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(54) Title: MACROMOLECULAR TREATMENT AGENTS FOR SURFACE MODIFICATION

(57) Abstract: Methods include generating a modified filler composition, including contacting: a filler; and a macromolecular treatment agent prepared from a reaction of: at least one bifunctional organosilane; and a polyfunctional nucleus having at least two nucleophilic functional groups and having a number average molecular weight of at least 400 Da. Methods include preparing a dispersion by admixing: a modified filler prepared by reacting a filler with at least one bifunctional organosilane and a polyfunctional nucleus having at least two nucleophilic functional groups and having a number average molecular weight of at least 400 Da; and a polyether polyol or polyether polyamine.

MACROMOLECULAR TREATMENT AGENTS FOR SURFACE MODIFICATION

Field

Embodiments relate to macromolecular treatment agents for modification of surfaces and inorganic fillers, particularly for use in polymer-forming materials and systems.

Introduction

The incorporation of inorganic fillers into polymer compositions is an emerging technical approach to develop new materials with desirable properties adapted to specific applications such as biomedical materials (e.g., dental restorative materials), batteries, ceramics, composites, magnetics, electronics packaging, solid propellants and adhesives. In some cases, inorganic fillers are applied in a high-volume ratio (i.e., above 20 vol%) to reach threshold concentrations that impart certain functions on the material, such as thermal conductivity, electroconductivity, and magnetorheological behaviors. For example, highly filled polymer systems have become popular thermal interfacial materials (TIMs) for electrical vehicles and the photovoltaic industry.

However, high concentrations of fillers are often accompanied by increased viscosity and energy dissipation from the particle-particle interactions, which can create difficulties in dispersing fillers in polymer-forming components and during application to substrates. To reduce the viscosity of the highly filled polymeric composites for easy processing, surface treatments may be employed to increase the compatibility of the filler with the surrounding phases. However, existing surface treatments continue to offer limited improvements for consistent viscosity reduction for high concentrations of inorganic fillers (e.g., above 20 vol% of inorganic fillers).

Summary

In an aspect, embodiments of the disclosure are directed to methods that include generating a modified filler composition, including contacting: a filler; and a macromolecular treatment agent prepared from a reaction of: at least one bifunctional organosilane; and a polyfunctional nucleus having at least two nucleophilic functional groups and having a number average molecular weight of at least 400 Da.

In another aspect, methods may include preparing a dispersion by admixing: a modified filler prepared by reacting a filler with at least one bifunctional organosilane and a polyfunctional nucleus having at least two nucleophilic functional groups and having a number average molecular weight of at least 400 Da; and a polyether polyol or polyether polyamine.

Detailed Description

Embodiments disclosed herein relate to macromolecular treatment agents for stabilizing fillers to increase compatibility with various polymers and polymer-forming systems.

Macromolecular treatment agents disclosed herein may be a product of a reaction between one or more bifunctional organosilanes and a polyfunctional nucleus having 2 or more nucleophilic functional groups and having a number average molecular weight of at least 400 Da.

Macromolecular treatment agents may be used to improve the interaction of the filler with polymer systems, and to improve the apparent viscosity and storage stability of polymer-forming components (e.g., polyol compositions and polyurethane forming components). In some cases, macromolecular treatment agents may be used to introduce higher levels of functionality to strengthen the interaction between the filler and a polymer system (e.g., increase the number of nucleophilic functional groups or alkoxysilane anchoring groups). Filler particles and surfaces may also be treated to modify the overall hydrophobicity/hydrophilicity and compatibility of the fillers with a wide array of polymer types (e.g., epoxy, polyurethane, acrylic).

Macromolecular treatment agents may be prepared from a reaction of a polyfunctional nucleus having two or more nucleophilic functional groups and one or more equivalents of bifunctional organosilane. The silane functional groups of the macromolecular treatment agent may react with functional groups on the surface of filler particles or substrates (e.g., silanization of hydroxyl groups on a silica surface to form Si-O-Si bonds). Surface functional groups may be naturally occurring or introduced through various chemical processes (e.g., plasma oxidation) or reagents (e.g., use of linkers, primerws, or intermediate layers). Once anchored to a surface, the nucleophilic functional groups on the polyfunctional nucleus may interact through covalent and/or non-covalent interactions with polymer systems or components, reducing viscosity and sedimentation behavior. The equivalents of bifunctional organosilane reacted with the polyfunctional nucleus may also be varied to modify the selected ratio of nucleophilic functional groups and silane functional groups.

Macromolecular treatment agents disclosed herein may be applied to fillers and/or surfaces prior to (ex situ) or in combination with (in situ) components to form a polymer system (e.g., polyurethane, epoxy, acrylic resin). In some cases, a macromolecular treatment agent may be combined with a filler as a pre-treatment prior to introduction into a polymer system or polymer-forming system (e.g., in an A-side and/or B-side). Using polyurethane systems as an example, a filler may be reacted with a macromolecular treating agent, which may improve storage and rheological properties of a treated component (e.g., isocyanate or isocyanate-reactive components) prior to or during reaction to form a polyurethane. Modified fillers may be generated by forming the macromolecular treatment agent and then combining with a filler, or may be generated by reacting a filler with a bifunctional organic silane, followed by reaction of the "activated" filler with a polyfunctional nucleus (e.g., polyol or polyamine). Modification of a filler may take place

in the presence of other components, including solvents or additives that do not substantially affect the modification chemistry.

Macromolecular treating agents may be prepared from a polyfunctional nucleus reacted with one or more equivalents of a bifunctional organosilane. A polyfunctional nucleus may include a polymer, copolymer, or oligomer having a functionality (number of nucleophilic functional groups) of two or more, such as a range from 2 to 10, or 2 to 8. As used herein, "nucleophilic functional group" refers to a functional group that donate an electron pair to form a covalent bond with an electrophile, such as hydroxy, primary or secondary amines, thiol, phenols, azides, and the like.

The polyfunctional nucleus may be derived from backbone structures of polyether, polyester, polydimethylsiloxane, polycarbonate, polybutadiene, polyolefin or their mixtures or co-polymers. Polyfunctional nuclei be generated from a polymerization or oligomerization with one or more starter compounds having >3 carbon atoms (e.g., sorbitol, glycerine) and one or more monomers (e.g., propylene oxide, butylene oxide, polyols, polyamines). Suitable polyfunctional nuclei may include polyether polyols prepared from a starter compound and one or more alkylene oxides, for example, ethylene oxide, propylene oxide, and/or butylene oxide. Starter compounds may include, but are not limited to, molecules having 1 to 8 hydroxyl groups per molecule, such as ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, 1,4-butanediol, 1,6-hexanediol, triethanolamine, diethanolamine, diisopropanolamine, bisphenol A, glycerol, diglycerol, triglycerol, trimethylolpropane, di(trimethylolpropane) pentaerythritol, dipentaerythritol, tripentaerythritol, sugars and sugar alcohols such as sucrose and sorbitol, and the like. It is understood for the purpose of this invention only, that the polyether polyols can also be a blend of any of these polyether polyols together with one or more starter compounds, and the polyether polyols can also be one or more starter compounds themselves. Polyether polyols may also include polyols reacted with polyethers formed from copolymers of alkylene oxides, including block copolymers and polyethers "capped" with hydroxyethyl and/or hydroxypropoyl oligomers or polymers.

Polyfunctional nuclei may function as a backbone or spacer that limits the steric effects between the alkoxysilane anchoring chemistry and the nucleophilic functional groups. The molecular weight of the polyfunctional nucleus may be selected such that the active hydrogen functional groups. In some cases, the polyfunctional nucleus may have a molecular weight of 400 Da or greater, 450 Da or greater, 1000 Da or greater, or be in a range of 400 Da to 50,000 Da, 400 Da to 10,000 Da, or 400 Da to 5,000 Da.

In some cases, the polyfunctional nucleus is selected to control hydrophilicity and compatibility with other polymer additives and phases. For example, a polyfunctional nucleus may minimize the content of hydrophilic components such as polyethylene glycol to increase compatibility with polymer systems having nonpolar or aromatic character.

Macromolecular treatment agents may be prepared by reacting a polyfunctional nucleus with one or more equivalents of a bifunctional organosilane. Bifunctional organosilanes may have at least one electrophilic functional group (e.g., isocyanate, epoxide, carbodiimide) and at least one alkoxysilane (e.g., alkoxysilanes such as trimethoxysilane, dimethoxysilane, triethoxysilane etc.) that can form Si-O-M bond with inorganic fillers (M indicates inorganic elements such as Si, Al, Mg, Zn, and the like).

Bifunctional organosilanes disclosed herein are "bifunctional" in that they include at least on silane functionality and at least one electrophilic functionality. In some cases, bifunctional organosilanes may have a general chemical structure of $Si(OR)_n(R'Y)_{4-n}$, where n is an integer from 1 to 3, R is independently a C1 to C5 alkyl group, R' is a C1 to C20 hydrocarbon, and Y is an electrophilic functional group. In some cases, R' is a linear or branched, saturated or unsaturated, cyclic or aromatic C1 to C20 hydrocarbon. Y is an electrophilic functional group, where "electrophilic functional group" refers to a configuration of ions or atoms that accept an electron pair to form a covalent bond with a nucleophile, such as isocyanates, epoxy, allyl, vinyl, carboxylic acid, anhydrides, succinates, aldehydes, acid chlorides, aziridine, carbodiimides, oxetanes, sulfonyl chlorides, and the like. For example, bifunctional organosilanes may include 3-isocyanatopropyltrimethoxysilane, 3-glycidyloxypropyltrimethoxysilane, isocyanatomethyltrimethoxysilane, and triethoxysilylpropyl succinic anhydride.

Bifunctional organosilanes may also include organopolysiloxanes having one or more functional groups, such as propylsuccinic anhydride functionalized linear, branched, resinous, and hyperbranched organopolysiloxanes; methylsuccinic anhydride functionalized linear, branched, resinous, and hyperbranched organopolysiloxanes; cyclohexenyl anhydride functional linear, resinous, and hyperbranched organopolysiloxanes; carboxylic acid functionalized linear, branched, resinous, and hyperbranched organopolysiloxanes such as carboxydecyl terminated oligomeric or polymeric polydimethylsiloxanes; and aldehyde functionalized linear, branched, resinous, and hyperbranched organopolysiloxanes such as undecylenic aldehyde-terminated oligomeric or polymeric polydimethylsiloxanes.

Macromolecular treatment agents may have a molar ratio between the polyfunctional nucleus and the bifunctional organosilane that is at most 1:(f-1), where f refers to the functionality of the polyfunctional nucleus. In some cases, the macromolecular treatment agent is prepared by

reacting the polyfunctional nucleus and the at least one bifunctional organosilane at a molar ratio in a range of 1:1 to 1:(f-1).

Macromolecular treatment agents may be used to treat filler surfaces, substrates, and/or particles of inorganic materials. Fillers disclosed herein may include one or more of silicas, silicates, aluminum trihydrate (ATH), natural or synthetic aluminum oxide (alumina), and the like. Fillers may include inorganic particles such as silica (SiO_2) particles, titania (TiO_2) particles, zinc oxide (ZnO) particles, zirconia (ZrO_2) particles, alumina (Al_2O_3) particles, and the like. In some cases, the filler may have a D_{10} in the range of 0.1 to 10 microns, D_{50} in the range of 5 to 50 microns, and D_{90} in the range of 50 to 200 microns.

In addition to fillers, macromolecular treating agents may be applied to reinforcement materials containing nucleophilic groups as discussed above. Suitable reinforcement materials include any one or more of glass fibers, carbon nanotubes, graphene, carbon fibers, polyester fibers, natural fibers, aramid fibers, nylon fibers, basalt fibers, boron fibers, silicon carbide fibers, asbestos fibers, whiskers, hard particles, metal fibers, functionalized derivatives thereof, and the like. Macromolecular treating agents may be applied to the filler as a pre-treatment prior to introduction into a polymer system or polymer-forming system (e.g., in an A-side and/or B-side). The concentration may vary depending on the nature of the treating agent and the thermally conductive filler type. Treating agents disclosed herein may be added to a filler as a pre-treatment at a percent by weight of the filler (wt%) of 0.5 wt% to 10 wt%, 0.5 wt% to 7.5 wt%, or 0.5 wt% to 5 wt%. While the disclosure discusses filler and particle types, for avoidance of doubt, treatment agents may also be applied to larger dimensioned substrates and parts of similar inorganic composition without departing from the disclosure.

Macromolecular treating agents may be used in combination with one or more fillers and can be used in various applications as a component of a polyol and/or polyamine formulation for use in a polymer system, e.g., polyurethane materials, polyurethane hybrid materials (e.g., polyurethan acrylate hybrids), and the like. In some cases, polymer systems may generally include a polymer matrix obtained from combining a two-component curable composition. For example, polymer systems may include multi-component polyurethane systems having an isocyanate component ("A-side") and an isocyanate-reactive component ("B-side"). During application, the A-side and B-side are mixed, initiating a curing reaction at room temperature, and forming the selected polymer matrix. In some cases, macromolecular treating agents may be combined with a filler separately or in the presence of a polyamine and/or polyol to form an isocyanate-reactive component.

In some cases, fillers modified with macromolecular treatment agents may be used as a component in a polymer system (e.g., polyurethane or polyurethane hybrid) to prepare polyurethane articles, including foams, composites, films, and high density solids. In some cases, polymer systems may be formulated as a low viscosity (e.g., <20 Pa.s, such as 2 Pa.s to 10 Pa.s) foam-forming compositions containing a modified filler at a percent by weight of less than 60 wt%, such as ranging from 10 wt% to 60 wt% filler. Foams produced that contain modified filler can be used in applications known in the industry. For example, as flexible foams used in applications such as vehicle parts, including seats, armrests, dashboards or instrument panels, sun visors, door linings, noise insulation parts, shoe soles, cloth interliners, appliance, furniture, bedding, and the like.

Polymer systems may also be formulated as high viscosity (e.g., >20 Pa.s) with higher concentrations of modified filler (e.g., greater than 60 wt%, 70%, or 80%) of filler. Polymer systems containing high concentrations of fillers may be formulated as thermally conductive adhesives, gap fillers, and other thermal interface materials. Polymer systems may also be applied in stationary energy storage applications in private and commercial settings. Polymer systems may be formulated to satisfy constraints for automotive and mobility solutions (e.g., EV), but may be modified outside of those constraints for other related electrical and stationary energy storage applications. For example, a stationary storage applications may be formulated at higher densities/weights (>1 g/mL) and higher thermal conductivities (e.g., >0.2 W/m.K), where concerns regarding overall weight and the absence of external cooling are not a driving factor.

While formulation components and properties have been disclosed individually, it is envisioned that component elements (e.g., compounds in isocyanate or isocyanate-reactive components) may be included, excluded, or combined in any manner or subcombination utilizing any of the above concentration ranges and nested subranges therein. Further, that the recited formulation properties may be similarly achieved through various combinations of the recited components within the recited ranges.

The numerical ranges disclosed herein include all values from, and including, the lower and upper value and all values in between. Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percentages are based on weight and all test methods are current as of the filing date of this disclosure.

Examples

The following examples are provided to illustrate the embodiments of the invention, but are not intended to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated. Table 1 lists the materials used in the following examples.

Table 1: Chemical components used in the examples			
Category	Chemical Name	Specification	Supplier
Polyfunctional nucleus	VORALUX™ HF 505	Mw = 12000, f = 6	Dow
Polyfunctional nucleus	SPECFLEX™ NC 138	Mw = 6000, f = 3	Dow
Polyfunctional nucleus	VORANOL™ 8010G	Mw = 3000, f = 3	Dow
Polyfunctional nucleus	VORANOL™ 222-056	Mw = 2000, f = 2	Dow
Polyfunctional nucleus	PPG400	Mw = 425, f = 2	Merck
Polyfunctional nucleus	Tripropylene glycol (TPG)	Mw = 192.25, f = 2	Merck
Polyfunctional nucleus	VORANOL™ 4701	Mw = 5000, f = 3	Dow
Polyfunctional nucleus	VORANOL™ CP 450	Mw = 450, f = 3	Dow
Polyfunctional nucleus	JEFFAMINE™ T-5000	Mw = 5000, f = 3	Huntsman
Bifunctional Organosilane	Decyltrimethoxysilane (Z-6210)	Mw = 346.62	Merck
Bifunctional Organosilane	3-isocyanatopropyl trimethoxysilane	Mw = 205.28	Merck
Bifunctional Organosilane	3-glycidyloxypropyl trimethoxysilane (Z-6040)	Mw = 236.34	DOW
Filler	Aluminum Hydroxide, KH-101, surface untreated	$Al(OH)_3$, D_{50} = 0.8-1.2μm	KC Corporation
Filler	Aluminum Hydroxide, Martinal 3620, surface untreated	$Al(OH)_3$, multi size distribution, D_{90} = 100 μm	Huber
Filler	Aluminum Hydroxide, Martinal 3810, surface treated	$Al(OH)_3$, multi size distribution, D_{90} = 100 μm	Huber
Filler	Spherical alumina, BAK-5, surface untreated	Al_2O_3, D_{50} = 4.38 μm	Bestry
Filler	Spherical alumina, BAK-5H4, surface treated	Al_2O_3, D_{90} = 4.38 μm	Bestry
Filler	Calcium Carbonate, G5, surface untreated	$CaCO_3$, D_{50} = 2.4 μm	Huagcc Tech (Nantong) Co., LTD, China
Comparative Treatment Agent	Decyltrimethoxysilane, Z 6210	Mw = 262.46	Dow

Macromolecular silanes used in the examples were prepared as follows. In a first step, all active hydrogen containing chemicals were dehydrated until the water content reach below 0.05 wt% while stirring under 20 mbar vacuum at 130 °C. The dehydrated chemicals were then cooled to room temperature under nitrogen atmosphere before further use.

For the reaction between hydroxyl and isocyanate groups, the system was heated to 50 °C under stirring, followed by addition of the stoichiometric amount of the silane-containing chemicals according to the formulations in Tables 2 and 3. After mixing at 50 °C for 30 min, the components were reacted at 80 to 85 °C for 1.5 hours, then at 88 to 92 °C for 1.5 hours. The mixture was then cooled to room temperature under nitrogen atmosphere.

For the reaction between amine and epoxy groups, the system was stirred under room temperature, followed by addition of the stoichiometric amounts of the epoxy- and silane-containing chemicals according to the formulations in Tables 2 and 3. The mixture was reacted at room temperature for 1.5 hours and then sealed with nitrogen atmosphere for future use.

Table 2: Components used in the preparation of macromolecular silane formulations

	Composition		1	2	3	4	5
			TPG-$Si(OMe)_3$	PPG400-$Si(OMe)_3$	222-056-$Si(OMe)_3$	NC138-$Si(OMe)_3$	8010G-$Si(OMe)_3$
Polyfunctional Nucleus	TPG	Mw = 192.25, f = 2	50.4	-	-	-	-
	PPG400	Mw = 425, f = 2	-	67.9	-	-	-
	VORANOL™ 222-056	Mw = 2000, f = 2	-	-	91.1	-	-
	SPECFLEX™ NC 138	Mw = 6000, f = 3	-	-	-	96.8	-
	VORANOL™ 8010G	Mw = 3000, f = 3	-	-	-	-	93.9
	VORALUX™ HF 505	Mw = 12000, f = 6	-	-	-	-	-
	JEFFAMINE™ T-5000	Mw = 5000, f = 3	-	-	-	-	-
Bifunctional Organosilane	3-isocyanatopropyl trimethoxysilane		49.6	32.1	8.9	3.2	6.1
	3-glycidyloxypropyl trimethoxysilane (Z-6040)		-	-	-	-	-
Total			100	100	100	100	100

Table 3: Components used in the preparation of macromolecular silane formulations

	Composition		6	7	8	9	10
			HF505-Si(OMe)$_3$	T-5000-Si(OMe)$_3$	HF505-2Si(OMe)$_3$	HF505-3Si(OMe)$_3$	HF505-5Si(OMe)$_3$
Polyfunctional Nucleus	TPG	Mw = 192.2, f = 2	-	-	-	-	-
	PPG400	Mw = 425, f = 2	-	-	-	-	-
	VORANOL™ 222-056	Mw = 2000, f = 2	-	-	-	-	-
	SPECFLEX™ NC 138	Mw = 6000, f = 3	-	-	-	-	-
	VORANOL™ 8010G	Mw = 3000, f = 3	-	-	-	-	-
	VORALUX™ HF 505	Mw = 12000, f = 6	98.4	-	96.8	95.2	92.0
	JEFFAMINE™ T-5000	Mw = 5000, f = 3	-	96.2	-	-	-
Bifunctional Organosilane	3-isocyanatopropyl trimethoxysilane		1.6	-	3.2	4.8	8.0
	3-glycidyloxypropyl trimethoxysilane (Z-6040)		-	3.8	-	-	-
Total			100	100	100	100	100

Polyol Compatibility Testing

In the following examples, polyol formulations were prepared with filler particles with varied surface treatments. Sample formulations and testing results are shown in Tables 4 to 7.

In a first step, all fillers were dehydrated in a vacuum oven at 130 °C for 3 hours under 25 mbar vacuum. Active hydrogen containing chemicals were dehydrated using procedures described above. Sample formulations for each sample were prepared by mixing the components indicated in Tables 4 to 7 and reacting the mixture with stirring at 145 °C for 3 hours and under 25 mbar vacuum. Samples were then sealed with nitrogen atmosphere and cooled to room temperature before testing.

Viscosity testing at various shear rates (0.01-100 s^{-1}) was performed using DHR-III Rheometer (TA Instruments) with 40 mm parallel plate at 0.5 mm gap and 25 °C.

The instability index (colloidal instability) for the samples was characterized using a LUMiSizer 6513-37 (12 channels, L.U.M GmbH) on 0.5 mL in a polyamide tube following centrifugation at 2500 rpm for 1 hour at 50 °C. Instability index is obtained through the machine-equipped software SEPView™ 6.4.177.7135 © L.U.M GmbH - www.lum-gmbh.de.

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Table 4: Comparison of polyol compositions containing surface treated fillers							
	Sample	11	13	14	15	16	17
		C1	C2	C3	I1	I2	I3
Treatment Agent	Z 6210	-	1		-	-	-
	TPG-Si(OMe)$_3$	-	-	1	-	-	-
	PPG400-Si(OMe)$_3$	-	-	-	1.8	-	-
	222-056-Si(OMe)$_3$	-	-	-	-	9	-
	NC138-Si(OMe)$_3$	-	-	-	-	-	9
	8010G-Si(OMe)$_3$	-	-	-	-	-	-
	HF505-Si(OMe)$_3$	-	-	-	-	-	-
	HF505-2Si(OMe)$_3$	-	-	-	-	-	-
	HF505-3Si(OMe)$_3$	-	-	-	-	-	-
	HF505-5Si(OMe)$_3$	-	-	-	-	-	-
	T-5000-Si(OMe)$_3$	-	-	-	-	-	-
Filler	KH 101 ATH (untreated)	40	40	40	40	40	40
Polyol	Voranol™ 4701	51	51	51	51	51	51
	Voralux™ HF 505	9	8	8	8	-	-
	JEFFAMINE™ T-5000	-	-	-	-	-	-
Total		100	100	100	100	100	100
Molar ratio of active hydrogen/silane in treatment agent		N/A	0	1	1	1	2
Mw. backbone between active hydrogen and silane in treatment agent		N/A	N/A	259	467	2067	4067
Low Shear Viscosity (Pa*s, 0.02 s^{-1})		14	12	21.88	11.41	4.9	6
High Shear Viscosity (Pa*s, 10 s^{-1})		6.9	7.5	7.04	5.98	5.1	5.5
Instability index (lower is better)		0.081	0.075	0.08	0.071	0.068	0.07

Table 5: Comparison of polyol compositions containing surface treated fillers							
	Sample	18	19	20	21	22	23
		I4	I5	I6	I7	C4	I8
Treatment Agent	Z 6210	-	-	-	-	-	-
	TPG-Si(OMe)$_3$	-	-	-	-	-	-
	PPG400-Si(OMe)$_3$	-	-	-	-	-	-
	222-056-Si(OMe)$_3$	-	-	-	-	-	-
	NC138-Si(OMe)$_3$	-	-	-	-	-	-
	8010G-Si(OMe)$_3$	9	-	-	-	-	-
	HF505-Si(OMe)$_3$		9	-	-	-	-
	HF505-2Si(OMe)$_3$	-	-	9	-	-	-
	HF505-3Si(OMe)$_3$	-	-	-	9	-	-

	HF505-5Si(OMe)$_3$	-	-	-	-	9	-
	T-5000-Si(OMe)$_3$	-	-	-	-	-	9
Filler	KH 101 ATH (untreated)	40	40	40	40	40	40
Polyol	Voranol™ 4701	51	51	51	51	51	51
	Voralux™ HF 505	-	-	-	-	-	-
	JEFFAMINE™ T-5000	-	-	-	-	-	-
Total		100	100	100	100	100	100
Molar ratio of active hydrogen/silane in treatment agent		2	5	2	1	0.2	1
Mw. backbone between active hydrogen and silane in treatment agent		2067	4067	4067	4067	4067	3387
Low Shear Viscosity (Pa*s, 0.02 s^{-1})		7.6	6.8	4.98	5.95	11.1	6.5
High Shear Viscosity (Pa*s, 10 s^{-1})		6.1	6.4	5.97	6.57	14.3	6.6
Instability index (lower is better)		0.059	0.064	0.05	0.05	0.03	0.05

Table 6: Comparison of polyol compositions containing surface treated fillers

	Composition	12	24	25	26	27
	Entry Type	C5	I9	C6	I10	C7
Treatment Agent	222-056-Si(OMe)$_3$	-	-	-	-	-
	NC138-Si(OMe)$_3$	-	-	-	9	-
	8010G-Si(OMe)$_3$	-	-	-	-	-
	HF505-Si(OMe)$_3$	-	9	-	-	-
	HF505-2Si(OMe)$_3$	-	-	-	-	-
	HF505-3Si(OMe)$_3$	-	-	-	-	-
	HF505-5Si(OMe)$_3$	-	-	-	-	-
	T-5000-Si(OMe)$_3$	-	-	-	-	-
Filler	KH 101 ATH (untreated)	50	50	-	-	-
	BAK-5 Al_2O_3 (untreated)	-	-	-	-	-
	BAK-5H4 Al_2O_3 (commercially treated)	-	-	-	-	-
	Martinal 3620 ATH (untreated)	-	-	80	80	-
	Martinal 3810 ATH (commercially treated)	-	-	-	-	80
	G5 $CaCO_3$ (*)	-	-	-	-	-
Polyol	Specflex NC 138	-	-	10	11	10
	Voranol 4701	41	41	10	-	10
	Voranol CP 450	-	-	-	-	-
	HF 505	9	-	-	-	-
Total		11.41	100	100	100	100
Molar ratio of active hydrogen/silane in treatment agent		N/A	5	N/A	2	N/A
Mw. backbone between active hydrogen and silane in treatment agent		N/A	4067	N/A	4067	N/A
Low Shear Viscosity (Pa*s, 0.02 s^{-1})		45	16.5	3480	250	1375

High Shear Viscosity (Pa*s, 10 s^{-1})	21	16.1	42	40	41
Instability index (lower is better)	0.07	0.05	0.21	0.07	0.19

Table 7: Comparison of polyol compositions containing surface treated fillers

	Composition	28	29	31	30	32
	Entry Type	C8	C9	I11	C10	C11
Treatment Agent	222-056-Si(OMe)$_3$	-	-	9		9
	NC138-Si(OMe)$_3$	-	-	-	-	-
	8010G-Si(OMe)$_3$	-	-	-	-	-
	HF505-Si(OMe)$_3$	9	-	-	-	-
	HF505-2Si(OMe)$_3$	-	-	-	-	-
	HF505-3Si(OMe)$_3$	-	-	-	-	-
	HF505-5Si(OMe)$_3$	-	-	-	-	-
	T-5000-Si(OMe)$_3$	-	-	-	-	-
Filler	KH 101 ATH (untreated)	-	-	-	-	-
	BAK-5 Al_2O_3 (untreated)	-	80	80	-	-
	BAK-5H4 Al_2O_3 (commercially treated)	-	-	-	80	80
	Martinal 3620 ATH (untreated)	-	-	-	-	-
	Martinal 3810 ATH (commercially treated)	-	-	-	-	-
	G5 $CaCO_3$ (*)	40	-	-	-	-
Polyol	Specflex NC 138	-	-	-	-	-
	Voranol 4701	51	-	-	-	-
	Voranol CP 450	-	20	11	20	11
	HF 505	-	-	-	-	-
Total		100	100	100	100	100
Molar ratio of active hydrogen/silane in stabilizer		5	N/A	1	N/A	1
Mw backbone between active hydrogen and silane in stabilizer		4067	N/A	2067	N/A	2067
Viscosity (Pa*s, 0.02 s^{-1})		6.1	7	1.7	6	6.3
Viscosity (Pa*s, 10 s^{-1})		5.5	1.1	0.9	1.8	1.9
Instability index		Sediment	0.31	0.21	0.21	0.18

As shown in Tables 4 and 5, comparative examples generally exhibit higher viscosities and higher instability index values relative to the inventive samples. Of note, comparative example C1 exhibited high viscosity and instability index due to untreated filler and lack of treatment agent. C2 exhibited slight viscosity reduction and slight stability improvement with commercially available low molecular weight surface modification agent/stabilizer Z 6210

(decyltrimethoxysilane) on the filler. C3 exhibited increased viscosity at low shear but unchanged viscosity at high shear. The lack of stability improvement was attributed to the short spacer between the silane and the hydroxyl groups (TPG-Si(OMet)$_3$, mw = 240 g/mol) of the bifunctional organosilane on ATH.

For inventive examples I1-I7, filler stabilized with macromolecular treatment agents show low viscosity at both high and low shear rates and colloidal stability (small values of instability index) relative to C1-C3 with 40 wt% filler loading. The difference is attributed to the larger constituent polyfunctional nucleus (Mw $\geq$ 400 g/mol of the backbone between active hydrogen and silane in the macromolecular treatment agent providing more intramolecular distance between the organosilane anchor and the reactive hydrogens.

C4 exhibits high viscosity, which is attributed to a low ratio of active hydrogen and silane groups (only 1:5) on the macromolecular treating agents, which leads to filler particle-particle aggregation and deterioration in viscosity as well as colloidal stability. In comparison, I8 exhibited better performances at viscosity reduction and stability improvement compared to C4 at 40 wt% loading of ATH, but using glycidyl-based T-5000-Si(OMet)$_3$ to prepare the macromolecular silane. C5 exhibited high viscosity and poor colloidal stability due to non-treated surface and increased loading of the filler, while I9 provides viscosity reduction and stability improvement compared to C5 at 50 wt% filler loading of ATH.

C6 containing commercial ATH fillers with broad size distribution and without surface modification exhibited high viscosity and instability index, while I10 showed improvement of the viscosity and colloidal stability with the incorporation of macromolecular treatment agent NC138-Si(OMet)$_3$.

C9 containing Al_2O_3 filler exhibited high viscosity and high instability index, while the addition of macromolecular treatment agent 222-056-Si(OMe)$_3$ in I11 provided improved viscosity and colloidal stability performance.

C7 containing commercial surface treated filler exhibited high viscosity and high instability. C8 also exhibited poor colloidal stability, which was unchanged through the addition of macromolecular treatment agent. This lack of change was attributed to the unavailability of hydroxyl groups on the surface of the filler that could interact with the organosilane of the treatment agent. Similarly, surface treated Al_2O_3 fillers in C10 exhibited high viscosity and high instability index, which is unchanged with the addition of macromolecular treatment agent C11 potentially due to unavailability of hydroxyl groups for reaction with the organosilane.

While the foregoing is directed to exemplary embodiments, other and further embodiments may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

CLAIMS

1. A method of generating a modified filler composition, comprising contacting:
a filler; and
a macromolecular treatment agent prepared from a reaction of:
at least one bifunctional organosilane; and
a polyfunctional nucleus having at least two nucleophilic functional groups and having a number average molecular weight of at least 400 Da.

2. The method of claim 1, wherein the macromolecular treatment agent comprises at least two nucleophilic groups.

3. The method of claim 1, wherein the macromolecular treatment agent comprises at least two alkoxysilanes.

4. The method of claim 1, wherein macromolecular treatment agent is prepared by reacting the polyfunctional nucleus and the at least one bifunctional organosilane at a molar ratio in a range of 1:1 to 1:(f-1), where f refers to the functionality of the polyfunctional nucleus.

5. The method of claim 1, wherein the modified filler is prepared by combining the filler with the at least one bifunctional organosilane, followed by a reaction with the polyfunctional nucleus.

6. The method of claim 1, wherein the modified filler composition further comprises a polyether polyol or polyether amine, and wherein the modified filler is present at a percent by weight (wt%) of the composition of at least 50 wt%.

7. The method of claim 6, wherein the filler is contacted with the macromolecular treatment agent prior to combination with a polyether polyol or polyether amine.

8. A modified filler produced by the method of claim 1.

9. A method comprising preparing a dispersion by admixing:

a modified filler prepared by reacting a filler with at least one bifunctional organosilane and a polyfunctional nucleus having at least two nucleophilic functional groups and having a number average molecular weight of at least 400 Da; and

a polyether polyol or polyether polyamine.

10. The method of claim 9, wherein the modified filler is prepared by combining the filler with the at least one bifunctional organosilane, followed by a reaction with the polyfunctional nucleus.

11. The method of claim 9, wherein the modified filler is prepared by combining the filler with the at least one bifunctional organosilane and the polyfunctional nucleus in the presence of the polyether polyol or polyether amine.

INTERNATIONAL SEARCH REPORT

International application No
PCT/CN2023/098801

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09C1/02 C09C1/40 C09C3/12
ADD.

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)
C09C

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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2010/041708 A1 (DENKI KAGAKU KOGYO KK [JP]; MIYAZAKI HAYATO [JP] ET AL.) 15 April 2010 (2010-04-15) PAJ-Abstract; example Comparative example 1 -----	1-11
A	JO S ET AL: "Surface modification using silanated poly(ethylene glycol)s - on the role of cleanliness, contamination, and preparation procedures", BIOMATERIALS, ELSEVIER, AMSTERDAM, NL, vol. 21, no. 6, 1 March 2000 (2000-03-01), pages 605-616, XP004187178, ISSN: 0142-9612, DOI: 10.1016/S0142-9612(99)00224-0 abstract, chapter "1. Introduction"; chapter "2. experimentals" ----- -/--	1-11

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

[x] See patent family annex.

* Special categories of cited documents :

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

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 February 2024	20/02/2024

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/CN2023/098801

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ZHANG ET AL: "Synthesis of poly(ethylene glycol) (PEG)-grafted colloidal silica particles with improved stability in aqueous solvents", JOURNAL OF COLLOID AND INTERFACE SCIENCE, ACADEMIC PRESS,INC, US, vol. 310, no. 2, 27 April 2007 (2007-04-27), pages 446-455, XP022057041, ISSN: 0021-9797, DOI: 10.1016/J.JCIS.2007.02.024 Chapter "1.Introduction" to "3. The new grafting procedure"; Figs 1 and 2; Chapter 4.4 PEGylation and purification -----	1-11

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/CN2023/098801

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010041708 A1	15-04-2010	JP 2011256214 A	22-12-2011
		WO 2010041708 A1	15-04-2010