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GLASS FIBER-PLASTIC COMPOSITES OF IMPROVED STRENGTH

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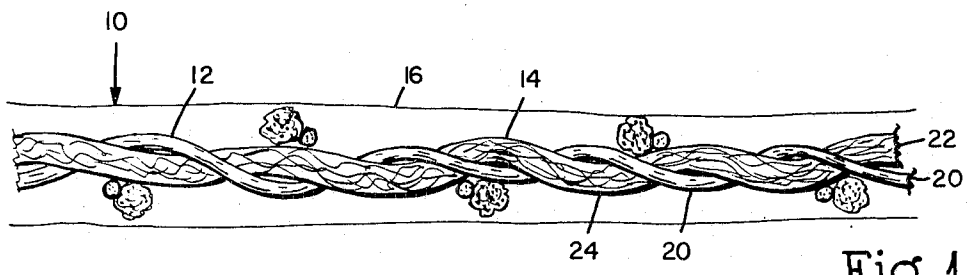


Fig. 1

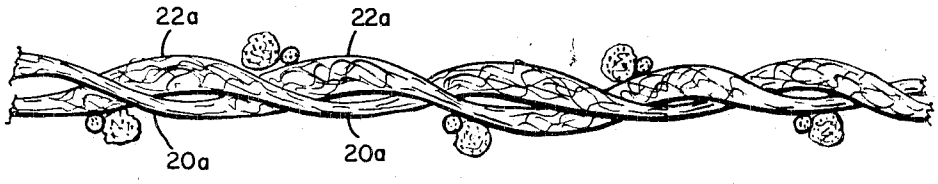


Fig. 2

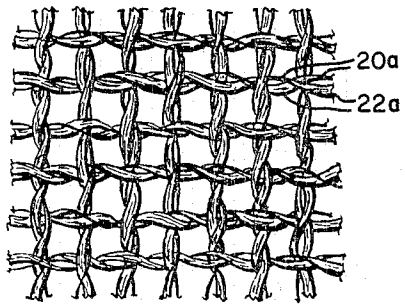


Fig. 3

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GLASS FIBER-PLASTIC COMPOSITES OF IMPROVED STRENGTH

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ABSTRACT OF THE DISCLOSURE

A composite wherein a plastic is reinforced by glass yarn, which yarn is formed by at least two strands twisted together to provide loops with the fibers of the loops being at least partially filamentized and longer than the fibers of the other strand which they overlay.

BACKGROUND OF THE INVENTION

The present invention relates to composites of the type wherein a plastic is strengthened or reinforced by glass fibers; and especially to such composites wherein the glass fibers are present in the form of a woven fabric.

In the Biefeld Patent 2,650,184, there is described a composite wherein a fabric of glass fibers reinforces a resin. The patent is directed to a method of improving the tear strength of such a composite by producing a partial or poor bond of the resin to the cloth. The patent appears to teach a composite wherein the plastic is forced down into the fabric in such a manner that the plastic does not fill all of the interstices of the fabric. The patent also appears to teach that improved tear resistance is had when the cloth is treated so that a poor bond is had between the resin and the fabric. The patent appears to also teach that because of the poor bond between the plastic and the cloth, the strands of the cloth are free to shift when a tear stress is applied thereto to prevent the plastic from concentrating shear on the individual fibers.

It has been found, however, that the materials of the Biefeld patent do not provide optimum strength and the concentrated loads cause the fibers to spread. Because of the weak attachment, stress applied to one fiber is not properly transmitted to another fiber through the plastic. In addition, the plastic does not provide total separation between the fibers so that flexing may produce abrasion of the fibers under certain conditions.

SUMMARY OF THE INVENTION

The present invention relates to a composite of glass fiber yarns surrounded by plastic with the yarn comprising at least two strands of glass fibers twisted together with sections of one of the twisted strands being of greater length than the section of the other twisted strand which it overlays to thereby provide fiber loops with plastic extending around the fiber loops.

The principal object of the present invention is the provision of a new and improved composite having improved abuse resistance.

A further object of the invention is the provision of a new and improved composite of the above described type wherein the plastic bonds to fibers of each strand so that the plastic is capable of transferring force from one fiber to another fiber, and so that breakage of some of the fibers do not proportionally decrease the strength of the composite.

Further objects and advantages of the invention will become apparent to those skilled in the art to which it relates from the following description of several preferred embodiments described with reference to the accompanying drawing forming a part of this specification.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a fragmentary sectional view through a composite of glass fibers and plastic and which embodies principles of the invention;

FIG. 2 is a cross sectional view similar to FIG. 1 showing another embodiment of the invention; and

FIG. 3 is a plan view of the woven glass fibers shown in FIG. 2.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The composite **10** shown in FIG. 1 generally comprises a woven fabric formed of multi-strand yarn **14** of glass fibers, and which yarn is surrounded by a stretchable plastic **16**. Yarn **12** is formed of two strands which are twisted together. One of the strands **20** comprises 408 monofilaments of E glass having a diameter of approximately 0.00025 inch. The other strand **22** likewise comprises 408 monofilaments of E glass of the same diameter, but the monofilaments of the strand **22** are separated in a manner similar to what is sometimes called texturizing. In addition to being texturized the monofilaments of the strand **22** are longer than are the monofilaments of the strand **20**. The excess length of the monofilaments of the strand **22** form loops **24** which extend around the strand **20**.

The yarn arrangement of the invention will provide increased strength when formed into composites with any type of resin, be it thermosetting or thermoplastic. Because thermoplastic resins, and particularly those having great stretchability, produce composites which tear easily, the reinforcing arrangement of the present invention will have particular advantages when reinforcing these stretchable resins. Suitable thermoplastic resins will include cellulose esters, including cellulose acetate, cellulose butrate or the like, cellulose ethers such as ethyl cellulose, benzyl cellulose, or nitro cellulose, polystyrene

or chlorinated polystyrene, acrylic esters, vinyl acetate, vinyl alcohol, vinyl chloride, vinyl acetals, copolymers of vinyl acetate and vinyl chlorides, polyvinylidene chloride-vinyl chloride copolymers, polybutene, polyethylene, polychloroprene, butadiene - acrylonitrile copolymers, polyesters, polyurethanes, the various natural and synthetic rubbers, silicones, etc.

Example 1

A woven fabric was made using 40 warp yarns per inch and 44 weft yarns per inch. Each yarn was made of two 408 filament strands, the monofilaments of which were made of E glass and had a diameter of 0.00025 inch. The yarn was texturized at the time the strands were twisted together and during which time one strand was overfed at a rate of 3 percent while the other strand was overfed at a rate of 70 percent. As the strands were twisted together and during the overfeeding operation, they were passed through an air jet which filamentized the strand that was overfed by 70 percent, into individual or small groups of filaments. By overfed is meant the feeding of the yarn to the air jet at a positive rate in excess of the rate which withdrawal rolls remove the yarn from the air jet.

The yarn which was processed as above described was coated with a conventional starch lubricant. The fabric after being woven was heat cleaned to remove the starch coating and provide a set to the weave. By heat cleaning is meant a process wherein the fabric is heated in air at a temperature of approximately 900° F. to burn off the organic materials.

The heat cleaned fabric was then coated with a ⅛ inch layer of a creamy emulsion having the following composition:

Ingredients:	Percent product by weight
Emulsion—50% solids, comprising 80% methamethacrylate, 20% vinylacetate	50
Water premix, 50% polyacrylic acid	5
Ammonium hydroxide (28–30% NH_3)	1
Gammamethacryloxy propyltrimethoxy silane	1
Water	Remainder

The coated fabric was dried at a temperature of approximately 212°F. The fabric was turned over, and a ⅛ inch thick layer of the same material was applied to the other side which was also dried in the oven at approximately 212° F. After being coated on both sides, the coated fabric was passed between calender rolls having surfaces heated to approximately 300° F., whereby the coatings were fused and pressed around the fibers to completely embed the fibers in the plastic.

The material made as above described has abuse resistance that is considerably improved over a conventional fabric made of untexturized yarn of the same filament count and of the same warp and weft count. It will be seen that the loops of the filamentized strand allow the plastic to become embedded between the filaments to totally and permanently separate the filaments and thereby prevent mutual abrasion. In addition, the plastic which permeates the filaments is greatly strengthened by the filaments to form a high strength region of the plastic having a strength and tear resistance considerably greater than that of the unreinforced plastic. The high strength regions formed by the plastic and impregnated loops distribute concentrated loads to the strand about which the loops are formed, as well as to the yarn which extends at right angles to the plastic impregnated loop. A concentrated load applied to the strand which is surrounded by the loop, causes the surrounded strand to become bowed to pull portions of the strand from either side of the concentrated load towards the concentrated load. Because the untexturized strand has plastic tightly bonded thereto by reason of other loops on either side of the concentrated load, the plastic is caused to grow towards the concentrated load, and thereby build up the amount of plastic which resists the pressure of the concentrated load.

By way of contrast, the prior art composites are thinned out in the region of a concentrated load to either leave the glass fibers exposed to the load, or to produce a rubbing action of the fibers against each other.

Shear forces applied to the edges of the composite of the present invention are also resisted by the high strength regions of the plastic that are formed by the plastic impregnated loops to thereby distribute the shear forces over a greater area of the strands. This reduces the angle at which the filaments of the strand are bent, and as is well known in the art, glass fibers are easily broken when they are bent at too sharp an angle.

In the above composition, the gammamethacryloxy propyltrimethoxy silane is a coupling agent which improves the attachment or bond of the resin to the fibers. Instead of mixing this material with the coating composition, it can also be applied as a pretreatment by dipping the fabric into a 1 to 5 percent solution, prior to the application of a coating material which does not include the coupling agent. Alternatively, an advantage will be had in some instances by applying the coupling agent only to the strand which is overfed by the greatest amount in the yarn forming operation to further enhance the bond of the resin to the looped fibers. This will not be necessary in most instances, however, because of the good physical bond which is achieved with the filamentized strand. Even nonheat cleaned starch size strands when filamentized will be satisfactory for most instances because of the good physical bond that is achieved with the filamentized strand. The solution may be either an organic solution, or in some instances, a water solution.

Example 2

A preferred type of yarn is shown in FIG. 2. The yarn of FIG. 2 is formed by twisting two 408 filament strands together. Each strand is formed by filaments of E glass having a diameter of approximately 0.00025 inch. Each of the strands are overfed by 10 percent during the time that they are passed over an air jet which alternately filamentizes or texturizes the strands. Both strands of the yarn are texturized at alternately spaced positions as seen in FIG. 2. A fabric of this material was made using 40 warp and 40 weft yarn per inch, following which the fabric was heat cleaned in the above described manner.

A plastisol of the following composition was prepared:

Ingredients:	Parts by weight
Particulate polyvinyl chloride resin (high M.W.)	100
Diisodecylphthalate	40
Dioctylphosphite	20
Epoxidized soya oil	7.5
Titanium dioxide	5
Lead phosphite	3
Vinyl trichloro silane	2

The composite is prepared by applying a ⅛ inch layer of the above material to the fabric of Example 2, and thereafter the material would be fused at a temperature in the range of 200–250° F. Thereafter, ⅛ inch layer is applied to the opposite side of the fabric and it is also is fused at a temperature of 200–250° F. The coated fabric is then passed through between heated rolls having a surface temperature of from 200–250° F. to thoroughly fuse the polyvinyl chloride material together and encase the fiber. A plan view of the fabric before coating is shown in FIG. 3. Those portions of the fabric shown in FIGS. 2 and 3 which correspond to similar portions of the fabric shown in FIG. 1 are designated by a like reference numeral characterized further in that a suffix *a* is affixed thereto.

It will be seen that both strands of a yarn of the fabric of Example 2 contain filamentized loops and that these loops are alternately spaced. The pattern of these loops is shown in FIG. 3, and these loops form reinforced areas

of plastic having a strength and a modulus considerably greater than the portions of the plastic which are not reinforced by the filaments. It will be seen that the strands of the yarn shown in FIGS. 2 and 3 are all anchored by filamentized loops whereas one strand in the yarn of the fabric shown in FIG. 1 is not filamentized and its anchorage is dependent upon force transferred from the filamentized loops to the unfilamentized strand.

When a concentrated load is applied to the fabric of FIGS. 2 and 3, loops on opposite sides of the concentrated load provide complete anchorage, so that plastic in the immediate vicinity of the concentrated load is progressively pulled towards the load as the force is applied. There is, therefore, a marked build up of stretchable plastic in the area of the concentrated load which in turn distributes the load onto the fibers running in both directions.

Instead of the vinyl trichloro silane being mixed with the plastisol composition, an organic solution thereof can be formed using one part vinyl trichloro silane and 99 parts toluene. Fabric can be dipped into the solution, or the solution can be otherwise applied to the fabric and the silane coated fabric dried at a temperature from 150–250° F. The plastisol mixture with or without an organosilane can then be applied.

Example 3

A formable composition was prepared from the following ingredients:

Ingredients:	Parts by weight
Polyvinylchloride emulsion polymerized resin (normal molecular weight)	50
Polyvinylchloride emulsion polymerized resin (low molecular weight)	50
Dioctyl phthalate	20
Diisodecylphthalate	50
Calcium carbonate filler	10
Sb_2O_3 fire retardant	5
Lead phosphite	5
Polyethylene glycol	2
Kerosen diluent	10–15
Azobisformamide blowing agent	5
RHB pigment	3–10

This material was prepared by adding the pigments to the plasticizer in a Hobart mixer. The fillers and fire retardants were mixed with another part of the plasticizer in a small mixer and then blended into the Hobart mixer. Thereafter, 100 parts of the normal and low molecular weight polyvinyl chloride powders were added to the Hobart mixer and blended together following which the diluent and ethylene glycol were added. This material is applied to both sides of the fabric of Example 2 and then foamed in situ by passing through an oven heated to 300° F. to foam the composition in situ. The filamentized loops are firmly embedded in the foam plastic and this composite has greately improved strength over a composite similarly formed except that the fabric used is a conventional untexturized one having the same fiber filament content.

Example 4

	Parts by weight
Oil extended butadiene-styrene rubber (SBR–1712)	80
Prebroken smoked sheet natural rubber (65 Mooney)	20
Zinc oxide	3
Stearic acid	1
Carbon black	50
Pine tar	5
Diphenylamine-acetone reaction product (Aminox)	1
Diphenylguanidine (DPG)	.2
N - cyclohexyl - 2 - benzothiazolesulfenamide (Santocure)	1
Sulphur	1.75

The oil extended butadiene-styrene rubber and the smoked sheet natural rubber is cut up into small pieces and fed to a Banbury mixer that is run at slow speed. After one minute of mixing, half of the carbon black, the zinc oxide, the stearic acid, and the diphenylamine-acetone reaction product is added and mixed for one minute. Thereafter, the remainder of the carbon black and the pine tar are added and mixed for two and one half minutes, following which the N-cyclohexyl-2-benzothiazolesulfenamide, the diphenylguanidine and the sulphur are added and mixed for a minute and a half. The compound at this stage is thoroughly blended and is then dumped from the Banbury mixer. The rubber compound is then cut up into small pieces and dropped into a container of toluene which is continually agitated by a paint stirrer or other mixer to form a solution containing about 33 percent by weight solids. The fabric of Example 2 is coated with the above mixture in two stages, the first of which works the mixture into the fabric, and the second of which provides a top dressing of approximately ⅛ inch thick. This material is then dried in an oven at approximately 200° F. following which the opposite side is coated in the same manner. Sheets of this material are then cured in a press at a temperature of about 350° F. until vulcanization is completed. The composites so formed has considerably greater abuse resistance than does a composite similarly formed of a fabric of like fiber and yarn count, differing only in that the yarn does not contain the filamentized loops, but is of a conventional strand.

From the above description, it will be apparent that both solid and/or foamable coatings can be applied to the fabric to provide solid or foam resin matrixes which are reinforced by the fibers. A coupling agent, such as an organosilane need not be used in all instances since the filamentized loops provide good mechanical anchorage without the use of a coupling agent. Where a coupling agent is used, however, more than approximately 0.5 percent based on total solids is necessary to produce a demonstrable effect, and more than 5 percent will not provide an appreciable improvement in most instances. For many instances, satisfactory results will be achieved using uncoronized starch sized strand without a coupling agent, either applied directly to the fibers or with the impregnating resin. This is because of the good mechanical anchorage which is achieved with the filamentized loops. The above examples show that improved tear strength is achieved even when the resin is applied to both sides of the fabric to thoroughly surround the fibers. It will be apparent that the synergistic effect is also achieved where the impregnating resin is applied to only one side of the fabric. From the above description, it will also be apparent that the glass fiber reinforcing need not be woven, but can be in the form of a mat formed by yarns containing the texturized loops above described. Still further modifications of the invention will occur to those skilled in the art, and it is my intention to cover hereby all novel adaptations, modifications, and arrangements thereof which come within the practice of those skilled in the art to which the invention relates and which fall within the purview of the following claims.

I claim:

1. A composite of glass fiber yarn surrounded by plastic, said yarn comprising at least two strands of glass fibers twisted together, at least one of said strands having been subjected to an air jet treatment so as to filamentize the strands into individual filaments or groups of filaments and both of said strands being overfed to the twisting operation by at least approximately 3% to cause each strand to have a length greater than that of the yarn, said yarn being embedded in plastic.

2. The composite of claim 1 in which said yarn comprises one of the mutually perpendicular yarns of a woven fabric.

3. The composite of claim 1 in which said yarn comprises both of the mutually perpendicular yarns of a woven fabric.

4. A composite of glass fiber yarn surrounded by plastic, said yarn comprising at least two strands of glass fibers twisted together, at least one of said strands having alternate sections that have been texturized by an air jet treatment so as to separate the sections into individual filaments or groups of filaments separated by generally untexturized sections, and both of said strands being overfed to the twisting operation by at least approximately 3% to cause each strand to havea length greater than that of the yarn, said yarn being embedded in plastic.

5. The composite of claim 4 wherein both strands are alternately texturized and untexturized.

6. The composite of claim 5 wherein the texturized portions of both strands are alternately spaced.

7. The composite of claim 5 wherein the yarn is in the form of a woven fabric.

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