The present invention relates to sizing compositions for glass fibers and glass fiber reinforced resins. In one embodiment, the present invention provides a sizing composition comprising at least one polyvinyl alcohol in an amount greater than about 65 weight percent of the sizing composition on a total solids basis, and at least one coupling agent in an amount greater than about 5 weight percent of the sizing composition on a total solids basis. Embodiments of the present invention also relate to fiber glass strands, glass fiber reinforced resin compositions, and methods for producing composites.
SIZING COMPOSITION FOR GLASS FIBERS, Sized FIBER GLASS PRODUCTS, AND COMPOSITES

FIELD OF THE INVENTION

[0001] The present invention relates to sizing compositions for glass fibers, to sized fiber glass products, and to materials reinforced with glass fibers at least partially coated with a sizing composition.

BACKGROUND OF THE INVENTION

[0002] Various chemical treatments exist for glass-type surfaces such as glass fibers to aid in their processability and applications. After formation and before bundling, glass filaments or fibers can be treated with a coating composition or sizing composition that is applied to at least a portion of the surface of the individual filaments to protect them from abrasion and to assist in processing. As used herein, the terms “sizing composition,” “sizing,” “binder composition,” “binder,” or “size” refer to a coating composition applied to the filaments after forming. Sizing compositions may provide protection through subsequent processing steps, such as those where the fibers pass by contact points as in the winding of the fibers and strands onto a forming package, drying the aqueous-based or solvent-based sizing composition to remove the water or solvent, twisting from one package to a bobbin, beaming to place the yarn onto very large packages ordinarily used as the warp in a fabric, chopping in a wet or dry condition, roving into larger bundles or groups of strands, unwinding for use as a reinforcement, or other downstream processes.

[0003] In addition, sizing compositions can play a dual role when placed on fibers that reinforce polymeric matrices in the production of fiber-reinforced plastics. In such applications, the sizing composition can provide protection and additionally can provide compatibility between the fiber and the matrix polymer or resin. Glass fibers in the forms of woven and nonwoven fabrics, mats, rovings, and chopped strands have been used with resins, such as thermosetting and thermostable resins, for reinforcement applications. In such applications, it can be desirable to maximize the compatibility between the surface of the fiber and the polymeric resin.

[0004] One example of a resin that has been reinforced by glass fibers is a polyamide resin. In the past, sizing compositions having polyurethanes as the major component have been used to coat glass fibers used in polyamide reinforcement applications. Polyurethanes demonstrate good compatibility with polyamides and other resins leading to compositions with desirable structural properties. However, while polyurethanes can provide good compatibility with certain resins, the use of polyurethanes as a major component of sizing compositions for glass fibers can be undesirable in some instances despite its good compatibility.

[0005] It would be desirable to provide sizing compositions comprising reduced or negligible amounts of polyurethane that demonstrate physical and chemical properties comparable to sizing compositions having polyurethane as a major component. It would additionally be desirable to provide composite materials comprising polymeric resins reinforced with glass fibers coated with sizing compositions comprising reduced or negligible amounts of polyurethane that exhibit physical and mechanical properties comparable to composites comprising glass fibers coated with sizing compositions having polyurethane as a major component.

SUMMARY OF THE INVENTION

[0006] Some embodiments of the present invention relate to aqueous sizing compositions and glass fibers at least partially coated with aqueous sizing compositions. Also provided in some embodiments are composite materials including glass fiber reinforced polymeric resins. Sizing compositions of the present invention can comprise reduced amounts of polyurethane while demonstrating physical and chemical properties comparable to sizing compositions having polyurethane as a major component in some embodiments.

[0007] In some embodiments, a sizing composition comprises at least one polyvinyl alcohol in an amount greater than about 65 weight percent of the sizing composition on a total solids basis and at least one coupling agent in an amount greater than about 5 weight percent on a total solids basis. In another embodiment, the polyvinyl alcohol can be present in an amount greater than about 70 weight percent of the sizing composition on a total solids basis. In another embodiment, the polyvinyl alcohol can be present in an amount greater than about 80 weight percent of the sizing composition on a total solids basis. In a further embodiment, the polyvinyl alcohol can be present in an amount greater than about 90 weight percent of the sizing composition on a total solids basis.

[0008] A sizing composition, in other embodiments, can comprise at least one polyvinyl alcohol in an amount greater than about 50 weight percent of the sizing composition on a total solids basis, at least one polyurethane, and at least one coupling agent. In some embodiments, the polyvinyl alcohol can be present in an amount greater than about 60 weight percent on a total solids basis. In some embodiments, the polyurethane can be present in an amount up to about 30 weight percent of the sizing composition on a total solids basis. The coupling agent, in some embodiments, can be present in an amount greater than about 5 weight percent of the sizing composition on a total solids basis.

[0009] Sizing compositions, according to some embodiments, can further comprise additional components including isocyanates, anhydrides, and acrylates. In one embodiment, a sizing composition can comprise at least one polyvinyl alcohol in an amount greater than about 40 weight percent of the sizing composition on a total solids basis, at least one coupling agent, and at least one additional component selected from the group consisting of polyurethane, blocked isocyanate, acrylate, anhydride, and combinations thereof. In some embodiments, at least one additional component comprises a plurality of components selected from the group consisting of polyurethane, blocked isocyanate, acrylate, anhydride and combinations thereof. In some embodiments, the coupling agent can be present in an amount greater than about 5 weight percent of the sizing composition on a total solids basis. In some embodiments, the at least one additional component can be present in an amount greater than about 40 weight percent of the sizing composition on a total solids basis.

[0010] Other embodiments of the present invention relate to glass fibers at least partially coated with a sizing composition of the present invention. Glass fibers at least partially coated with a sizing composition of the present invention can be gathered into strands. In some embodiments, a glass
A fiber strand can comprise at least one glass fiber at least partially coated with a sizing composition comprising at least one polyvinyl alcohol in an amount greater than about 50 weight percent of the sizing composition on a total solids basis, at least one polyurethane, and at least one coupling agent.

The present invention can additionally provide polymeric resins reinforced with glass fibers, wherein the glass fibers are at least partially coated with a sizing composition according to embodiments of the present invention. Polymeric resins can comprise thermoplastic resins and thermoset resins. In some embodiments, the polymeric resin can comprise a polyamide resin.

In other embodiments, the present invention provides methods for producing fiber reinforced polymeric composite materials. A method for producing a fiber reinforced polymeric composite material, in one embodiment, comprises providing a plurality of glass fibers at least partially coated with a residue of a sizing composition of the present invention, incorporating the plurality of glass fibers into a polymeric resin, and molding the polymeric resin into a composite.

These and other embodiments of the present invention are described in greater detail in the detailed description of the invention which follows.

**DETAILED DESCRIPTION**

For the purposes of this specification, unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

It is further noted that, as used in this specification, the singular forms “a,” “an,” and “the” include plural referents unless expressly and unequivocally limited to one referent.

Some embodiments of the present invention relate to sizing compositions having reduced amounts of polyurethane. In some embodiments, such sizing compositions, when at least partially coated on glass fiber, can result in the glass fibers demonstrating properties comparable to sizing compositions having polyurethane as a major component. In some embodiments, the sizing compositions can be useful for coating glass fibers to be used in reinforcing polymeric resins.

Embodiments of the present invention will be discussed generally in the context of their use in the production, assembly, and application of glass fibers and composite materials comprising glass fibers. One of skill in the art, however, would understand that the present invention may be useful in the processing of other textile materials.

In some embodiments, a sizing composition of the present invention comprises at least one polyvinyl alcohol in an amount greater than about 65 weight percent of the sizing composition on a total solids basis and at least one coupling agent in an amount greater than about 5 weight percent on a total solids basis. In another embodiment, the polyvinyl alcohol can be present in an amount greater than about 70 weight percent of the sizing composition on a total solids basis. In another embodiment, the polyvinyl alcohol can be present in an amount greater than about 80 weight percent of the sizing composition on a total solids basis. In a further embodiment, the polyvinyl alcohol can be present in an amount greater than about 90 weight percent of the sizing composition on a total solids basis.

A sizing composition, according to some embodiments of the present invention, comprises at least one polyvinyl alcohol in an amount greater than about 50 weight percent of the sizing composition on a total solids basis, at least one polyurethane, and at least one coupling agent. In some embodiments, the polyvinyl alcohol is present in an amount greater than about 60 weight percent on a total solids basis. In some embodiments, the polyurethane can be present in an amount up to about 30 weight percent of the sizing composition on a total solids basis. The coupling agent, in some embodiments, can be present in an amount greater than about 5 weight percent of the sizing composition on a total solids basis.

Sizing compositions, according to some embodiments of the present invention, can further comprise additional components including isocyanates, anhydrides, and acrylates. In one embodiment, a sizing composition can comprise at least one polyvinyl alcohol in an amount greater than about 40 weight percent of the sizing composition on a total solids basis, at least one coupling agent, and at least one additional component selected from the group consisting of polyurethane, blocked isocyanate, acrylate, anhydride, and combinations thereof. In some embodiments, the at least one additional component comprises a plurality of components selected from the group consisting of polyurethane, blocked isocyanate, acrylate, anhydride, and combinations thereof. In some embodiments, the at least one additional component can be present in an amount greater than about 5 weight percent of the sizing composition on a total solids basis. In some embodiments, the at least one additional component can be present in an amount greater than about 40 weight percent of the sizing composition on a total solids basis. In other embodiments, the at least one additional component can be present in an amount greater than about 50 weight percent of the sizing composition on a total solids basis. In a further embodiment, the at least one additional component can be present in an amount greater than about 60 weight percent of the sizing composition on a total solids basis.

Turning now to components that can be included in various embodiments of sizing compositions of the present invention, sizing compositions of the present invention comprise polyvinyl alcohol.

Polyvinyl alcohols suitable for use in sizing compositions of the present invention can be derived from polyvinyl acetate by hydrolysis or saponification processes. A wide variety of grades of polyvinyl alcohol are available and are often classified according to degrees of hydrolysis.
and viscosity. Suppliers of polyvinyl alcohol typically characterize their polyvinyl alcohol products based on degree of hydrolysis, and the term "degree of hydrolysis" is intended to have the same meaning herein as understood by the those of ordinary skill in the art.

[0024] In the present application, polyvinyl alcohol may be characterized in terms of degree of hydrolysis. In some embodiments, a polyvinyl alcohol for use in sizing compositions of the present invention can be greater than 80% hydrolyzed. In other embodiments, the polyvinyl alcohol can be greater than 85% hydrolyzed. In other embodiments, the polyvinyl alcohol can be greater than 98% hydrolyzed.

[0025] The polyvinyl alcohol component of sizing compositions, according to some embodiments of the present invention, can comprise polyvinyl alcohol having a particular average degree of hydrolysis. In other embodiments, the polyvinyl alcohol component comprises a mixture of polyvinyl alcohols having different average degrees of hydrolysis. In one embodiment, for example, the polyvinyl alcohol component of a sizing composition can comprise a mixture of a polyvinyl alcohol greater than 85% percent hydrolyzed and a polyvinyl alcohol greater than 98% hydrolyzed. Embodiments of the present invention contemplate mixtures of polyvinyl alcohols discussed herein in any combination.

[0026] Non-limiting examples of commercially available polyvinyl alcohols for use in embodiments of sizing compositions of the present invention can include CELVOL® series polyvinyl alcohols available from Celanese Corporation. Several examples of CELVOL® series polyvinyl alcohols that can be used in various embodiments of sizing compositions of the present invention are provided in Table 1.

<table>
<thead>
<tr>
<th>CELVOL® Series Polyvinyl Alcohols</th>
<th>Hydrolysis %</th>
<th>Viscosity mPa (4%/20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CELVOL® 205</td>
<td>88</td>
<td>5.7</td>
</tr>
<tr>
<td>CELVOL® 203</td>
<td>88</td>
<td>4.0</td>
</tr>
<tr>
<td>CELVOL® 502</td>
<td>88</td>
<td>3.4</td>
</tr>
<tr>
<td>CELVOL® 305</td>
<td>98.4</td>
<td>5.0</td>
</tr>
<tr>
<td>CELVOL® 103</td>
<td>98.4</td>
<td>4.0</td>
</tr>
</tbody>
</table>

[0027] Additional non-limiting examples of commercially available polyvinyl alcohols that can be used in various embodiments of sizing compositions of the present invention comprise MOWIOL® series polyvinyl alcohols available from Kunany Specialities Europe. Several examples of MOWIOL® series polyvinyl alcohols that can be used in various embodiments of sizing compositions of the present invention are provided in Table 2.

<table>
<thead>
<tr>
<th>MOWIOL® Series Polyvinyl Alcohols</th>
<th>Hydrolysis %</th>
<th>Viscosity mPa (4%/20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOWIOL® 4-88</td>
<td>87.7</td>
<td>4.0</td>
</tr>
<tr>
<td>MOWIOL® 3-83</td>
<td>82.6</td>
<td>3.0</td>
</tr>
<tr>
<td>MOWIOL® 3-98</td>
<td>98.4</td>
<td>3.5</td>
</tr>
</tbody>
</table>

[0028] Embodiments of sizing compositions of the present invention can comprise varying amounts of polyvinyl alcohol. The amount of polyvinyl alcohol in sizing compositions of the present invention can depend upon several factors such as, but not limited to, compatibility with the resin to be reinforced, the fuzz and fly and strand integrity of a glass fiber, compatibility with other components of the sizing composition, and the useful viscosity of the sizing composition. Polyvinyl alcohol can demonstrate good film forming properties and can provide good strand integrity to a glass fiber. Moreover, the polarity of polyvinyl alcohol can facilitate compatibility with various thermoplastic resins, including polyamides.

[0029] In some embodiments, polyvinyl alcohol can be present in an amount greater than 50 weight percent of the sizing composition on a total solids basis. In some embodiments, polyvinyl alcohol can be present in an amount greater than 80 weight percent of the sizing composition on a total solids basis. In other embodiments, polyvinyl alcohol can be present in an amount greater than 90 weight percent of the sizing composition on a total solids basis. Amounts of polyvinyl alcohol present in sizing compositions according to different embodiments of the present invention are provided in Table 3.

<table>
<thead>
<tr>
<th>TABLE 3: Ranges of Amounts of Polyvinyl Alcohol in Sizing Compositions</th>
<th>AMOUNT IN WEIGHT PERCENT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>≥50</td>
<td>50–65</td>
</tr>
<tr>
<td>≥50</td>
<td>65–70</td>
</tr>
<tr>
<td>≥50</td>
<td>70–80</td>
</tr>
<tr>
<td>≥80</td>
<td>80–85</td>
</tr>
<tr>
<td>≥80</td>
<td>85–90</td>
</tr>
<tr>
<td>≥90</td>
<td>90–95</td>
</tr>
<tr>
<td>≥90</td>
<td>95–100</td>
</tr>
</tbody>
</table>

*Based on total solids

[0030] Some embodiments of sizing compositions of the present invention can comprise at least one coupling agent. In some embodiments, sizing compositions of the present invention can comprise a plurality of coupling agents. Coupling agents suitable for use in the present invention can comprise a functional group or functional groups operable for reacting with a surface of a glass fiber or otherwise be attracted, but not necessarily bound to the glass surface by, for example, Van der Waals, dipole-dipole, or other intermolecular interactions. In embodiments where the glass fibers have contact with a resin, one or more coupling agents can interact with the resin to facilitate adhesion of the resin to the glass fiber. Interactions between coupling agents and resins according to embodiments of the present invention can comprise various chemical reactions, electrostatic interactions, or other attractive intermolecular interactions, although typically the interaction between the coupling agent and the resin is a chemical reaction.

[0031] Embodiments of sizing compositions of the present invention comprising a plurality of coupling agents can provide glass fibers coated with the sizing compositions that can be used in variety or processes and applications. For example, the plurality of coupling agents can facilitate
favorable interactions with a variety of resins systems and/or other matrices, such as, for example, a variety of polyamide resins and matrices.

[0032] Coupling agents, according to embodiments of the present invention, can comprise organosilanes. Organosilanes useful in some embodiments of the present invention can comprise aminofunctional silanes. Aminofunctional silanes can be useful, for example, in at least partially coating glass fibers used to reinforce polyamide resins. Two examples of aminofunctional silanes that can be used in some embodiments of the present invention are aminopropyltriethoxysilane and dimethyldichlorosilane. Non-limiting examples of aminopropyltriethoxysilane for use in some embodiments of sizing compositions of the present invention comprise γ-aminopropytrimethoxysilane and γ-aminopropytrimethoxysilane. Commercially available γ-aminopropytrimethoxysilane comprise DYNASILYAN AME0 from DeGussa AG of Dusseldorf, Germany and A-1100 from OSI Specialties of Tarrytown, N.Y. Non-limiting examples of dimethyldichlorosilane that can be used in some embodiments of sizing compositions include N-[β-(aminobutyl)γ-aminopropyltrimethoxysilane (DYNASILYAN 1189), N-[β-(aminomethyl)aminopropyltrimethoxysilane, and N-[β-(aminomethyl)]γ-aminopropyltrimethoxysilane (DYNASILYAN DAMO).

[0033] The amount and type of coupling agent in sizing compositions of the present invention can depend upon various factors such as, but not limited to, the coupling agent's affinity for a particular resin, and the coupling agent's compatibility with the other components of the sizing composition. Table 4 provides exemplary ranges of the amount of coupling agent that can be used in various embodiments of sizing compositions of the present invention.

**TABLE 4**

<table>
<thead>
<tr>
<th>AMOUNT IN WEIGHT PERCENT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤5</td>
</tr>
<tr>
<td>5-10</td>
</tr>
<tr>
<td>≤15</td>
</tr>
</tbody>
</table>

*Based on Total Solids

[0034] In some embodiments, a sizing composition of the present invention can comprise at least one polyurethane. Polyurethanes are generally synthesized via the formation of carbamate linkages by the reaction of polyfunctional isocyanates and alcohols. Polyurethanes useful in embodiments of the present invention can be produced from aliphatic, cycloaliphatic, or aromatic polyfunctional isocyanates. Polyurethanes produced from aliphatic isocyanates, for example, can demonstrate desirable color characteristics in some embodiments. In some embodiments, polyurethanes can be introduced into sizing compositions of the present invention as aqueous dispersions.

[0035] In some embodiments, the polyurethane component comprises a single polyurethane species. In other embodiments, the polyurethane component of sizing compositions of the present invention can comprise a mixture of polyurethanes. Some embodiments of the present invention contemplate mixtures of polyurethanes discussed herein in any combination.

[0036] Non-limiting examples of polyurethanes useful in sizing compositions of the present invention comprise WITCOBOND® 60X, WITCOBOND® W-213, WITCOBOND® 234, WITCOBOND® W-290H, and WITCOBOND® W-296 commercially available from Crompton Corporation-Uniroyal Chemical. Additional non-limiting examples of polyurethanes useful in sizing compositions of the present invention include BAYBOND® PU-130, BAYBOND® PU-400S and BAYBOND® XP-7055 available from Bayer Material Science.

[0037] Polyurethanes have been previously been used as film-formers in sizing compositions used to at least partially coat glass fibers for reinforcement applications, such as the reinforcement of polyamide resins. In such sizing compositions, polyurethanes were usually the component present in the largest amount, other than water. Some embodiments of the present invention relate to sizing compositions in which polyurethanes do not represent the major constituent (e.g., another component, such as polyvinyl alcohol, is present in a greater amount). In some embodiments, polyurethanes represent a minor constituent (e.g., not the largest, non-water component of the sizing composition). As polyurethanes can be expensive, the use of a less expensive component to reduce the amount of polyurethane needed in a sizing composition for a particular application can be desirable.

[0038] Thus, in embodiments of sizing compositions that comprise polyurethane, varying amounts of polyurethane can be used. The amount of polyurethane that can be used in some embodiments of sizing compositions of the present invention can depend upon various factors including, but not limited to, compatibility with other components in the sizing composition, and the cost of the polyurethane such that the sized glass fibers are commercially viable product. In some embodiments, polyurethane can be present in an amount up to about 30 weight percent of the sizing composition on a total solids basis. Table 5 represents exemplary ranges of the amount of polyurethanes that can be used in various embodiments of sizing compositions of the present invention that comprise polyurethane.

**TABLE 5**

<table>
<thead>
<tr>
<th>AMOUNT IN WEIGHT PERCENT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-5</td>
</tr>
<tr>
<td>6-10</td>
</tr>
<tr>
<td>11-15</td>
</tr>
<tr>
<td>16-20</td>
</tr>
<tr>
<td>21-25</td>
</tr>
<tr>
<td>26-30</td>
</tr>
</tbody>
</table>

*Based on Total Solids

[0039] In some embodiments, sizing compositions of the present invention can further comprise isocyanates, such as blocked isocyanates. As used herein, the term “blocked isocyanate” refers to any isocyanate where the isocyanate groups have been reacted with a compound so that the resultant blocked isocyanate is stable to active hydrogens at 25°C, and reactive with active hydrogens at a temperature below the temperature at which any film former present in the sizing composition reacts. In some embodiments, two or more isocyanates may be used jointly.

[0040] In the preparation of blocked organic isocyanates, any suitable organic polyisocyanate may be used. A suitable
organic polyisocyanate may be determined by the polyisocyanate's ability to form cross links with a film-former in a sizing composition, by the polyisocyanate's ability to interact with a polyamide resin, and/or by the polyisocyanate's ability to interact with other components of the sizing composition, such as, but not limited to, during drying of the sizing composition and during extrusion. Non-limiting examples of suitable organic polyisocyanates are aliphatic compounds such as trimethylene, tetramethylene, hexamethylene and butylidene diisocyanate, or isophorone diisocyanate (IPDI); cycloalkylene compounds such as 1,4-cyclohexane diisocyanate; aromatic compounds such as p-phenylene diisocyanate; aliphatic-aromatic compounds such as 4,4' diphenylene methane diisocyanate, 2,4- or 2,6-tolylene diisocyanate or mixtures thereof. Non-limiting examples of suitable higher polyisocyanates comprise triisocyanates such as triphenylmethane-4,4',4''-trisocyanate and 2,4,6-trisocyanatoluene. Additional examples of organic polyisocyanates that may be used when practicing this invention include those of the biuret type and those for which a di- or trimerization reaction has produced four-, five- or six-membered rings. Among the six-membered rings, there may be mentioned the isocyanurate rings derived from a homo- or hetero-trimerization of various diisocyanates alone, with other isocyanate(s) (e.g., mono-, di- or polyisocyanate(s)) or with carbon dioxide. In this latter case, a nitrogen from the isocyanurate ring is replaced by an oxygen.

A suitable blocking agent may be determined by its ability to prevent the blocked isocyanate from reacting until a desired temperature is achieved. Non-limiting examples of compounds which may be suitable blocking agents include, but are not limited to, oximes such as methyl ethyl ketoxime, acetone oxime and cyclohexanone oxime, lactams such as epsilon-caprolactam, and pyrazoles. Use of oximes, lactams, and pyrazoles can be desirable because polyisocyanates blocked with oximes, lactams, and pyrazoles can unblock and react at lower temperatures relative to polyisocyanates blocked with alcohols.

In an embodiment, a blocked isocyanate comprises epsilon-caprolactam blocked aliphatic polyisocyanate aqueous emulsion from Bayer Chemical as NAJ-1058.

The amount of blocked isocyanate in the sizing composition may depend upon several factors such as, but not limited to, the blocking agent's compatibility with other components of the sizing composition, the type and amount of any film-former used in the sizing composition, and the useful viscosity of the sizing composition. For example, the lower limit of the amount of blocked isocyanate in the sizing composition may be determined by the amount effective to improve or maintain the strength of a reinforced thermoplastic resin. Table 6 represents exemplary ranges of the amount of blocked isocyanates that can be used in various embodiments of sizing compositions of the present invention that comprise blocked isocyanates.

### TABLE 6

<table>
<thead>
<tr>
<th>Amount in Weight Percent*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-5</td>
</tr>
<tr>
<td>6-10</td>
</tr>
<tr>
<td>11-15</td>
</tr>
<tr>
<td>16-20</td>
</tr>
</tbody>
</table>

*Based on Total Solids

Some embodiments of sizing compositions of the present invention can further comprise at least one lubricant. Lubricants can be used to reduce interfilament abrasion between glass fibers and to reduce abrasion between glass fibers and contact points during processing. Lubricants can comprise any cationic, anionic, or non-ionic glass fiber lubricants or mixtures thereof compatible with other components of the sizing composition. Non-limiting examples of lubricants useful in sizing compositions of the present invention can include condensates of a fatty acid and polyethyleneimine and an amide substituted polyethyleneimine. In some embodiments, a sizing composition of the present invention can comprise a first lubricant comprising a partially amidated polyethyleneimine, such as EMERTM-6717, commercially available from Henkel Corporation of Kankakee, Ill., or Congis Corporation of Cincinnati, Ohio, and a second lubricant comprising a carboxylic acid copolymer with ethylene oxide, such as DAPRAL®GE202 available from Akzo Nobel, Netherlands. In some embodiments, a sizing composition can comprise either of these lubricants.

The amount of lubricant included in a sizing composition can depend upon one or more factors such as, but not limited to, the amount sufficient to reduce interfilament abrasion, the amount sufficient to facilitate processability of the fiber glass in manufacturing operations, and the amount compatible with the other components of the sizing composition. In some embodiments, the amount of lubricant in a sizing composition of the present invention can be less than about 10 weight percent on a total solids basis. In other embodiments, the lubricant can be present in an amount up to about 5 weight percent on a total solids basis.

In some embodiments, sizing compositions of the present invention can further comprise additional components such as anhydrides, acrylates, or combinations thereof.

Anhydrides, as used herein, can comprise monomeric, oligomeric, and polymeric forms of anhydrides as well as their hydrolyzed and neutralized forms. In one embodiment, for example, anhydrides can comprise maleic anhydride or itaconic anhydride in a monomeric form. In other embodiments, anhydrides can comprise oligomers and polymers having one or more anhydride moieties. In such embodiments, the anhydride moieties can be incorporated into the backbone of the oligomers and polymers or can otherwise be substituents coupled to the backbone. In some embodiments, maleic anhydride and/or itaconic anhydride can be copolymerized with one or more additional monomers to produce an anhydride oligomer or polymer. Anhydrides, in some embodiments, can comprise MALDENE 286 from Lindan Chemicals, Inc. and ZEMAC E400 from Zeeland Chemicals Inc.

Acrylates, as used herein, can comprise monomeric, oligomeric, and polymeric forms of acrylates, including acrylic acids, as well as their neutralized forms. In one embodiment, for example, acrylates can comprise methacrylate and methylmethacrylate monomers. In other embodi-
ments, acrylates can comprise oligomers and polymers having one or more acrylic acid moieties. In such embodiments, the acrylic acid moieties can be incorporated into the backbone of the oligomers or polymer or can otherwise be substituents coupled to the backbone.

[0049] Anhydrides and acrylates can generally improve hydrolysis resistance of fiber reinforced thermoplastic resins. In some embodiments, anhydrides, acrylates, or combinations thereof can be present in a sizing composition of the present invention in an amount up to about 75 weight percent of the sizing composition on a total solids basis. In other embodiments, anhydrides, acrylates, or combinations thereof can be present in sizing compositions of the present invention in an amount greater than about 40 weight percent of the sizing composition on a total solids basis. In another embodiment, anhydrides, acrylates, or combinations thereof can be present in sizing compositions of the present invention in an amount greater than about 50 weight percent of the sizing composition on a total solids basis. In a further embodiment, anhydrides, acrylates, or combinations thereof can be present in a sizing compositions of the present invention in an amount greater than or equal to about 60 weight percent of the sizing composition on a total solids basis.

[0050] The present invention also provides fiber glass strands comprising glass fibers at least partially coated with sizing compositions of the present invention. Embodiments of the present invention contemplate fiber glass strands comprising at least one glass fiber at least partially coated with a sizing composition of the present invention. Sizing compositions used to at least partially coat glass fibers, according to embodiments of the present invention, can comprise any combination and any amount of the sizing composition components consistent with that described herein.

[0051] In some embodiments, a fiber glass strand of the present invention comprises at least one glass fiber at least partially coated with a sizing composition comprising at least one polyvinyl alcohol in an amount greater than about 80 weight percent of the sizing composition on a total solids basis and at least one coupling agent in an amount greater than about 5 weight percent of the sizing composition on a total solids basis.

[0052] In some embodiments, a fiber glass strand of the present invention can comprise at least one glass fiber at least partially coated with a sizing composition comprising at least one polyvinyl alcohol in an amount greater than about 50 percent by weight of the sizing composition on a total solids basis, at least one polyurethane, and at least one coupling agent.

[0053] The type of glass fibers to be sized may be determined by various factors such as, but not limited to, the intended end use of the sized glass fibers. The glass fibers, in some embodiments, may be any type so long as the glass fibers are compatible with a thermoplastic or thermostet resin. In one embodiment, the glass fibers can be used to reinforce a thermoplastic composite. Glass fibers suitable for reinforcing thermoplastic or thermostet resins include chopped type fibers and long fibers, such as continuous rovings. The length and diameter of the chopped glass fibers used for reinforcing thermoplastic resins may be determined by various factors such as, but not limited to, the ease of handling when glass fibers are melt-kneaded with a thermoplastic resin, the reinforcing effect of the glass fibers, and glass fiber dispersing ability. In some embodiments, the length of glass fibers can be greater than 1 mm. In other embodiments, the length of glass fibers can be less than 50 mm. In other embodiments, the length of glass fibers can be between 3.175 mm (1/8 inch) and 12.7 mm (1/2 inch).

[0054] In some embodiments, the average diameter of the glass fibers can be greater than 8 μm. In some embodiments, the average diameter of the glass fibers can be less than 25 μm.

[0055] Non-limiting examples of glass fibers suitable for use in the present invention can include those prepared from fiberizable glass compositions such as “E-glass”, “A-glass”, “C-glass”, “S-glass”, “ECR-glass” (corrosion resistant glass), and fluorine and/or boron-free derivatives thereof. Typical formulations of glass fibers are disclosed in K. Lowenstein, The Manufacturing Technology of Continuous Glass Fibers, (3rd Ed. 1993).

[0056] The present invention also provides glass fiber reinforced resin compositions and methods of producing glass fiber reinforced resin compositions. Sizing compositions used to at least partially coat glass fibers for resin reinforcement applications, according to embodiments of the present invention, can comprise any combination and any amount of the sizing composition components consistent with that described herein.

[0057] Resin compositions reinforced with glass fibers, according to embodiments of the present invention, can comprise thermoset resins and/or thermostet resins. Non-limiting examples of thermoplastic materials comprise polyolefins, polyacets, polyamide, polycarbonates, polyesters, styrene-acrylonitrile copolymers, acrylonitrile-butadiene styrene (ABS) copolymers, polyvinyl chloride, polyethylene terephthalates, polybutylene terephthalates, and blends of thermoplastic resins.

[0058] Some embodiments of glass fibers according to the present invention can be particularly suited for reinforcing polyamide resins. Polyamide resins reinforced with glass fibers, in some embodiments, can comprise nylon 6, nylon 6/6, nylon 12, polycarbonate, polylactic acid, polyamides 6T (polyhexamethylene terephthalamide), polyamide 6i (polyhexamethylene isophthalamide) or mixtures thereof. A particular polyamide resin can be chosen based on a resin’s mechanical characteristics, heat resistance, glass transition temperature, moldability, and appearance of the moldings.

[0059] The polyamide thermoplastic resins can be lubricated with a fatty acid metal salt such as sodium, lithium, calcium, magnesium, zinc or aluminum salt of a fatty acid having 9 or more carbon atoms such as capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, cetic acid, montanac acid, melissic acid, oleic acid, and erucic acid. Additionally, two or more fatty acid metal salts may be jointly used. The fatty acid metal salt can be used to reduce shear stress during melt-kneading of the thermoplastic polyamide resin and sized glass fibers in an extruder, to improve the mold release characteristics of the resin, or improve the melt flow of the resin during injection molding. In one embodiment, metal stearate is used to lubricate a polyamide resin to be reinforced with sized glass fibers. A caprolactam blocked isocyanate, as described in connection with sizing compositions of the present invention, can improve the strength of the calcium stearate lubricated polyamide resin.
[0060] In some embodiments, a fiber reinforced resin composition comprises a polyamide resin and glass fibers at least partially coated with the residue of a sizing composition of the present invention. In some embodiments, the sizing composition comprises polyvinyl alcohol and a coupling agent, wherein the polyvinyl alcohol is present in an amount greater than about 50 weight percent of the sizing composition on a total solids basis. In other embodiments, the polyvinyl alcohol can be present in an amount greater than about 90 weight percent of the sizing composition on a total solids basis. In some embodiments, the sizing composition can also comprise a polyurethane.

[0061] In some embodiments, methods for producing a fiber reinforced resin composition provide for a plurality of glass fibers at least partially coated with a residue of a sizing composition of the present invention, incorporating the plurality of glass fibers into a resin, and molding the resin into a composite. In some embodiments, the sizing composition comprises polyvinyl alcohol and a coupling agent, wherein the polyvinyl alcohol is present in an amount greater than about 50 weight percent of the sizing composition on a total solids basis. In some embodiments, the polyvinyl alcohol is present in an amount greater than 90 weight percent of the sizing composition on a total solids basis. Sizing compositions used to at least partially coat glass fibers in methods of producing fiber reinforced resin compositions, according to embodiments of the present invention, can comprise any combination and any amount of the sizing composition components consistent with that described herein.

[0062] Sizing compositions of the present invention can be prepared by addition of the components using any suitable method known to those skilled in the art. For example, the components can be added sequentially to each other, or they may be prediluted in a carrier before they are combined to form the sizing composition.

[0063] Sizing composition can be applied to glass fibers by suitable methods known to one of skill in the art such as, but not limited to, by contacting glass fibers with a static or dynamic applicator, such as a roller or belt applicator, or by spraying, or by other means. The overall concentration of the non-volatile components in the sizing composition can be adjusted over a wide range according to the means of application to be used, the character of the glass fiber to be sized, and the weight of dried size coating desired for intended use of the sized glass fibers.

[0064] In some embodiments, the sizing composition can be applied to glass fibers in a single step during the forming operation of the fibers as is known to those of skill in the art. After the sizing composition is applied to the continuous glass fibers, the fibers can then be dried to remove the carrier in some embodiments.

[0065] The sizing composition can be a multi-part sizing composition in some non-limiting embodiments, such that the sizing composition is applied to glass fibers in a plurality of steps. In one non-limiting embodiment, for example, the sizing composition can comprise a two-part sizing composition with the sizing composition applied in two steps. In one example of such an embodiment, a first portion of the sizing composition can comprise a silane component and a lubricant component that is applied in a first step, such as during fiber formation. A second portion of the sizing composition can comprise a polyvinyl alcohol component, any polyurethane that might be part of the composition, and/or additional silane components, and could be applied in a second step after formation of a fiber glass strand.

[0066] The fiber glass strands can be chopped in some embodiments. The fiber glass strands can be chopped before drying in some embodiments, or after drying in other embodiments. Continuous fiber glass strands may be chopped using techniques known to those of skill in the art including, but not limited to, direct chop processes and remote chop processes.

[0067] As discussed above, the length of chopped glass fiber can vary depending on various factors such as, but not limited to, the type of thermoplastic resin in which the chopped glass fiber will be used to reinforce and the intended use of a glass fiber reinforced thermoplastic resin article. As discussed above, in embodiments where the sized chopped fiber is used to reinforce polyamide resins, the length may have a lower limit of 1 mm. Further, the sized chopped fiber used to reinforce polyamide resins may have an upper limit of length of 50 mm.

[0068] The amount of sizing composition on a fiber may be measured as “loss on ignition” or “LOI.” As used herein, the term “loss on ignition” or “LOI” means the weight percent of dried sizing composition present on the fiber glass as determined by Equation 1:

\[
\text{LOI} = \frac{100 \times (W_{\text{dry}} - W_{\text{raw}})}{W_{\text{dry}}} 
\]

wherein \(W_{\text{dry}}\) is the weight of the fiber plus the weight of the coating after drying in an oven at 220°F (about 104°C) for 60 minutes, and \(W_{\text{raw}}\) is the weight of the bare fiber glass after heating the fiber glass in an oven at 1150°F (about 621°C) for 20 minutes and cooling to room temperature in a desiccator.

[0069] Glass fibers coated with sizing compositions of the present invention, according to some embodiments, can have a loss on ignition ranging from about 0.1 to 1.0 weight percent.

[0070] The sized glass fibers can be incorporated into thermoplastic resins in any suitable molding process known to those skilled in the art using either chopped strand, continuous strand, or mixtures thereof. The sized chopped fiber strands can be mixed with a thermoplastic resin in a dry powder mixture. The mixture can be compression or injection molded to produce a glass fiber reinforced thermoplastic resin article. The glass fiber reinforced thermoplastic resins may be used in molding processing such as injection molding, extrusion molding, blow molding, or press molding.

[0071] One embodiment of the present invention will now be illustrated by the following non-limiting example.

**EXAMPLE 1**

[0072] One non-limiting example of a sizing composition of the present invention was prepared in accordance with the formulation set forth in Table 7.

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (kg)</th>
<th>Weight Percent Total Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silane</td>
<td>0.805</td>
<td>10.0</td>
</tr>
<tr>
<td>Polyvinyl Alcohol</td>
<td>3.4</td>
<td>67.7</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>2.275</td>
<td>20.4</td>
</tr>
<tr>
<td>Lubricant</td>
<td>0.00525</td>
<td>1.3</td>
</tr>
</tbody>
</table>
The amounts of components listed in Table 7 represent the amounts that can be used to prepare 100 kg of the sizing composition. Other amounts of the sizing composition can be prepared by adjusting the amounts shown.

Preparation of the Sizing Composition of Example 1

The sizing composition provided in Table 7 was generally prepared according to the procedure described below. The amount of water used to prepare the individual components prior to adding the components to the main mix tank may have varied depending on the technique preparing the sizing composition. The amount of water cited below would be sufficient for preparation of the sizing composition in Table 7. Water can be added at the end of the procedure to dilute the sizing composition to a desired final volume.

20 kg of water at 25 °C were added to a main mix tank. 0.2675 kg of acetic acid and 0.805 kg silane were added to the water in the main mix tank and the resulting mixture was agitated for 10 minutes. 1 kg of water at 70 °C was added to a side mix tank. 0.0245 kg of acetic acid and 0.06525 kg of a lubricant were added to the water in the side mix tank. The resulting lubricant solution was stirred for 15 minutes and subsequently added to the main mix tank. 1 kg of water at 70 °C was added to a side mix tank. 0.0352 kg of another lubricant was added to the water in the side mix tank. The resulting lubricant solution was stirred for 10 minutes and subsequently added to the main mix tank. The specified amount of polyurethane was added to the main mix tank and the resulting solution agitated.

15 kg of water at 70 °C were added to an emulsion tank. The specified amount of polyvinyl alcohol was added to the emulsion tank. The resulting mixture was stirred for 60 minutes and then added to the main mix tank. Subsequent to the addition of the polyvinyl alcohol, the resulting mixture in the main mix tank was agitated and additional water was added to bring the mixture to its final volume. The sizing composition had the weight percent solids and pH specified in Table 7.

Desirable characteristics, which can be exhibited by the present invention, include, but are not limited to, the provision of sizing compositions for reinforcing polymeric materials that comprise polyvinyl alcohol as a major constituent; the provision of sizing compositions for reinforcing polymeric materials that comprise polyurethane as a minor constituent; and the provision of sizing compositions that can at least partially coat glass fibers for use in reinforcing polyamide materials that comprise polyurethane as a minor constituent; and others.

Various embodiments of the invention have been described in fulfillment of the various objects of the invention. It should be recognized that these embodiments are merely illustrative of the principles of the present invention. Numerous modifications and adaptations thereof will be readily apparent to those skilled in the art without departing from the spirit and scope of the invention.

That which is claimed is:

1. An aqueous sizing composition for glass fibers, comprising:
   at least one polyvinyl alcohol in an amount greater than about 65 weight percent of the sizing composition on a total solids basis, and
   at least one coupling agent in an amount greater than about 5 weight percent of the sizing composition on a total solids basis.

2. The sizing composition of claim 1, wherein the at least one polyvinyl alcohol is present in an amount greater than about 80 weight percent of the sizing composition on a total solids basis.

3. The sizing composition of claim 1, wherein the at least one coupling agent comprises at least one aminofunctional coupling agent.

4. The sizing composition of claim 1, further comprising at least one lubricant.

5. The sizing composition of claim 1, further comprising at least one polyurethane.

6. The sizing composition of claim 1, further comprising at least one blocked isocyanate.

7. The sizing composition of claim 1, further comprising at least one of maleic anhydride and acrylate.

8. A fiber glass strand comprising at least one glass fiber at least partially coated with the sizing composition of claim 1.

9. A glass fiber reinforced resin composition comprising:
   at least one polyamide resin; and
   glass fibers at least partially coated with the residue of the sizing composition of claim 1.

10. A method for producing a polyamide composite comprising:
   providing a plurality of glass fibers at least partially coated with the residue of the sizing composition of claim 1;
   incorporating the plurality of glass fibers into a polyamide resin; and
   molding the polyamide resin into a composite.

11. An aqueous sizing composition for glass fibers, comprising:
   at least one polyvinyl alcohol in an amount greater than about 50 weight percent of the sizing composition on a total solids basis, and
   at least one polyurethane; and
   at least one coupling agent.

12. The sizing composition of claim 11, wherein the at least one polyurethane is present in an amount up to about 30 weight percent of the sizing composition on a total solids basis.
13. The sizing composition of claim 11, wherein the at least one coupling agent is present in an amount greater than about 5 weight percent of the sizing composition on a total solids basis.

14. The sizing composition of claim 11, wherein the at least one polyvinyl alcohol is present in an amount greater than about 60 weight percent of the sizing composition on a total solids basis.

15. The sizing composition of claim 11, wherein the at least one coupling agent comprises at least one aminofunctional coupling agent.

16. The sizing composition of claim 11, further comprising at least one lubricant.

17. The sizing composition of claim 11, further comprising at least one blocked isocyanate.

18. The sizing composition of claim 11, further comprising at least one of maleic anhydride and acrylate.

19. A fiber glass strand comprising at least one glass fiber at least partially coated with the sizing composition of claim 11.

20. A glass fiber reinforced resin composition comprising: at least one polyamide resin; and glass fibers at least partially coated with the residue of the sizing composition of claim 11.

21. A method for producing a polyamide composite comprising:

providing a plurality of glass fibers at least partially coated with the residue of the sizing composition of claim 11; and

incorporating the plurality of glass fibers into a polyamide resin; and

molding the polyamide resin into a composite.

22. The glass fiber reinforced resin composition comprising: at least one polyamide resin, and glass fibers at least partially coated with residue of a sizing composition, the sizing composition comprising at least one polyvinyl alcohol and at least one coupling agent,

wherein the at least one polyvinyl alcohol is present in an amount greater than about 50 weight percent of the sizing composition on a total solids basis.

23. The glass fiber reinforced resin composition of claim 22, wherein the at least one polyvinyl alcohol is present in an amount greater than about 90 weight percent of the sizing composition on a total solids basis.

24. The glass fiber reinforced resin composition of claim 22, wherein the sizing composition further comprises at least one polyurethane.

25. The glass fiber reinforced resin composition of claim 24, wherein the at least one polyurethane is present in an amount up to about 30 weight percent of the sizing composition on a total solids basis.

26. The glass fiber reinforced resin composition of claim 22, wherein the sizing composition further comprises at least one blocked isocyanate.

27. The glass fiber reinforced resin composition of claim 22, wherein the sizing composition further comprises at least one of maleic anhydride and acrylate.

28. The glass fiber reinforced resin composition of claim 22, wherein the polyamide resin comprises nylon 6, nylon 6/6, nylon 4.6, nylon 6/12, nylon 12, or mixtures thereof.

29. An aqueous sizing composition for glass fibers, consisting essentially of:

at least one polyvinyl alcohol;

at least one polyurethane; and

at least one aminofunctional coupling agent, wherein the sizing composition is adapted to at least partially coat glass fibers to reinforce a thermoplastic resin.

30. A method for producing a polyamide composite comprising:

providing a plurality of glass fibers at least partially coated with the residue of a sizing composition, the sizing composition comprising polyvinyl alcohol and coupling agent, the polyvinyl alcohol being present in an amount greater than about 50 weight percent of the sizing composition on a total solids basis; and incorporating the plurality of glass fibers into a polyamide resin; and

molding the polyamide resin into a composite.

31. A aqueous sizing composition for glass fibers comprising:

at least one polyvinyl alcohol in an amount greater than about 40 weight percent of the sizing composition on a total solids basis;

at least one coupling agent in an amount greater than about 5 weight percent of the sizing composition on a total solids basis; and

at least one additional component selected from the group consisting of polyurethane, blocked isocyanate, acrylate, maleic anhydride, and combinations thereof.

32. The sizing composition of claim 31, wherein the total amount of the at least one additional component is greater than about 40 weight percent of the sizing composition on a total solids basis.

33. The sizing composition of claim 31, wherein the total amount of the at least one additional component is greater than about 50 weight percent of the sizing composition on a total solids basis.

34. The sizing composition of claim 31, wherein the at least one additional component comprises polyurethane and maleic anhydride.

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