiments. The patentable scope of the invention is defined by the claims, and may include other embodiments that occur to those skilled in the art.

We claim:

1. A method for synthesizing a core-shell nanoparticle, comprising the steps of:

providing a polymeric seed in a solvent, the seed including a mono-vinyl monomer cross-linked with a cross-linking agent to form the core of the nanoparticle, the core having an average diameter of about 5 nanometers to about 10,000 nanometers, and the core having polymer chains with living ends;

adding a stabilizer to stabilize the seed and prevent the seed from precipitating out of solution; and

grafting and/or polymerizing a shell species onto the living ends of the core to form the shell of the nanoparticle.

2. The method of claim 1 wherein the stabilized seed is made by living dispersion polymerization.

3. The method of claim 1 wherein the seed is formed by polymerizing the mono-vinyl monomer with an initiator, and cross-linking the resulting polymer with a multiple-vinyl monomer cross-linking agent.

4. The method of claim 1 further comprising the step of polymerizing the shell species with anionic initiator.

5. The method of claim 1 wherein the shell species is a preformed polymer.

6. The method of claim 1 wherein the cross-linking agent and anionic initiator are added in one charge to the hydrocarbon solvent, mono-vinyl aromatic monomer, and stabilizer.

7. The method of claim 1, with the proviso that emulsion polymerization is not used to synthesize the seed.

8. The method of claim 1, wherein the solvent comprises a hydrocarbon solvent.

9. The method of claim 1, further comprising the step of adding a functional terminator to terminate the living ends of the shell.

10. The method of claim 1, wherein the core has an average diameter of from about 50 nanometers to about 125 nanometers.

11. The method of claim 1, wherein the shell species is selected from the group consisting of polyvinyl, polyurethane, polyester, polyether, polyimide, polyamine, poly(carbonate), poly(epoxide), poly(siloxane), and polyvinyl alcohol.

12. The method of claim 1, wherein the shell species contains a heteroatomic species selected from the group consisting of O, N, S, P, halogens, Ti, and Si.

13. The method of claim 1 wherein the shell species is a functional oligomer or macromolecule, or a functional terminator that includes a heteroatom.

14. The method of claim 1 wherein the shell species is a synthetic oil, a fatty acid ester, triglycerides, or a vegetable oil.

15. A method for making a rubber composition, the method comprising:

making core-shell nanoparticles according to claim 1; and

adding the core-shell nanoparticles to a vulcanizable rubber matrix.

16. A method for making a tire, the method comprising:

making core-shell nanoparticles according to claim 1;

adding the core-shell nanoparticles to a rubber composition;

molding the rubber composition into a tire tread; and

constructing a tire using the tire tread.

17. A core-shell nanoparticle comprising:

a core formed from a polymeric seed that includes a mono-vinyl monomer core species cross-linked with a cross-linking agent, the core having an average diameter of from about 5 nanometers to about 10,000 nanometers;

a shell comprising a shell species attached to the core, the shell being substantially uncrosslinked.

18. The core-shell nanoparticle of claim 17 wherein less than about 10% of the shell species are crosslinked.

19. The core-shell nanoparticle of claim 17 comprising a residue of a stabilizer.

20. The core-shell nanoparticle of claim 17, wherein the core is formed by living dispersion polymerization.

21. The core-shell nanoparticle of claim 17, wherein the shell species comprise monomers that include a heteroatom.

22. The core-shell nanoparticle of claim 17, wherein the core has an average diameter of about 50 nanometers to about 125 nanometers.

23. The core-shell nanoparticle of claim 17, further comprising a functional group in the shell.

24. The core-shell nanoparticle of claim 17, wherein a Tg of the core is higher than a Tg of the shell.

25. The core-shell nanoparticle of claim 17, wherein the shell species is selected from the group consisting of polyvinyl, polyurethane, polyester, polyether, polyimide, polyamine, poly(carbonate), poly(epoxide), poly(siloxane), and polyvinyl alcohol.

26. The core-shell nanoparticle of claim 17, wherein the shell species is synthetic oil, a fatty acid ester, triglycerides, or vegetable oil.