

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
12 August 2010 (12.08.2010)

(10) International Publication Number
WO 2010/091135 A1

(51) International Patent Classification:
C08G 10/00 (2006.01)

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(21) International Application Number:
PCT/US2010/023129

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(22) International Filing Date:
4 February 2010 (04.02.2010)

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/150,129 5 February 2009 (05.02.2009) US

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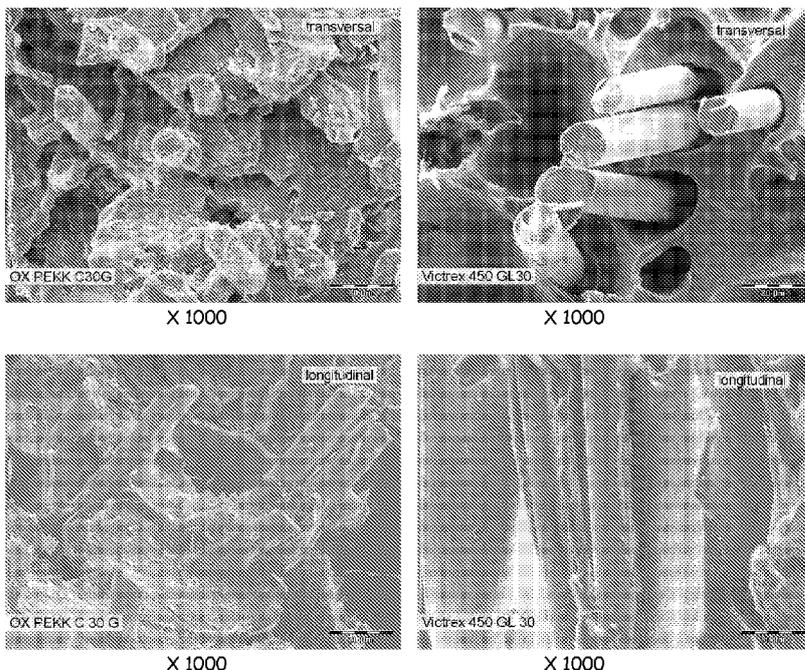
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ,

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(54) Title: FIBERS SIZED WITH POLYETHERKETONEKETONES

FIGURE 1

Cryofracturing of glass filled PEKK (left) and PEEK (right) composite samples



(57) Abstract: Fibers sized with a coating of amorphous polyetherketoneketone are useful in the preparation of reinforced polymers having improved properties, wherein the amorphous polyetherketoneketone can improve the compatibility of the fibers with the polymeric matrix.

TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, — *of inventorship (Rule 4.17(iv))*
ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, **Published:**
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, — *with international search report (Art. 21(3))*
ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

FIBERS SIZED WITH POLYETHERKETONEKETONES

FIELD OF THE INVENTION

The invention relates to fibers sized with a coating of amorphous polyetherketoneketone as well as reinforced polymers that include such sized fibers.

5 DISCUSSION OF THE RELATED ART

Various chemical treatments exist for the surfaces of fibers such as glass fibers and carbon fibers to aid in their handling, improve processability for compounding and downstream processes such as injection molding, and improve strength and other properties for specific end-use applications. Before bundling the filaments together
10 after formation, a coating composition or sizing composition is applied to at least a portion of the surface of the individual filaments to protect them from abrasion and to assist in processing. Sizing compositions may provide protection through subsequent processing steps, such as those where the fibers pass by contact points as in the winding of the fibers and strands onto a forming package, drying the aqueous-based
15 or solvent-based sizing composition to remove the water or solvent (if the sizing has been applied to the fibers using a solution), twisting from one package to a bobbin, beaming to place the yarn onto very large packages ordinarily used as the warp in a fabric, chopping in a wet or dry condition, roving into larger bundles or groups of strands, unwinding for use as a reinforcement, and other downstream processes.

20

In addition, sizing compositions can play a dual role when placed on fibers that reinforce polymeric matrices in the production of fiber-reinforced plastics. In such applications, the sizing composition provides protection and also can provide compatibility between the fiber and the matrix polymer or resin. For instance, fibers
25 in the forms of woven and nonwoven fabrics and mats, rovings and chopped strands have been used with resins, such as thermosetting and thermoplastic resins, for impregnation by, encapsulation by, or reinforcement of the resin. In such applications, it is desirable to maximize the compatibility between the surface and the polymeric resin while also improving the ease of processability and manufacturability. However,
30 many polymeric resins, especially highly crystalline engineering thermoplastics such as crystalline polyaryletherketones, do not exhibit good adhesion to various fiber

surfaces. Poor adhesion at the interface between the fiber surface and the polymeric resin matrix makes it difficult to take full advantage of the property improvements potentially realizable through incorporation of the fibers into such matrices.

5 Additionally, many of the sizing compositions that have been developed to date have unsatisfactory stability at the high processing temperatures typically required to admix fibers into engineering thermoplastics.

Accordingly, it would be desirable to develop alternative approaches to enhance the compatibility of engineering thermoplastics and the like with fibers of various types so that composites having improved properties can be obtained.

10 BRIEF SUMMARY OF THE INVENTION

The present invention provides a sized fiber comprising a fiber having a coating of amorphous polyetherketoneketone, as well as a method of making a sized fiber comprising coating a fiber with amorphous polyetherketoneketone. In another aspect, the invention provides a reinforced polymer comprising a polymer matrix and sized
15 fibers comprising fibers having a coating of amorphous polyetherketoneketone.

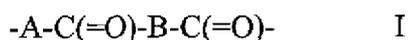
BRIEF DESCRIPTION OF THE DRAWINGS

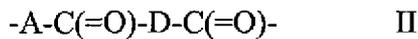
Figure 1 Shows micrographs of fibers sized with PEKK and PEEK, and demonstrates the failure mode in fibers of each sizing.

20 DETAILED DESCRIPTION OF CERTAIN EMBODIMENTS OF THE INVENTION

Sized fibers in accordance with the present invention are advantageously manufactured by coating fibers with a polymeric composition comprised of an amorphous (non-crystalline) polyetherketoneketone.

The amorphous polyetherketoneketones suitable for use in the present invention
25 comprise (and preferably consist essentially of or consist of) repeating units represented by the following Formulas I and II:





where A is a p,p'-Ph-O-Ph- group, Ph is a phenylene radical, B is p-phenylene, and D is m-phenylene. The Formula I : Formula II (T:I) isomer ratio in the polyetherketoneketone is selected so as to provide an amorphous polymer. An
5 amorphous polymer, for purposes of this invention, means a polymer that does not exhibit a crystalline melting point by differential scanning calorimetry (DSC).

Polyetherketoneketones are well-known in the art and can be prepared using any suitable polymerization technique, including the methods described in the following patents, each of which is incorporated herein by reference in its entirety for all
10 purposes: U.S. Pat. Nos. 3,065,205; 3,441,538; 3,442,857; 3,516,966; 4,704,448; 4,816,556; and 6,177,518. Mixtures of polyetherketoneketones may be employed.

In particular, the Formula I : Formula II ratio (sometimes referred to in the art as the T/I ratio) can be adjusted as desired by varying the relative amounts of the different monomers used to prepare the polyetherketoneketone. For example, a
15 polyetherketoneketone may be synthesizing by reacting a mixture of terephthaloyl chloride and isophthaloyl chloride with diphenyl ether. Increasing the amount of terephthaloyl chloride relative to the amount of isophthaloyl chloride will increase the Formula I : Formula II (T/I) ratio. Generally speaking, a polyetherketoneketone having a relatively high Formula I : Formula II ratio will be more crystalline than a
20 polyetherketoneketone having a lower Formula I : Formula II ratio. An amorphous polyetherketoneketone having a T/I ratio of from about 55:45 to about 65:35 is particularly suitable for use in the present invention.

Suitable amorphous polyetherketoneketones are available from commercial sources, such as, for example, certain of the polyetherketoneketones sold under the brand name
25 OXPEKK by Oxford Performance Materials, Enfield, Connecticut, including OXPEKK-SP polyetherketoneketone.

The polymeric composition used as a fiber sizing may additionally be comprised of components other than the amorphous polyetherketoneketone, such as stabilizers, pigments, processing aids, fillers, and the like. If the sizing is to be applied to the
30 fibers in solution form, such additional components should preferably be soluble in

the solvent or mixture of solvents employed. In certain embodiments of the invention, the polymeric composition consists essentially of or consists of amorphous polyetherketoneketone. For example, the polymeric composition may be free or essentially free of any type of polymer other than amorphous polyetherketoneketone.

5 The present invention is useful in connection with any type of fiber, but particularly fibers that are to be used as reinforcements or fillers in polymeric matrices. Suitable fibers include, for example, glass fibers, carbon fibers, polymeric fibers, metallic fibers, mineral (ceramic, inorganic) fibers and the like. Glass fibers (fiberglass) may be obtained from any type of glass, e.g., A glass, E glass, S glass, or D glass. Carbon
10 fibers (which include graphite fibers) are typically prepared by pyrolysis of organic or polymeric fibers (such as PAN). Polymeric fibers include fibers made from any of the known types of thermoplastic polymers such as polyamides, polyolefins, polyaramids, polyesters, poly(p-phenylene-2,6-benzobisoxazole)(PBO), and the like. Suitable metallic fibers include fibers prepared using any type of metal or metal alloy,
15 such as iron, steel, aluminum, aluminum alloys, copper, titanium, nickel, gold, silver and the like. Mineral fibers that can be used in the present invention are fibers made from natural or synthetic minerals, refractory oxides or metal oxides and include, but are not limited to, mineral wool, rock wool, stone wool, basalt fibers, alumina fibers, beryllia fibers, magnesia fibers, thoria fibers, zirconia fibers, silicon carbide fibers,
20 quartz fibers, boron fibers, asbestos fibers and high silica fibers and the like.

Fibers of any diameter or length may be sized with a coating of amorphous polyetherketoneketone in accordance with the present invention. For example, the fiber may be from 1 micron to 1 mm in diameter. Typically, the fiber is many times longer than its diameter. For example, the fiber length may be at least 10, 100, 1000
25 or 10,000 times the fiber diameter.

In one embodiment of the invention, the amorphous polyetherketoneketone is applied to the fiber as a sizing composition comprised of the polyetherketoneketone and a suitable solvent or mixture of solvents and the solvent or solvent mixture then removed by drying so as to deposit a relatively thin coating of the
30 polyetherketoneketone on the fiber surface. Any substance capable of dissolving the polyetherketoneketone may be utilized as the solvent, including, for example, halogenated (preferably, chlorinated) organic compounds such as o-dichlorobenzene,

1,2-dichloroethane, dichloromethane (methylene chloride), alpha-chloronaphthalene and tetrachloroethylene. Other suitable solvents may include benzophenone, diphenylsulfone, 2-phenylphenol, p-methoxyphenol, 2-methoxynaphthalene, ethyl-4-hydroxybenzoate, N-cyclohexyl-2-pyrrolidone, pentafluorophenol, dimethylphthalate, nitrobenzene and phenyl benzoate. Aqueous mineral acids (e.g., sulfuric acid and/or nitric acid) are examples of other solvents that could be used for this purpose. In one embodiment of the invention, the amorphous polyetherketoneketone is synthesized in a suitable solvent and the resulting polymerization reaction product used as the sizing composition (thereby avoiding the need to isolate the polyetherketoneketone from the polymerization reaction mixture and then redissolve it). The solvent should be selected based on its compatibility with the fibers that are to be sized in accordance with the present invention. For example, the solvent should not dissolve or degrade the fibers.

The amorphous polyetherketoneketone preferably forms a relatively thin coating on the fiber surface. For example, the polyetherketoneketone coating may be from about 1 to about 50 microns thick. In one embodiment of the invention, the fiber surfaces are completely covered by the polyetherketoneketone coating, although in other embodiments certain portions of the fiber surfaces remain uncoated. Typically, the amorphous polyetherketoneketone coating may comprise from about 0.01 to about 10 % by weight of the sized fibers.

The fiber may be in the form of individual filaments, twisted yarns, threads, strands, rovings, mats, meshes, scrim or a fabric (woven or non-woven) at the time it is sized with the amorphous polyetherketoneketone. After sizing, the fibers may be further processed (e.g., individual filaments may be sized and the sized filaments then converted into yarns, threads, strands, rovings, mats, meshes, scrim, woven fabric, non-woven fabric and the like). In one embodiment, the fiber is in continuous form (e.g., an unbroken filament, thread, strand or yarn) at the time it is sized, but then converted into discontinuous form by cutting, chopping or other such operation. The discontinuous sized fibers may, for example, be from about 0.5 to about 20 mm in length. The sized fibers may be used, in continuous or discontinuous form, in the manufacture of fiber reinforced composites.

Means for applying the sizing composition include, but are not limited to, pads, sprayers, rollers or immersion baths, which allow a substantial amount of the surfaces of the individual filaments of the fiber to be wetted with the sizing composition. The sizing composition may be applied to the fibers by dipping, spraying, roll coating, extruding, pultrusion, or the like. In one embodiment, the sizing composition is applied to the fibers continuously.

If solvent is present in the sizing composition, the solvent is removed after the sizing composition is applied to the fiber. The solvent may be removed by heating the fiber to evaporate the solvent, by allowing the solvent to evaporate at ambient temperature and pressure and/or by subjecting the fiber to vacuum. When the solvent is removed by heating, the temperature will vary depending on the types of solvent and fiber used. The solvent may be removed continuously, for example, by passing the fiber through a heater, such as a tube furnace. The time required to remove the solvent will vary depending on the temperature and the solvent, however, the time required is typically several seconds to several hours, preferably 10 to 20 seconds. If an acidic solution has been used, the fibers may be passed through water to remove residual acid (extractive dilution) or passed through a basic solution to remove and/or neutralize residual acid.

Although sized fibers in accordance with the present invention can be combined with or compounded into any type of polymeric matrix, including thermoplastic or thermosettable polymeric matrices, they are particularly useful where it is desired to provide fiber reinforcement to a polymeric matrix comprised, consisting essentially of, or consisting of a crystalline and/or high temperature thermoplastic as these materials often exhibit interfacial adhesion to various types of fiber surfaces that is not completely satisfactory. A sizing of amorphous polyetherketoneketone on the fiber in accordance with the present invention helps to improve such adhesion, thereby enhancing the mechanical and other properties of the resulting composite. Suitable crystalline and/or high temperature thermoplastics include, but are not limited to, polyaryletherketones (such as crystalline polyetherketone (PEK), crystalline polyetheretherketone (PEEK), crystalline polyetherketoneketone (PEKK), polyetheretheretherketone (PEEEK), polyetheretherketoneketone (PEEKK), polyetherketoneetheretherketone (PEKEKK), and polyetherketoneketoneketone

(PEKKK)), polyimides, polyetherimides, polyamideimides, polysulfones, polyethersulfones, polyarylethers, polycarbonates, liquid crystal polymers, polyphenylene sulfides, polyarylenes (polyphenylenes), polyamides, polyphthalamides, polyaromatic esters and the like.

- 5 In one embodiment of the invention, chopped fibers sized with amorphous polyetherketoneketone may be mixed with a polymeric resin and supplied to a compression- or injection-molding machine to be formed into fiber-reinforced composites. Typically, the chopped fibers are mixed with pellets of a thermoplastic polymer resin in an extruder. For example, polymer pellets can be fed into a first
- 10 port of a twin screw extruder and the chopped sized fibers then fed into a second port of the extruder with the melted polymer to form a fiber/resin mixture. Alternatively, the polymer pellets and chopped fibers can be dry mixed and fed together into a single screw extruder where the resin is melted and the fibers are dispersed throughout the molten resin to form a fiber/resin mixture. Next, the fiber/resin mixture is degassed
- 15 and formed into pellets. The fiber/resin pellets can then be fed to a molding machine and formed into molded composite articles that have a substantially homogeneous dispersion of fibers throughout the composite article.

The sized fibers of the present invention may also be used in long-fiber thermoplastic applications. Fiber-reinforced thermoplastic polymer structural components can be

20 manufactured from long fiber thermoplastic (LFT) granulates (pellets), glass mat thermoplastic (GMT) sheets, or pultruded sections wherein the fibers have been sized with amorphous polyetherketoneketone. Long fiber-reinforced granulates can comprise sized fiber bundles encapsulated with a thermoplastic through a cable coating or a pultrusion process. The LFT granulates, which contain fibers equal in

25 length to the pellet, e.g., 1 to 25 mm, can be injection molded, but can also be extrusion compression molded in order to preserve fiber length in the finished product.

Polymer components reinforced with sized fibers in accordance with the present invention may also be manufactured using continuous in-line extrusion methods

30 known in the art. Such methods involve the plastication of a polymer in a first single screw extruder from which the output is fed to a second single screw extruder. Fibers are introduced in the polymer melt in the second extruder, either in chopped-

segmented form or as continuous strands under a predetermined tension. The fiber-reinforced polymer is fed into an accumulator and then applied automatically or in a separate step to a compression molding tool wherein the fiber-reinforced polymer is shaped as required for a particular application. Alternatively, the fiber-reinforced polymer may be continuously extruded onto a conveyor and sectioned thereupon. The conveyor delivers the sectioned fiber-reinforced polymer to a placement assembly which removes the sectioned material from the conveyor and places the material upon the compression molding tool.

The process of compounding and molding the sized reinforcing fiber and the matrix resin to form a composite may be accomplished by any means conventionally known in the art. Such compounding and molding means include, but are not limited to, extrusion, wire coating, blow molding, compression molding, injection molding, extrusion-compression molding, extrusion-injection-compression molding, long fiber injection, and pushtrusion.

The orientation of the sized fibers within the polymeric matrix of the composite produced in accordance with the present invention may be varied and controlled as desired using the techniques known to those skilled in the field. For example, the fibers may be continuous and aligned, or discontinuous and aligned, or discontinuous and randomly oriented.

The amount of fiber included in the composite is generally about 1% to about 90% by weight, based on the total weight of the composite formulation.

The amorphous polyetherketoneketone provides a coating on the reinforcing fibers that improves compatibility and adhesion with the resin matrix, and results in composites with more desirable properties such as higher short-term and long-term mechanical properties.

Reinforced polymers prepared in accordance with the present invention may be utilized in any of the end use applications where such materials conventionally are employed or have been proposed to be employed. Representative applications include composites for aerospace/aircraft, automobiles and other vehicles, boats, machinery, heavy equipment, storage tanks, pipes, sports equipment, tools, biomedical devices

(including devices to be implanted into the human body, such as load-bearing orthopedic implants), building components, and the like. Benefits of the invention described herein include higher tensile strength, higher compressive strength, improved resistance to crack initiation and propagation, greater creep resistance, and
5 higher resistance to attack by various chemicals and solvents, as compared to reinforced polymers prepared using fibers that are not sized with amorphous polyetherketoneketone.

Fiber-reinforced composites in accordance with the present invention can, for example, be used to prepare laminar panels that are stacked and bonded to each other
10 or can be used as face sheets in the production of sandwich panels having honeycomb or foamed cores.

EXAMPLES

Example 1: Sizing a fiber from a solution – A solution of an amorphous grade of Polyetherketoneketone (A-PEKK) such as OXPEKK SP from Oxford Performance
15 materials) with a high ratio of isophthalate (T/I = 55-45 to 65-35 but most preferably 60/40) is produced by dissolving XX gm of PEKK in 100 gm of concentrated sulfuric acid. The solution is placed in a bath of suitable construction so as not to react with the strong mineral acid and a glass fiber yarn made from a group of fibers is passed through the bath so as to produce a fairly even coating of the solution. The acidic
20 solution is then neutralized or simply diluted by passage through a second bath containing a basic solution or just water. The act of neutralizing or diluting the solution thus renders the polymer insoluble and leaves a coating of the polymer on the fiber.

Example 2: Sizing the fiber by powder coating and heating – A fine powder is
25 produced from an amorphous grade of A-PEKK, as described in example 1, and used to powder coat a metal fiber. Two general methods can be employed for the powder coating. In the first, an electrostatic spray of the fine powder is applied to the fiber just prior to the fiber entering an oven heated to a temperature such that the A-PEKK melts (c.a 320°C) and forms a generally continuous coating on the fiber. Alternatively
30 the fiber can be heated prior to entering a fluidized bath containing the fine A-PEKK powder. More details on specific powder coating methods can be found in references such as: Powder Coating. The Complete Finisher's Handbook, 1997, Powder Coating

Inst., ISBN: 0964309106 or Organic Coatings: Science and Technology (Society of
Plastics Engineers Monographs) (Vol 2), Z.W. Wicks Jr, Frank N. Jones and S. P.
Pappas (Authors). For the application described here there is no need for an
impermeable A-PEKK coating but rather only a reasonably complete layer of A-
5 PEKK needs to be applied.

Example 3: Sizing Woven Mats - Complete woven, or otherwise formed mats of
metal or glass strands can be sized after production by passing the preformed mat or
cloth through the solution described in example 1 or by powder coating as described
in example 2.

10 Example 4: Incorporation of the A-PEKK sized fibers into a matrix – The A-PEKK
sized fibers can be incorporated into an article by any manner of polymer processing.
Chopped fiber is routinely incorporated by compounding the fiber into a polymer
using a twin screw extruder and continuous fiber incorporation can be accomplished
by pultrusion etc. As the A-PEKK sizing is compatible with a variety of other high
15 temperature polymer matrices and PEKK has very good adhesion properties the A-
PEKK sizing can diffuse into the matrix promoting incorporation or dispersion of the
fibers within the matrix polymer and improve the adhesion of the fibers to the matrix.
The pictures of Figure 1 illustrate the adhesion developed by PEKK to a glass fiber
vs. that developed by another high temperature polymer, in this case
20 polyetheretherketone PEEK. As the picture illustrates the failure in the PEKK
composite is cohesive as the failure is in the PEKK matrix. The fracture surface in this
case shows significant ductility produced as a consequence of the effective load
transfer between the fiber and the PEKK matrix. In contrast, the failure in the PEEK
system is adhesive as the fibers are cleanly pulled from the matrix. The fractured
25 surface shows a clean brittle rupture process, indicating that in this case the
interaction of the fiber with the matrix is not as effective. Load transfer is not
expected to be efficient in this system. The energy of breaking a piece by cohesive
failure is dependant on the strength of the matrix itself and is generally regarded as
higher than an adhesive failure.

What is claimed is:

1. A sized fiber comprising a fiber having a coating of amorphous polyetherketoneketone.
2. The sized fiber of Claim 1, wherein said fiber is a monofilament.
3. The sized fiber of Claim 1, wherein said fiber is a multifilament.
4. The sized fiber of Claim 1, wherein said fiber has a diameter of about 50 microns to about 1 mm.
5. The sized fiber of Claim 1, wherein said fiber is selected from the group consisting of glass fibers, carbon fibers, mineral fibers, metal fibers and polymeric fibers.
6. The sized fiber of Claim 1, wherein said coating has a thickness of from about 1 to about 50 microns.
7. The sized fiber of Claim 1, wherein the amorphous polyetherketoneketone has a T:I ratio of from about 55:45 to about 65:35.
8. The sized fiber of Claim 1, wherein the amorphous polyetherketoneketone comprises repeating units represented by Formulas I and II:

$$\text{-A-C(=O)-B-C(=O)-} \quad \text{I}$$

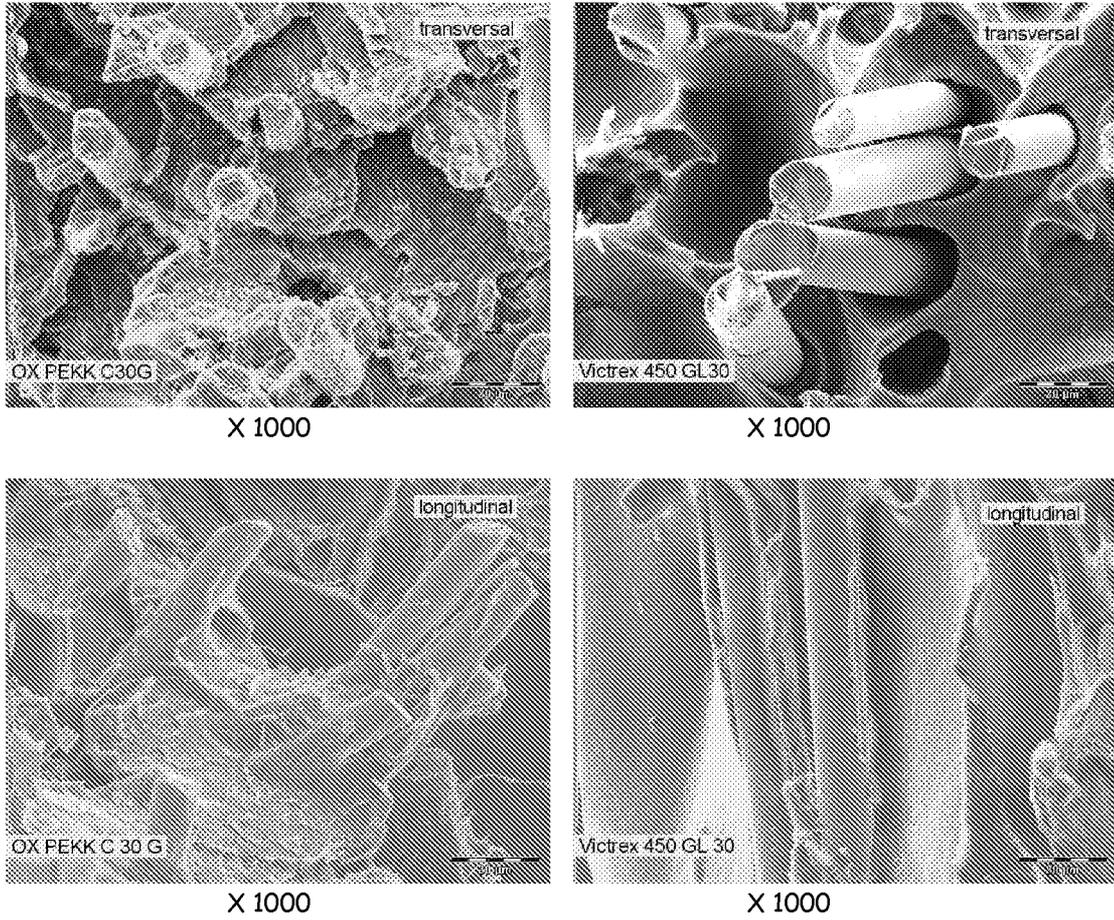
$$\text{-A-C(=O)-D-C(=O)-} \quad \text{II}$$

where A is a p,p'-Ph-O-Ph- group, Ph is a phenylene radical, B is p-phenylene, and D is m-phenylene.
9. A reinforced polymer comprising a polymer matrix and sized fibers comprising fibers having a coating of amorphous polyetherketoneketone.
10. The reinforced polymer of Claim 9, wherein said polymer matrix is comprised of a crystalline and/or high temperature thermoplastic.

11. The reinforced polymer of Claim 9, wherein said polymer matrix is comprised of a crystalline poly(aryletherketone).
12. A method of making a sized fiber, said method comprising coating a fiber with amorphous polyetherketoneketone.
13. The method of Claim 12, wherein a sizing composition comprised of amorphous polyetherketoneketone and a solvent is applied to the surface of the fiber and the solvent is removed by drying.
14. The method of Claim 12, wherein a sizing composition comprised of amorphous polyetherketoneketone and acid is applied to the surface of the fiber and the acid is removed by extractive dilution and/or neutralized.
15. A method of making a reinforced polymer, said method comprising combining a polymer with sized fibers comprising fibers coated with amorphous polyetherketoneketone.

FIGURE 1

Cryrofracturing of glass filled PEKK (left) and PEEK (right) composite samples



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/23129

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08G 10/00 (2010.01)

USPC - 528/125; 525/391

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)
USPC - 528/125; 525/391Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 442/3,19,43,46,58,59,60,101,104,107,109,108,110,117,118,126,148; 528/125; 525/391 (text search - see search terms below)Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST (PGPB,USPT,OC,EPAB,JPAB); DialogPro (General Research); Google Patents
size, coat, fiber, amorphous, random, peek, pekk, filament, diameter, micron, glass, carbon, mineral, metal, polymer, thick, T.I, ratio, formula, reinforced, matrix, crystalline, thermoplastic, aryl, solvent, dry, remove, extract, dilute, acid, neutralize

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,409,757 A (MUZZY et al.) 25 April 1995 (25.04.1995), abstract, col 1, ln 20-31, col 6, ln 30-46, col 8, ln 18-64, col 10, ln 16-38, col 14, ln 10 - col 15, ln 13 and claim 5.	1-15
Y	US 5,238,725 A (EFFING et al.) 24 August 1993 (24.08.1993), col 1, ln 5-10, col 1, ln 50-60, col 3, ln 11-15, col 4, ln 16-56.	1-15
Y	US 5,260,104 A (BRYANT et al.) 09 November 1993 (09.11.1993), abstract, col 1, ln 5-10, col 3, ln 27-66.	2 and 4
Y	US 5,049,340 A (MOSS et al.) 17 September 1991 (17.09.1991), abstract, col 1, ln 6-10, col 2, ln 1-40, col 4, ln 54 - col 5, ln 26.	6-8
Y	US 4,891,084 A (SENIOR) 02 January 1990 (02.01.1990), col 1, ln 46 - col 2, ln 10, col 4, ln 61 - col 5, ln 35, col 5, ln 66 - col 6, ln 6.	10, 11 and 15
Y	US 4,992,485 A (KOO et al.) 12 February 1991 (12.02.1991), eabstract, col 1, ln 5-15 and col 4, ln 1-47.	14
A	US 4,816,556 A (GAY et al.) 28 March 1989 (28.03.1989), entire document.	5-8
A	US 2008/0312387 A1 (EL-HIBRI et al.) 18 December 2008 (18.12.2008), abstract, para [0018]-[0021], [0133]-[0135], [0139], [0250], [0263]-[0267], [0275]-[0278].	11
A	US 5,034,157 A (MERRELL et al.) 23 July 1991 (23.07.1991), entire document (teaches polyether ketone coatings as fiber/fabric sizings).	1-15

 Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

15 March 2010 (15.03.2010)

Date of mailing of the international search report

24 MAR 2010

Name and mailing address of the ISA/US

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/23129

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,666,612 A (Angelo) 30 May 1972 (30.05.1972), entire document.	1-15