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(54) Title: IMPROVED FIBERGLASS REINFORCED COMPOSITES

(57) **Abrégé/Abstract:**

A fiberglass reinforced composite is provided with improved physical properties. The fiberglass reinforced composite incorporates core-shell rubber nanoparticles within the resinous binder of the composite and/or within a sizing composition coated directly onto the individual glass fibers.



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IMPROVED FIBERGLASS REINFORCED COMPOSITES

[0001] The present application claims priority to U.S. provisional application nos. 61/679,196, filed on August 3, 2012 and 61/727,453, filed on November 16, 2012, which are hereby incorporated by reference in their entireties.

BACKGROUND

[0002] Conventional asphalt roofing shingles are made by applying an asphalt coating to a fiberglass web, embedding sand or other roofing granules in the asphalt coating while still soft, and then subdividing the web so formed into individual shingles once the asphalt has hardened. The fiberglass web is normally made from glass fibers bound together by a suitable resinous binder. In addition, a finely ground inorganic particulate filler is normally included in the asphalt coating to reduce cost, improve the heat distortion resistance of the shingle, and reduce asphalt UV degradation.

[0003] Commonly assigned U.S. Patent No. 7,951,240, the entire disclosure of which is incorporated herein by reference, indicates that the tear strength of roofing shingles made in this way can be affected by the type of particulate filler contained in the asphalt coating. In particular, this patent indicates that the tear strength of such roofing shingles may be compromised if hard fillers such as dolomite, silica, slate dust, high magnesium carbonate and the like are used.

[0004] It has been found that the physical properties of many types of fiberglass reinforced polymer composites may be improved by including core-shell rubber nanoparticles in a resinous binder that is applied to glass fibers before they are combined with the polymer forming the matrix or body of a composite, such as a fiberglass mat for use in making shingles.

[0005] Moreover, it has also been found that glass fibers carrying these core-shell rubber nanoparticles can be easily made by including them in the size that is applied to the fibers as they are made rather than including them in a separate polymer binder subsequently applied to the fibers in a later manufacturing process, in which the previously-sized glass fibers are used to make useful products.

SUMMARY

[0006] In some exemplary embodiments of the present invention, it has been found that the physical properties of a fiberglass reinforced composite may be improved by incorporating core-shell rubber nanoparticles within the resinous binder of the composite.

[0007] In various exemplary embodiments of the present invention, the fiberglass reinforced composite comprises an improved roofing mat for use in making asphalt roofing shingles. Some exemplary aspects of the improved roofing mat comprise a fiberglass mat composed of multiple glass fibers and a resinous binder holding the individual glass fibers together, wherein the resinous binder includes rubber core-shell nanoparticles.

[0008] Moreover, in accordance with further exemplary aspects of this invention, it has been found that glass fibers carrying these core-shell rubber nanoparticles may be made by including core-shell rubber nanoparticles in the size that is applied to the fibers as they are made rather than, or in addition to, including the nanoparticles in a separate polymer binder subsequently applied to the fibers in a later manufacturing process.

[0009] Thus, exemplary aspects of this invention provide a fiberglass reinforced polymer composite is provided comprising a matrix polymer and glass fibers dispersed in the matrix polymer, wherein the surfaces of the glass fibers carry a coating of core-shell rubber nanoparticles.

[00010] In accordance with other exemplary aspects of the present invention, glass filaments and fiber for use in making a fiberglass reinforced polymer composite is provided. The glass filaments and fibers comprise a glass filament or fiber substrate carrying a coating of an aqueous size composition, the aqueous size composition comprising a film-forming polymer, an organosilane coupling agent and core-shell rubber nanoparticles.

[00011] Further exemplary aspects of the present invention also provide a continuous process for making glass fibers comprising charging molten glass through multiple orifices in a bushing to produce molten streams of glass, allowing the molten streams of glass to solidify to form individual filaments. The individual filaments may be coated with an incipient size composition containing a lubricant, a film forming resin and an organosilane coupling agent, and combined together to form the fiber. The process may further comprise applying a coating of core-shell rubber nanoparticles to the fiber.

[00012] Some exemplary embodiments provide fiberglass reinforced polymer composite comprising a plurality of individual glass fibers fiberglass and a resinous binder, wherein

core-shell rubber nanoparticles are incorporated within the resinous binder of the composite. The individual glass fibers may form a fiberglass mat held together by the resinous binder. The resinous binder may include 0.1 to 20 wt.% rubber core-shell nanoparticles, or 0.5 to 10 wt.% wt.% rubber core-shell nanoparticles, based on the total amount of resin in the binder. The average particle size of the rubber core-shell nanoparticles may be 250 nm or less. The resinous binder may be formed from a urea formaldehyde resin, an acrylic resin or a mixture thereof.

[00013] In some exemplary embodiments, the core of the rubber core-shell nanoparticles is made from a synthetic polymer rubber selected from the group consisting of styrene/butadiene, polybutadiene, silicone rubber (siloxanes), acrylic rubbers and mixtures thereof.

[00014] In other exemplary embodiments, the composite is an asphalt roofing shingle.

[00015] In various exemplary embodiments, an improved roofing mat for use in making asphalt roofing shingles is provided. The improved roofing mat may comprise a fiberglass mat composed of multiple glass fibers and a resinous binder holding the individual glass fibers together. The resinous binder may include rubber core-shell nanoparticles. The resinous binder may include 0.1 to 20 wt.% rubber core-shell nanoparticles, based on the total amount of resin in the binder. The average particle size of the rubber core-shell nanoparticles may be 250 nm or less. The resinous binder may be formed from a urea formaldehyde resin, an acrylic resin or a mixture thereof. The core of the rubber core-shell nanoparticles may be made from a synthetic polymer rubber selected from the group consisting of styrene/butadiene, polybutadiene, silicone rubber (siloxanes), acrylic rubbers and mixtures thereof.

[00016] In yet other exemplary embodiments, an improved asphalt roofing shingle is provided comprising a fiberglass roofing mat composed of multiple glass fibers and a resinous binder holding the individual glass fibers together and an asphalt coating covering the fiberglass roofing mat. The asphalt coating may include an inorganic particulate filler. The asphalt coating may further contain roofing granules embedded therein. In some exemplary embodiments, the resinous binder of the fiberglass roofing mat includes rubber core-shell nanoparticles. The resinous binder may include 0.1 to 20 wt.% rubber core-shell nanoparticles, or from 0.5 to 10 wt.% rubber core-shell nanoparticles, based on the total amount of resin in the binder. The average particle size of the rubber core-shell nanoparticles may be 250 nm or less. The resinous binder may be formed from a urea formaldehyde resin, an acrylic resin or a mixture thereof. The core of the rubber core-shell nanoparticles may be

made from a synthetic polymer rubber selected from the group consisting of styrene/butadiene, polybutadiene, silicone rubber (siloxanes), acrylic rubbers and mixtures thereof. The asphalt coating may include 30 to 80 wt.%, based on the entire weight of the filled asphalt, of an inorganic particular filler selected from the group consisting of dolomite, silica, slate dust and high magnesium carbonate.

[00017] In various exemplary embodiments, a fiberglass reinforced polymer composite is provided comprising a matrix polymer and glass fibers dispersed in the matrix polymer. The surfaces of the glass fibers may carry a coating of core-shell rubber nanoparticles. In other exemplary embodiments, the surfaces of the glass fibers carry a coating comprising a mixture of core-shell rubber nanoparticles and a film-forming polymer. In other exemplary embodiments, the surfaces of the glass fibers carry a first coating of an incipient size composition applied to the fibers during fiber manufacture, the incipient size composition comprising core-shell rubber nanoparticles, a film-forming polymer and an organosilane coupling agent. The incipient size composition may contain a hydrocarbon wax.

[00018] In some exemplary embodiments, the glass fibers are made by combining multiple attenuated glass filaments together to form individual fibers and the incipient size composition is applied to the individual glass filaments before they are combined.

[00019] In some exemplary embodiments, a second coating of a secondary incipient size composition applied to the fibers during fiber manufacture after the individual glass filaments are combined, the secondary incipient size composition comprising additional core-shell rubber nanoparticles and a film-forming polymer.

[00020] The glass fibers may be made by combining multiple attenuated glass filaments together to form individual fibers, wherein the surfaces of the glass fibers carry a first coating of an incipient size composition applied to the individual glass filaments before they are combined, the incipient size composition comprising a film-forming polymer and an organosilane coupling agent, and further wherein the surfaces of the glass fibers carry a second coating of a secondary incipient size composition applied to the fibers during fiber manufacture after the individual glass filaments are combined, the secondary incipient size composition comprising core-shell rubber nanoparticles and a film-forming polymer.

[00021] The average particle size of the core-shell rubber nanoparticles may be 250 nm or less. The core of the rubber core-shell nanoparticles may be made from a synthetic polymer rubber selected from the group consisting of styrene/butadiene, polybutadiene, silicone rubber (siloxanes), acrylic rubbers and mixtures thereof.

[00022] In some exemplary embodiments, the core-shell rubber nanoparticles are applied to the reinforcing glass fibers in the form of a mixture of the core-shell rubber nanoparticles and a film forming resin, and further wherein the mixture includes 0.1 to 20 wt.% rubber core-shell nanoparticles, 0.5 to 10 wt.% wt.% rubber core-shell nanoparticles, based on the total amount of film forming resin in the mixture.

[00023] In some exemplary embodiments, the fiberglass reinforced polymer composite is roofing shingle.

[00024] In some exemplary embodiments, a glass filament for use in making a fiberglass reinforced polymer composite is provided. The glass filament may include a glass filament substrate carrying a coating of an incipient size composition, the incipient size composition comprising a film-forming polymer, an organosilane coupling agent and core-shell rubber nanoparticles.

[00025] In other exemplary embodiments, a glass fiber for use in making a fiberglass reinforced polymer composite is provided. The glass fiber may comprise a glass fiber substrate carrying a coating comprising a film forming polymer and core-shell rubber nanoparticles.

[00026] The glass fiber may be composed of multiple glass filaments combined together, the surfaces of the glass filaments carrying a first coating of an incipient size composition applied to the filaments before being combined, the incipient size composition comprising a film-forming polymer, an organosilane coupling agent and core-shell rubber nanoparticles.

[00027] The surfaces of the glass fiber carry a second coating of a secondary incipient size composition applied to the fiber after the filaments forming the fiber are combined, the secondary incipient size composition comprising additional core-shell rubber nanoparticles and a film-forming polymer.

[00028] In other exemplary embodiments, a glass fiber is made by combining multiple attenuated glass filaments together to form the fiber, wherein the surfaces of the glass fiber carry a first coating of an incipient size composition applied to the individual glass filaments before they are combined, the incipient size composition comprising a film-forming polymer and an organosilane coupling agent. The surfaces of the glass fiber may additionally carry a second coating of a secondary incipient size composition that is applied to the fiber after the individual glass filaments are combined, the secondary incipient size composition comprising a film-forming polymer and core-shell rubber nanoparticles.

[00029] The average particle size of the core-shell rubber nanoparticles may be 250 nm or less. Additionally, the core of the rubber core-shell nanoparticles may be made from a

synthetic polymer rubber selected from the group consisting of styrene/butadiene, polybutadiene, silicone rubber (siloxanes), acrylic rubbers and mixtures thereof.

[00030] The core-shell rubber nanoparticles may be applied to the glass filaments or fiber in the form of a mixture of the core-shell rubber nanoparticles and a film forming resin, and further wherein the mixture includes 0.1 to 20 wt.% core-shell rubber nanoparticles, based on the total amount of film forming resin in the mixture.

[00031] In yet further exemplary embodiments, a continuous process for making glass fiber is provided that includes charging molten glass through multiple orifices in a bushing to produce molten streams of glass, allowing the molten streams of glass to solidify to form individual filaments, coating the individual filaments with an incipient size composition containing a lubricant, a film forming resin and an organosilane coupling agent, and combining the individual filaments together to form the fiber. The process may further comprises applying a coating of core-shell rubber nanoparticles to the fiber.

[00032] The core-shell rubber particles may be applied to the glass fiber by including the core-shell rubber particles in the incipient size composition.

[00033] In some exemplary embodiments, the core-shell rubber particles are applied to the glass fiber by coating the glass fiber after it is formed with a secondary incipient size composition comprising core-shell rubber nanoparticles and a film-forming polymer. The incipient size may also contains core-shell rubber nanoparticles.

[00034] The average particle size of the core-shell rubber nanoparticles may be 250 nm or less and the core of the rubber core-shell nanoparticles may be made from a synthetic polymer rubber selected from the group consisting of styrene/butadiene, polybutadiene, silicone rubber (siloxanes), acrylic rubbers and mixtures thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[00035] This invention may be better understood by reference to the following drawings wherein:

[00036] Fig. 1 is a box plot of data illustrating the tensile strengths of two certain fiberglass mats;

[00037] Fig. 2 is a box plot of data illustrating the tear strengths of two certain fiberglass mats;

[00038] Fig. 3 is a box plot of data illustrating the tensile strengths of two certain asphalt roofing shingles;

[00039] Fig. 4 is a bar chart showing the effect the core-shell rubber nanoparticles of this invention have on the burst strengths of glass fiber wound high pressure composite pipes made in accordance with this invention;

[00040] Fig. 5 is a graph showing the effect these core-shell rubber nanoparticles have on the interlaminar shear strength of the glass fiber wound high pressure composite pipes of Fig. 1; and

[00041] Fig. 6 is a graph showing the effect these core-shell rubber nanoparticles have on the tension exerted on the glass fibers used to form the glass fiber wound high pressure composite pipes of Fig. 4 during their manufacture.

DETAILED DESCRIPTION

Rubber Core-Shell Particles

[00042] Rubber core-shell particles are known articles of commerce described in several patents. For example, they are described in EP 2 053 083 A1, EP 5 830 086 B2, U.S. 5,002,982, U.S. 2005/0214534, JP 11207848, U.S. 4,666,777, U.S. 7,919,549 and U.S. 2010/0273382, the disclosures of each being incorporated herein by reference in their entireties. Generally speaking, they are composed of nanoparticles having a thermoplastic or thermosetting polymer shell and a core made from a synthetic polymer rubber such as styrene/butadiene, polybutadiene, silicone rubber (siloxanes) or acrylic rubbers. Generally, they have average particle sizes of about 250 nm or less, more commonly about 200 nm or less, about 150 nm or less or even about 100 nm or less and a fairly narrow particles size distribution. They are commercially available from a number different sources including Kenaka Corporation of Pasadena, Texas.

Fiberglass Manufacture

[00043] Glass fibers are typically made by a continuous manufacturing process in which molten glass is forced through the holes of a "bushing," the streams of molten glass thereby formed are solidified into filaments, and the filaments are combined together to form a fiber or "roving" or "strand." Glass fiber manufacturing processes of this type are known and described in numerous patents. Examples include U.S. 3,951,631, U.S. 4,015,559, U.S. 4,309,202, U.S. 4,222,344, U.S. 4,448,911, U.S. 5,954,853, U.S. 5,840,370 and U.S. 5,955,518, the disclosures of each being incorporated herein by reference in their entireties. The rate at which glass fibers are typically produced by such processes is on the order of 4,000 to 15,000 feet per minute (about 1,220 to 4,572 meters per minute). It will therefore be appreciated that the time over which such glass manufacturing processes occur, that is to say the period between the time when the molten glass leaves the bushing and the time when the

fully sized and formed glass fibers or strands are packaged, stored and/or used is very short, on the order of a fraction of a second.

[00044] The glass fibers can be made from any type of glass. Examples include A-type glass fibers, C-type glass fibers, E-type glass fibers, S-type glass fibers, ECR-type glass fibers (e.g., Advantex[®] glass fibers commercially available from Owens Corning), Hiper-tex[™], wool glass fibers, and combinations thereof. In addition, synthetic resin fibers such as those made from polyester, polyamide, aramid, and mixtures thereof can be also be included in the fiberglass mats of this invention. Similarly, fibers made from one or more naturally occurring materials such cotton, jute, bamboo, ramie, bagasse, hemp, coir, linen, kenaf, sisal, flax, henequen, and combinations thereof can also be included, as can carbon fibers.

[00045] Normally, an aqueous coating or “size” is applied to glass filaments after they have solidified but before they are contacted with the rotating spindle for attenuation. Such sizes typically contain a lubricant to protect the fibers from damage by abrasion, a film-forming resin to help bond the fibers to the polymer forming the body or matrix of the composite in which the fibers will be used, and an organosilane coupling agent to improve the adhesion of the film-forming resin and matrix polymer to the surfaces of the glass fibers. Although such sizes can be applied by spraying, they are typically applied by passing the filaments over a pad or roller containing the size on its surfaces.

[00046] Sized glass fibers made in this way are used in the manufacture of a variety of different fiberglass reinforced polymer composites. In the majority of these manufacturing processes, the sized glass fibers are combined with the matrix polymer forming the body or matrix of the composite before the glass fibers are arranged in final form in the product to be made. In another approach, the sized glass fibers are first assembled into a “perform, which is then impregnated with the matrix resin forming the body of the composite. This is the approach used in the manufacture of roofing shingles, in which the glass fibers are formed into a self-supporting web (perform) and the web so made coated with asphalt, which then solidifies to form the final asphalt shingle product.

[00047] The fiberglass performs used in this approach are normally self-supporting or at least coherent in the sense that the individual sized glass fibers will not separate from one another when exposed to the stresses and forces occurring when the preform is manipulated and/or impregnated with the matrix resin. For this purpose, the sized glass fibers are normally coated with an additional film forming resin to bond the fibers together. For convenience, coating compositions used for this purpose are referred to in this document as “binder sizes.” These binder sizes will be understood to be different from the size

compositions applied to the glass filaments and fibers as part of their manufacturing process, which are referred to in this document as “incipient sizes” or “incipient size compositions.”

[00048] From the above, it should be clear that processes for making glass fibers and processes for using glass fibers are regarded in industry as separate and distinct from one another. For this reason, process steps or operations which occur during manufacture of glass fibers are typically referred to as “in-line” steps or operations. In contrast, process steps or operations which occur during the use of previously-made glass fibers, such as in the manufacture of fiberglass reinforced polymer composites, are typically referred to as “off-line” steps or operations. This terminology is used, for example, in the above-mentioned U.S. 5,840,370, as well as U.S. 8,163,664, U.S. 7,279,059, U.S. 7,169,463, U.S. 6,896,963 and especially U.S. 6,846,855. The disclosures of each of these patents being incorporated herein by reference in their entireties. This terminology is also used in this disclosure.

Fiberglass Reinforced Polymer Composites

[00049] Various aspects of this invention also relate to making any type fiberglass reinforced polymer composite. Such products are well known in industry, and are often referred to as “fiberglass reinforced plastics.” They are composed of glass reinforcing fibers and a polymer resin forming the body or “matrix” of the composite. For convenience, these polymers are sometimes referred to in this document as “matrix polymers.” Also, in the context of this case, “polymer resin” and “polymer” are used in their broadest sense as including both manmade synthetic resins as well as naturally occurring resinous materials such as asphalt and the like.

[00050] The fiberglass reinforced polymer composites of this invention can be made from any type of glass fiber. Examples include A-type glass fibers, C-type glass fibers, E-type glass fibers, S-type glass fibers, ECR-type glass fibers (*e.g.*, Advantex[®] glass fibers commercially available from Owens Corning), Hiper-tex[™], and combinations thereof.

[00051] The inventive fiberglass reinforced polymer composites can also include fibers made from materials other than glass, examples of which include synthetic resin fibers such as those made from polyester, polyamide, aramid, and mixtures thereof. Similarly, fibers made from one or more naturally occurring materials such cotton, jute, bamboo, ramie, bagasse, hemp, coir, linen, kenaf, sisal, flax, henequen, and combinations thereof can also be included, as can carbon fibers. Similarly, inventive fiberglass reinforced polymer composites can also include non-fibrous fillers, examples of which include calcium carbonate, silica sand and wollastonite.. Preferably, the fiberglass reinforced polymer composites of this invention contain a combined total of no more than about 5 wt.% of non-glass fibers and fillers, based

on the weight of all the fibers and fillers in the composite. More preferably, all or essentially all of the fibers in the fiberglass composites of this invention are glass fibers.

[00052] Similarly, the fiberglass reinforced polymer composites of this invention can be made from any resinous binder which has previously been used or may be used in the future as the matrix polymer for making the body or matrix of fiberglass reinforced plastic composites. Examples include polyolefins, polyesters, polyamides, polyacrylamides, polyimides, polyethers, polyvinylethers, polystyrenes, polyoxides, polycarbonates, polysiloxanes, polysulfones, polyanhydrides, polyimines, epoxies, acrylics, polyvinylesters, polyurethane, maleic resins, urea resins, melamine resins, phenol resins, furan resins, polymer blends, alloys and mixtures thereof. Epoxy resins are especially preferred.

[00053] The amount of resinous binder that should be included in the fiberglass reinforced polymer composites of this invention can vary widely and any conventional amount can be used. In some exemplary embodiments, in the case of fiberglass mats, the amount of resinous binder will be about 10 to 30 wt.%, more typically about 14 to 25 wt.% or even about 16 to 22 wt.%, based on the weight of the fiberglass mat as a whole.

[00054] Fiberglass reinforced polymer composites can be made by a variety of different manufacturing techniques including simple coating and laminating processes, but are most commonly made by molding. Two different types of molding processes are commonly used, wet molding processes and composite molding processes. In wet molding processes, the glass reinforcing fibers and the matrix polymer are combined in the mold immediately prior to molding. For instance, fiberglass mats produced in accordance with this invention may be made by a wet laid molding process in which wet chopped glass fibers, after being deposited onto a moving screen from an aqueous slurry, are coated with an aqueous dispersion of a resin binder which is then dried and cured. The formed non-woven web is an assembly of randomly dispersed, individual glass filaments bound together at their interstices by the resinous binder.

[00055] As stated above, the fiberglass mats of this invention include a resinous binder for holding the fibers together. For this purpose, any resinous binder which has previously been used or may be used in the future for making fiberglass mats used in the manufacture of asphalt roofing shingles can be used as the resinous binder of this invention. Examples include urea formaldehyde resins, acrylic resins, polyurethane resins, epoxy resins, polyester resins and so forth. Urea formaldehyde resins and acrylic resins are preferred, while mixtures of urea formaldehyde resins and acrylic resins are even more preferred. In such mixtures, the amount of acrylic resin is desirably about 2 to 30 wt.%, more desirably about 5 to 25 wt.% or

even about 10 to 20 wt.% of the combined amounts of urea formaldehyde resin and acrylic resin in the binder, on a dry solids basis.

[00056] The amount of resinous binder that should be included in the fiberglass mats of this invention can vary widely and any conventional amount can be used. Normally, the amount of resinous binder will be about 10 to 30 wt.%, more typically about 14 to 25 wt.% or even about 16 to 22 wt.%, based on the weight of the fiberglass mat as a whole.

[00057] The physical structure of the fiberglass mat of this invention is not critical and any physical structure which has previously been used, or may be used in the future for making fiberglass mats for asphalt roofing shingles, can be used for making the fiberglass mat of this invention. For example, nonwoven webs of glass fibers as well as woven and nonwoven fiberglass fabrics or scrim can be used for making the fiberglass mats of this invention.

[00058] Most commonly, however, the fiberglass mat of this invention will be made by a wet laid process in which wet chopped glass fibers, after being deposited onto a moving screen from an aqueous slurry, are coated with an aqueous dispersion of a resin binder which is then dried and cured. The formed non-woven web is an assembly of randomly dispersed, individual glass filaments bound together at their interstices by the resinous binder.

Roofing Shingle

[00059] In some exemplary embodiments, an inventive asphalt roofing shingle is made from the inventive fiberglass web, as described above, using conventional production methods, *i.e.*, by applying a molten asphalt coating composition to the inventive fiberglass web, embedding sand or other roofing granules in this asphalt coating while still soft, and then subdividing the web so formed into individual roofing shingles once the coating asphalt has hardened. Any production method may be used that has been used, or used in the future, may be suitable in producing the inventive fiberglass mat and shingles. Any fiberglass mat that has previously been used, or may be used in the future, for making asphalt roofing shingles can be suitable for use in making the inventive fiberglass mats and shingles.

[00060] For this purpose, any asphalt coating composition which has previously been used or may be used in the future for making asphalt roofing shingles may be suitable for use as the asphalt coating in this invention. As described in the above-noted U.S. 7,951,240, such asphalt coating compositions include a substantial amount of inorganic particulate filler. In addition, they can be made from a variety of different types and grades of asphalt and can also include various different optional ingredients such as polymeric modifiers, waxes and the like. Any of the different grades of asphalt described there, as well as any of the different

inorganic particulate fillers and optional ingredients described there, may be suitable for making the roofing shingles of this invention.

[00061] In addition to these ingredients, the asphalt coating composition used in this invention also includes an inorganic particulate filler. For this purpose, any inorganic particulate filler which is or becomes known for use in making asphalt roofing shingles can be used. For example, calcite (crushed limestone), dolomite, silica, slate dust, high magnesium carbonate, rock dust other than crushed limestone, and the like can be used. Concentrations on the order of 30 to 80 wt.%, based on the entire weight of the asphalt coating, can be used although concentrations of about 40 to 70 wt.% or even of about 50 to 70 wt.% are more typical.

[00062] As indicated above, some of these inorganic particulate fillers are known to adversely affect the tear strength of asphalt roofing shingles made with these materials. In particular, inorganic fillers which exhibit a high degree of hardness (*i.e.*, a hardness greater than about 3 Moh) such as dolomite, silica, slate dust, high magnesium carbonate, etc., are known to produce asphalt shingles having lower tear strengths than otherwise identical shingles made from softer inorganic filler such as calcite (crushed limestone) and the like. Therefore, it is common practice in this industry to use calcite or other soft inorganic particulate as the asphalt filler, at least when asphalt shingles of superior tear strengths are desired. Tear strength is an important property because it reflects the ability of an installed shingle to resist being destroyed or otherwise torn off a roof substrate by a strong wind. The same cannot be said for tensile strength, as tear strength and tensile strength do not normally correlate with one another, at least in asphalt roofing shingles and the fiberglass mats from which they are made. Indeed, tear strength and tensile strength can even be inversely proportional in some of these products.

Core-Shell Fiberglass Mats

[00063] In accordance with various aspects of this invention, it has been found that the poor tear strength problem of traditional asphalt roofing shingles can be overcome or otherwise obviated by incorporating core-shell rubber particles into the resin binder used to make the fiberglass mat from which the inventive asphalt roofing shingle is made. Therefore, in accordance with various aspects of this invention, asphalt roofing shingles exhibiting superior tear strengths can be produced even though hard inorganic fillers such as dolomite, silica, slate dust, high magnesium carbonate, and the like are included in their asphalt coating compositions.

[00064] Once the asphalt coating composition of this invention is applied to the inventive fiberglass mat, a conventional roofing granule such as sand or the like is applied to and embedded in this asphalt coating while still soft, such as in a conventional manner. The asphalt coating is then allowed to harden, and the hardened web so formed is then subdivided into individual roofing shingles.

[00065] It has already been proposed to use latexes of these rubber core-shell nanoparticles as binders for fiberglass mats. *See*, for example, the above-noted EP 2 053 083 A1, EP 5 830 086 B2 and U.S. 2005/0214534. In such use, however, the fiberglass binder is composed entirely of these rubber core-shell nanoparticles. In contrast, in some exemplary aspects of this invention, these rubber core-shell nanoparticles may be incorporated in small but suitable amounts as additives for improving the properties of a polymer resin which forms the body of the resin binder. According to some aspects of the present invention, the amount of these rubber core-shell nanoparticles included in the resin binder of the fiberglass mat is about 0.1 to 20 wt.%, more typically about 0.5 to 10 wt.% or even about 1 to 4 wt.%, based on the total amount of the other polymer resins in the binder, *i.e.*, excluding the weight of the rubber core-shell nanoparticles themselves.

[00066] It is also already known that the tensile strength of a solid polymer mass (as reflected by its fracture toughness, peel strength and lap shear strength) can be enhanced by including these rubber core-shell nanoparticles in the mass as fillers. However, as indicated above, tear strength and tensile strength do not correlate with one another in the field of asphalt roofing shingles. This is shown in Figs. 1 and 2, which are box plots showing the tensile strengths and tear strengths of fiberglass mats made with different conventional binders. *See, also*, Fig. 3, which is a similar box plot showing the tear strength of asphalt roofing shingles made with these different fiberglass mats. As shown in Fig. 1, the tensile strength of the mat made with binder A was better than the tensile strength of the mat made with binder B. In contrast, both the tear strength of the mat made with binder A (Fig. 2) and the tear strength of the asphalt roofing shingle made with binder A (Fig. 3), were worse than the tear strengths of the mat and shingle made with binder B. This shows that there is no direct correlation between tear strength and tensile strength in asphalt roofing shingles and their associated fiberglass mats. This, in turn, demonstrates that the improved tear strengths of the inventive mats and shingles is a different phenomenon from the improved tensile strengths shown in the prior art.

[00067] The shell of the rubber core-shell nanoparticles used in this invention can be formed from essentially any thermoplastic or thermosetting polymer so long as it is compatible with

the polymer used to form the resinous binder of the fiberglass mat used in this invention. And by “compatible” is meant that the polymer forming the shell does not adversely react with the resinous binder, either by adversely affecting its physical or chemical stability or generating obnoxious or unwanted by product.

Additional Fiberglass Reinforced Composites

[00068] In accordance with other exemplary embodiments, fiberglass reinforced composites are formed by composite molding, wherein the glass reinforcing fibers and the matrix polymer are combined into a “prepreg” before being charged into the mold. Such prepregs can take the form of self-supporting objects in which the glass fibers are randomly oriented, such as the fiberglass sheets or “veils” used to form asphalt shingles. In addition, they can also take the form of self-supporting objects in which the glass fibers are oriented in predetermined directions, such as the three dimensional “skeletons” used to form load bearing products of complex shape such as rocker arms for automobile suspensions. Such prepregs can also take the form of pellets, pastilles or agglomerates composed of the matrix polymer containing randomly distributed chopped glass fiber.

[00069] Specific examples of molding processes that can be used to make the fiberglass reinforced polymer composites of this invention include injection molding, bladder molding, compression molding, vacuum bag molding, mandrel wrapping, wet layup, chopper gun application, filament winding, extrusion molding, pultrusion, resin transfer molding and vacuum assisted resin transfer molding.

[00070] In accordance with some exemplary embodiments, the fiberglass reinforced polymer composite includes pressure-bearing vessels such as pipes (tubes) and tanks formed by filament winding or mandrel wrapping, especially products of this type in which the matrix polymer is an epoxy resin. Such products are well-known and described, for example, in U.S. 5,840,370 and U.S. 7,169,463, mentioned above. As described in these patents, such pressure bearing vessels are normally made by winding a continuous glass fiber which has been impregnated with some or all of the matrix polymer needed to form the vessel around a rotating steel mandrel in specific orientations. Any additional matrix polymer is then added, and the matrix polymer is then cured and the mandrel withdrawn, thereby producing the product vessel. Alternatively, such products can be made by wrapping a preformed sheet or veil of glass fibers, preimpregnated with some or all of the matrix polymer needed to form the vessel, around a stationary steel mandrel followed by adding additional matrix polymer if needed, curing the matrix polymer and withdrawing the mandrel. As further described in these patents, the glass fibers used to form such products are normally sized during fiber

manufacture with a binder size containing a lubricant, a film forming resin, and a coupling agent which is normally an organosilane.

[00071] In accordance with some exemplary aspects of this invention, core-shell rubber nanoparticles may be incorporated into the incipient size that is applied to the glass fibers as they are made. It has been discovered that incorporating these nanoparticles onto the fibers in this way is not only very convenient from a manufacturing standpoint but also effective in producing glass fibers with improved reinforcing properties when used in a variety of different fiberglass reinforced polymer composite applications.

[00072] Generally speaking, it is desirable in accordance with this invention for the average particle size of the core-shell rubber particles used in this invention to be 100 times smaller (*i.e.*, less than 1%) of the average diameter of the glass reinforcing fibers to which they are applied. Average particle sizes of 150 times smaller (*i.e.*, less than 0.67%) or even 200 times smaller (*i.e.*, less than 0.5%) of the glass reinforcing fibers are interesting as well.

[00073] As explained above, it is known that the tensile strength of a solid polymer mass (as reflected by its fracture toughness, peel strength and lap shear strength) can be enhanced by including these core-shell rubber nanoparticles in the mass as fillers. *See*, "Structure-Property Relationship In Core-Shell Rubber Toughened Epoxy Nanocomposites," A Dissertation by Ki Tak Gam Submitted to the Office of Graduate Studies of Texas A&M University in partial fulfillment of the requirements for the degree of Doctor Of Philosophy December 2003. However, as detailed above, the tear strength of an asphalt roofing shingle and its tensile strength do not correlate with one another. This demonstrates that the improved tear strengths of the asphalt roofing shingles made in accordance with this invention is a different phenomenon from the improved tensile strengths shown in the prior art.

[00074] In this regard, it should be appreciated that the tensile strength of a solid polymer mass is understood to be a function of its cohesive strength, *i.e.*, the ability of the mass to hold itself together when under a tensile load. In contrast, the tear strength of an asphalt roofing shingle is understood to be a function of an entirely different phenomenon, *i.e.*, the ability of the binder size composition coating the glass fiber veil of the shingle to promote adhesion between the veil and the subsequently applied asphalt coating (matrix polymer). Furthermore, when core-shell rubber particles are used to improve the tensile strength of a solid polymer mass, enough of these nanoparticles are used to fill the entire polymer mass. In contrast, a much smaller amount of core-shell rubber nanoparticles is used in this invention, since these nanoparticles are present only on the surfaces of the glass fibers themselves and

are not distributed in the mass of matrix polymer forming the body of the inventive fiberglass reinforced polymer composites.

[00075] In accordance with this invention, the core-shell rubber nanoparticles of this invention can be applied to the glass reinforcing fibers anytime prior to the application of the matrix polymer forming the body of the inventive fiberglass reinforced polymer composites. So, for example, the core-shell rubber nanoparticles can be applied to the glass reinforcing fibers in a binder size after they are made and stored, in a separate application step as part of the manufacturing process for producing the fiberglass reinforced polymer composites of this invention.

[00076] Alternatively, they can be applied to the glass fibers “in-line” during fiberglass manufacture as part of the glass fiber manufacturing process itself. Normally, this will be done by including these core-shell rubber nanoparticles in the incipient size composition applied to the individual glass filaments used to form the glass fiber, before these filaments are combined together to form the fiber. Alternatively, these core-shell rubber nanoparticles can be applied to the glass fibers after they are formed in a separate aqueous size composition. For convenience, these separate size compositions are referred to in this document as “secondary incipient sizes.” In a third approach, both of these procedures can be used, some the core-shell rubber particles being applied to the individual filaments in the incipient size before the glass fibers are formed and the remainder being applied in a secondary incipient size after the fibers are formed.

[00077] Regardless of which of these approaches is used, in-line application enables these core-shell rubber particles to be conveniently applied during glass fiber manufacture, which in turn eliminates the need for a separate “off-line” process step during subsequent manufacture of the inventive fiberglass reinforced polymer composites. In addition, in-line application of the core-shell rubber nanoparticles can reduce the amount of film-forming polymer that is ultimately applied to the glass fibers, at least when the nanoparticles are included in the incipient size composition used during fiber manufacture. This is because, to promote adhesion of the core-shell rubber nanoparticles to the glass fibers, the nanoparticles should be applied together with a film-forming polymer. Therefore, combining these nanoparticles with the incipient glass size eliminates the need for a second, subsequent film-forming resin coating.

[00078] As indicated above, the core-shell rubber nanoparticles of this invention may be applied to glass fiber or filament substrates together with a suitable film forming resin. For

this purpose, any film forming resin which has previously been used or may be used in the future as a film forming resin in a glass fiber and/or filament size may be suitable for use.

[00079] As appreciated in the art, it is conventional practice when selecting the film forming resin to be used in an incipient size or a binder size to select a resin which is compatible with the matrix resin that will be used to make the fiberglass composite ultimately being produced. For example, if a particular fiberglass composite is to be made with an epoxy resin matrix, then a compatible epoxy resin will normally be selected as the film forming resin for the glass fiber size. This same customary practice is followed in accordance with this invention, *i.e.*, the film forming resin used in the size containing the core-shell rubber nanoparticles of this invention is desirably selected to be compatible with the matrix resin of the fiberglass reinforced polymer composite being produced

[00080] As further indicated above, this invention finds particular use in making fiberglass reinforced polymer composites from epoxy resins, because of the superior physical properties (*e.g.*, tensile strength) and chemical resistance of these polymers. For this purpose, in some exemplary embodiments, it is desirable to select as the film forming resin in the size containing the core-shell rubber particles, a linear bisphenol A type epoxy resin of moderate molecular weight. In this context, "moderate molecular weight" means a weight average molecular weight of about 10,000 to 250,000. Weight average molecular weights of 15,000 to 100,000 or even 20,000 to 50,000 are preferred. Linear bisphenol A type epoxies are desirable because many fiberglass reinforced polymer composites, and especially those requiring high strength and good chemical resistance, are made from linear bisphenol A type epoxy matrix resins. These molecular weights are desirable, because the epoxy resin will not effectively form a film if its molecular weight is too high and will undergo unwanted crystallization in the coating equipment if its molecular weight is too low.

[00081] In addition to linear bisphenol A type epoxies, modified epoxy resins can also be used. For example, epoxy novolacs can also be used.

[00082] Specific examples of commercially available epoxy resins which are useful as the film forming resin to be used together with the core-shell rubber nanoparticles of this invention are AD-502 epoxy aqueous emulsion from AOC, Neoxil 962/D aqueous emulsion from DSM, EpiRez 5003 from Momentive, EpiRez 3511 epoxy emulsion from Momentive. Blends also are effective, especially AD-502 + EpiRez 5003 in a 95:5 ratio.

[00083] The amount of film forming resin that can be present in the aqueous size containing the core-shell rubber nanoparticles of this invention can vary widely, and essentially any amount can be used that will provide an effective coating composition. Typically, the

amount of film forming resin will be about 60 to 90 wt.% of the aqueous size on a dry solids basis (*i.e.*, excluding water). Concentrations on the order of about 65 to 85 wt.%, or even 73 to 77 wt.%, on a dry weight basis are preferred.

Sizes with Combination Particles

[00084] As indicated above, the aqueous size containing the core-shell rubber nanoparticles of this invention may also contain a film forming resin. While each of these ingredients can be separately supplied to and contained in this aqueous size composition, in a particularly interesting embodiment of this invention these ingredients are combined together in the emulsified particles contained in this aqueous size composition.

[00085] Core-shell rubber nanoparticles are commercially available in a variety of different forms. One such form is an organic emulsion of the rubber nanoparticles dispersed in neat (*i.e.*, solvent free) liquid epoxy resin. Examples of these products include the Kane AceTM MX line of CSR Liquid Epoxy Emulsions available from Kaneka Belgium NV. These liquid epoxy/rubber nanoparticle emulsions comprise stable dispersions of about 25 to 40 wt.% CSR (core shell rubber nanoparticles) in various different kinds of liquid epoxy resin system including bisphenol-A type liquid epoxy resins, bisphenol-F type liquid epoxy resins, epoxidized phenol novolac type liquid epoxy resins, triglycidyl p-aminophenol type liquid epoxy resins, tetraglycidyl methylene dianiline type liquid epoxy resins, and cycloaliphatic type liquid epoxy resins. They are well known articles of commerce which have been previously used for toughening epoxy and other matrix resins, including matrix resins used for forming fiberglass reinforced polymer composites such as filament wound pipes and the like.

[00086] In this regard, it should be remembered that a significant difference between this invention and prior technology for making fiberglass reinforced composites containing core shell rubber nanoparticles is that, in this invention, the core shell rubber nanoparticles are coated onto the glass reinforcing fibers of the composite before these fibers are combined with the matrix resin forming the body of the composite. This is completely different from earlier technology in which the core shell rubber nanoparticles are dispersed throughout the entire mass of matrix resin. Thus, a difference between this invention and prior technology in connection with using these commercially available liquid epoxy core shell rubber nanoparticle emulsions is that, in this invention, these emulsions are used to form the incipient size that is coated onto the glass fibers before these fibers are combined with the matrix resin. In contrast, in earlier technology, these emulsions are used to form the matrix resin itself.

[00087] These commercially available liquid epoxy/rubber nanoparticle emulsions represent a convenient source of the core-shell rubber nanoparticles of this invention, because they already contain two major ingredients of the incipient sizes of this invention, *i.e.*, the core shell rubber particles and the epoxy resin film former.

[00088] According to some exemplary embodiments, before these commercially available liquid epoxy/rubber nanoparticle emulsion can be used to make the incipient sizes of this invention, they are converted into aqueous emulsions. This can easily be done by using conventional high shear emulsification techniques. For example, a rubber nanoparticle aqueous size composition in which the weight ratio of rubber nanoparticles to epoxy resin is 25/75 can be made by emulsifying an organic emulsion containing 25 wt.% rubber nanoparticles and 75 wt.% liquid epoxy resin using conventional high shear mixing techniques and conventional epoxy-suitable surfactants such as ethylene oxide/propylene oxide block copolymers.

[00089] The amount of core-shell rubber particles that will be applied to a glass fiber or filament substrate in accordance with this invention will typically represent about 0.01 to 25 wt.% of the solids content of the aqueous size compositions in which they are contained. More commonly, the amount of core-shell rubber particles will be about 0.1 to 5 wt.%, about 0.3 to 2 wt.%, about 0.5 to 1.5 wt.%, or even about 0.7 to 1.3 wt.% of these solids. Accordingly, the rubber nanoparticle aqueous size compositions of this invention will typically be made by combining at least two different aqueous resin dispersions, one whose emulsified resin particles contain a combination of film forming resin and core-shell rubber nanoparticles, the other whose emulsified resin particles contain only the film forming resin.

Additional Ingredients

[00090] In addition to the film forming resin, the aqueous size composition containing the core-shell rubber nanoparticles of this invention can also contain various additional optional ingredients.

[00091] For example, these aqueous size compositions may contains about 5 to 30 wt.%, more commonly about 8 to 20 wt.% or even about 10 to 15 wt.% of an organosilane coupling agent based on the solids content. For this purpose, any organosilane coupling agent that has previously been used or may be used in the future for enhancing the bonding strength of a film forming binder resin to a glass fiber substrate can be used in this invention. In addition, as in the case of the binder resin, the organosilane coupling agent should be selected to be compatible with the particular film forming binder resin being used.

[00092] Specific examples of useful organosilane coupling agents are Silquest A-1524 ureidosilane, Silquest A-1100 aminosilane, Silquest A-1387 silylated polyazimide in methanol, Y-19139 silylated polyazimide in ethanol from Momentive, Silquest A-174 methacryloxysilane, Silquest A-187 epoxy silane, Silquest A-1170 trimethoxy bis-silane, Silquest A-11699 triethoxy bis-silane, all from Momentive and Silquest A1120. Silquest A-1524 as well as blends of Silquest A-1387 and Silquest A-1100 are preferred for use with epoxy resin film forming resins.

[00093] Another ingredient that can be included in the rubber nanoparticle-containing aqueous size compositions used in this invention is a lubricant. Examples of commercially available lubricants that are suitable for this purpose include Katex 6760 (also known as Emery 6760) cationic lubricant, PEG400 monooleate (PEG400 MO, Emerest 2646), PEG-200 monolaurate (Emerest 2620), PEG400 monostearate (Emerest 2640), PEG600 monostearate (Emerest 2662). Cationic lubricants such as Katex 6760 are typically used in amounts from 0.001 to 2 wt.%, more typically 0.2 to 1 wt.%, or even about 0.5 wt.%, of size solids. Meanwhile, PEG lubricants are typically used in amounts of 0.1 to 22 wt.%, more typically about 1 to 10 wt.%, or even about 7 wt.% of solids content.

[00094] Yet another conventional lubricant that can be included in the rubber nanoparticle-containing aqueous size compositions used in this invention is a wax. Any wax which has been or may be used as a lubricant wax in a glass fiber aqueous sizing composition can be used as the wax in the rubber nanoparticle aqueous size compositions of this invention. Michelman Michemlube 280 wax is a good example. Concentrations on the order of about 0.1 to 10 wt% of size solids are useable, while concentrations of about 2 to 6 wt% or even 4 to 5 wt% are preferred.

[00095] Still other conventional ingredients that can be included in the rubber nanoparticle-containing aqueous size compositions of this invention include acetic, citric or other organic acid in an amount sufficient to efficiently hydrolyze the silanes that are present, which typically requires a pH of about 4-6 in the case of Silquest A-1100. Final size pH will typically be in the 5 – 6.5 range.

[00096] Other additives such as Coatosil MP 200 multifunctional epoxy oligomer, aqueous urethane polymers such as Michelman U6-01 or Baybond PU-403 from Bayer, Witco W-296 or W-298 from Chemtura or and the like can also be included in the rubber nanoparticle-containing aqueous size compositions of this invention for their known functions in conventional amounts.

Water Content and Loadings

[00097] The rubber nanoparticle-containing aqueous size compositions of this invention are applied to their glass fiber and/or filament substrates in a conventional way using conventional coating equipment. Therefore, they are formulated with sufficient amounts of water so that their rheological properties are essentially the same or at least comparable to that of conventional aqueous sizes. Accordingly, these aqueous size compositions will typically contain a total solids content of about 2 to 10 wt.%, more commonly 4 to 8 wt.% or even 5 to 7 wt.%, based on the total weight of the aqueous size composition.

[00098] In addition, these nanoparticle-containing aqueous size compositions are also applied to their glass fiber and/or filament substrates in conventional amounts. For example, these size compositions will normally be applied in amounts such that the LOI (loss on ignition) of the sized glass fibers and filaments obtained is about 0.2 to 1.5 %, more typically 0.4 to 1.0 % or even 0.5 to 0.8%. Inasmuch as the concentration of core-shell rubber nanoparticles in these sizes will typically be on the order of about 0.3 to 2 wt.%, about 0.5 to 1.5 wt.%, or even about 0.7 to 1.3 wt.% on a dry solids basis, this means that the amount of these core-shell rubber nanoparticles that will be applied to their glass fiber and/or filament substrates in terms of LOI will normally be about 0.001 to 0.015%, more typically about 0.002 to 0.010% or even about 0.0025 to 0.0080%.

WORKING EXAMPLES

[00099] In order to more thoroughly describe this invention, the following working examples are provided.

Example 1 and Comparative Example A

[000100] Two fiberglass mats were made by a conventional wet laid coating process in which wet chopped glass fibers, after being deposited onto a moving screen from an aqueous slurry, were coated with an aqueous dispersion of a resin binder and then dried and cured. The resin binders applied to both webs were each prepared using a commercially-available acrylic latex (Rhoplex GL 720 available from Dow Chemical) and a commercially-available urea formaldehyde resin latex (FG 654A available from Momentive). The amounts resins applied were selected so that the weight ratio of acrylic resin to urea formaldehyde resin in both binders was the same on a dry solids basis (15/85) and further so that the total amount of binder applied to each web was essentially the same. The resin binder of Example 1 also included 1.7 wt.%, based on the combined weights of urea formaldehyde and acrylic resins in the binder, of a commercially-available rubber core-shell nanoparticles, in particular Kane Ace MX-113 rubber core-shell nanoparticles available from Kenaka Corporation of Pasadena, Texas.

[000101]The fiberglass mats so obtained were then tested for tensile strength and tear strength in the cross or transverse direction. Because fiberglass mats and their associated asphalt roofing shingles are generally weaker in their transverse direction than in their machine direction, tensile and tear strengths in the transverse direction give a better indication of the overall strength of the product.

[000102]In addition to these tests, the tear strengths of these fiberglass mats in the transverse direction was also determined by a rock dusted mat performance test. In this test, each mat was first dusted with the same amount of a powdered rock and then measured for tear strength in the transverse direction. This test was used, because it provides a good simulation of the adverse effect on fiberglass mat properties that can be caused by the inorganic particulate fillers contained in a subsequently applied asphalt coating. This rock dust mat performance test was carried out three times for each sample, with the average values obtained for each test being reported below.

[000103]The results obtained are set forth in the following Table 1:

TABLE 1

Tensile and Tear Strengths of Fiberglass Mats of Example 1 and Comparative Example A

	BW	LOI	Transverse Tensile	Transverse Tear (no rock dust)	Transverse Tear (rock dusted)	Tear Retention(%): (RD tear/tear no RD)
Comp Ex A	1.82	19.1	73	466	306	66
Ex 1	1.81	18.8	71	633	488	77

[000104]In the above table, "BW" refers to basis weight, which is the weight of cured mat (fiberglass plus cured binder) pounds per 100 square feet. Meanwhile, "LOI" refers to loss on ignition, which is a standard measure in this industry indicating the portion of the aqueous binder originally applied to the web, in percent, which remains on the web after the binder has dried and cured. The total amount of binder applied to the web after drying and curing, *i.e.*, on a dry solids basis, can be determined by multiplying BW by LOI.

[000105]As can be seen from Table 1, the presence of rubber core-shell nanoparticles in the binder of Example 1 caused essentially no effect on the tensile strength of the fiberglass mat made from this binder (the difference in Table 1 is within the experiment error), but the tear strength of this mat to increase, in the transverse direction relative to the control fiberglass mat of Comparative Example A. In addition, Table 1 also shows that, while rock dusting caused a significant decrease in the tear strength of both mats, this decrease was more

pronounced in the case of Comparative Example A. Specifically, Table 1 shows that the presence of these rubber core-shell nanoparticles enabled the mat of Example 1 to retain 77% of its original tear strength, whereas the mat of Comparative Example A retained only 66% of its original tear strength, when both mats were rock dusted.

[000106] This data shows that the addition of these rubber core-shell nanoparticles improves the tear strength of fiberglass mats in the transverse direction, not only in an “as-made” (uncoated) condition but also in a simulated use condition.

Example 2 and Comparative Example B

[000107] Eight additional mats were prepared, four representing this invention and four being controls in which no rubber core-shell nanoparticles were used. These mats were made using the same procedures and ingredients as used in Example 1, except that the amount rubber core-shell nanoparticles included in the binders representing this invention was 1.85 wt.%.

[000108] Each fiberglass mat obtained was then formed into an asphalt roofing shingle by coating the mat with an asphalt coating composition made from of a coating asphalt, the asphalt coating composition also containing 65 wt.% based on the asphalt coating composition as a whole of a calcite inorganic particulate filler.

[000109] The tensile strength of each roofing shingle in the machine direction was measured, as was the tear strength of each roofing shingle in both the machine and transverse directions. In addition, the total tear strength of each roofing shingle was determined by adding the machine and transverse tear strengths together. Finally, these measured tear and tensile strengths were normalized by shingle weight.

[000110] The results obtained are set forth in the following Table 2.

TABLE 2

Tensile and Tear Strengths of Roofing Shingles of Example 2 and Comparative Example B

	Machine MD Tensile	Transverse Tear	Total Tear
Comp Ex B	192	1870	3317
Ex 2	185	2037	3615
% of Change	-3.65	8.93	8.98

[000111] Table 2 shows that adding rubber core-shell nanoparticles to the binder of a fiberglass mat used to make an asphalt roofing shingle imparts essentially the same effect on the shingle as it imparts on the mat. In particular Table 2 shows that, like the fiberglass mats

of Example 1, asphalt shingles made with these nanoparticles exhibit significantly greater tear strengths in the transverse direction than control shingles made without these nanoparticles. In addition, Table 2 further shows that these nanoparticles also cause a slight decrease in the tensile strength of these shingles, in this case in the machine direction rather than in the transverse direction as reported in Example 1 above.

Example 3

[000112] In the following examples, filament wound high pressure composite pipes were made by winding around a mandrel glass fibers having previously been impregnated with a commercially available aqueous epoxy matrix resin dispersion. The winding so formed was then heated to cure the epoxy matrix resin and the mandrel then withdrawn to produce the final product pipe.

[000113] The glass fibers used to make each composite were made by a conventional glass fiber manufacturing process as described above in which the attenuated glass filaments, prior to being combined into fiber, were coated with an incipient size. Three different experiments were done. In the first experiment representing the prior art, the incipient size contained no core-shell rubber nanoparticles. In the remaining two experiments, the incipient size contained 0.5 wt.% core-shell rubber nanoparticles and 1 wt.% core-shell rubber nanoparticles, respectively.

[000114] The amount of incipient size applied to each glass fiber is set forth in the following Table 3, while the specific composition of each incipient size is set forth in the following Table 4.

TABLE 3
Size Loadings

Example	% Rubber Particles in Size	LOI, %	Yardage, Yards/pound	Tex, g/kg
Control	0	0.55	243.98	2033.20
4	0.5	0.57	251.74	1970.51
5	1.0	0.63	251.69	1970.94

TABLE 4
Chemical Composition of Incipient Sizes

Ingredient		Concentration, wt.% solids		
Identity	Function	Control	Example 1	Example 2
Citric Acid	pH control	0.53	0.53	0.53

Uredosilane	Coupling agent	13.02	13.03	13.04
Aqueous Epoxy Resin Emulsion		77.46	76.42	73.42
Aqueous Nanoparticle Emulsion*		0	2.01	4.00
PEG 400	Lubricant	3.89	3.92	3.92
Wax	Lubricant	4.69	4.70	4.70
Cationic Lubricant	Lubricant	0.39	0.39	0.39

* Aqueous emulsion of Kaneka's Kane Ace™ MX-125 epoxy emulsion containing 75 wt.% epoxy resin and 25 wt.% core shell rubber nanoparticles

[000115]The filament wound composite pipes so obtained were subjected to two different analytical tests. In the first, the burst strength of the product pipes obtained was determined. In the second, the interlaminar shear strength (ILSS) of the product pipes when exposed to boiling water for 500 hours was determined in accordance with the NOL Ring Test Method, Accession No. AD0449719, Naval Ordinance Laboratory, White Oak, Maryland. In addition to these analytical tests, during manufacture of each pipe, the tension generated on the glass fibers used to make the pipes during the winding operation was determined and recorded. The results obtained are set forth in Figs. 3-6.

[000116]As shown in Fig. 3, the burst strengths of the inventive product pipes were about 8-11% greater than the burst strength of the control pipe. This shows that the core-shell rubber nanoparticles of this invention provide a substantial improvement in the mechanical properties of glass fiber reinforced polymer composites made in accordance with this invention.

[000117]Meanwhile, Fig. 4 shows that the core-shell rubber nanoparticles of this invention imparted essentially no adverse effect on the interlaminar strength of the inventive product pipes after 500 hours of exposure to boiling water. This suggests that the core-shell rubber nanoparticles of this invention do not adversely affect the chemical resistance of the inventive glass fiber reinforced polymer composites in any significant way.

[000118]Finally, Fig. 5 shows that tension generated on the glass fibers during the winding operation used to form the inventive filament wound composite pipes was essentially unaffected by the core-shell rubber nanoparticles of this invention. This shows that the core-shell rubber nanoparticles of this invention do not adversely affect the manufacturing process

used to produce the inventive glass fiber reinforced polymer composites in any significant way.

[000119] Although only a few embodiments of this invention have been described above, it should be appreciated that many modifications can be made without departing from the spirit and scope of this invention. For example, it is possible and even desirable in some instances to combine the core-shell rubber nanoparticle technology of this invention with other technologies for making fiberglass reinforced polymer composites.

[000120] For example, the above-mentioned commonly assigned U.S. 5,840,370 describes a process for making a glass/polymer prepreg in which application of some or all of the matrix polymer forming the ultimate fiberglass reinforced polymer composite is applied “in-line” as part of the glass manufacturing process. That technology can be combined with the technology of this invention by applying the core-shell rubber nanoparticles of this invention first, followed by impregnating the coated glass fibers so formed with the matrix polymer of the polymer composite second.

[000121] All such modifications are intended to be included within the scope of this invention and the related general inventive concepts, which are to be limited only by the following claims.

Claims:

1. A fiberglass reinforced polymer composite comprising a plurality of individual glass fibers fiberglass and a resinous binder, wherein core-shell rubber nanoparticles are incorporated within the resinous binder of the composite.
2. The fiberglass reinforced polymer composite of claim 1, wherein said individual glass fiber form a fiberglass mat held together by the resinous binder.
3. The fiberglass reinforced polymer composite of claim 1, wherein the resinous binder includes 0.1 to 20 wt.% rubber core-shell nanoparticles, based on the total amount of resin in the binder.
4. The fiberglass reinforced composite of claim 1, wherein the average particle size of the rubber core-shell nanoparticles is 250 nm or less.
5. The fiberglass reinforced composite of claim 1, wherein the resinous binder is formed from a urea formaldehyde resin, an acrylic resin or a mixture thereof.
6. The fiberglass reinforced composite of claim 1, wherein the core of the rubber core-shell nanoparticles is made from a synthetic polymer rubber selected from the group consisting of styrene/butadiene, polybutadiene, silicone rubber (siloxanes), acrylic rubbers and mixtures thereof.
7. The fiberglass reinforced composite of claim 1, wherein said composite is an asphalt roofing shingle.
8. An improved roofing mat for use in making asphalt roofing shingles, the improved roofing mat comprising a fiberglass mat composed of multiple glass fibers and a resinous binder holding the individual glass fibers together, wherein the resinous binder includes rubber core-shell nanoparticles.
9. The roofing mat of claim 8, wherein the resinous binder includes 0.1 to 20 wt.% rubber core-shell nanoparticles, based on the total amount of resin in the binder.

10. The roofing mat of claim 8, wherein the resinous binder is formed from a urea formaldehyde resin, an acrylic resin or a mixture thereof.
11. The roofing mat of claim 8, wherein the core of the rubber core-shell nanoparticles is made from a synthetic polymer rubber selected from the group consisting of styrene/butadiene, polybutadiene, silicone rubber (siloxanes), acrylic rubbers and mixtures thereof.
12. An improved asphalt roofing shingle comprising a fiberglass roofing mat composed of multiple glass fibers and a resinous binder holding the individual glass fibers together, an asphalt coating covering the fiberglass roofing mat, the asphalt coating including an inorganic particulate filler therein, the asphalt coating further containing roofing granules embedded therein, wherein the resinous binder of the fiberglass roofing mat includes rubber core-shell nanoparticles.
13. The asphalt roofing shingle of claim 12, wherein the resinous binder includes 0.1 to 20 wt.% rubber core-shell nanoparticles, based on the total amount of resin in the binder.
14. The asphalt roofing shingle of claim 12, wherein the resinous binder is formed from a urea formaldehyde resin, an acrylic resin or a mixture thereof.
15. The asphalt roofing shingle of claim 12, wherein the core of the rubber core-shell nanoparticles is made from a synthetic polymer rubber selected from the group consisting of styrene/butadiene, polybutadiene, silicone rubber (siloxanes), acrylic rubbers and mixtures thereof.
16. The asphalt roofing shingle of claim 12, wherein the asphalt coating includes 30 to 80 wt.%, based on the entire weight of the filled asphalt of an inorganic particular filler selected from the group consisting of dolomite, silica, slate dust and high magnesium carbonate.
17. A fiberglass reinforced polymer composite comprising a matrix polymer and glass fibers dispersed in the matrix polymer, wherein the surfaces of the glass fibers carry a coating of core-shell rubber nanoparticles.

18. The fiberglass reinforced polymer composite of claim 17, wherein the surfaces of the glass fibers carry a coating comprising a mixture of core-shell rubber nanoparticles and a film-forming polymer.

19. The fiberglass reinforced polymer composite of claim 17, wherein the glass fibers are made by combining multiple attenuated glass filaments together to form individual fibers, and further wherein the incipient size composition is applied to the individual glass filaments before they are combined.

20. The fiberglass reinforced polymer composite of claim 17, wherein the surfaces of the glass fibers carry a second coating of a secondary incipient size composition applied to the fibers during fiber manufacture after the individual glass filaments are combined, the secondary incipient size composition comprising additional core-shell rubber nanoparticles and a film-forming polymer.

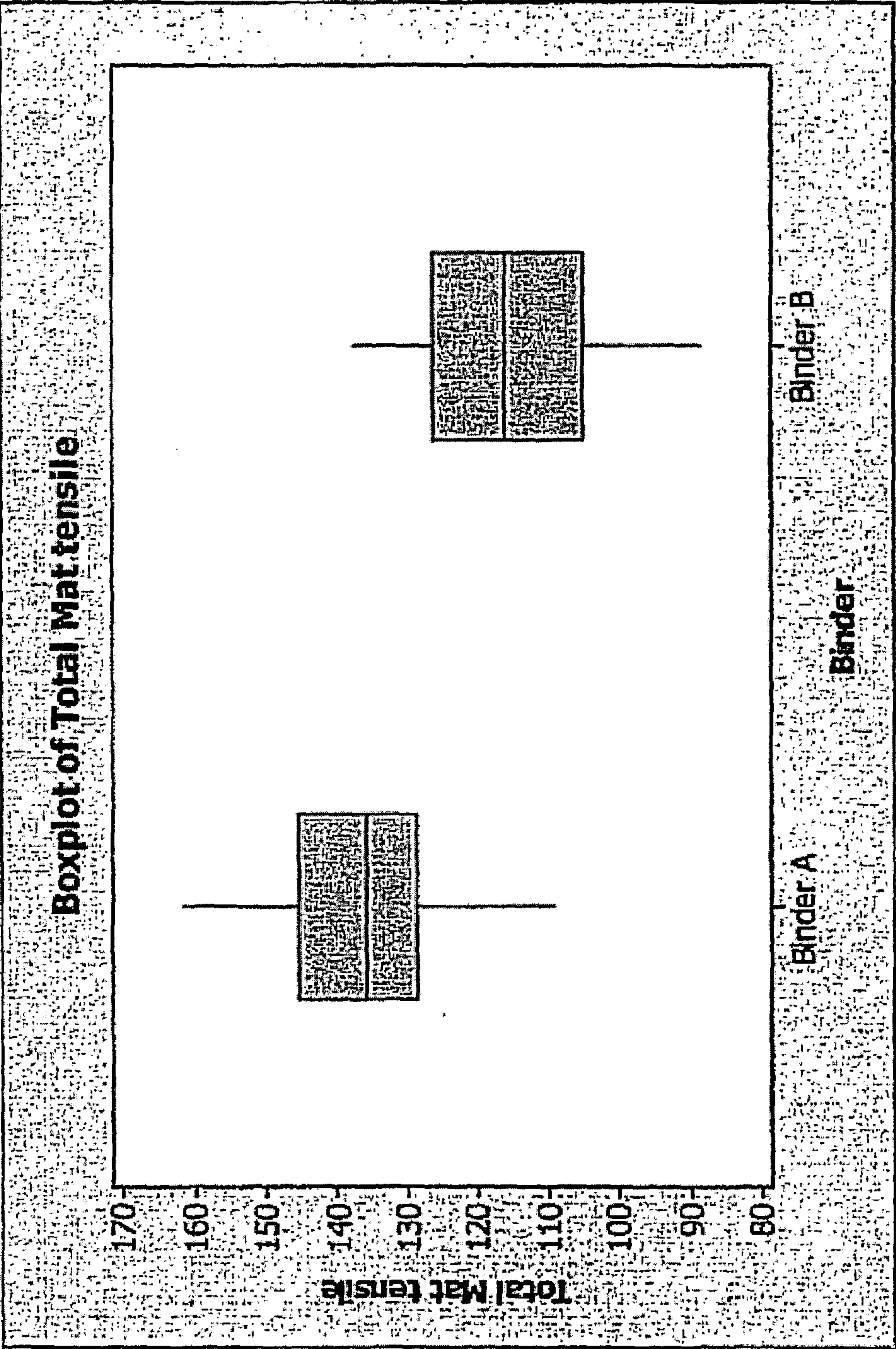


Figure 1

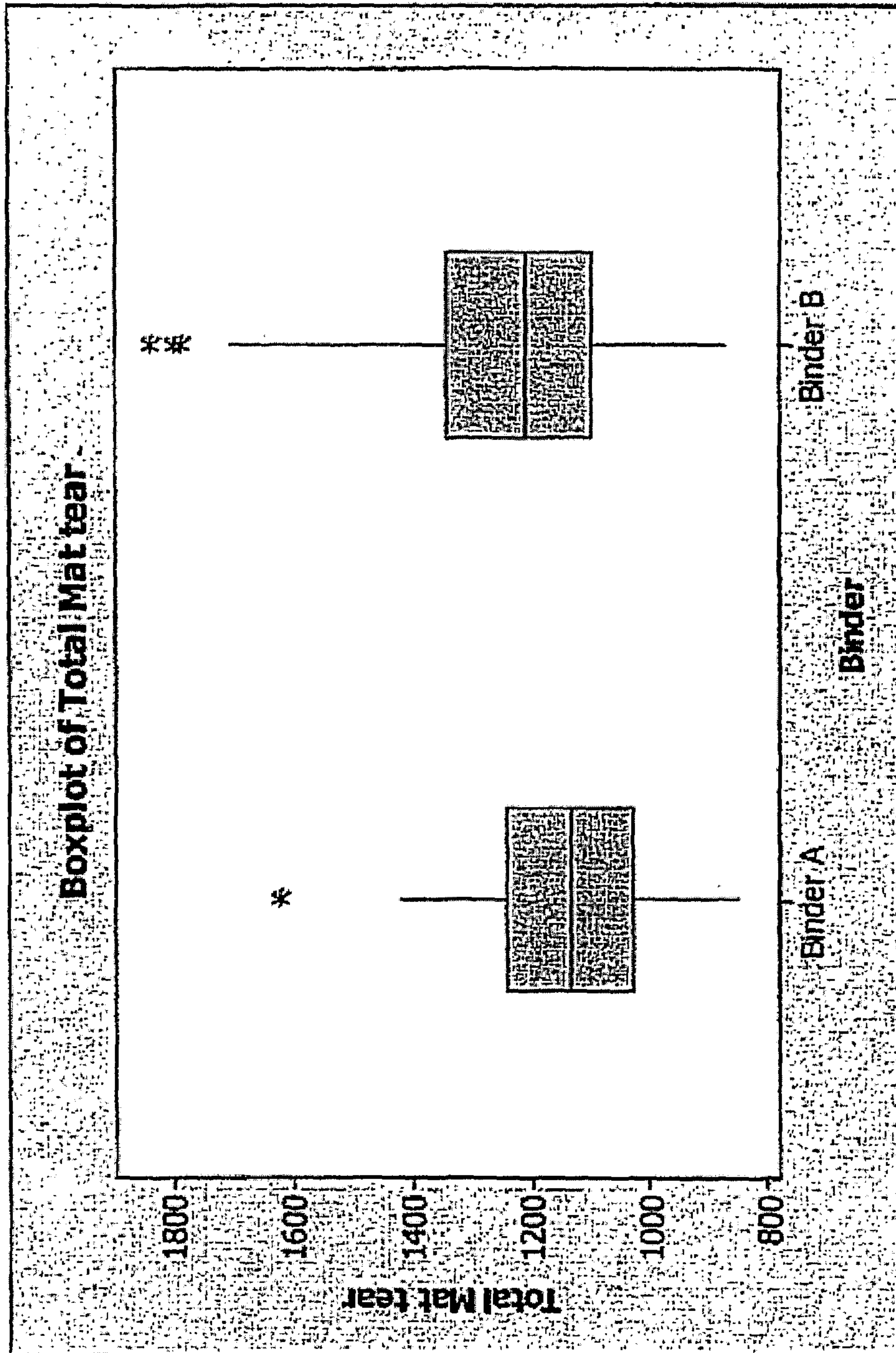


Figure 2

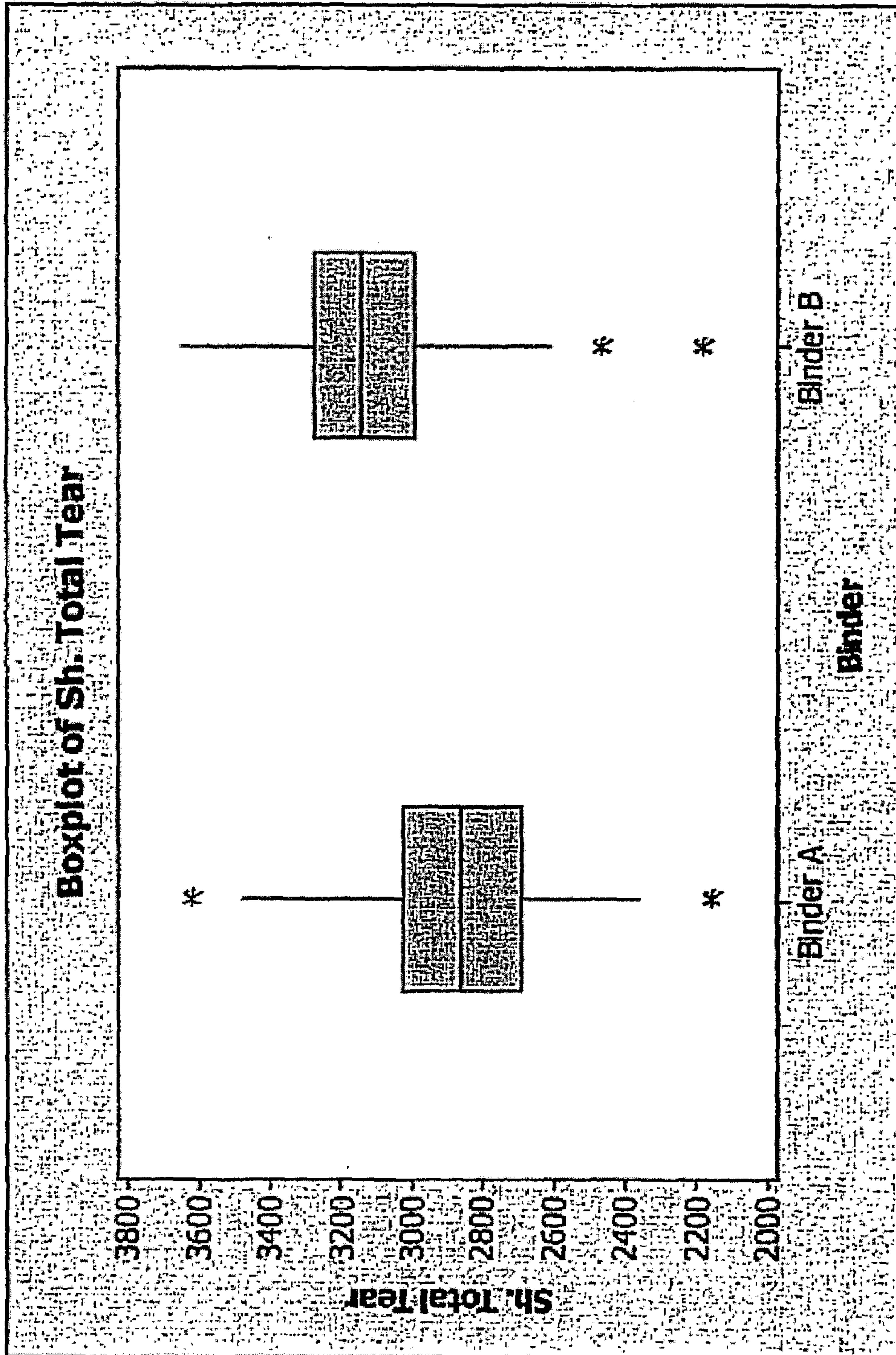


Figure 3

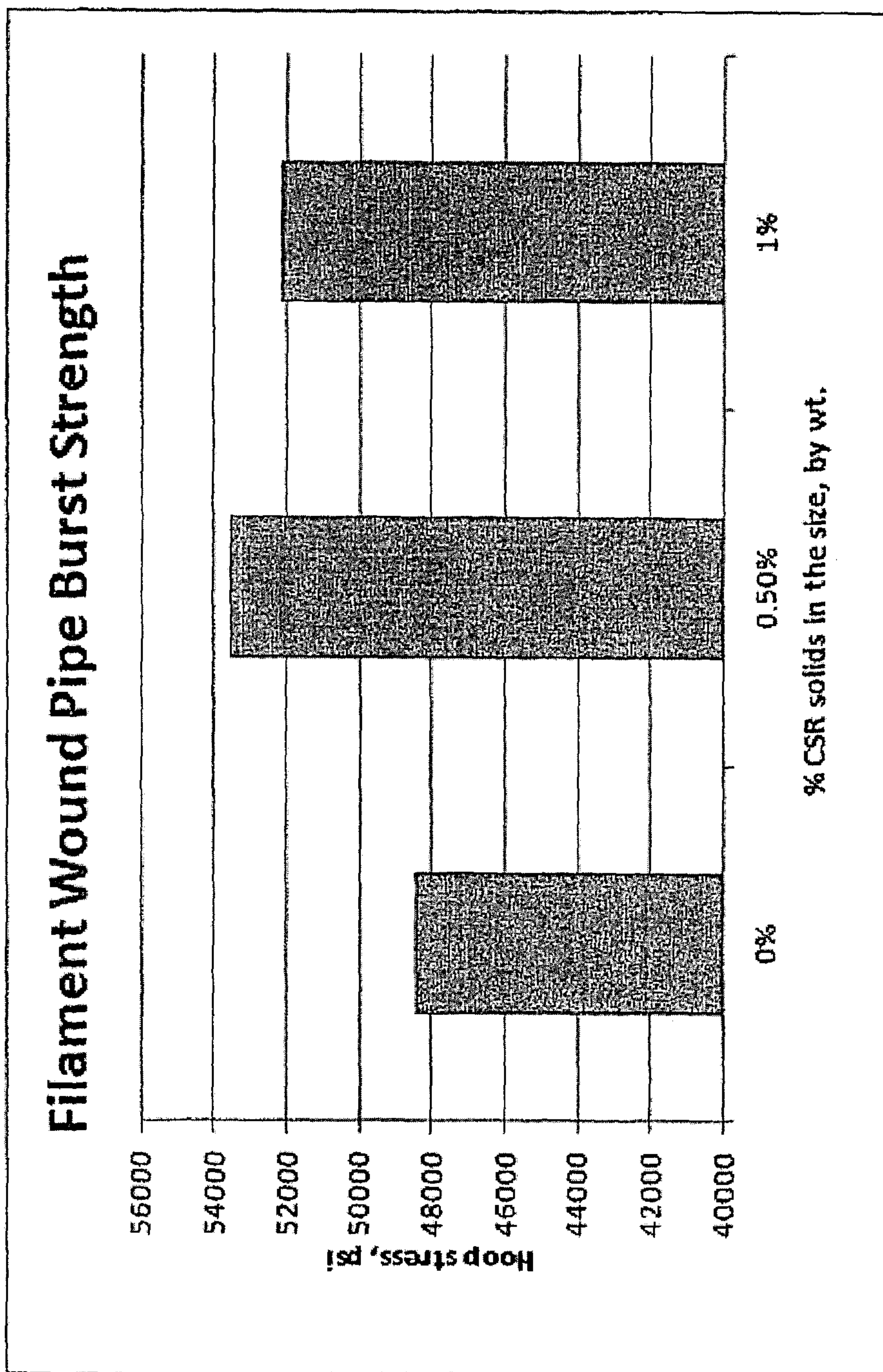


Figure 4

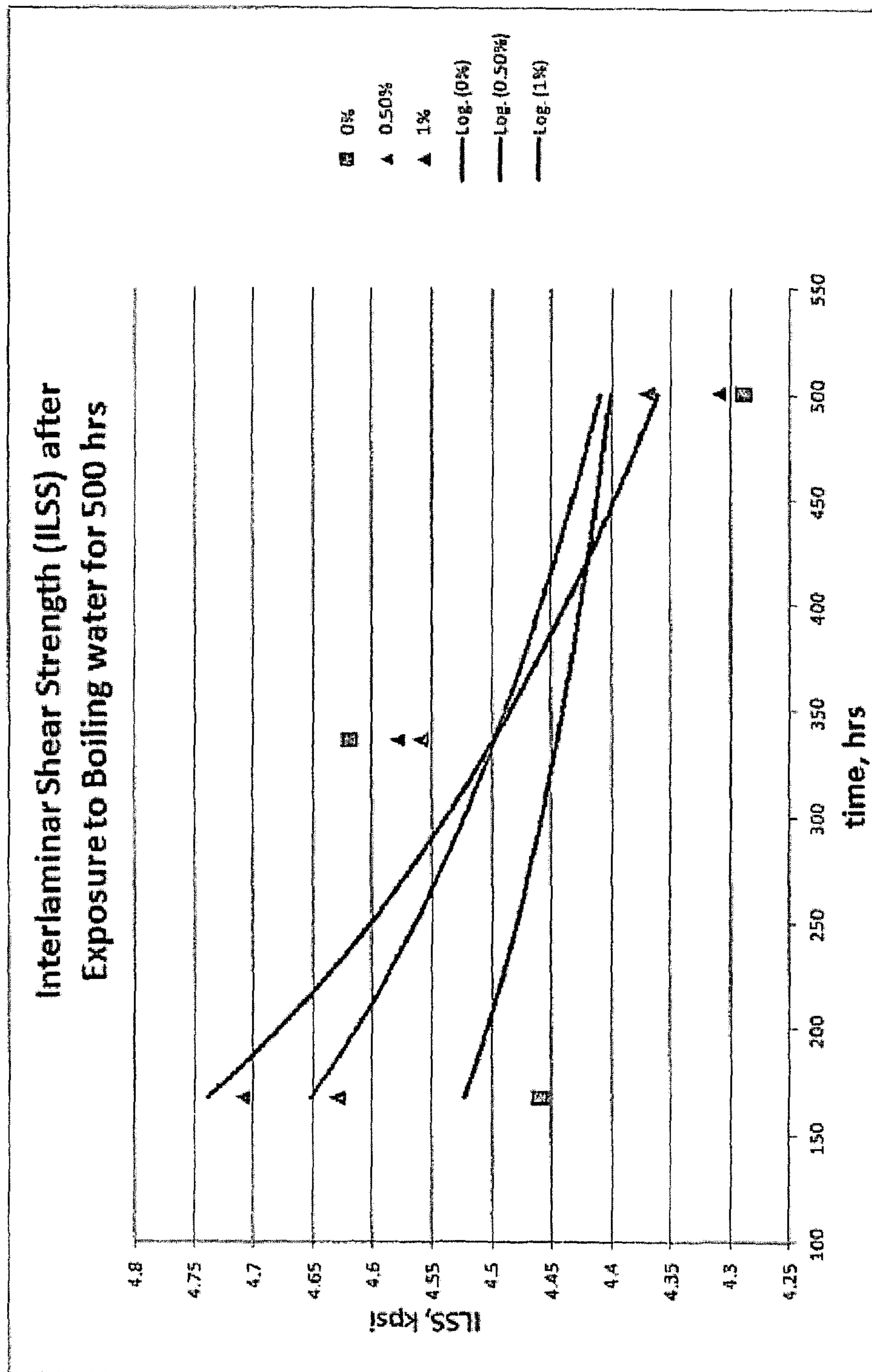


Figure 5

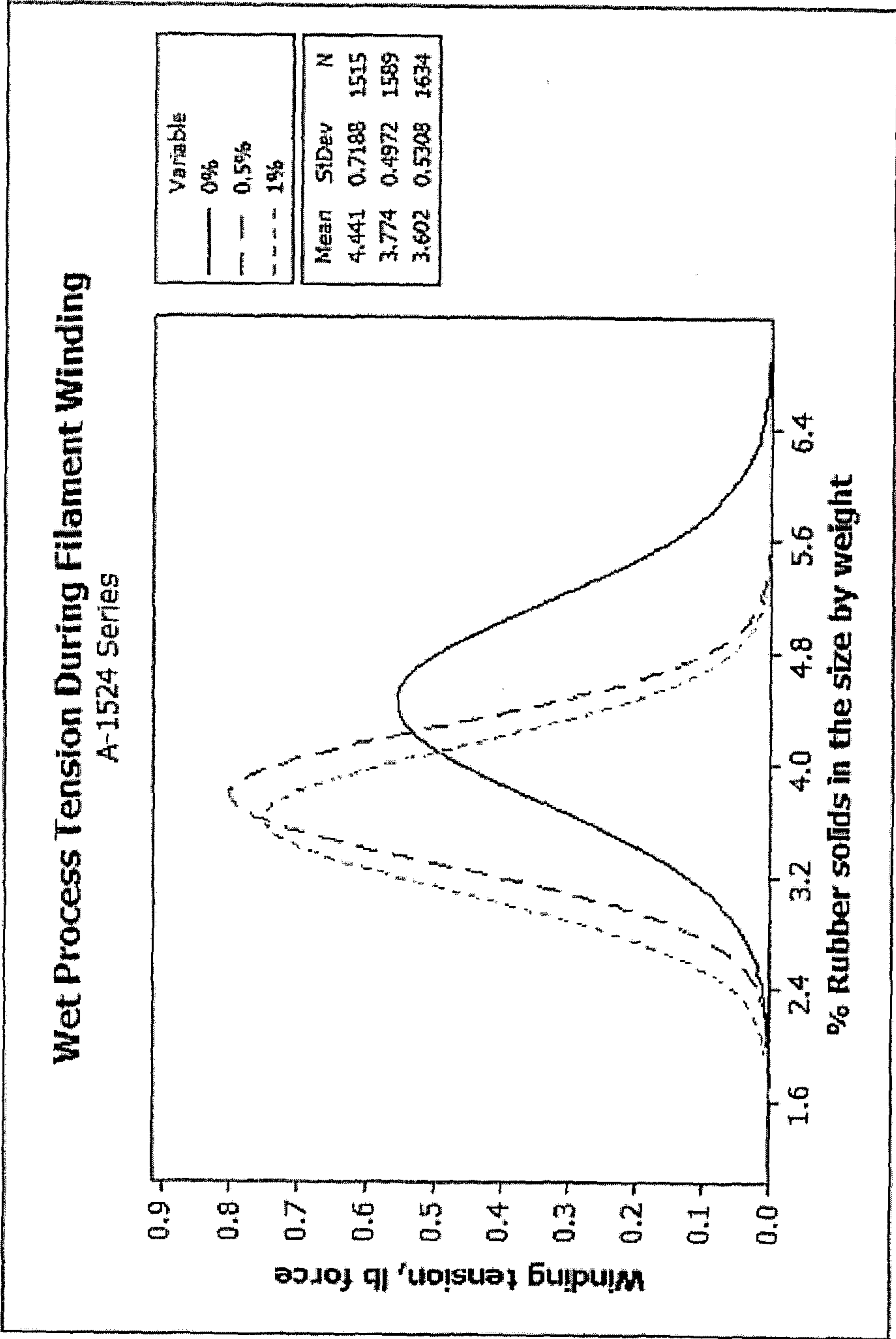


Figure 6