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(54) TWO-PART SIZING COMPOSITION FOR REINFORCEMENT FIBERS

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(57) **ABSTRACT**

A two-part sizing formulation that imparts improved strength of reinforced composites including a size composition and a binder composition is provided. The size composition may include one or more coupling agents and one or more film forming agents. The binder composition includes a high acid number copolymer formed from the polymerization of maleic anhydride or maleic acid and at least one other desired monomer and/or a high acid number polycarboxylic acid. In a preferred embodiment, the binder composition includes an ethylene-maleic acid copolymer formed by the hydrolysis of an ethylene-maleic anhydride copolymer. The size composition may be applied to a reinforcing fiber material before the binder size material is applied. The two-part size composition may be applied to a reinforcing fiber material to form a reinforcing fiber product which may then be densified or compacted to form a densified reinforcing fiber product, such as a pellet.

FIGURE 1

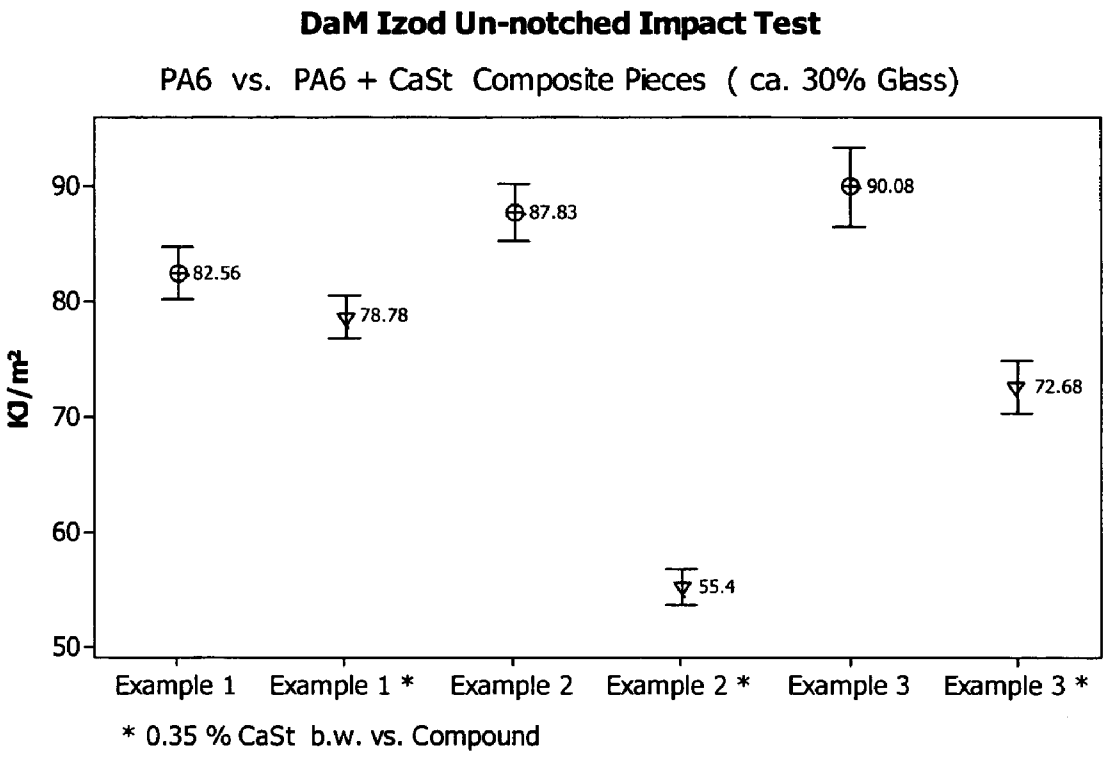

DaM Izod Un-notched Impact Test
PA6 vs. PA6 + CaSt Composite Pieces (ca. 30% Glass)
KJ/m²
90
80
70
60
50
82.56
78.78
87.83
55.4
90.08
72.68
Example 1
Example 1 *
Example 2
Example 2 *
Example 3
Example 3 *
* 0.35 % CaSt b.w. vs. Compound

FIGURE 2

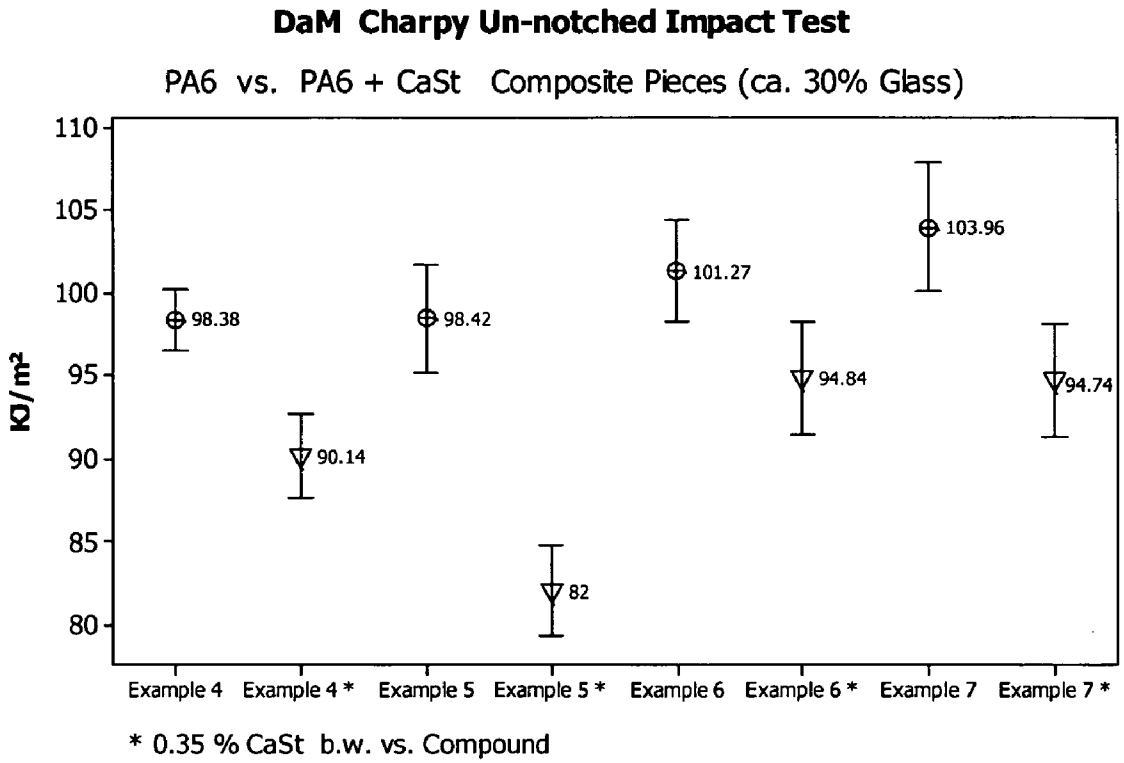

DaM Charpy Un-notched Impact Test
PA6 vs. PA6 + CaSt Composite Pieces (ca. 30% Glass)
KJ/m²
110
105
100
95
90
85
80
98.38
90.14
98.42
82
101.27
94.84
103.96
94.74
Example 4
Example 4 *
Example 5
Example 5 *
Example 6
Example 6 *
Example 7
Example 7 *
* 0.35 % CaSt b.w. vs. Compound

FIGURE 3

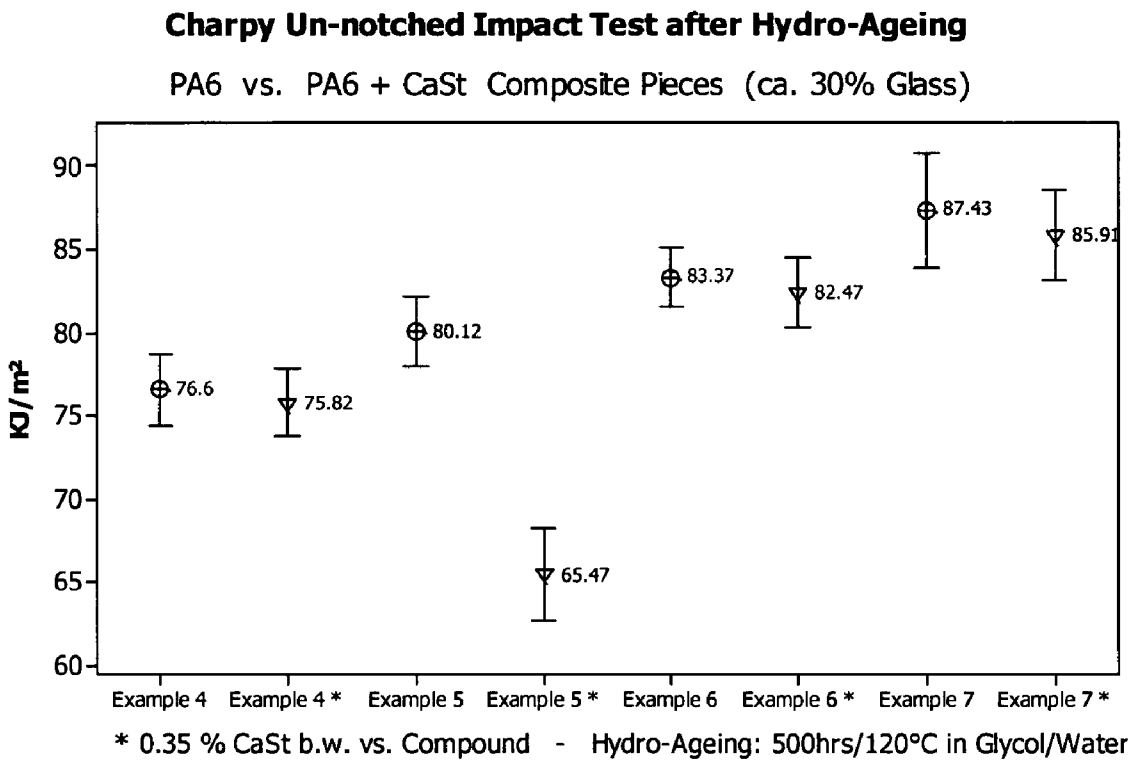

Charpy Un-notched Impact Test after Hydro-Ageing
PA6 vs. PA6 + CaSt Composite Pieces (ca. 30% Glass)
KJ/m²
90
85
80
75
70
65
60
76.6
75.82
80.12
65.47
83.37
82.47
87.43
85.91
Example 4
Example 4 *
Example 5
Example 5 *
Example 6
Example 6 *
Example 7
Example 7 *
* 0.35 % CaSt b.w. vs. Compound - Hydro-Ageing: 500hrs/120°C in Glycol/Water

FIGURE 4

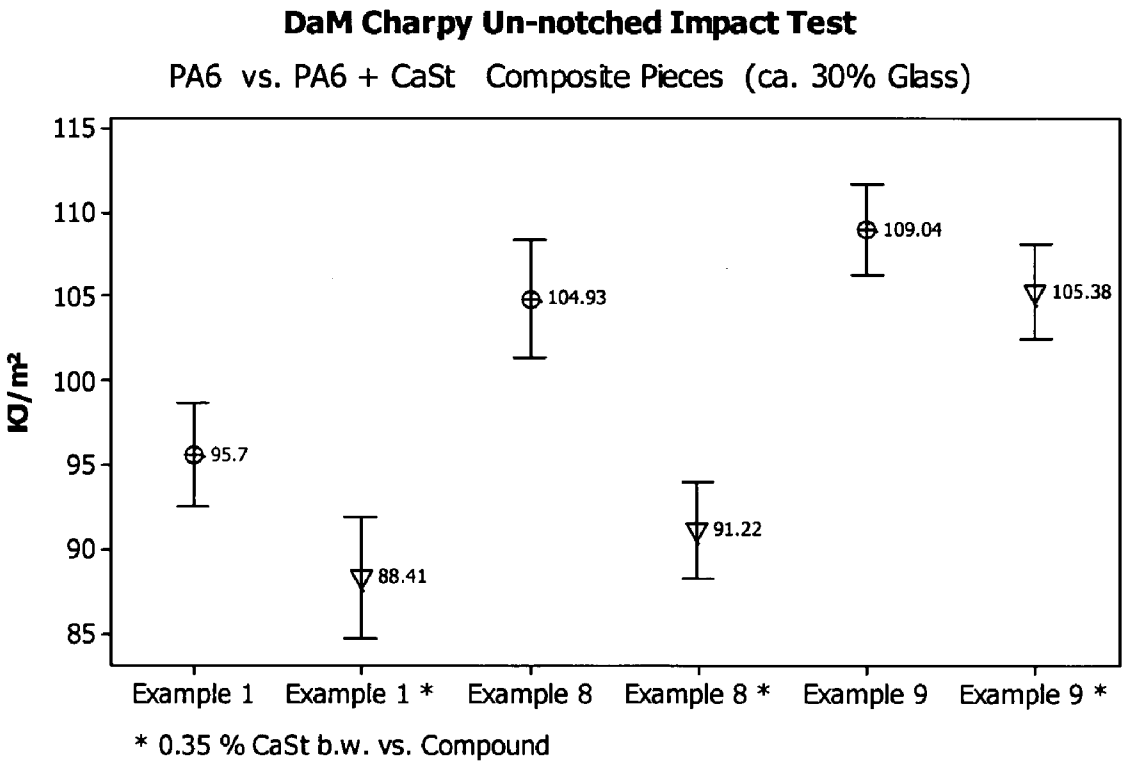
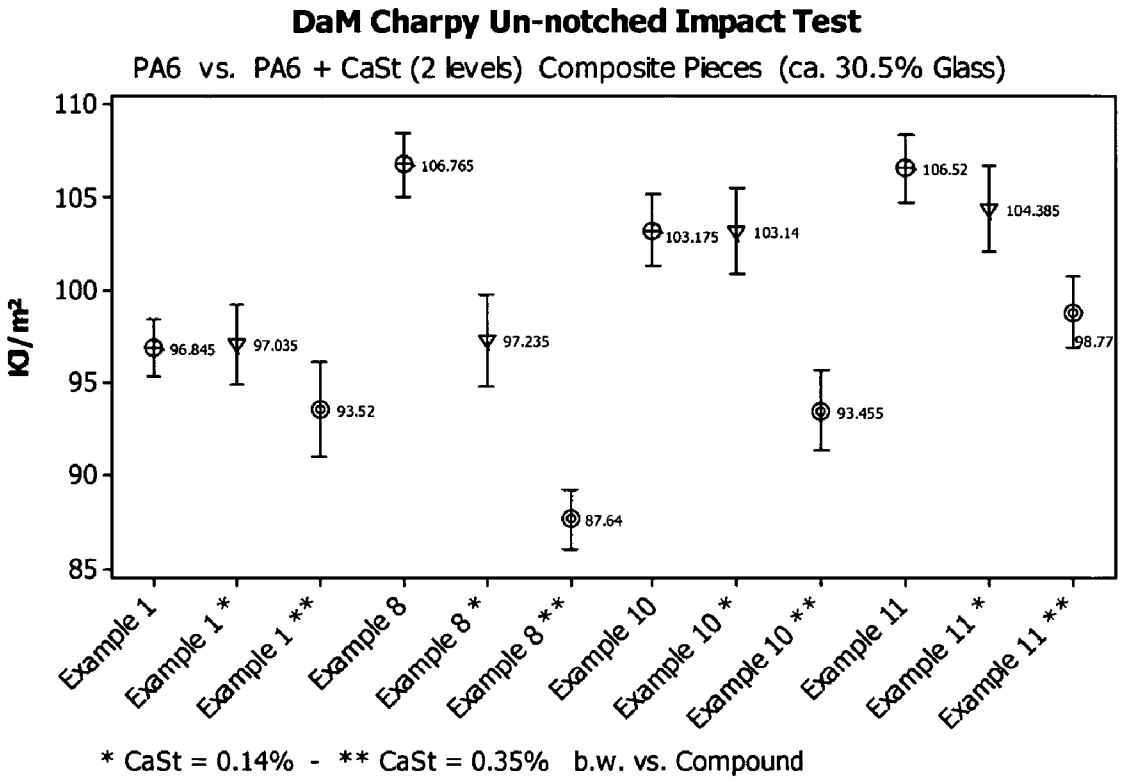

DaM Charpy Un-notched Impact Test
PA6 vs. PA6 + CaSt Composite Pieces (ca. 30% Glass)
KJ/m²
115
110
105
100
95
90
85
95.7
88.41
104.93
91.22
109.04
105.38
Example 1
Example 1 *
Example 8
Example 8 *
Example 9
Example 9 *
* 0.35 % CaSt b.w. vs. Compound

FIGURE 5



* CaSt = 0.14% - ** CaSt = 0.35% b.w. vs. Compound

TWO-PART SIZING COMPOSITION FOR REINFORCEMENT FIBERS

TECHNICAL FIELD AND INDUSTRIAL APPLICABILITY OF THE INVENTION

[0001] The present invention relates generally to a sizing composition for a reinforcing fiber material, and more particularly, to a two-part sizing formulation that imparts improved strength to reinforced composites which includes a size composition and a binder composition. A composite article formed from a reinforcing fiber material sized with a two-part sizing formulation is also provided.

BACKGROUND OF THE INVENTION

[0002] Glass fibers are useful in a variety of technologies. For example, glass fibers are commonly used as reinforcements in polymer matrices to form glass fiber reinforced plastics or composites. Glass fibers have been used in the form of continuous or chopped filaments, strands, rovings, woven fabrics, nonwoven fabrics, meshes, and scrims to reinforce polymers. It is known in the art that glass fiber reinforced polymer composites possess higher mechanical properties compared to unreinforced polymer composites, provided that the reinforcement fiber surface is suitably modified by a sizing composition. Thus, better dimensional stability, tensile strength and modulus, flexural strength and modulus, impact resistance, and creep resistance may be achieved with glass fiber reinforced composites.

[0003] Chopped glass fibers are commonly used as reinforcement materials in reinforced composites. Conventionally, glass fibers are formed by attenuating streams of a molten glass material from a bushing or orifice. The glass fibers may be attenuated by a winder that collects gathered filaments into a package or by rollers that pull the fibers before they are collected and chopped. An aqueous sizing composition, or chemical treatment, is typically applied to the fibers after they are drawn from the bushing. After the fibers are treated with the aqueous sizing composition, they may be dried in a package or chopped strand form.

[0004] Chopped strand segments may be mixed with a polymeric resin and supplied to a compression- or injection-molding machine to be formed into glass fiber reinforced composites. Typically, the chopped strand segments are mixed with pellets of a thermoplastic polymer resin in an extruder. In one conventional method, polymer pellets are fed into a first port of a twin screw extruder and the chopped glass fibers are fed into a second port of the extruder with the melted polymer to form a fiber/resin mixture. Alternatively, the polymer pellets and chopped strand segments are dry mixed and fed together into a single screw extruder where the resin is melted, the integrity of the glass fiber strands is destroyed, and the fiber strands are dispersed throughout the molten resin to form a fiber/resin mixture. Next, the fiber/resin mixture is degassed and formed into pellets. These dry fiber strand/resin dispersion pellets are then fed to a molding machine and formed into molded composite articles that have a substantially homogeneous dispersion of glass fiber strands throughout the composite article.

[0005] Unfortunately, chopped glass fibers are often bulky and do not flow well in automated equipment. As a result, the chopped fiber strands may be compacted into rod-shaped bundles or pellets to improve their flowability and to enable the use of automated equipment, such as, for example, for transporting the pellets and mixing the pellets with the polymer resins. U.S. Pat. No. 5,578,535 to Hill et al. discloses glass fiber pellets that are from about 20% to 30% denser than the individual glass strands from which they are made, and approximately 5 to 15 times larger in diameter. These pellets are prepared by hydrating cut fiber strand segments to a hydration level sufficient to prevent separation of the fiber strand segments into individual filaments but insufficient to cause the fiber strand segments to agglomerate into a clump. The hydrated strand segments are then mixed for a period of time sufficient for the strand segments to form pellets. Suitable mixing methods include processes that keep the fibers moving over and around one another, such as by tumbling, agitating, blending, commingling, stirring and/or intermingling the fibers.

[0006] Sizing compositions, such as are used in reinforced composites, are well-known in the art and conventionally include a polyacid polymeric component, a film forming polymeric component, a coupling agent, and a lubricant. A polyacid sizing composition is typically added to glass fibers to reduce interfilament abrasion and to make the glass fibers compatible with the polymeric matrices they are intended to reinforce. The sizing composition also ensures the integrity of the strands of glass fibers, e.g., the interconnection of the glass filaments that form the strand.

[0007] One fundamental problem associated with polyacid conventional sizing compositions used in reinforced composites is the presence of a di-cationic species, such as a metallic salt of a long chain carboxylic acid, in the polymer used to form a reinforced composite article. The interaction of the di-cationic lubricant with the polyacid conventional sizing compositions causes a decrease in mechanical strength. For example, polyamide composites reinforced with conventional sizing compositions often demonstrate a reduction in impact strengths (e.g., Charpy or Izod, unnotched or notched) as well as a reduction in tensile strength and elongation at break when such tests are run on hydroaged composite pieces. Thus, there exists a need in the art for a sizing composition that confers improved mechanical strength to reinforced composites that contain a di-cationic lubricant.

SUMMARY OF THE INVENTION

[0008] It is an object of the present invention to provide a two-part sizing formulation that imparts improved dry-as-molded (DaM) mechanical properties and hydrolysis resistance to reinforced polymer composites (e.g., reinforced polyamide composites), even when such composites contain di-cationic or higher valency cation additives such as a calcium stearate lubricant. The two-part sizing formulation includes a size composition and a binder composition. The size composition may be applied to a reinforcing fiber material before the binder composition is applied. The reinforcing fiber material may be one or more strands of glass (e.g., Advantex® glass), natural fibers, carbon fibers, or one or more synthetic polymers. According to at least one exemplary embodiment of the present invention, the size composition includes one or more coupling agents and one or more resinous film forming agents. Preferably, the coupling agent is an aminosilane or a diaminosilane. In addition, the size composition may optionally include conventional additives such as lubricants, wetting agents, pH adjusters,

antioxidants, antifoaming agents, processing aids, antistatic agents, and/or non-ionic surfactants.

[0009] The binder composition includes a high acid number copolymer formed from the polymerization of maleic anhydride or maleic acid and at least one other desired monomer and/or a high acid number polycarboxylic acid. The maleic anhydride or acid copolymer may be a pure copolymer or a derivative in the anhydride, acid, salt, or partial-ester, -amide, or -imide form. Suitable copolymers include C_2-C_5 α-olefins, such as butadiene-, ethylene-, propylene- or (iso)butylene-maleic acid copolymers, and methyl vinyl ether-maleic acid copolymers. In a preferred embodiment, the binder composition includes an ethylene-maleic acid copolymer formed by the hydrolysis of an ethylene-maleic anhydride copolymer. The binder composition may also include a film forming agent, which may be the same as, or different from, the film forming agent in the size composition. Conventional additives such as lubricants, surfactants, and anti-static agents may also be included in the binder composition.

[0010] It is yet another object of the present invention to provide a process for making a densified reinforcing fiber product. The process for making a densified reinforcing fiber product may be an in-line process that includes applying a two-part sizing formulation as described above to a strand of a reinforcing fiber material, chopping the strand of sized reinforcing fibers into segments, applying a binder composition as described above to the segments, and pelletizing and/or densifying the segments to form the densified reinforcing fiber product. Pellet formation and densification may occur in separate tumbling apparatuses, such as in a rotary drum (e.g., pelletizer) and rotating zig-zag tube (e.g., densifier). Alternatively, pellet formation and densification may occur in separate regions within a single apparatus, such as in a "Zig-Zag" blender commercially available from Patterson Kelly. The size composition may be applied to the fibers as they are being formed and the binder composition may be applied to the sized fibers in a pelletizer. By applying the binder composition in the pelletizer, an application efficiency of approximately 95% to 100% for the binder composition may be obtained. In addition, applying the binder composition separately from the size composition outside the fiber-forming environment permits the inclusion of materials that are not desirably applied during the fiber-forming process because of safety, flammability, irritation, stability, low compatibility with aminosilanes, viscosity, toxicity, cleanliness, odor, cost, and/or shear sensitivity.

[0011] It is an advantage of the present invention that a high loss-on-ignition (LOI) of the high acid number maleic anhydride copolymer, ethylene maleic acid copolymer, or polycarboxylic acid in the sizing composition provides for improved dry-as-molded mechanical properties and improved hydrolysis resistance.

[0012] It is another advantage of the present invention that polyurethane film formers present in the sizing composition demonstrate good compatibility with polyamide matrices, which helps to improve the dispersion of the reinforcement fiber bundles in the melt (e.g., in extrusion process or injection molding process) when forming a composite article. This increased fiber dispersion may cause a reduction of defects such as visual defects in the final product, a reduction in processing breaks, and/or low mechanical properties in the final article.

[0013] It is a further advantage of the present invention that the polyurethane dispersion present in the sizing composition improves the compatibility of the sizing composition with the di-cationic species containing polymer to improve the dispersion of the fibers during further processing to form a composite article.

[0014] It is yet another advantage that the present invention imparts improved physical properties such as improved dry-as-molded (DaM) mechanical properties of the composite part or after aging the composite part in severe hydrolysis conditions to composites formed from industrially processable and easily dispersible pellets.

[0015] It is also an advantage of the present invention that the two-part sizing formulation has improved stability over conventional sizing formulations that contain an aminosilane and a polyacid in the same mixture.

[0016] The foregoing and other objects, features, and advantages of the invention will appear more fully hereinafter from a consideration of the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The advantages of this invention will be apparent upon consideration of the following detailed disclosure of the invention, especially when taken in conjunction with the accompanying drawings wherein:

[0018] FIG. **1** is a graphical illustration of dry-as-molded (DaM) Izod Un-notched Impact tests on polyamide 6 and polyamide 6/calcium stearate composite pieces;

[0019] FIG. **2** is a graphical illustration of dry-as-molded (DaM) Charpy Un-notched Impact tests on polyamide 6 and polyamide 6/calcium stearate composite pieces;

[0020] FIG. **3** is a graphical illustration of Charpy Un-notched Impact tests after hydro-aging polyamide 6 and polyamide 6/calcium stearate composite pieces;

[0021] FIG. **4** is a graphical illustration of dry-as-molded (DaM) Charpy Un-notched Impact tests on polyamide 6 and polyamide 6/calcium stearate composite pieces; and

[0022] FIG. **5** is a graphical illustration of dry-as-molded (DaM) Charpy Un-notched Impact tests on polyamide 6 and polyamide 6/calcium stearate composite pieces.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS OF THE INVENTION

[0023] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are described herein. All references cited herein, including published or corresponding U.S. or foreign patent applications, issued U.S. or foreign patents, and any other references, are each incorporated by reference in their entireties, including all data, tables, figures, and text presented in the cited references. The terms "film forming agent" and "film former" may be used interchangeably herein. In addition, the terms "reinforcing fiber material" and "reinforcing fiber" may be used interchangeably herein.

[0024] The present invention relates to a two-part sizing formulation that improves the mechanical performance of reinforced composites. In particular, the two-part sizing formulation of the invention imparts improved dry-as-molded mechanical properties and hydrolysis resistance to polymer reinforced composites, such as a polyamide reinforced composite, even when such composites contain di-cationic or higher valency additives such as a calcium stearate lubricant. It is to be appreciated that although any di-cation or higher valency cation may applicable to the present invention, di-cations are discussed in detail herein for ease of discussion. The two-part sizing formulation includes a size composition and a binder composition. The two-part sizing formulation may be applied to a reinforcing fiber material to form a reinforcing fiber product, which may then be densified or compacted to form a densified reinforcing fiber product, such as pellets. The densified pellets provide a convenient form for storage and handling of the chopped fibers used as reinforcing materials in composite structures.

[0025] The size composition may be applied to a reinforcing fiber material before the binder composition is applied. The reinforcing fiber material may be one or more strands of glass formed by conventional techniques such as by drawing molten glass through a heated bushing to form substantially continuous glass fibers. These fibers may subsequently be collected into a glass strand. Any type of glass, such as A-type glass, C-type glass, E-type glass, S-type glass, or ECR-type glass such as Owens Corning's Advantex® glass fibers. Preferably, the reinforcing fiber material is E-type glass or Advantex® glass.

[0026] Alternatively, the reinforcing fiber material may be strands of one or more synthetic polymers such as polyester, polyamide, aramid, and mixtures thereof. The polymer strands may be used alone as the reinforcing fiber material, or they can be used in combination with glass strands such as those described above. As a further alternative, natural fibers may be used as the reinforcing fiber material. The term "natural fiber" as used in conjunction with the present invention refers to plant fibers extracted from any part of a plant, including, but not limited to, the stem, seeds, leaves, roots, or phloem. Examples of natural fibers suitable for use as the reinforcing fiber material include cotton, jute, bamboo, ramie, bagasse, hemp, coir, linen, kenaf, sisal, flax, henequen, and combinations thereof. Carbon or polyaramide fibers may be also used as the reinforcing fiber material.

[0027] The reinforcing fiber material may include fibers that have a diameter of from about 6 microns to about 24 microns and may be cut into segments approximately 1 mm to about 50 mm in length. Preferably, the fibers have a diameter from about 7 microns to about 14 microns and a length from about 3 mm to about 6 mm. Most preferably, the fibers have a diameter of approximately 10 microns. Prior to the densification of the reinforcing fiber material as described below, each strand may contain from approximately 500 fibers to approximately 8,000 fibers.

[0028] After the reinforcing fibers are formed, and prior to their collection into a strand, they may be coated with a size composition. A suitable size composition according to at least one exemplary embodiment of the present invention includes one or more coupling agents and one or more film forming agents. Optionally, conventional additives such as, but not limited to, lubricants, wetting agents, pH adjusters, antioxidants, antifoaming agents, processing aids, antistatic agents, and non-ionic surfactants may be present in the size composition. The size composition may be applied to the reinforcement fibers in an amount sufficient to achieve a Loss on Ignition (LOI) of from about 0.05% to about 1.0% on the dried fiber, and preferably in an amount of from 0.15% to about 0.40%. LOI may be defined as the percentage of organic solid matter deposited on the glass fiber surfaces measured by the reduction in weight experienced by the fibers after heating them to a temperature sufficient to burn or pyrolyze the organic size from the fibers.

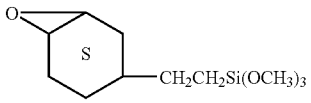
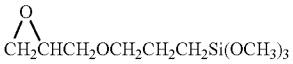
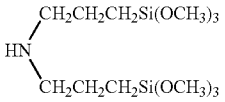
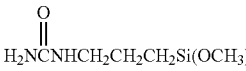
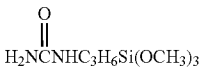
[0029] The size composition includes one or more coupling agents. Preferably, the coupling agent is a silane coupling agent. Besides their role of coupling the surface of the reinforcement fibers and the plastic matrix, silanes also function to enhance the adhesion of the polycarboxylic acid component to the reinforcement fibers and to reduce the level of fuzz, or broken fiber filaments, during subsequent processing. Examples of silane coupling agents that may be used in the present size composition may be characterized by the functional groups amino, epoxy, vinyl, methacryloxy, ureido, isocyanato, and azamido. In preferred embodiments, the silane coupling agents include silanes containing one or more nitrogen atoms that have one or more functional groups such as amine (primary, secondary, tertiary, and quarternary), amino, imino, amido, imido, ureido, isocyanato, or azamido.

[0030] Suitable silane coupling agents include, but are not limited to, aminosilanes, silane esters, vinyl silanes, methacryloxy silanes, epoxy silanes, sulfur silanes, ureido silanes, and isocyanato silanes. Specific non-limiting examples of silane coupling agents for use in the instant invention include γ-aminopropyltriethoxysilane (A-1100), n-phenyl-γ-aminopropyltrimethoxysilane (Y-9669), n-trimethoxy-silyl-propyl-ethylene-diamine (A-1120), methyltrichlorosilane (A-154), γ-chloropropyl-trimethoxy-silane (A-143), vinyl-triacetoxy silane (A-188), methyltrimethoxysilane (A-1630), γ-ureidopropyltrimethoxysilane (A-1524). Other examples of suitable silane coupling agents are set forth in Table 1. All of the silane coupling agents identified above and in Table 1 are available commercially from GE Silicones.

TABLE 1

Silanes	Label	Formula
Silane Esters		
octyltriethoxysilane	A-137	$CH_3(CH_2)_7(Si(OCH_2CH_3)_3$
methyltriethoxysilane	A-162	$CH_3Si(OCH_2CH_3)_3$
methyltrimethoxysilane	A-163	$CH_3Si(OCH_3)_3$

TABLE 1-continued

Silanes	Label	Formula
proprietary	A-1230	proprietary
tris-[3-(trimethoxysilyl)propyl] isocyanurate	Y-11597	—
Vinyl Silanes		
proprietary	RC-1	proprietary
vinyltriethoxysilane	A-151	$CH_2{=}CHSi(OCH_2CH_3)_3$
vinyltrimethoxysilane	A-171	$CH_2{=}CHSi(OCH_3)_3$
vinyl-tris-(2-methoxyethoxy) silane	A-172	$CH_2{=}CHSi(OCH_2CH_2OCH_3)_3$
Methacryloxy Silanes		
γ-methacryloxypropyl-trimethoxysilane	A-174	$CH_2{=}C(CH_3)CO_2CH_2CH_2CH_2Si(OCH_3)_3$
Epoxy Silanes		
β-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane	A-186	
γ-glycidoxypropyltrimethoxysilane	A-187	
Sulfur Silanes		
γ-mercaptopropyltrimethoxysilane	A-189	$HSCH_2CH_2CH_2Si(OCH_3)_3$
proprietary polysulfidesilane	RC-2	proprietary
Amino Silanes		
γ-aminopropyltriethoxysilane	A-1101	$H_2NCH_2CH_2CH_2Si(OCH_2CH_2)_3$
	A-1102	
aminoalkyl silicone	A-1106	$(H_2NCH_2CH_2CH_2SiO_{1.5})_n$
modified aminoorganosilane	A-1108	—
γ-aminopropyltrimethoxysilane	A-1110	$H_2NCH_2CH_2CH_2Si(OCH_3)_3$
N-β-(aminoethyl)-γ-	A-1120	$H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$
modified aminoorganosilane	A-1126	—
modified aminosilane	A-1128	—
triaminofunctional silane	A-1130	$H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$
bis-(γ-trimethoxysilylpropyl)amine	A-1170	
oganomodified plydimethylsiloxane	Y-11343	$CH_3SiO[CH_3)_2SiO]_x[CH_3SiO]_y[CH_3SiO]_z SiCH_3)_3$ (NR_2; $NHR'Si(OR')_3$)
polyazamide silylated silane	A-1387	—
Ureido Silanes		
γ-ureidopropyltrialkoxysilane	A-1160	
γ-ureidopropyltrimethoxysilane	Y-11542	
Isocyanato Silanes		
γ-isocyanatopropyltriethoxysilane	A-1310	$O{=}C{=}NCH_2CH_2CH_2CH_2Si(OCH_2CH_3)_3$

[0031] Additional examples of suitable silane coupling agents include the products from Chisso having the trade designations set forth in Table 2.

TABLE 2

S-310	n-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane
S-320	n-(2-aminoethyl)-3-aminopropyltrimethoxysilane
S-350	n-[2-(vinylbenzylamino)ethyl]-3-aminopropyl-trimethoxysilane monohydrochloride (methanol solution)
S-510	3-glycidoxypropyltrimethoxysilane
S-610	3-chloropropylmethydimethoxysilane
S-620	3-chloropropyltrimethoxysilane

[0032] The silane coupling agents used in the present invention may be replaced by alternative coupling agents or mixtures. For example, A-1387 may be replaced by a version in which the methanol solvent is replaced by ethanol. A-1126, an aminosilane coupling agent including a mixture of approximately 24% by weight diaminosilane modified by a surfactant in a methanol solution (GE Silicones), may be replaced with trimethoxy-silyl-propyl-ethylene-diamine (Z-6020 from Dow Corning). A-1120 or Z-6020 may be substituted by a pre-hydrolyzed version. Z-6020 may be replaced by Z-6137, a pre-hydrolyzed version lacking the alcohol solvent and including 33% diaminosilane in water at a concentration of 24% solids (commercially available from Dow Corning). In addition, A-1100 may be replaced by its hydrolyzed form Y-9244, which will reduce or eliminate the ethanol emission.

[0033] Preferably, the silane coupling agent is an aminosilane or a diaminosilane.

[0034] The size composition may include one or more of the above-identified coupling agents. The coupling agent may be applied to the fibers in an amount sufficient to achieve a Loss on Ignition (LOI) of from about 0.02% to about 0.30% on the dried fiber, and preferably in an amount of from about 0.04% to about 0.08%.

[0035] In addition, the size composition may include at least one resinous film forming agent. Any conventional film forming agent known to those of skill in the art may be utilized in the size composition. In addition, the film former may be the same as or different from the film forming agent present in the binder composition described in detail below. In the size composition, the film former acts as a polymeric binding agent to provide additional protection to the reinforcing fibers and improves processability, such as a reduction in fuzz generated by high speed chopping. The film forming agent may be present on the reinforcement fibers in an amount sufficient to provide an LOI from 0% to about 1.0%. Preferably, the film forming agent is present on the fibers in an amount sufficient to provide an LOI from about 0.15% to about 0.60%.

[0036] In an alternative embodiment of the present invention, the size composition contains a lubricant to facilitate manufacturing instead of, or in addition to, a film forming agent. Examples of suitable lubricants include, but are not limited to, lubricants such as water-soluble ethyleneglycol stearates (e.g., polyethyleneglycol monostearate, butoxyethyl stearate, polyethylene glycol monooleate, and butoxyethylstearate), ethyleneglycol oleates, ethoxylated fatty amines, glycerin, emulsified mineral oils, and organopolysiloxane emulsions. Other examples of lubricants include alkyl imidazoline derivatives (e.g., a cationic softener which has a solids content of approximately 90% and is available commercially from Th. Goldschmidt AG), stearic ethanolamide (e.g., Lubesize K12 (AOC)), and a polyethyleneimine polyamide salt commercially available at 50% active solid from Cognis under the trade name Emery 6760. The lubricant may be present on the fibers in an amount sufficient to provide an LOI up to about 0.10%.

[0037] Although the size composition is effective at any pH level, the pH preferably falls within the range of from 7 to 11. The pH may be adjusted depending on the intended application, or to facilitate the compatibility of the ingredients of the size composition. Any suitable pH adjuster (e.g., a weak organic acid such as acetic acid or a base such as ammonia), may be added to the size composition in an amount sufficient to adjust the pH to a desired level.

[0038] The size composition may be made by dissolving each of the ingredients into a premix with agitation. The separate premixes may then be combined with deionized water to form a main mixture and to achieve the appropriate concentration and control the mix of solids. The premixes may be added in any order. If necessary, the pH of the main mixture may be adjusted to a desired level. The premixes may be added separately, or they may be added at the same time to form the main mixture.

[0039] As described above, the two-part sizing formulation also includes a binder composition. The binder composition includes a high acid number copolymer formed from the polymerization of maleic anhydride or maleic acid and at least one other desired monomer and/or a high acid number polyacid. As used herein, the phrase "high acid number" is intended to designate a polyacid with an acid number or acid value of greater than about 300. In addition, the binder composition may include any suitable additive identified by one of skill in the art, such as, for example, adhesive film forming polymers, lubricants, a surfactant or a mixture of surfactants, antistatic agents, and crosslinking agents. The binder composition may be applied to the fiber with an LOI of from about 0.20% to about 2.0%, depending on the desired application.

[0040] The maleic anhydride or maleic acid copolymer may be a pure copolymer or a derivative in an anhydride, acid, partial-salt, partial-ester, partial-amide, or partial-imide form. Suitable copolymers include C_2-C_5 α-olefins, such as ethylene-, propylene-, (iso)butylene-, or butadiene-maleic acid copolymers, and methyl vinyl ether-maleic acid copolymers. The copolymer is poorly soluble when dispersed in water at room temperature, but when it is heated to temperatures above approximately 90° C., it dissolves by virtue of the hydrolysis of the anhydride groups of the polymer to form the corresponding polyacids. In such a reaction, one mole of anhydride is hydrolyzed to two moles of diacid in an exothermic reaction. The aqueous solution formed by the hydrolysis may then be used to formulate the binder composition. Similar reactions may be employed using ammonia or an amine in water, or an alcohol or an amine in a non-reactive solvent, to form, respectively, solutions of the partial-ammonium salt, partial-ester, partial-amide, or partial-imide derivatives.

[0041] In a preferred embodiment, the binder composition includes an ethylene-maleic acid (EMA) copolymer formed by the hydrolysis of an ethylene-maleic anhydride copolymer. The ethylene-maleic anhydride copolymer may be formed by the radical copolymerization between ethylene and maleic anhydride in the presence of a peroxide catalyst. This copolymerization leads to an alternating copolymer that includes a high level of maleic units which gives the ethylene-maleic acid copolymer a high polyacid functionality.

[0042] In at least one exemplary embodiment, the copolymer is an aqueous solution of the polyacid, (partial) ammonium salt, partial-ester, partial-amide, or partial-imide derivative of an alternating block copolymer of maleic anhydride, or mixtures thereof. Mixtures of different ethylene maleic acid copolymers or maleic anhydride copolymers with other high acid number polycarboxylic acids such as acrylic or maleic acid homo- or co-polymers or derivates thereof such as those described above may used in the binder composition to achieve desired properties, such as improved strength in the reinforced fiber product or improved fiber processability, and also to reduce the total binder cost.

[0043] As discussed above, the binder composition may include a high acid number (e.g., high acid value) polyacid alternatively, or in addition to, the maleic anhydride or maleic acid copolymer. Desirably, the polyacid is a polycarboxylic acid. A suitable polycarboxylic acid polymer for use in the binder composition is an organic polymer that contains numerous pendant carboxylic acid groups and is characterized by a high acid number. The acid number or acid value of a substance may be described as a measure of the free acid content, and may be expressed as the number of milligrams of potassium hydroxide neutralized by the free acid present in one gram of the substance. In the binder composition, the high acid number polyacid may have an acid number of at least about 300. In at least one exemplary embodiment, the binder composition has an acid number of about 300 to about 950.

[0044] The polycarboxylic acid polymer may be a homopolymer or copolymer prepared from unsaturated carboxylic acids including, but not limited to, acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, maleic acid, cinnamic acid, 2-methylmaleic acid, itaconic acid, 2-methylitaconic acid, and α,β-methyleneglutaric acid. Alternatively, the polycarboxylic acid polymer may be prepared from unsaturated anhydrides such as maleic anhydride, itaconic anhydride, acrylic anhydride, methacrylic anhydride, and mixtures thereof. Methods for polymerizing these acids and anhydrides are known by those of ordinary skill in the art, and will not be discussed in detail herein. In addition, the polycarboxylic acid polymer may include a copolymer of one or more of the unsaturated carboxylic acids or anhydrides described above and one or more vinyl compounds including, but not limited to, styrene, α-ethylstyrene, acrylonitrile, methacrylonitrile, methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, methyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, glycidyl methacrylate, vinyl methyl ether, vinyl acetate, 1-olefins (e.g., ethylene, isobutene) vinyl and allyl alkyl ethers (e.g., methyl vinyl ether, ethyl vinyl ether), substituted acrylamides, and sulfonic and sulfonate monomers (e.g., allylsulfonic acid, vinylsulfonic acid). Such polyacids are described in detail in U.S. Pat. No. 5,236,982 to Cossement, et al., which is hereby incorporated by reference in its entirety.

[0045] The high acid number maleic anhydride copolymer, high acid number ethylene maleic acid copolymer, or high acid number polycarboxylic acid in the binder composition may be present on the fibers in an amount sufficient to provide an LOI up to about 2.0%, preferably from about 0.10% to about 2.0%, and even more preferably from about 0.40% to about 1.0%. It is to be appreciated that when the high acid number maleic anhydride copolymer, high acid number ethylene maleic acid copolymer, or high acid number polycarboxylic acid comes in contact with a polymer containing a di-cation, there is an interaction between the carboxylic acid moieties and the di-cations in which the carboxylic acid moieties are consumed or become otherwise unable to interact favorably with the polymer matrix. Although not wishing to be bound by theory, it is believed that a ratio higher than 2:1 (equivalent carboxylic acid of the polyacid:equivalent di-cation respectively) retains the presence of carboxylic acid moieties after the interaction of the polyacid moieties with the di-cation. Therefore, it is desirable that an excess of carboxylic acid moieties be present in the size/binder composition to compensate for the polyacid that is consumed by the di-cations such that improved dry-as-molded mechanical properties and improved hydrolysis resistance may be achieved. However, the specific amount of carboxylic acid moieties present in the binder composition needed to achieve an excess (and improved physical properties) is dependent upon the amount of di-cations present in the polymer. It is believed that it is the difference between the number of equivalents of carboxylic acid moieties present on the reinforcing fiber and the number of equivalents of di-cationic additive present in the polymer that targets the % LOI of the maleic anhydride copolymer, ethylene maleic acid copolymer, or high acid number polycarboxylic acid. It is to be noted that the use of a high LOI polyacid does not alter the efficiency of the calcium stearate in its primary role as a lubricant/demolding agent.

[0046] In addition to a maleic anhydride copolymer, an ethylene maleic acid copolymer, or a high acid number polycarboxylic acid, the binder composition may also include one or more film forming agents. Film formers are agents which create improved adhesion between the reinforcing fibers, which results in improved strand integrity. Suitable film formers include thermosetting and thermoplastic polymers which promote the adhesion of sizing compositions. Polyurethane film formers are a preferred class of film formers for use in the binder composition because they demonstrate good compatibility with polyamide matrices and help to improve the dispersion of the glass fiber bundles in the melt (e.g., extrusion process or injection molding process) when forming the composite article, which causes a reduction or elimination of defects in the final article that caused by poor dispersion of the reinforcement fibers (e.g., visual defects, processing breaks, and/or low mechanical properties). The polyurethane dispersions utilized in the two-part sizing formulation of the present invention may be part of a dispersion that either is based or is not based on a blocked isocyanate. In addition, as discussed above, the film former present in the binder composition may or may not be the same as the film former present in the size composition.

[0047] Examples of suitable urethane film formers that are not based on blocked isocyanates that may be used in the binder composition include, but are not limited to, Baybond® XP-2602 (a non-ionic polyurethane dispersion (Bayer Corp.)); Baybond® PU-401 and Baybond® PU-402 (anionic urethane polymer dispersions (Bayer Corp.)); Baybond® VP-LS-2277 (an anionic/non-ionic urethane polymer dispersion (Bayer Corp.)); Aquathane 518 (a non-ionic polyurethane dispersion (Dainippon, Inc.)); and Witcobond 290H (polyurethane dispersion (Witco Chemical Corp.)). Other examples of suitable film forming agents for use in the binder composition include, but are not limited to, polyvinylpyrrolidone homo- and co-polymers and other polymers bearing amide-like functionality such as polyamide, polyvinylformamide, or polyacrylamide. In at least one exemplary embodiment, the film forming agent is an aqueous polyurethane dispersion that is not part of a dispersion that includes a polyurethane and a blocked isocyanate.

[0048] Examples of suitable urethane film formers based on blocked isocyanates which may be used in the binder composition include, but are not limited to, Baybond® XW-116; Baybond® XP-055; Baybond® PU-330; Baybond® PU-400-S; Baybond® PU-401 (polyurethane dispersions based on blocked isocyanates (available from Bayer Corp.)); Baybond® VP-LS-2277 and Baybond® VP-LS-2297 (anionic/non-ionic urethane polymer dispersions (Bayer Corp.)); Baybond® PU-130 (an anionic/non-ionic urethane polymer dispersion (Bayer Corp.)); Baybond® PU-403 (a polyurethane dispersion (Bayer Corp.)); Baybond® PU-239 (a crosslinkable anionic/non-ionic urethane polymer dispersion (Bayer Corp.)); Baybond® PU-2435 (an anionic/non-ionic urethane polymer dispersion (Bayer Corp.)); and Witcobond 296B (an aqueous blocked polyurethane dispersion, available from Baxenden Chemicals).

[0049] The film former(s) may be present in the binder composition in an amount sufficient to provide an LOI up to about 1.0%, and preferably from about 0.10% to about 0.40%. It is desirable that the amount of film former present in the two-part sizing formulation is such that the two-part sizing formulation provides the desired level of compatibility for the reinforcement fibers and the polymer matrix to help fiber dispersion during processing to form a composite part without affecting the positive effect of the polyacid moieties to improve dry-as-molded and hydro-aged mechanical properties and without developing static and/or an undesirable color in the reinforcing fiber product.

[0050] The binder composition may be formed by mixing a solution of the desired high acid number polyacid(s) (e.g., a polycarboxylic acid obtained by hydrolysis of the parent polyanhydride in hot water) with a solution of the film forming agent. Optionally, the solution may be diluted with water. It may be necessary to adjust the pH of the polyacid solution with a base before mixing it with the film former solution to reduce or eliminate the occurrence of destabilization phenomena. Any suitable pH adjuster may be added to the binder composition to adjust the pH to a desired level; however, it is preferred that ammonia (NH_4) be added to adjust the pH. The pH of the binder composition may fall in the range of from 2.5-10.

[0051] The total LOI for the two-part sizing formulation on the reinforcing fiber material may be from about 0.25% to about 2.05%, preferably from about 0.60% to about 1.10%.

[0052] One advantage of the two-part sizing formulation of the present invention is that the product resulting from the application of the two-part sizing formulation, which may contain up to about 2.0% LOI of the high acid number maleic anhydride copolymer, high acid number ethylene maleic acid copolymer, or high acid number polycarboxylic acid, provides improved mechanical properties, even when the polyamide matrix contains a di-cation additive such as calcium stearate.

[0053] In addition, the two-part sizing formulation of the present invention imparts improved physical properties, such as improved dry-as-molded (DaM) mechanical properties of the composite part after aging the composite part in severe hydrolysis conditions, to composites formed from industrially processable and easily dispersible pellets.

[0054] The present invention is also advantageous in that the polyurethane film formers present in the two-part sizing formulation demonstrate good compatibility with polymer matrices (such as polyamide matrices) that contain di-cationic lubricants, which helps to improve the dispersion of the reinforcement fiber bundles in the melt (e.g., in extrusion process or injection molding process) when forming a composite article. This increased dispersion of the reinforcement fibers causes a reduction of defects such as visual defects, processing breaks, and/or low mechanical properties in the final product.

[0055] Further, the two-part sizing formulation of the present invention has improved stability over conventional sizing formulations containing an aminosilane and a polyacid in the same mixture. Mixtures containing both aminosilanes and polyacids may not be stable due to chemical interactions between the two compounds. By placing substantially all (if not all) of the aminosilane in the size composition and the polyacid in the binder composition, both the size composition and the binder composition have increased shelf lives.

[0056] The process for making a densified reinforcing fiber product may be an in-line process that permits the application of the size composition, the chopping of the glass fibers, the application of the binder composition, and pelletizing the reinforcing fiber material. Such an in-line process forms a pellet product that exhibits superior physical properties, such as improved strength, when integrated into a composite (e.g., when compared to pellets produced by processes previously known in the art). Although not wishing to be bound by theory, such superior properties are believed to be due to the improved compatibility of the size composition and binder composition, which permits a better coating of the reinforcing fiber material.

[0057] The process for making a densified reinforcing fiber product according to the invention may employ an apparatus that includes: (a) an apparatus for applying a size composition to a continuous fiber material; (b) an apparatus for cutting the glass fiber strands to form chopped strand segments; (c) an apparatus for conveying the chopped strand segments to a first tumbling apparatus; (d) an apparatus for applying a binder composition to the chopped strand segments; (e) a first tumbling apparatus for imparting a tumbling action to the chopped strand segments to disperse the binder composition and cause the chopped strand segments to align and coalesce into pellets; (f) optionally, an apparatus for conveying the pellets to a second tumbling apparatus; (g)

optionally, a second tumbling apparatus for tumbling the pellets to compact them and increase their density; (h) an apparatus for conveying the densified pellets to a drying apparatus; and (i) a drying apparatus adapted to receive and dry the pellets.

[0058] Initially, the size composition may be applied to the reinforcing fiber material by any conventional means, including kiss roll, dip-draw, and slide or spray applicators. Preferably, the precursor size is applied by passing the reinforcing fiber material, e.g., strands of glass or polymer, over a kiss roll applicator. The size composition is preferably applied to the strands in an amount sufficient to provide the strands with a moisture content of from about 8% by weight to about 13% by weight, more preferably about 10% to about 11% by weight.

[0059] The sized strands may then be chopped into strand segments. The strand segments may have a length of from approximately 2 mm to approximately 50 mm. Preferably, the strands have a length of from about 3 to about 4 mm. Any suitable method or apparatus known to those of ordinary skill for chopping glass fiber strands into segments may be used.

[0060] Next, the binder composition may be applied to the chopped strand segments. The coated chopped strand segments are then pelletized by any suitable method known to those of ordinary skill in the art, such as, for example, tumbling or otherwise agitating the chopped strand segments in a pelletizer. Processes suitable for pelletizing the chopped strand segments are disclosed in U.S. Pat. Nos. 5,868,982, 5,945,134, 6,365,090, and 6,659,756 to Strait et al., and U.S. Pat. No. 5,693,378 to Hill et al., all of which are incorporated by reference in their entireties. The amount of moisture in the binder composition serves to adjust the moisture content of the strand segments to a level suitable for the formation of pellets when the strand segments are tumbled in the pelletizer. Although the moisture content of the strand segments can be adjusted prior to their introduction into the pelletizer, it is preferred that the segments are hydrated to a moisture content suitable for pellet formation in the pelletizer itself.

[0061] Preferably, the moisture content of the chopped strand segments in the pelletizer is from about 12% by weight to about 16% by weight, and more preferably from about 13% by weight to about 14% by weight, based on the total weight of the binder-sized, chopped strand segments. If the moisture content is too low, the strand segments tend not to combine into pellets and will remain in a strand formation. On the other hand, if the moisture content is too high, the strands tend to agglomerate or clump or form pellets having a large diameter and an irregular, non-cylindrical shape.

[0062] The binder composition may be applied to the chopped strand segments as they enter the pelletizer, or after the chopped segments are placed in the pelletizer but prior to tumbling. In an alternative embodiment, the binder composition may be sprayed onto the strands before they are chopped. In this alternative embodiment, it is preferable to use a pelletizer that is specially equipped with tumbling means such as baffles to ensure adequate tumbling and formation of the pellets.

[0063] To ensure good coverage of the chopped segments, the binder composition is preferably applied to the chopped strand segments as they enter the pelletizer but before they begin to coalesce into pellets. If the binder composition is applied at other locations within the pelletizer, pellets may form before the strand segments are completely coated with the binder composition, which results in pellets containing fibers that are not coated with the binder composition. When such pellets are used in the manufacture of fiber reinforced composite articles, the uncoated fibers lack the interfacial coating required to provide good reinforcing characteristics, and the resulting composite article will have less than optimal properties. Preferably, the pelletizer is equipped with a spray nozzle, located adjacent to the strand segment inlet, for spraying the binder size onto the strand segments as they enter the pelletizer.

[0064] The pelletizer may be any apparatus capable of tumbling the strand segments in such a way that: (1) they become substantially uniformly coated with the binder composition, and (2) multiple chopped strand segments align and coalesce into pellets having a desired dimension. Such a tumbling apparatus should have an average residence time sufficient to insure that the strand segments become substantially coated with the binder size and form pellets, but insufficient for the pellets to be damaged or degraded through abrasion (e.g., by rubbing against one another). Preferably, the residence time in the tumbling apparatus is from about 1 minute to about 10 minutes. More preferably, the residence time in the tumbling apparatus is from about 1 minute to about 3 minutes.

[0065] A preferred pelletizer is a rotating drum, such as that disclosed in U.S. Pat. No. 5,868,982, as referenced herein above. U.S. Pat. No. 5,868,982 discloses an apparatus for making reinforcing fiber pellets, which is preferably provided with a system for monitoring and/or adjusting various process parameters. The moisture content of the strand segment input may be monitored and controlled using suitable method. In one embodiment in which the binder composition is applied to the strand segments before they are placed in the pelletizer, the rotating drum is adapted to accommodate a spray head for applying the binder composition to the strand segments as they enter the drum. The binder composition and a solvent, such as water, may be combined into one fluid stream and dispersed through the nozzle orifice. This stream may be combined with two jets of air positioned approximately 180 degrees apart and at an angle of 60 degrees to the direction of the stream flow. Mixing the binder composition with the forced air streams effectively creates a mist that is propelled onto the surface of the tumbling strand segments in the drum.

[0066] Rotation of the drum causes the wet strand segments to tumble around one another while the surface tension created by the wet sizing or coating causes strand segments contacting one another over a substantial portion of their length to align with one another and coalesce into a cylindrically shaped pellet. By such action, any fines or single fibers created during the chopping operation are recombined with and incorporated into the forming pellets to essentially eliminate individual fine fibers from the resulting pellets. Preferably, the drum is tilted slightly so that the end of the drum from which the pellets exit is lower than the end in which they enter to ensure that the pellets formed in the drum do not remain in the drum for an excessive period of time.

[0067] The size of the pellets formed in the drum is controlled primarily by the moisture content of the strand segments. If the moisture content is maintained at a high level, a greater number of strand segments will coalesce into a pellet and the pellet will have a larger diameter. On the other hand, if the moisture is maintained at a lower level, fewer strand segments will coalesce into a pellet and the pellet will have a smaller diameter. The amount of binder composition that is discharged onto the strands may be controlled by a computer which monitors the weight of wet glass entering the pelletizer and adjusts the amount of the binder composition to obtain a final chopped strand having a strand solids content of from about 0.25% to about 2.05% by weight.

[0068] Preferably the pellets formed have a diameter of from about 20% to about 65% of their length. Such pellets are typically formed by combining from about 70 strand segments to about 175 strand segments, each containing from about 500 individual filaments per strand to about 8000 individual filaments per strand.

[0069] The size of the pellets may also be affected by drum throughput. For example, the higher the drum throughput, the shorter the residence time of the strand segments in the drum. As a result, smaller pellets may be formed because the binder composition is not adequately dispersed on the strands which may cause the strands not to coalesce into a pellet. In addition, pellets that are formed in the drum for a shorter period of time are less compacted than those pellets that formed in the drum for a longer period of time.

[0070] Although some compaction of the formed pellets invariably occurs in the pelletizer, it is typically insufficient to increase the pellet density to a level providing optimum flowability. For this reason, after their formation in the pelletizer, the pellets may optionally be fed into a second tumbling apparatus or densifier, wherein the pellets are further compacted and densified. Any low-impact tumbling apparatus that will compact the pellets without degrading them through abrasion or otherwise damaging the pellets may be used. Preferably, the densifier is a zig-zag tube adapted to be rotated about its longitudinal axis, such as is described in U.S. Pat. Nos. 5,868,982, 5,945,134, 6,365,090, and 6,659,756 to Strait et al.

[0071] Preferably, the densifier has a gentler, less vigorous tumbling action than that of the pelletizer to minimize degradation of the pellets. As the zig-zag tube is rotated, pellets placed therein are gently tumbled about by the tube's rotation as they are pulled through the tube by gravity. As with the rotating drum described above, the zig-zag tube densifier is preferably tilted at a slight angle to ensure that the pellets flow through the apparatus without excessive residence times. Furthermore, the densifier preferably has an average residence time of less than approximately 5 minutes to reduce any abrasion that may occur. Preferably, the average residence time in the densifier is from about 1 minute to about 2 minutes.

[0072] Although pellet formation and densification may occur in separate apparatuses, such as a separate rotary drum and a rotating zig-zag tube linked by a conveyor, the pelletizing process may be accomplished using any suitable apparatus. For example, pellet formation and densification may occur in separate tumbling regions or zones within a single apparatus. A preferred example of such an apparatus is a "Zig-Zag" blender commercially available from Patterson Kelly. In a preferred embodiment of this device, a drum is equipped with an interior baffle to reduce the free-fall distance of the glass pellets and strand segments during rotation of the drum. By reducing this distance, less deterioration of the glass fibers and pellets through impact and abrasion occurs, resulting in improved physical properties in the glass fiber reinforced molded articles manufactured therefrom.

[0073] After densification, the pellets may be delivered onto a conveyor belt and dried, e.g., using a hooded oven supplied with hot air and cooling air or any other suitable drying apparatus easily identified by one of skill in the art. To reduce drying time to a level acceptable for commercial mass production, it is preferred that the fibers are dried at elevated temperatures of up to approximately 260° C. in a fluidized-bed oven. After drying, the densified pellets may be classified by size using a screen or other suitable device.

[0074] By varying the throughput and moisture content of the strand segments, glass fiber pellets can be made that are from about 13% to about 60% denser than the corresponding unpelleted strand segments, and from about 10 times to about 65 times larger in diameter. For example, chopped 4 mm (length) segments of a 2000 filament strand composed of 14 micron (diameter) fibers typically have a bulk density of from about 33 lb/ft^3 (528.66 kg/m^3) to 36 lb/ft^3 (576.72 kg/m^3). After being hydrated to a moisture content of from about 13% to about 14% and formed into densified pellets such as is described above, according to the process of the invention, the resulting dried pellets typically have a bulk density of from about 40 lb/ft^3 (640.8 kg/m^3) to about 55 lb/ft^3 (881.1 kg/m^3). As a result of their increased diameter-to-length ratio and increased density, the resulting pellets exhibit significantly improved flowability in comparison to the unpelleted chopped strand product.

[0075] The size composition and the binder composition facilitate treating reinforcing fiber materials, e.g., glass, during a continuous process that includes forming the fibers as well as subsequent processing or handling. By applying the binder composition in the pelletizer, an application efficiency of about 95% to about 100% for the binder composition may be obtained. This high application efficiency reduces waste water contamination in the plant. Further, because the binder composition can be applied efficiently, the binder composition may be applied with a reduction in cost.

[0076] In addition, by applying the binder composition separately from the sizing composition outside the fiber-forming environment permits, materials that are not desirably applied during the fiber-forming process because of toxicity, safety, flammability, irritation, stability, low compatibility with aminosilanes, viscosity, toxicity, cleanliness, odor, cost, or shear sensitivity may be applied to the glass fibers. Also, because the polyacid in the binder composition can be applied to the glass fibers in a more concentrated form in the pelletizer than if it were applied directly to the glass strands as they are being formed, there is reduced fiber logging and waste as compared to conventional in-line processes.

[0077] Although the invention is highly suitable for in-line manufacturing processes, such as described above, it may also be used in an off-line process in which the size composition and the binder composition are applied to previously formed and packaged reinforcing fiber materials,

or in which the size composition and the binder composition are applied to the reinforcing fiber material at different times. For example, the size composition may be applied to a formed fiber strand, after which the strand may be wound and stored before subsequent unwinding, chopping into segments and application of the binder composition.

[0078] Having generally described this invention, a further understanding can be obtained by reference to certain specific examples illustrated below which are provided for purposes of illustration only and are not intended to be all inclusive or limiting unless otherwise specified.

EXAMPLES

[0079] Two-Part Sizing Formulations

[0080] The two part sizing compositions set forth in Table 2 were prepared as described below.

Preparation of Examples 1-3 of Table 2

[0081] In Examples 1-3, the components of Table 3 were mixed to prepare the size composition. The size composition was applied to 10 μm Advantex® glass fibers to achieve a strand Loss-On-Ignition (LOI) of 0.60% on the glass fibers. A conventional loss on ignition (LOI) method, ASTM 2854, was used to determine how much of the applied size composition was on the glass fibers. The glass fibers were then collected into a strand and chopped wet in-line by a chopper into segments of approximately 4 mm in length.

TABLE 2

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11
Size Composition											
AX-1100 Silane[a]	0.07	0.07	0.07	0.04	0.04	0.04	0.04	0.04	0.07	0.06	0.06
Lubesize K-12[b]								0.02			
Zonyl FS-300[c]								0.005			
Baybond PU403[d]				0.31	0.31	0.31	0.31		0.18		
Witcobond 296B[e]	0.53	0.53	0.53								
Baybond XP-2602[f]										0.16	0.16
Binder Composition											
Glascol E5[g]		0.28			0.40	0.65	0.95		0.14		
Glascol C95[h]								0.04			0.12
ZeMac E400[i]			0.30					0.24	0.47		0.38
ZeMac E60[j]										0.40	
Ammonia											
Baybond PU-403[d]				0.40							
Baybond XP-2602[e]										0.21	
Aquathane 518[k]								0.19			
AX-1100 Silane[a]								0.02			
Jeffamine ED2003[l]								0.09			
Pluronic F-77[m]								0.0008			
Pluronic PE-103[n]								0.0022			
Pluronic L-101[o]								0.0009			
Triton X-100[p]								0.0022			
Polyacid LOI	0.00	0.28	0.30	0.00	0.40	0.65	0.95	0.28	0.61	0.40	0.50
Total LOI (%)	0.60	0.88	0.90	0.75	0.75	0.95	1.30	0.65	0.86	0.83	0.72

[a]AX-1100 Silane γ-aminopropyltriethoxysilane (GE Silicones)

[b]K12 Lubesize tetraethylenepentamine reacted with stearic acid (AOC)

[c]Zonyl FS-300 fluoroalkyl alcohol substituted polyethylene glycol (DuPont)

[d]Baybond PU-403 blocked isocyanate polyurethane dispersion (Bayer Corp.)

[e]Witcobond 296B blocked polyurethane dispersion (Baxenden Chemicals)

[f]Baybond XP-2602 non ionic polyurethane dispersion (Bayer Corp.)

[g]Glascol E5 solution of low Mw acrylic acid homopolymer (Ciba)

[h]Glascol C95 solution of low Mw acrylic acid homopolymer partially neutralized by ammonia (Ciba)

[i]ZeMac E400 alternating copolymer of ethylene and maleic anhydride with a Mw of approx 400,000 (Zeeland Chemicals)

[j]ZeMac E60 alternating copolymer of ethylene and maleic anhydride with a Mw of approximately 60,000 (Zeeland Chemicals)

[k]Aquathane 518 polyurethane dispersion (D.I.C.)

[l]Jeffamine ED2003 water-soluble aliphatic diamine derived from a propylene oxide-capped poly(ethyleneoxide) (Huntsman Corp.)

[m]Pluronic F-77 oxirane (EO-PO copolymer) (BASF)

[n]Pluronic PE-103 oxirane (EO-PO copolymer) (BASF)

[o]Pluronic L-101 oxirane (EO-PO copolymer) (BASF)

[p]Triton X-100 octylphenoxypolyethoxyethanol (Union Carbide Corp.)

TABLE 3

Component	Amount of Component
Witcobond 296B[a]	78.4 kg as received in 400 L of deionized water
AX-1100 Silane[b]	19.91 kg as received in 500 L of deionized water
Deionized Water	to 1000 L

[a]blocked polyurethane dispersion (Baxenden Chemicals)
[b]γ-aminopropyltriethoxysilane (GE Silicones)

[0082] The chopped segments were then collected and approximately 1-2 days later treated under rotation in a lab pelletizer where the corresponding binder set forth in Table 2 was sprayed onto the chopped segments. In Example 1, no binder was applied during the pelletization. In Example 2, Glascol E5, a 25% solids solution of a low molecular weight acrylic acid homopolymer available from Ciba, was diluted to 15% solids by deionized water and used as the binder. In Example 3, the binder composition was prepared by dispersing 132 g of ZeMac 400, an alternating copolymer of ethylene and maleic anhydride available from Zeeland Chemicals, in 870 g of deionized water and dissolved by heating to approximately 95° C. under agitation. The various binder compositions were applied to achieve the corresponding LOI % set forth in Table 2. The densified glass pellets were collected and dried in a moving belt lab oven for approximately 16 minutes at a maximum temperature of 220° C.

Preparation of Examples 4-7 of Table 2

[0083] In Examples 4-7, the components of Table 4 were mixed to prepare the size composition. The size composition was applied to 10 μm Advantex® glass fibers to achieve a strand Loss-On-Ignition (LOI) of 0.35% on the glass fibers. A conventional loss on ignition (LOI) method, ASTM 2854, was used to determine how much of the applied size composition was on the glass fibers. The glass fibers were then collected into a strand and chopped wet in-line by a chopper into segments of approximately 4 mm in length.

TABLE 4

Component	Amount of Component
Baybond PU-403[a]	160.20 kg as received in 450 L of deionized water
AX-1100 Silane[b]	14.5 kg as received hydrolyzed in 65 L of deionized water
Deionized Water	to 1400 L

[a]blocked isocyanate polyurethane dispersion (Bayer Corp.)
[b]γ-aminopropyltriethoxysilane (GE Silicones)

[0084] The chopped segments were then collected and approximately 1-2 days later treated under rotation in a lab pelletizer where the corresponding binder set forth in Table 2 was sprayed onto the chopped segments. In Example 4, Baybond PU-403, a 39% solids blocked isocyanate polyurethane dispersion available from Bayer Corp., was diluted to 15% solids by deionized water and used as the binder. In Examples 5-7, the binder was prepared by diluting Glascol E5, a 25% solids solution of a low molecular weight acrylic acid homopolymer, to 15% solids by deionized water. The various binder compositions were applied to achieve the corresponding LOI % set forth in Table 2. The densified glass pellets were collected and dried in a moving belt lab oven for approximately 16 minutes at a maximum temperature of 220° C.

Preparation of Example 8 of Table 2

[0085] The size composition of Example 8 was prepared according to the description of Table 7 set forth in U.S. Patent Publication No. 2004/0209991 A1 to Piret et al., which is hereby incorporated by reference in its entirety. In particular, the size composition as set forth in Table 5 was prepared and applied to 10 μm Advantex® glass fibers as they were produced in a continuous in-line process. The glass fibers were then formed into strands and chopped into strand segments having a length of approximately 4.0 mm. The molten glass was fed through the bushing at approximately 215 lbs/hour. The size composition was applied with a conventional kiss roll type applicator turning in the direction of the strand at 15 meters per minute. The size composition was applied at a concentration of 0.69% to achieve a strand LOI of 0.06% solid on the glass.

TABLE 5

Component	% by Weight of Active Solids
AX-1100 Silane[a]	51
Lubesize K12[b]	40
Zonyl FS-300[c]	9

[a]γ-aminopropyltriethoxysilane (GE Silicones)
[b]tetraethylenepentamine reacted with stearic acid (AOC)
[c]fluoroalkyl alcohol substituted polyethylene glycol (DuPont)

[0086] The chopped segments were then conveyed to a pelletizer where the binder composition according to Table 6 was sprayed onto the chopped segments. The binder composition was applied to achieve a strand LOI of 0.59% solid on the glass fibers. The total Loss-On-Ignition (LOI) of the glass was 0.65%. The densified glass pellets were conveyed to a conveyor-type or fluidized bed oven for drying.

TABLE 6

Component	% by Weight of Active Solids
ZeMac E400[a]	40
Jeffamine ED-2003[b]	14
Glascol C95[c]	7
AX-1100 Silane[d]	7
Aquathane 518[e]	31
Pluronic F-77[f]	0.13
Pluronic PE-103[g]	0.36
Pluronic L-101[h]	0.15
Triton X-100[i]	0.36

[a]alternating copolymer of ethylene and maleic anhydride with a Mw of approx 400,000 (Zeeland Chemicals)
[b]water-soluble aliphatic diamine derived from a propylene oxide-capped poly(ethyleneoxide) (Huntsman Corp.)
[c]solution of low Mw acrylic acid homopolymer partially neutralized by ammonia
[d]γ-aminopropyltriethoxysilane (GE Silicones)
[e]polyurethane dispersion (D.I.C.)
[f]oxirane (EO-PO copolymer) (BASF)
[g]oxirane (EO-PO copolymer) (BASF)
[h]oxirane (EO-PO copolymer) (BASF)
[i]octylphenoxypolyethoxyethanol (Union Carbide Corp.)

Preparation of Example 9 of Table 2

[0087] In Example 9, components of Table 7 were mixed to prepare the size composition. The size composition was applied to 10 μm Advantex® glass fibers to achieve a strand Loss-On-Ignition (LOI) of 0.25% on the glass fibers. A

conventional loss on ignition (LOI) method, ASTM 2854, was used to determine how much of the applied size composition was on the glass fibers. The glass fibers were then collected into a strand and chopped wet in-line by a chopper into segments of approximately 4 mm in length.

TABLE 7

Component	Amount of Component
Baybond PU-403[a]	131.10 kg as received in 1000 L of deionized water
AX-1100 Silane[b]	33.80 kg as received hydrolyzed in 1000 L of deionized water
Deionized Water	to 2440 L

[a]blocked isocyanate polyurethane dispersion (Bayer Corp.)
[b]γ-aminopropyltriethoxysilane (GE Silicones)

[0088] The chopped segments were then collected and approximately 1-2 days later treated under rotation in a lab pelletizer where the binder was sprayed onto the chopped segments. The binder composition was prepared by dispersing 13.43 kg of ZeMac 400 EMA powder in 47.85 kg of deionized water and dissolving the powder by heating the water to approximately 95° C. under agitation. After the ZeMac 400 EMA powder was dissolved, the solution was further diluted by adding 19 kg of deionized water. 18.61 kg of Glascol C95, a solution of a low molecular weight acrylic acid homopolymer partially neutralized by ammonia which is available from Ciba, was then added with agitation at a temperature lower than 60° C. The binder composition was applied to achieve a strand LOI of 0.61% solid on the glass fibers. The total Loss-On-Ignition (LOI) of the glass fibers was 0.86%. The densified glass pellets were collected and dried in a moving belt lab oven for approximately 16 minutes at a maximum temperature of 220° C.

Preparation of Example 10 of Table 2

[0089] In Example 10, components of Table 8 were mixed to prepare the size composition. The size composition was applied to 10 μm Advantex® glass fibers to achieve a strand Loss-On-Ignition (LOI) of 0.22% on the glass fibers. A conventional loss on ignition (LOI) method, ASTM 2854, was used to determine how much of the applied size composition was on the glass fibers. The glass fibers were then collected into a strand and chopped wet in-line by a chopper into segments of approximately 4 mm in length.

TABLE 8

Component	Amount of Component
Baybond XP-2602[a]	143.23 kg as received in 800 L of deionized water
AX-1100 Silane[b]	34.81 kg as received hydrolyzed in 1000 L of deionized water
Deionized Water	to 2200 L

[a]non-ionic polyurethane dispersion (Bayer Corp.)
[b]γ-aminopropyltriethoxysilane (GE Silicones)

[0090] The chopped segments were then conveyed to a pelletizer where the binder was sprayed onto the chopped segments as they passed through the entrance chamber of the pelletizer. The binder composition was prepared by dispersing 32.00 kg of ZeMac 60 EMA powder in 80.80 kg of deionized water and dissolving the powder by heating the water to approximately 95° C. with agitation. After the ZeMac 60 EMA powder was dissolved, the solution was cooled to 25° C. and the pH was adjusted to about 3.5 by the addition of approximately 9.10 kg of a 25% ammonia solution. 52.37 kg of Baybond XP-2602, a non-ionic polyurethane dispersion available from Bayer Corp., was then added slowly with agitation. The densified glass pellets were conveyed to a conveyor or conveyor-type or fluidized bed oven for drying. The binder composition was applied to achieve a strand LOI of 0.61% solid on the glass fibers. The total LOI of the glass fibers was 0.83%.

Preparation of Example 11 of Table 2

[0091] In Example 11, components of Table 9 were mixed to prepare the size composition. The size composition was applied to 10 μm Advantex® glass fibers to achieve a strand Loss-On-Ignition (LOI) of 0.22% on the glass fibers. A conventional loss on ignition (LOI) method, ASTM 2854, was used to determine how much of the applied size composition was on the glass fibers. The glass fibers were then collected into a strand and chopped wet in-line by a chopper into segments of approximately 4 mm in length.

TABLE 9

Component	Amount of Component
Baybond XP-2602[a]	143.23 kg as received in 800 L of deionized water
AX-1100 Silane[b]	34.81 kg as received hydrolyzed in 1000 L of deionized water
Deionized Water	to 2200 L

[a]non-ionic polyurethane dispersion (Bayer Corp.)
[b]γ-aminopropyltriethoxysilane (GE Silicones)

[0092] The chopped segments were then conveyed to a pelletizer where the binder was sprayed onto the chopped segments as they passed through the entrance chamber of the pelletizer. The binder composition was prepared by dispersing 13.43 kg of ZeMac 400 EMA powder in 47.85 kg of deionized water and dissolving the powder by heating the water to approximately 95° C. under agitation. After the ZeMac 400 EMA powder was dissolved, the solution was further diluted by adding 19 kg of deionized water. 18.61 kg of Glascol C95, a solution of a low molecular weight acrylic acid homopolymer partially neutralized by ammonia which is available from Ciba, was then added with agitation at a temperature lower than 60° C. The densified glass pellets were then conveyed to a conveyor-type or fluidized bed oven for drying. The binder composition was applied to achieve a strand LOI of 0.50% solid on the glass fibers. The total LOI of the glass fibers was 0.72%.

[0093] Comparative Testing

[0094] The glass fiber pellets were compounded with molding pellets of polyamide 6 (Ultramid B3 from BASF with or without added Calcium Stearate) using a twin screw co-rotating intermeshing extruder (ZSK30 Werner-Pfleiderer (Coperion)) while feeding the pellets into the melt of the second port of the extruder. The fiber/resin mixture was then degassed and formed into compounded glass/resin pellets.

[0095] Next, the compounded glass/resin pellets were dried for 12 hours at 95° C. by a molecular sieve circulating hot air dryer. After drying, the pellets were injection-molded by an injection-molding machine (Demag DC80 or Arburg 420C) into Axxicon ISO molds to form standardized com-

posite specimens. The molded specimens were placed in metallic vessels containing silicagel to keep them dry.

[0096] A portion of the composite specimens were cross-mixed between different autoclaves to simulate the same aging for each composite specimen. During hydrolysis (hydro-aging) testing, the composites were fully immersed in an ethylene glycol/water (50/50) mixture and placed under pressure for 500 hours at a temperature of 120° C. When each of the hydrolysis tests were completed, the vessel was cooled to room temperature before the tensile strengths and the Charpy un-notched impact strengths were determined. Dry-as-Molded (DaM) properties such as Tensile Strength, Charpy un-notched impact strength, and Izod un-notched and notched impact strength were measured on the dry, molded specimens. The results are set forth below.

[0097] The tests to determine tensile strength were conducted according to the procedures set forth in ISO 527-4/1B/10. The Charpy un-notched impact strength was measured according to the procedures set forth in ISO 179-1/1 Eu. The Izod un-notched and notched (2 mm notch) were measured according to ISO 180/A. The lab conditions were set as described in ISO 291.

Example 1

Loss of Properties of Polyacid-Based Glass Fibers in the Presence of Calcium Stearate

[0098]

[0099] In Table 10, the general negative effects of the presence of calcium stearate on physical properties such as Tensile strength, Charpy un-notched and Izod notched and un-notched impact strengths can be seen. As shown in Table 10, when calcium stearate is present in the Polyamide 6, such as in Examples 2 and 3, the Tensile, Charpy and Izod properties are significantly lower compared to when there is no calcium stearate present in the polyamide. For example, in Examples 2 and 3, the Izod un-notched impact strengths decreased from 87.8 KJ/m^2 to 55.4 KJ/m^2 (Example 2) and from 90.1 KJ/m^2 to 72.7 KJ/m^2 (Example 3) when calcium stearate was present. Similar decreases in the Charpy un-notched and Izod notched impact strengths were obtained when calcium stearate was present. As indicated by the strongly negative values of the delta for Examples 2 and 3, the losses were most severe in Example 2. Although the negative delta values for Example 3 were less severe, they are still significant when compared to the smaller negative delta values obtained for the polyacid-free composite of Example 1. It is to be noted that although Examples 2 and 3 contain a polyacid, the amount of polyacid moieties present in the two-part sizing formulation is not sufficient to overcome the negative effects of the di-cations present in the Polyamide 6.

[0100] It can also be seen from Table 10 that when no calcium stearate is present in the Polyamide 6, Examples 2 and 3, which contain a polyacid, perform as well as, and sometimes better than, the polyacid-free composite of Example 1. For example, the results of the Charpy impact

TABLE 10

Dry-as-Molded Properties of (Polyamide 6) vs. (Polyamide 6 + 0.35% Calcium Stearate) Composite Pieces

		Glass Content (%)	Tensile Strength (MPa)	Charpy Un-notched (KJ/m^2)	Izod Un-notched. (KJ/m^2)	Izod Notched (KJ/m^2)
Example 1 of Table 2[a]	Polyamide 6	30.1	178.4	95.1	82.6	13.6
	Polyamide 6 + Calcium Stearate	30.0	175.8	90.5	78.8	13.6
	Delta[d]		−1.4%	−4.8%	−4.6%	0%
Example 2 of Table 2[b]	Polyamide 6	30.1	176.8	103.5	87.8	14.2
	Polyamide 6 + Calcium Stearate	29.9	150.2	64.3	55.4	9.3
	Delta		−15%	−37.8%	−36.9%	−34.7%
Example 3 of Table 2[c]	Polyamide 6	29.6	176.2	99.7	90.1	14.5
	Polyamide 6 + Calcium Stearate	29.2	171.0	82.8	72.7	12.8
	Delta		−3.0%	−17%	−19.3%	−11.6%

[a]blocked polyurethane dispersion (Baxenden Chemicals)/γ-aminopropyltriethoxysilane (GE Silicones)
[b]blocked polyurethane dispersion (Baxenden Chemicals)/γ-aminopropyltriethoxysilane (GE Silicones) + polyacrylic acid (low polyacid content)
[c]blocked polyurethane dispersion (Baxenden Chemicals)/γ-aminopropyltriethoxysilane (GE Silicones) + EMA (low polyacid content)
[d]value of property in (Polyamide 6 + calcium stearate) minus the value of the property in Polyamide 6/value of property in Polyamide 6

strength in Examples 2 and 3 and the Izod un-notched and notched impact tests were superior to the corresponding results obtained for Example 1. The improved performance of Examples 2 and 3 in Polyamide 6 without calcium stearate with respect to the Izod un-notched impact strength can be seen graphically in FIG. **1**, as well as the strong losses in the same properties when calcium stearate is present in the Polyamide 6.

Example 2

Influence of Polyacid Level on Performance of Calcium Stearate Containing Polyamide 6 Composites

[0101]

TABLE 11

Dry-as-Molded Properties of (Polyamide 6) vs. (Polyamide 6 + 0.35% Calcium Stearate) Composite Pieces

		Glass Content (%)	Tensile Strength (MPa)	Charpy Un-notched (KJ/m^2)	Izod Un-notched. (KJ/m^2)	Izod Notched (KJ/m^2)
Example 4 of Table 2[a]	Polyamide 6	29.7	176.6	98.4	77.3	14.4
	Polyamide 6 + Calcium Stearate	30.0	180.6	90.1	78.1	14.6
	Delta[e]		+2.3%	−8.4%	1.0%	+1.2%
Example 5 of Table 2[b]	Polyamide 6	29.8	181.4	98.4	87.0	14.8
	Polyamide 6 + Calcium Stearate	30.0	179.4	82	72.1	14
	Delta		−1.1%	−16.7%	−17.1%	−5.3%
Example 6 of Table 2[c]	Polyamide 6	29.9	183.4	101.3	90.4	15.8
	Polyamide 6 + Calcium Stearate	29.9	183.1	94.8	82.2	15.1
	Delta		−0.2%	−6.4%	−9.0%	−4.3%
Example 7 of Table 2[d]	Polyamide 6	29.7	183.9	104.0	92.9	15.2
	Polyamide 6 + Calcium Stearate	29.4	183.9	94.7	84.1	14.7
	Delta		0%	−8.9%	−9.5%	−3.7%

[a]γ-aminopropyltriethoxysilane (GE Silicones) + blocked isocyanate polyurethane dispersion (Bayer Corp.)
[b]γ-aminopropyltriethoxysilane (GE Silicones) + blocked isocyanate polyurethane dispersion (Bayer Corp.) + solution of low Mw acrylic acid homopolymer (Ciba) (low polyacid content)
[c]γ-aminopropyltriethoxysilane (GE Silicones) + blocked isocyanate polyurethane dispersion (Bayer Corp.) + solution of low Mw acrylic acid homopolymer (Ciba) (medium polyacid content)
[d]γ-aminopropyltriethoxysilane (GE Silicones) + blocked isocyanate polyurethane dispersion (Bayer Corp.) + solution of low Mw acrylic acid homopolymer (Ciba) (high polyacid content)
[e]value of property in (Polyamide 6 + calcium stearate) minus the value of the property in Polyamide 6/value of property in Polyamide 6

[0102]

TABLE 12

Properties of (Polyamide 6) vs. (Polyamide 6 + 0.35% Calcium Stearate) Composite Pieces After Aging in Water/Glycol Mixture for 500 Hours at 120° C.

		Glass Content (%)	Tensile Strength (MPa)	Charpy Un-notched (KJ/m^2)
Example 4 of Table 2[a]	Polyamide 6	29.7	69.4	76.6
	Polyamide 6 + Calcium	30.0	68.4	75.8

TABLE 12-continued

Properties of (Polyamide 6) vs. (Polyamide 6 + 0.35% Calcium Stearate) Composite Pieces After Aging in Water/Glycol Mixture for 500 Hours at 120° C.

		Glass Content (%)	Tensile Strength (MPa)	Charpy Un-notched (KJ/m^2)
	Stearate Delta[e]		−1.3%	−1%
Example 5 of Table 2[b]	Polyamide 6	29.8	81.0	80.1
	Polyamide 6 + Calcium Stearate	30.0	66.5	65.4
	Delta		−17.8%	−18.3%
Example 6 of Table 2[c]	Polyamide 6	29.9	81.7	83.4
	Polyamide 6 + Calcium Stearate	29.9	78.5	82.5
	Delta		−3.9%	−1.1%
Example 7 of Table 2[d]	Polyamide 6	29.7	79.5	87.4
	Polyamide 6 + Calcium Stearate	29.4	82.3	85.9
	Delta		+3.5%	−1.8%

[a]γ-aminopropyltriethoxysilane (GE Silicones)/blocked isocyanate polyurethane dispersion (Bayer Corp.)
[b]γ-aminopropyltriethoxysilane (GE Silicones) + blocked isocyanate polyurethane dispersion (Bayer Corp.) + solution of low Mw acrylic acid homopolymer (Ciba) (low polyacid content)
[c]γ-aminopropyltriethoxysilane (GE Silicones) + blocked isocyanate polyurethane dispersion (Bayer Corp.) + solution of low Mw acrylic acid homopolymer (Ciba) (medium polyacid content)
[d]γ-aminopropyltriethoxysilane (GE Silicones) + blocked isocyanate polyurethane dispersion (Bayer Corp.) + solution of low Mw acrylic acid homopolymer (Ciba) (high polyacid content)
[e]value of property in (Polyamide 6 + calcium stearate) minus the value of the property in Polyamide 6/value of property in Polyamide 6

[0103] It can be seen from the data obtained and illustrated in Tables 11 and 12 that the negative effects caused by the presence of calcium stearate in the Polyamide 6 on the Tensile strength, the Charpy un-notched, and Izod notched and un-notched impact strengths are reduced by the presence of a suitable amount of polyacid in the two part inventive sizing composition. It is to be noted that Examples 5, 6, and 7 differ only in the amount of polyacid content, and increase in polyacid content from Example 5 (low acid content) to Example 6 (medium acid content) to Example 7 (high acid content) respectively. Referring to Table 11, one example of the reduction of the negative effects caused by the presence of calcium stearate in the polyamide is shown by Example 6. Although the Charpy un-notched impact strength decreased from 101.3 KJ/m^2 to 94.8 KJ/m^2 when calcium stearate was present, this data demonstrates an improvement over the Charpy un-notched impact strength of the polyacid-free composite of Example 4 in which the Charpy un-notched impact strength decreased from 98.4 KJ/m^2 to 90.1 KJ/m^2 when calcium stearate was present. By including a suitable amount of polyacid in the inventive two-part sizing formulation, the Charpy un-notched impact strength was higher (94.8 KJ/m^2) than the Charpy impact strength of the polyacid-free composite of Example 4 (90.1 KJ/m^2) in the presence of calcium stearate. The reduction in the negative effects of the presence calcium stearate is also demonstrated by Example 7, in which the Charpy un-notched impact strength decreased from 104.0 KJ/m^2 to 94.7 KJ/m^2 in the presence of calcium stearate. The data obtained from Examples 6 and 7 show a small difference in the Charpy un-notched impact strength (94.8 KJ/m^2 for Example 6 and 94.7 KJ/m^2 for Example 7), indicating that there may be a plateau for the number of polyacid moieties needed to achieve improved dry-as-molded mechanical properties in the composite product. Similar results demonstrating a decrease in the negative effects of calcium stearate in the polyacid were obtained with respect to the Tensile strength and Izod notched and un-notched impact strengths.

[0104] With respect to Example 5, it can be seen that the relatively low level polyacid-containing composite resulted in better mechanical performance than the polyacid-free, polyurethane-based composite formed by the two-part sizing formulation of Example 4. This is particularly noticeable for the dry-as-molded (DaM) Izod un-notched properties (Table 11) and for the Tensile strength properties after hydro-aging when no calcium stearate is present (Table 12). However, when calcium stearate was present in the Polyamide 6, the polyacid-containing composite of Example 5 showed a loss of mechanical properties. For example, the polyacid-containing composite of Example 5 demonstrated a loss of dry-as-molded Charpy and Izod (notched and un-notched) impact strengths (Table 11) and Tensile strength and Charpy un-notched impact strength after hydro-aging (Table 12) compared to these same mechanical properties in the absence of calcium stearate. These losses of mechanical properties are clearly highlighted by the strongly negative delta values associated with the separate properties. Although not wishing to be bound by theory, it is believed that the amount of polyacid present in the binder of the two-part sizing formulation forming the composite product of Example 5 is not high enough to compensate for the carboxylic acid moieties consumed in the negative interaction with the calcium stearate, and as a result, there is a decrease in the mechanical properties tested. On the other hand, as discussed above, Examples 6 and 7 contain a higher polyacid content than Example 5 and are less sensitive to the presence of calcium stearate, as indicated by the smaller negative delta values for the dry-as-molded or properties after hydro-aging. In Examples 6 and 7, the amount of polyacid present in the two-part sizing formulation is high enough to compensate for the negative interaction with the calcium stearate. This excess in polyacid moieties result in improved and superior mechanical properties, as can be seen in FIGS. **2** and **3**.

Example 3

Performance of High vs. Low Polyacid Content Glass Fiber in Calcium Stearate Containing Polyamide 6 Composites

[0105]

TABLE 13

Dry-as-Molded Properties of (Polyamide 6) vs. (Polyamide 6 + 0.35% Calcium Stearate) Composite Pieces

		Glass Content (%)	Tensile Strength (MPa)	Charpy Un-notched (KJ/m^2)	Izod Un-notched. (KJ/m^2)	Izod Notched (KJ/m^2)
Example 1 of Table 2[a]	Polyamide 6	29.5	180.4	95.7	83.1	13.0

TABLE 13-continued

Dry-as-Molded Properties of (Polyamide 6) vs. (Polyamide 6 + 0.35% Calcium Stearate) Composite Pieces

		Glass Content (%)	Tensile Strength (MPa)	Charpy Un-notched (KJ/m^2)	Izod Un-notched. (KJ/m^2)	Izod Notched (KJ/m^2)
	Polyamide 6 + Calcium Stearate	28.9	179.4	88.4	75.4	11.9
	Delta[d]		−0.6%	−7.6%	−9.3%	−8.6%
Example 8 of Table 2[b]	Polyamide 6	29.3	180.5	104.9	92.6	14.4
	Polyamide 6 + Calcium Stearate	29.9	180.8	91.2	80.6	13.2
	Delta		+0.2%	−13.1%	−12.9%	−8.4%
Example 9 of Table 2[c]	Polyamide 6	29.4	186.8	109.0	95.0	15.3
	Polyamide 6 + Calcium Stearate	29.6	190.4	105.4	91.2	14.6
	Delta		+1.9%	−3.4%	−4.0%	−5.1%

[a]γ-aminopropyltriethoxysilane (GE Silicones)/blocked polyurethane dispersion (Baxenden Chemicals)
[b]γ-aminopropyltriethoxysilane (GE Silicones) + tetraethylenepentamine reacted with stearic acid (AOC) + fluoroalkyl alcohol substituted polyethylene glycol (DuPont) + solution of low Mw acrylic acid homopolymer partially neutralized by ammonia (Ciba) + alternating copolymer of ethylene and maleic anhydride (Zeeland Chemicals) + polyurethane dispersion (D.I.C.) + water-soluble aliphatic diamine derived from a propylene oxide-capped poly(ethyleneoxide) (Huntsman Corp.) + mixture of oxiranes (EO-PO copolymers) (BASF) (low polyacid content)
[c]γ-aminopropyltriethoxysilane (GE Silicones) + blocked isocyanate polyurethane dispersion (Bayer Corp.) + solution of low Mw acrylic acid homopolymer (Ciba) + alternating copolymer of ethylene and maleic anhydride (Zeeland Chemicals) (high polyacid content)
[d]value of property in (Polyamide 6 + calcium stearate) minus the value of the property in Polyamide 6/value of property in Polyamide 6

[0106]

TABLE 14

Properties of (Polyamide 6) vs. (Polyamide 6 + 0.35% Calcium Stearate) Composite Pieces After Aging in Water/Glycol Mixture for 500 hours at 120° C.

		Glass Content (%)	Tensile Strength (MPa)	Charpy Un-notched (KJ/m^2)
Example 1 of Table 2[a]	Polyamide 6	29.5	56.2	63.7
	Polyamide 6 + Calcium Stearate	28.9	55.6	57.6
	Delta[d]		−1.1%	−9.5%
Example 8 of Table 2[b]	Polyamide 6	29.3	82.2	88.4
	Polyamide 6 + Calcium Stearate	29.9	68.9	60.7
	Delta		−16.5%	−31.3%
Example 9 of Table 2[c]	Polyamide 6	29.4	83.7	88.1

TABLE 14-continued

Properties of (Polyamide 6) vs. (Polyamide 6 + 0.35% Calcium Stearate) Composite Pieces After Aging in Water/Glycol Mixture for 500 hours at 120° C.

		Glass Content (%)	Tensile Strength (MPa)	Charpy Un-notched (KJ/m^2)
	Polyamide 6 + Calcium Stearate	29.6	77.3	72.4
	Delta		−7.6%	−17.8%

[a]γ-aminopropyltriethoxysilane (GE Silicones)/blocked polyurethane dispersion (Baxenden Chemicals)
[b]γ-aminopropyltriethoxysilane (GE Silicones) + tetraethylenepentamine reacted with stearic acid (AOC) + fluoroalkyl alcohol substituted polyethylene glycol (DuPont) + solution of low Mw acrylic acid homopolymer partially neutralized by ammonia (Ciba) + alternating copolymer of ethylene and maleic anhydride (Zeeland Chemicals) + polyurethane dispersion (D.I.C.) + water-soluble aliphatic diamine derived from a propylene oxide-capped poly(ethyleneoxide) (Huntsman Corp.) + mixture of oxiranes (EO-PO copolymers) (BASF) (low polyacid content)
[c]γ-aminopropyltriethoxysilane (GE Silicones) + blocked isocyanate polyurethane dispersion (Bayer Corp.) + solution of low Mw acrylic acid homopolymer (Ciba) + alternating copolymer of ethylene and maleic anhydride (Zeeland Chemicals) (high polyacid content)
[d]value of property in (Polyamide 6 + calcium stearate) minus the value of the property in Polyamide 6/value of property in Polyamide 6

[0107] It can be seen from the data obtained and illustrated in Tables 13 and 14 that the negative effects caused by the presence of calcium stearate in the Polyamide 6 on the Tensile strength, the Charpy un-notched, and Izod notched and un-notched impact strengths are reduced by the presence of a suitable amount of polyacid in the two-part inventive sizing composition. In the absence of calcium stearate, the polyacid-based glass fiber composite of Example 8 demonstrated an improvement in the dry-as-molded Charpy un-notched and Izod notched and un-notched impact properties (Table 13) and Tensile strength and Charpy un-notched impact strength after hydro-aging (Table 14) versus the polyacid-free, polyurethane-based commercial glass fiber of Example 1. Thus, the polyacid performed its expected function of improving the mechanical properties when no calcium stearate was present.

[0108] In the presence of calcium stearate, however, the level of polyacid present in the two-part sizing formulation of Example 8 was not enough to compensate for the level of calcium stearate present in the polyamide, and, as a result, the polyacid moieties were consumed by the negative interaction with the calcium stearate di-cation. The low level of polyacid present in Example 8 results in lower-than-expected performance (e.g., results that are well below the results that are observed with Polyamide 6 without calcium stearate) of the dry-as-molded Charpy un-notched and Izod (notched and un-notched) impact strengths (Table 13) and the Tensile strength and Charpy un-notched impact strength after hydro-aging (Table 14). The high sensitivity to calcium stearate of the low polyacid level of Example 8 is also clearly highlighted by the high negative delta value for these properties. On the other hand, the composite product of Example 9 contained a higher level of polyacid in the two-part sizing formulation. It can be seen from Tables 13 and 14 that when calcium stearate was present in the Polyamide 6, the losses induced by the calcium stearate in the dry-as-molded Charpy un-notched and Izod (notched and un-notched) impact strengths (Table 13) and the Tensile

strength and Charpy un-notched impact strength after hydro-aging (Table 14) of Example 9 were less severe compared to the composite product of Example 8. The improvement of the dry-as-molded Charpy un-notched impact strength of Example 9 is illustrated graphically in FIG. **4**. The excess of polyacid present in the two-part sizing formulation resulted in a high mechanical performance of the composite pieces tested both before and after hydro-aging both with and without the presence of calcium stearate in the Polyamide 6. Such improved mechanical properties demonstrated by the composite product of Example 9 confirms the superior and unexpected properties of the two-part sizing formulation of the present invention.

Example 4

Influence of Calcium Stearate Level Present in Polyamide 6 on the Performance of Polyamide 6 Reinforced by Polyacid-Based Fibers

[0109]

TABLE 15

Dry-as-Molded Properties of (Polyamide 6) vs. Polyamide 6 + 0.14% Calcium Stearate (1) and Polyamide 6 + 0.35% Calcium Stearate (2) Composite Pieces

		Glass Content (%)	Tensile Strength (MPa)	Charpy Un-notched (KJ/m^2)	Izod Notched (KJ/m^2)
Example 1 of Table 2[a]	Polyamide 6	30.3	185.9	96.8	13.3
	Polyamide 6 + Calcium Stearate (1)	30.4	187.5	97.0	13.8
	Polyamide 6 + Calcium Stearate (2)	30.4	186.5	93.5	13.9
	Delta[e]		+0.3%	−3.4%	+4.0%
Example 8 of Table 2[b]	Polyamide 6	30.2	185.0	106.8	15.8
	Polyamide 6 + Calcium Stearate (1)	30.5	187.6	97.2	14.6
	Polyamide 6 + Calcium Stearate (2)	30.3	186.0	87.6	13.8
	Delta		+0.5%	−17.9%	−12.8%
Example 10 of Table 2[c]	Polyamide 6	30.6	184.7	103.2	15.8
	Polyamide 6 + Calcium Stearate (1)	30.4	186.5	103.1	15.4
	Polyamide 6 + Calcium Stearate (2)	30.4	185.5	93.4	14.1
	Delta		+0.4%	−9.4%	−10.8%
Example 11 of Table 2[d]	Polyamide 6	30.3	183.1	106.5	16.3
	Polyamide 6 + Calcium Stearate (1)	30.2	185.1	104.4	15.4

TABLE 15-continued

Dry-as-Molded Properties of (Polyamide 6) vs. Polyamide 6 + 0.14% Calcium Stearate (1) and Polyamide 6 + 0.35% Calcium Stearate (2) Composite Pieces

	Glass Content (%)	Tensile Strength (MPa)	Charpy Un-notched (KJ/m^2)	Izod Notched (KJ/m^2)
Polyamide 6 + Calcium Stearate (2)	30.2	184.6	98.8	14.8
Delta		+0.8%	−7.3%	−9.4%

[a]γ-aminopropyltriethoxysilane (GE Silicones)/blocked polyurethane dispersion (Baxenden Chemicals)
[b]γ-aminopropyltriethoxysilane (GE Silicones) + tetraethylenepentamine reacted with stearic acid (AOC) + fluoroalkyl alcohol substituted polyethylene glycol (DuPont) + solution of low Mw acrylic acid homopolymer partially neutralized by ammonia (Ciba) + alternating copolymer of ethylene and maleic anhydride (Zeeland Chemicals) + polyurethane dispersion (D.I.C.) + water-soluble aliphatic diamine derived from a propylene oxide-capped poly(ethyleneoxide) (Huntsman Corp.) + mixture of oxiranes (EO-PO copolymers) (BASF) (low polyacid content)
[c]γ-aminopropyltriethoxysilane (GE Silicones) + non ionic polyurethane dispersion (Bayer Corp.) + alternating copolymer of ethylene and maleic anhydride (Zeeland Chemicals)
[d]γ-aminopropyltriethoxysilane (GE Silicones) + non ionic polyurethane dispersion (Bayer Corp.) + solution of low Mw acrylic acid homopolymer partially neutralized by ammonia + alternating copolymer of ethylene and maleic anhydride (Zeeland Chemicals)
[e]value of property in (Polyamide 6 + calcium stearate (2) minus the value of the property in Polyamide 6/value of property in Polyamide 6

[0110] Another way to exemplify the results of the high polyacid content of glass fibers versus traditional polyacid-free or low polyacid-based glass fibers is to compare their performance in polyamide formulations that contain increasing levels of calcium stearate. Table 15 shows the mechanical properties from Polyamide 6 composite pieces based on four different glass fibers that were produced on an industrial scale. For each example, data on the mechanical properties of the composites were collected for Polyamide 6 (with no calcium stearate), for Polyamide 6 containing 0.14% by weight vs. compound of calcium stearate (1), and for Polyamide 6 containing 0.35% by weight vs. compound of calcium stearate (2). The level of polyacid (as LOI) increases from Example 1 to Example 8 to Example 10 to Example 11 respectively. The specific LOI for each example is set forth in Table 2.

[0111] It can be seen in Table 15, that when calcium stearate is not present, all of the polyacid-based products perform as well as (e.g., tensile strength) or better than (e.g., Charpy and Izod notched impact strength) the polyacid-free, polyurethane-based glass fiber of Example 1. At intermediate levels of calcium stearate, the impact properties of the low polyacid content candidate of Example 8 are markedly affected. On the other hand, the higher polyacid content composites of Examples 10 and 11 present acceptable impact properties under intermediate levels of calcium stearate, as well as in presence of even higher amount of calcium stearate. These results are illustrated in FIG. **5**, which shows the relative performance of the glass fibers in the related Charpy un-notched property of DaM-tested polyamide 6 composites containing differing levels of calcium stearate. It is to be noted that the tensile strength properties are less dependent on the level of calcium stearate present in the compound.

[0112] The foregoing description of the specific embodiments will so fully reveal the general nature of the invention that others can, by applying knowledge within the skill of the art (including the contents of the references cited herein), readily modify and/or adapt for various applications such specific embodiments, without undue experimentation, without departing from the general concept of the present invention. Therefore, such adaptations and modifications are intended to be within the meaning and range of equivalents of the disclosed embodiments, based on the teaching and guidance presented herein. It is to be understood that the phraseology or terminology herein is for the purpose of description and not of limitation, such that the terminology or phraseology of the present specification is to be interpreted by the skilled artisan in light of the teachings and guidance presented herein, in combination with the knowledge of one of ordinary skill in the art.

[0113] The invention of this application has been described above both generically and with regard to specific embodiments. Although the invention has been set forth in what is believed to be the preferred embodiments, a wide variety of alternatives known to those of skill in the art can be selected within the generic disclosure. The invention is not otherwise limited, except for the recitation of the claims set forth below.

Having thus described the invention, what is claimed is:

1. A two-part sizing formulation for sizing a reinforcing fiber used to form a composite product when combined with a polymer that includes a di-cation or a higher valency cation, said two-part sizing formulation comprising:

a size composition; and

a binder composition including at least one high acid number polyacid containing acid moieties, said acid moieties being present in an amount that is greater than the amount of said di-cation or said higher valency cation present in said polymer.

2. The two-part sizing formulation of claim 1, wherein said amount of said acid moieties is sufficient to retain at least a portion of said acid moieties after interacting with said di-cation or said higher valency cation when forming said composite material.

3. The two-part sizing formulation of claim 1, wherein said at least one high acid number polyacid is present on said reinforcing fiber in an amount sufficient to provide a loss-on-ignition up to about 2.0%.

4. The two-part sizing formulation of claim 1, wherein said at least one high acid number polyacid is a polyacid selected from a high acid number copolymer formed from the polymerization of maleic anhydride and at least one other monomer copolymerized therewith, a copolymer formed from the polymerization of maleic acid and at least one other monomer copolymerized therewith, and a high acid number polycarboxylic acid.

5. The two-part sizing formulation of claim 4, wherein said at least one high acid number polyacid is an ethylene-maleic acid copolymer.

6. The two-part sizing formulation of claim 1, wherein said high acid number is from about 300 to about 950.

7. The two-part sizing formulation of claim 1, wherein said size composition comprises a coupling agent and a first film forming agent.

8. The two-part sizing composition of claim 1, wherein said binder composition further comprises a second film forming agent, said first and second film forming agents being the same as or different from each other.

9. The two part sizing formulation of claim 8, wherein at least one of said first and second film forming agents is a polyurethane film forming agent based on a non-blocked isocyanate.

10. A two-part sizing formulation for sizing a reinforcing fiber used to form a composite material when combined with a polymer that includes a di-cation or a higher valency cation, said two-part sizing formulation comprising:

a size composition containing a first film former; and

a binder composition including at least one high acid number polyacid selected from a copolymer formed from the polymerization of maleic anhydride and at least one other monomer copolymerized therewith, a copolymer formed from the polymerization of maleic acid and at least one other monomer copolymerized therewith, and a high acid number polycarboxylic acid.

11. The two-part sizing formulation of claim 10, wherein said at least one high acid number polyacid contains acid moieties, said acid moieties being present in an amount that is greater than the amount of said di-cation or said higher valency cation present in said polymer.

12. The two-part sizing formulation of claim 11, wherein said high acid number is from about 300 to about 950.

13. The two-part sizing formulation of claim 10, wherein said high acid number polyacid is present on said reinforcing fiber in an amount sufficient to provide a loss-on-ignition up to about 2.0%.

14. The two-part sizing formulation of claim 13, wherein said binder composition further comprises a second film forming agent, said first and second film forming agents being the same as or different from each other.

15. The two-part sizing formulation of claim 14, wherein at least one of said first and second film forming agents is a polyurethane film forming agent based on a non-blocked isocyanate.

16. A reinforced composite product comprising:

a polymer matrix containing a di-cation or a higher valency cation; and

a plurality of strands of a reinforcing fiber, the strands including:

an inner coating of a size composition; and

an outer coating of a binder composition including at least one high acid number polyacid containing acid moieties, said acid moieties being present in an amount that is greater than the amount of said di-cation or said higher valency cation present in said polymer matrix.

17. The reinforced composite product of claim 16, wherein said at least one high acid number polyacid is a polyacid selected from a copolymer formed from the polymerization of maleic anhydride and at least one other monomer copolymerized therewith, a copolymer formed from the polymerization of maleic acid and at least one other monomer copolymerized therewith, and a polycarboxylic acid.

18. The reinforced composite product of claim 17, wherein said at least one high acid number polyacid is

present on said reinforcing fiber in an amount sufficient to provide a loss-on-ignition up to about 2.0%.

19. The reinforced composite product of claim 18, wherein said at least one high acid number polyacid is an ethylene-maleic acid copolymer.

20. The reinforced composite product of claim 16, wherein said at least one high acid number is from about 300 to about 950.

21. The reinforced composite product of claim 16, wherein said size composition comprises a first film forming agent.

22. The reinforced composite product of claim 21, wherein said binder composition further comprises a second film forming agent, said second film forming agent being the same as or different from said first film forming agent.

23. The reinforced composite product of claim 22, wherein at least one of said first and second film forming agents is a polyurethane film forming agent based on a non-blocked isocyanate.

24. A sized reinforcing fiber used to form a composite product when combined with a polymer that includes a di-cation or a higher valency cation, said sized reinforcing fiber comprising:

a reinforcing fiber at least partially coated with a two-part sizing formulation, said two-part sizing formulation including:

a size composition; and

a binder composition including at least one high acid number polyacid containing acid moieties, said acid moieties being present in an amount that is greater than the amount of said di-cation or said higher valency cation present in said polymer.

25. The sized reinforcing fiber of claim 24, wherein said amount of said acid moieties is sufficient to retain at least a portion of said acid moieties after interacting with said di-cation or said higher valency cation when forming said composite material.

26. The sized reinforcing fiber of claim 24, wherein said at least one high acid number polyacid is present on said reinforcing fiber in an amount sufficient to provide a loss-on-ignition up to about 2.0%.

27. The sized reinforcing fiber of claim 24, wherein said high acid number is from about 300 to about 950.

28. The sized reinforcing fiber of claim 24, wherein said size composition comprises a coupling agent and a first film forming agent.

29. The sized reinforcing fiber of claim 28, wherein said binder composition further comprises a second film forming agent, said first and second film forming agents being the same as or different from each other.

30. The sized reinforcing fiber of claim 28, wherein at least one of said first and second film forming agents is a polyurethane film forming agent based on a non-blocked isocyanate.

31. The sized reinforcing fiber of claim 24, wherein said at least one high acid number polyacid is a polyacid selected from a high acid number copolymer formed from the polymerization of maleic anhydride and at least one other monomer copolymerized therewith, a copolymer formed from the polymerization of maleic acid and at least one other monomer copolymerized therewith, and a high acid number polycarboxylic acid.

32. A sized reinforcing fiber comprising:

a reinforcing fiber at least partially coated with a two-part sizing formulation, said two-part sizing formulation including:

a size composition containing a first film former; and

a binder composition including at least one high acid number polyacid selected from a copolymer formed from the polymerization of maleic anhydride and at least one other monomer copolymerized therewith, a copolymer formed from the polymerization of maleic acid and at least one other monomer copolymerized therewith, and a high acid number polycarboxylic acid.

33. The sized reinforcing fiber of claim 32, wherein said high acid number is from about 300 to about 950.

34. The sized reinforcing fiber of claim 32, wherein said high acid number polyacid is present on said reinforcing fiber in an amount sufficient to provide a loss-on-ignition up to about 2.0%.

35. The sized reinforcing fiber of claim 32, wherein said binder composition further comprises a second film forming agent, said first and second film forming agents being the same as or different from each other.

36. The sized reinforcing fiber of claim 32, wherein at least one of said first and second film forming agents is a polyurethane film forming agent based on a non-blocked isocyanate.

37. A method of preparing a sized reinforcing fiber for reinforcing a composite article that contains a di-cation or higher valency cation comprising:

applying a size composition to at least a portion of a reinforcing fiber to form a coated reinforced fiber material; and

applying a binder composition to said coated reinforced fiber material, said binder composition including at least one high acid number polyacid containing acid moieties, said acid moieties being present in an amount that is greater than the amount of said di-cation or said higher valency cation in said composite article.

38. The method of claim 37, wherein said size composition comprises a film forming agent.

39. The method of claim 38, wherein said amount of said acid moieties is sufficient to retain at least a portion of said acid moieties after interacting with said di-cation or said higher valency cation.

40. The method of claim 37, wherein said at least one high acid number polyacid is present on said reinforcing fiber in an amount sufficient to provide a loss-on-ignition up to about 2.0%.

41. A method of forming reinforcing fiber pellets comprising:

at least partially coating reinforcing fibers with a size composition to form coated reinforcing fibers, said size composition including a first film forming agent;

chopping the coated reinforcing fibers to produce reduced length coated reinforcing fibers;

at least partially coating said reduced length coated reinforcement fibers with a binder composition to form binder-coated reduced length reinforcement fibers, said binder composition including at least one high acid

number polyacid selected from a copolymer formed from the polymerization of maleic anhydride and at least one other monomer copolymerized therewith, a copolymer formed from the polymerization of maleic acid and at least one other monomer copolymerized therewith, and a high acid number polycarboxylic acid; and

pelletizing the binder-coated reduced length reinforcement fibers to form reinforcing fiber pellets.

42. The method of claim 41, further comprising:

densifying said reinforcing fiber pellets.

43. The method of claim 42, wherein said at least one high acid number polyacid is present on said binder-coated reduced length reinforcement fibers in an amount sufficient to provide a loss-on-ignition up to about 2.0%.

44. The method of claim 43, wherein said binder composition further comprises a second film forming agent, said first and second film forming agents being the same as or different from each other.

45. The sized reinforcing fiber of claim 44, wherein at least one of said first and second film forming agents is a polyurethane film forming agent based on a non-blocked isocyanate.

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