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(54) Title: GLASS FIBER SIZING		
(57) Abstract A glass fiber for use in reinforcing thermoplastics is provided which has, in addition to water, a mixture of an epoxy functional acrylic polymer and a vinyl acetate polymer, a silane coupling agent, an emulsified polypropylene composition, a lubricant, and an adhesion promoter. The strength of molded thermoplastics reinforced with glass fibers sized as taught herein is superior to that of others.		

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GLASS FIBER SIZING

5

BACKGROUND OF THE INVENTION

The present invention is directed to chemically
10 treated glass fibers, strands or yarn where the fibers impart
improved strength in reinforcing thermoplastics such as
polypropylene.

Glass fibers may be in various forms such as
chopped or unchopped, woven, twisted or as a mat. The fibers
15 are generally treated upon formation with various chemical
treatments or sizings to increase their compatibility with
different polymers and to make the fibers more easy to
process.

It is an object of this invention to provide
20 chemically treated fibers resulting in improved mechanical
strength when used to reinforce thermoplastics. The
thermoplastics to be reinforced are preferably chemically
coupled polypropylenes.

SUMMARY OF THE INVENTION

25 The objects of this invention are achieved with
glass fibers which have been treated with a sizing having from
0.5 to 20 weight percent on a non-aqueous basis of a
thermoplastic compatible film former mixture or an epoxy
functional acrylic polymer and a vinyl acetate copolymer; from
30 0.5 to 10 weight percent on a non-aqueous basis of a silane
coupling agent; from 25 to 75 weight percent on a non-aqueous
basis of an emulsified polypropylene composition; from 0.01 to
10 weight percent on a non-aqueous basis of a lubricant; from
10 to 30 weight percent on a non-aqueous basis of an adhesion
35 promoter; and water in an amount to produce an aqueous sizing
composition. Other components may optionally be added to the

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invention and more than one of the above components may be used.

DETAILED DESCRIPTION OF THE INVENTION

Any glass fiber suitable for reinforcing may
5 suitably be treated in accordance with the present invention. The production of glass fibers is well known in the art and is described, for example, in The Manufacturing Technology of Continuous Glass Fibers by K. L. Lowenstein, published in 1973 by Elsevier Scientific Publishing Company, Library of Congress
10 Card Number 72-97429.

Application of sizing to glass fibers is well known in the art and may be accomplished by conventional methods such as a belt applicator, a "kiss-roll" applicator, by spraying, etc. The amount of sizing deposited on the glass is
15 around 0.01 to 5 weight percent of the treated glass fiber strand. After the strands have been sized, they are usually at least partially dried to remove residual moisture.

After sizing and before or after drying, the glass fiber strands are collected and where intended for use as
20 reinforcement, are generally cut or chopped into lengths from about a sixteenth (1.6 mm) to about 3 (76.2 mm) inches. The fibers may also be collected as continuous strand roving for long fiber applications and may also be made into a mat of either chopped strands or continuous fibers.

25 The sized glass fibers of this invention are advantageously used to reinforce thermoplastics such as polypropylene and other polyolefins such as polyethylene, polybutylene, 5-methyl-pentene, etc. The thermoplastic may be a homopolymer or copolymer and may be chemically coupled.
30 Chemically coupled polypropylene is the preferred thermoplastic for use with the sized fibers of this invention.

"Chemically coupled" is a term used to identify the product resulting from the grafting of a polar moiety into a non-polar hydrocarbon such as polypropylene, to enhance

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adhesion to other polar molecules. Suitable polar moieties are anhydrides like maleic anhydride, or acrylic acids. In a typical chemically coupled hydrocarbon, the actual quantity of grafted polar moiety is small as compared to the hydrocarbon
5 matrix, accounting for less than 0.1 weight percent of the solids of the base hydrocarbon. Because the level is low, maleic anhydride grafted polypropylene is often referred to as "chemically coupled propylene homopolymer". Chemically
coupled versions of various polyolefins at varying levels of
10 polar moieties which provide the desired levels of chemical coupling are commercially available.

The components of the sizing of this invention are from 0.5 to 20 weight percent on a non-aqueous basis of a thermoplastic compatible mixture of certain film formers; from
15 0.5 to 10 weight percent on a non-aqueous basis of a silane coupling agent; from 5 to 20 weight percent on a non-aqueous basis of an emulsified polypropylene composition; from 0.01 to 20 weight percent on a non-aqueous basis of a lubricant; from
1 to 10 weight percent on a non-aqueous basis of an adhesion
20 promoter; and water in an amount to produce an aqueous sizing composition.

A specific thermoplastic compatible film former mixture particularly useful in this invention comprises an epoxy functional acrylic polymer and a vinyl acetate polymer.

25 The epoxy-functional acrylic polymer is a polymer having a backbone derived by polymerizing one or more acrylic monomers and having pendant epoxy groups. The pendant epoxy groups are normally obtained from a monomer such as glycidyl acrylate or methacrylate. Homopolymers of epoxy functional
30 acrylic monomers may be used, but also useful are interpolymers of such monomers with other copolymerizable acrylic monomers such as acrylic acid, methacrylic acid and alkyl esters of acrylic and methacrylic acid. Such comonomers may include, at least in small proportion, monomers having

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other functional groups, such as urethane or urethane-producing moieties, carbonyl, amido groups, etc., and non-acrylic ethylenic monomers such as styrene. The epoxy equivalent of the epoxy-functional polymer is preferably
5 between about 125 to about 165, however, polymers with epoxy equivalents outside of this preferred range would also function, since epoxy-functionality of any amount would have some effect.

The preferred epoxy-functional acrylic polymer is a
10 glycidyl methacrylate polymer, i.e., a homopolymer of glycidyl methacrylate or a copolymer of glycidyl methacrylate with minor amounts of one or more other monomers, such as acrylic or methacrylic acids or esters.

A glycidyl methacrylate polymer is commercially
15 available as Fulatex® PN-3620J emulsion from the H.B. Fuller Company and has an epoxy equivalent of about 142, a solids percentage of 44 to 46 percent (Ohaus Moisture Balance), a viscosity of 10 to 150 cps (Brookfield Viscometer Model RVF, at 20 RPM at 25°C), a density of about 8.8 pounds per gallon,
20 an opaque white color and a glass transition temperature (Tg) of 56 ± 2°C.

The vinyl acetate polymer may be poly(vinyl acetate) or may be a vinyl acetate copolymer which contains at least 80% vinyl acetate copolymerized with other monomers,
25 which may contain various functional groups. Other monomers which may be used include, for example, alkylacrylates and methacrylates, acrylamide, methylacrylamide, N-ethylacrylamide, acrylic acid, styrene and similar copolymerizable ethylenic monomers.

30 The preferred vinyl acetate polymer is that available as a stiff self-reactive emulsion of a copolymer of vinyl acetate and acrylamide which has 52% solids, a viscosity of 5800 cps (RVF Brookfield viscosity, #3 spindle, 20 RPM at 70°F), a density of 9.2 pounds per gallon at 72°F, and a

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particle size of about 1 micron. Such a material is commercially available as Resyn 2828 from National Starch & Chemical.

The epoxy-functional acrylic polymer may be present
5 in an amount of 0.5 to 10 weight percent on a non-aqueous basis of the components (i.e., the components other than water) and the vinyl acetate polymer in an amount of 0.5 to 10 weight percent on a non-aqueous basis. It is preferred that the weight ratio of the epoxy functional acrylic polymer to
10 vinyl acetate polymer be about 1:1 based on the solids or non-volatiles.

The silane coupling agent may be an organofunctional silane or one or more of its hydrolysis products. Any suitable organofunctional silanes known to those skilled in
15 the art may be used. Particularly suitable silanes are the amino- and mercapto- functional silanes. Examples of different types of these silane coupling agents and their amounts are disclosed in U.S. Patents Nos. 4,271,229 and 4,457,970. The preferred silanes for this invention is gamma-
20 aminoalkyltrialkoxo silanes, an example of which is gamma-aminopropyltriethoxy silane available under the tradename A-1100 from Union Carbide Corporation.

The emulsified polypropylene composition used in this invention is an emulsion of polypropylene polymer, the
25 polypropylene having been modified to provide dispersibility in water by grafting small amounts of acid or anhydride groups which are then neutralized. Such emulsions may be prepared, for example, by reacting an acid or anhydride, such as maleic anhydride, with polypropylene and then neutralizing the
30 anhydride grafted polypropylene resin with an organic amine or an alkali metal hydroxide like potassium hydroxide and dispersing the neutralized anhydride grafted polypropylene through the use of a non-ionic emulsifier. The preferred product is a maleic anhydride grafted polypropylene

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neutralized with an organic amine such as diethylethanolamine
The material may be emulsified in water using a surfactant
such as an alkoxyated phenol or others known in the art.

The preferred emulsified polypropylene composition
5 is a maleonated polypropylene which has a percent solids of
32%, is a tan to grey color, has a specific gravity of 0.98
and is available as Protolube RL-5440 from National Starch and
Chemical Corporation, Proctor Chemicals of Salisbury, NC.
Another useful emulsified polypropylene composition is
10 maleonated polypropylene available as Protolube RL-3974, also
from National Starch and Chemical Corporation.

Various lubricants as known in the fiber glass
sizing art be used in this invention. Particularly useful are
polyether polyols, such as polyalkylene or polyoxyalkylene
15 polyol. The polyether polyol may be either solid or liquid so
long as it is dispersible or emulsifiable or soluble in water.
The most effective molecular weight of the polyol is that
which forms a non-homogeneous lubricious phase with non-rigid
film forming polymers. Examples of the suitable average
20 molecular weight range of these polyether polyols is generally
about 300 to about 12,000 and preferably about 700 to around
10,000.

One suitable polyether polyol is an ethylene
glycol-propylene glycol copolymer sold as Pluracol® V-10
25 polyol by BASF-Wyandotte Corporation and having the properties
shown below.

PLURACOL® V-10 POLYOL TYPICAL PHYSICAL PROPERTIES

Appearance	Pale, yellow, clear viscous fluid
Viscosity at 210°F	6,000 cst (ASTM D445-53T)
30 at 100°F	45,000 cst (ASTM D445-53T)
Specific Gravity 60/60°F	1,089 (BWC test)
Flash point	510°F (ASTM D92-52)
Fire point	535°F (ASTM D92-52)

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	Surface tension (1% aq.)	54.7 dynes/cm at 75°F (ASTM D1331-56)
5		48.4 dynes/cm at 105°F (ASTM D1331-56)
		44.2 dynes/cm at 110°F (ASTM D-1331-56)
10	Shear Stability (in a typical fire-resistant fluid) change in viscosity 12,000 cycles, 1000 psi	+1% (nod. VVL 791 method 3471)

15

Another suitable class of lubricant are the water soluble, nonionic poly(ethylene oxide) homopolymers ranging in molecular weight from 100,000 to 5,000,000. The general formula of such polyether resins is $-(O-CH_2CH_2)_n-$, where n may range from about 2000 to about 100,000. These resins are available from the Union Carbide Corporation under the designation Polyox® water soluble resins. Preferred is Polyox® WSR-301 resin which has an approximate molecular weight of 4,000,000.

By "adhesion promoter" is meant a substance which increases the adhesion, through crosslinking or otherwise, between the thermoplastic and the glass fiber. A number of such adhesion promoters are known in the art and used in sizing compositions and can be used in this invention.

Particularly suitable adhesion promoters are blocked organic polyisocyanates, preferably those comprising an aliphatic diisocyanate such as trimethylene, tetramethylene, hexamethylene, 1,4-cyclohexane diisocyanates and the like. The blocking agent may be a ketoxime, caprolactam, phenol, alcohol or other typical blocking agent known to those skilled in the art. The preferred blocking agents are ketoximes. The preferred adhesion promoter is 1,6 hexamethylene diisocyanate commercially available as a light brown to yellow liquid with a specific gravity of 1.1 at 25°C,

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and a bulk density of 9.2 pounds per gallon, sold by Mobay Corp., Pittsburgh, PA under the product name Baybond XW-116 Crosslinker.

The sizing is mixed with water to have an amount of
5 solids less than 40% and preferably about 7%, as is known to those skilled in the art.

The following is an example of the preparation of the sizing of the invention.

EXAMPLE

10 Add 85.1 pounds (38,600 grams) of maleonated polypropylene emulsion (Protolube RL-5440) to 20 gallons (75.7 liters) of deionized water at room temperature in a large tank with gentle stirring. It is important to avoid air entrainment and foam generation in the mixture.

15 In a separate tank, add 10.6 pounds (4808 grams) of gamma-aminopropyltriethoxy silane to 20 gallons of deionized water at room temperature. After gentle stirring for about 10 minutes, add to the prior mixture with moderate stirring.

In a separate tank, add 0.6 pounds (270 grams) of
20 ethylene glycol-propylene glycol copolymer (Pluracol V-10) to about 3 gallons (11.4 liters) of hot (140°F/60°C) deionized water to dissolve it. Cool the solution with about 3 gallons of room temperature deionized water and add to the prior mixture with moderate stirring.

25 In a separate tank, add 4.7 pounds (2120 grams) of glycidyl methacrylate homopolymer emulsion (Fulatex® PN-3620-J) to about 8 gallons (30.3 liters) of room temperature deionized water. Add 3.8 pounds (1740 grams) of N-methylacrylamide-vinyl acetate copolymer (Resyn 2828) with
30 stirring and then add the entire mixture to the prior mixture with moderate stirring.

In separate tank, add 17 pounds (7700 grams) of a ketoxime-blocked 1,6-hexamethylene di-isocyanate (Baybond XW-116) to about 8 gallons of hot (140°F/60°C) deionized water

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with moderate stirring until dissolved. Cool the mixture with about 8 gallons of room temperature deionized water and then add to the prior mixture.

These ingredients are in tabular form below.

5	Active Ingredient	
	<u>in weight percent</u>	<u>Description</u>
	55	Emulsified polypropylene
	13	Silane coupling agent
	1	Polyol lubricant
10	4	Epoxy film former
	4	Vinyl acetate film former
	23	Adhesion promoter (blocked isocyanate)

Glass fibers were sized with the sizing prepared as described above, with a roller applicator, and were then chopped in the wet state and subsequently dried. The fibers were then compound extruded with a commercially available chemically coupled polypropylene at a 30 weight percent glass content. This chemically coupled polypropylene was one which contained about 0.05 to 0.07 weight percent maleic anhydride and is available as PC072 from Himont Chemical Co. The pellets of extruded glass and polypropylene were molded in a 200 ton injection molding unit and then tested for strength. A number of competitive glass fibers, sold commercially for use in reinforcing thermoplastics and having thereon sizes not having the combination of components used in the sizing of this invention were similarly compounded and molded with the same type of polypropylene and similarly tested. The results of the tests are shown in table I.

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TABLE I

	<u>Tensile</u> <u>Strength (psi)</u>	<u>Impact Strength (FPI)</u> <u>Izod</u>	<u>Unnotched</u>
5 Example 1	13600	2.3	11.1
Competitive I	12600	1.8	8.8
Competitive II	12100	1.9	10.0
Competitive III	12300	2.0	10.5

10 The tensile and Izod strength tests were carried
out in accordance with test procedures ASTM-D638 and ASTM-D256
respectively. The unnotched impact test was carried out by
the same procedure as the Izod test except that the notch was
deleted. The fibers sized as taught herein clearly enhanced
15 the strength of the molded polypropylene to a greater degree
than did the competitive fibers.

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I CLAIM:

1. A glass fiber having thereon the dried residue of an aqueous sizing which comprises:
 - a.) from 0.5 to 20 weight percent on a non-aqueous basis of a thermoplastic compatible film former mixture of an epoxy-functional acrylic polymer and a vinyl acetate polymer;
 - b.) from 0.5 to 10 weight percent on a non-aqueous basis of a silane coupling agent;
 - c.) from 25 to 75 weight percent on a non-aqueous basis of an emulsified polypropylene composition;
 - d.) from 0.01 to 10 weight percent on a non-aqueous basis of a lubricant;
 - e.) from 10 to 30 weight percent on a non-aqueous basis of an adhesion promoter; and
 - f.) water in an amount to produce an aqueous sizing composition.
2. The glass fiber of claim 1 wherein the film former mixture is a mixture of a glycidyl methacrylate polymer and a vinyl acetate polymer.
3. The glass fiber of claim 1 wherein the adhesion promoter is a blocked 1,6-hexamethylene di-isocyanate.
4. The glass fiber of claim 1 wherein the silane coupling agent is selected from the group consisting of amino- and mercapto- functional silanes.
5. The glass fiber of claim 4 wherein the silane coupling agent is gamma-aminopropyltriethoxy silane.
6. The glass fiber of claim 1 wherein the lubricant is a polyoxyalkylene polyol.

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7. The glass fiber of claim 1 wherein the epoxy functional acrylic polymer is glycidyl methacrylate polymer and the vinyl acetate polymer is N-methylacrylamide-vinyl acetate copolymer and said polymer and copolymer are in a weight ratio of approximately 1:1 on a non-volatile basis.
8. A glass fiber having thereon the dried residue of an aqueous sizing which comprises:
- a.) from 0.5 to 20 weight percent on a non-aqueous basis of a thermoplastic compatible film former mixture of an epoxy functional acrylic polymer having an epoxy equivalent of at least 125, and a vinyl acetate copolymer containing at least 80% vinyl acetate functionality;
 - b.) from 0.5 to 10 weight percent on a non-aqueous basis of an amino functional silane coupling agent;
 - c.) from 25 to 75 weight percent on a non-aqueous basis of an emulsified polypropylene composition;
 - d.) from 0.01 to 10 weight percent on a non-aqueous basis of a polyoxyalkylene polyol lubricant;
 - e.) from 10 to 30 weight percent on a non-aqueous basis of a blocked 1,6-hexamethylene di-isocyanate; and
 - f.) water in an amount to produce an aqueous sizing composition.
9. The glass fiber of claim 8 wherein the silane coupling agent is gamma-aminopropyltriethoxy silane.
10. The glass fiber of claim 8 wherein the epoxy functional acrylic polymer and vinyl acetate

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copolymer are in a weight ratio of approximately 1:1 on a non-volatile basis.

11. A glass fiber for reinforcing chemically coupled polypropylene having thereon the dried residue of an aqueous sizing which comprises:

- a.) from 0.5 to 20 weight percent on a non-aqueous basis of a mixture of a glycidyl methacrylate polymer and an N-methylacrylamide-vinyl acetate copolymer;
- b.) from 0.5 to 10 weight percent on a non-aqueous basis of an amino-functional silane coupling agent;
- c.) from 25 to 75 weight percent on a non-aqueous basis of an emulsified polypropylene composition;
- d.) from 0.01 to 10 weight percent on a non-aqueous basis of a polyoxyalkylene polyol lubricant;
- e.) from 10 to 30 weight percent on a non-aqueous basis of an adhesion promoter which is a blocked 1,6-hexamethylene di-isocyanate, and
- f.) water in an amount to produce an aqueous sizing composition.

12. The glass fiber of claim 11 wherein the silane coupling agent is gamma-aminopropyltriethoxy silane.

13. The glass fiber of claim 11 wherein the glycidyl methacrylate polymer and the N-methylacrylamide-vinyl acetate copolymer are in a weight ratio of approximately 1:1 on a non-volatile basis.

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14. The glass fiber of claim 11 wherein the emulsified polypropylene composition is a maleic anhydride-grafted polypropylene neutralized with an organic amine and emulsified with an alkoxylated phenol.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/00353

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C03C 25/02; C08F 8/46; C08K 5/54; C08L 31/04, 37/00

US CL : 523/214; 524/262, 501, 517, 524; 428/391

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/214; 524/262, 501, 517, 524; 428/391

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,803,069 (MCWILLIAMS ET AL.) 09 APRIL 1974, See column 2, lines 14-63 and column 3, lines 27-40.	1-14
Y	US, A, 3,814,715 (NALLEY ET AL.) 04 JUNE 1974, See Abstract column 2, lines 40-65 and column 3, lines 42-76.	1-14
Y	US, A, 4,271,229 (TEMPLE) 02 JUNE 1981, See column 2, lines 33-53, column 4, lines 46-68, column 5, lines 1-37 and 45-56 and column 7, lines 8-23.	1-14
Y	US, A, 4,457,970 (DAS ET AL.) 03 JULY 1984, See column 3, line 35 to column 4, line 25, column 5, line 51 to column 6, line 6, column 7, column 9, line 45 to column 10, line 12 and column 12, lines 43-66.	1-14

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
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"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

02 MARCH 1994

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/00353

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,608,304 (ROSTHAUSER) 26 AUGUST 1986, See column 1, line 55 to column 2, lines 5, column 3, lines 14-41 and column 4, lines 4-48.	6, 8-14