COMPOSITE MATERIAL OF CONTINUOUS FIBER AND ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE

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ABSTRACT
A composite material composed of continuous high strength fibers such as carbon, aramid or glass, and ultra high molecular weight polyethylene (UHMW PE), wherein the UHMW PE comprises a continuous matrix among and surrounding the fibers. The resultant composite material exhibits extraordinarily high strength, stiffness and other fiber dominated properties in the directions parallel to the fibers and exhibits its lowest strength and stiffness in directions perpendicular to the fibers. It also exhibits superb abrasion resistance, good impact strength, excellent chemical resistance, a low coefficient of friction and other beneficial properties of UHMW PE.
Tensile Strength (psi)  14,500  32,625
Flexural Modulus (psi) 580,000  2,784,000
Izod Impact Strength - 1.12  1.10
0.01 in. notch (ft. lb./in.)

PRIOR ART

FIG. 1
<table>
<thead>
<tr>
<th></th>
<th>APC-2 in fiber direction</th>
<th>APC-2 perpendicular to fibers</th>
<th>PEEK (unreinforced)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (psi)</td>
<td>300,000</td>
<td>12,500</td>
<td>14,500</td>
</tr>
<tr>
<td>Flexural Modulus (psi)</td>
<td>18,100,000</td>
<td>1,290,000</td>
<td>580,000</td>
</tr>
</tbody>
</table>

**PRIOR ART**

**FIG. 2**
GUR 2126 UHMW PE *
(Unreinforced)

Tensile Yield Strength (psi) 2,466
(ISO 527)

Tensile Modulus (psi) 114,000
(ISO 527)

Coefficient of Friction () 0.2

Charpy Impact Strength (ft. lb./ft²) >8,230
(with 14° V-notch both sides)
(ISO DIS11542, part 2)

Abrasion Resistance 100
(sand slurry test)

Electrical Volume Resistivity (Ohm ft.) >3.3x10¹²
(IEC 6093)

Thermal Conductivity (BTU in./hr. ft² °F) 2.84

Coefficient, Thermal Expansion (in/in.°F) 1.1 x10⁻⁴
(ISO 11359, part 2)

FIG. 3
COMPOSITE MATERIAL OF CONTINUOUS FIBER AND ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE

CROSS REFERENCE TO RELATED APPLICATIONS


FIELD OF THE INVENTION

[0002] This invention relates generally to the art of composite materials, more particularly to composite materials comprising thermoplastics and high strength fibers.

BACKGROUND OF THE INVENTION

[0003] Thermoplastics are plastics that are made by heating resin pellets or powders (the raw material) until they melt, molding the material to a desired shape, and then resolidifying the material through a cooling process. Because the chemistry of the plastic does not change, this process can be performed multiple times. In other words, thermoplastics can be reprocessed or recycled with additional heating and cooling. Additionally, the manufacturing process for thermoplastic products can be as quick as the heating, molding, and cooling processes can occur (e.g., seconds). Hence thermoplastics have the manufacturing advantages of rapid processing and multi-step manufacturing, both of which can translate and have translated to significant benefits and cost savings.

[0004] Some common thermoplastics are polyethylene “PE”, polypropylene “PP”, polyamide “PA” (more commonly known as nylon) and polyethylene terephthalate “PET” (more commonly known as polyester). Products made from such thermoplastics are very diverse, for example, toys, rope, clothing and bottles. Melt temperatures for most thermoplastics fall between 125° C. and 300° C. In their softened or partially melted state thermoplastics flow under pressure and thus can be shaped by processes such as injection molding, blow molding and extrusion.

[0005] Thermoplastics have many excellent qualities. Metals, however, generally have much higher strength and stiffness than thermoplastics. To increase the strength and/or stiffness of thermoplastics it has long been known that mixing thermoplastic resins with short high strength fibers results in a product with substantially increased strength and/or stiffness. Often higher temperature properties are also improved. This mixing is done either before melting the thermoplastic resin or as the thermoplastic resin is melted but in either case before forming the product by extrusion or injection molding, as disclosed for example in U.S. Pat. No. 3,577,378. Types of fiber commonly used for this purpose may be glass, carbon, aramid or other materials which have suitably high strength and/or stiffness and melt temperatures above the thermoplastic of choice.

[0006] These materials are sometimes referred to as short fiber composites or more commonly fiber reinforced plastics “FRP”. Such FRP materials typically comprise 10 to 30 percent fiber by weight with the balance being the thermoplastic of choice. The fibers are typically 0.1 to 5 mm in length. The use of higher percentages of fiber and/or longer fibers is typically avoided because of difficulties achieving good flow of the mixture and good uniform dispersion and distribution of the fibers, unacceptable accumulation of the fibers in the nozzle of the injection molding equipment, and unacceptable reduction in toughness and impact strength in the product.

[0007] Typically with the short fibers from 0.1 to 5 mm in length, FRP thermoplastics have tensile and/or flexural strength and stiffness up to 5 times greater than the same thermoplastic without the reinforcing fibers.

[0008] U.S. Pat. No. 3,577,378 teaches that the added tensile and flexural strength and stiffness is due to the high strength and stiffness of the fibers coupled with the excellent mixing and distribution of the fibers in the polymer and the ease with which the molten FRP material flows in the extruder and injection mold. There is possibly, however, a characteristic loss of impact strength in the short fiber FRP product compared with the unreinforced thermoplastic product as reported with respect to polycarbonate in U.S. Pat. No. 3,577,378.

[0009] A more current example of the enhanced strength and stiffness properties of FRP comes from Victrex plc, headquartered at Hillhouse International in Lancashire, UK. Victrex is the world’s largest producer of certain high performance high temperature engineered thermoplastics, in particular polyetheretherketone (PEEK). Published Victrex data for unreinforced “150G” PEEK and 30% short carbon fiber reinforced “150CA30” PEEK is indicative of the difference in properties that successful introduction of short fibers can produce, as illustrated in FIG. 1. This data is excerpted from Victrex USA Inc. publication 1100/2.5m titled PEEK Material Properties Guide. Both materials are suitable for extrusion and injection molding.

[0010] Engineers and designers, however, continue to seek materials which have strength and stiffness that exceed conventional FRP short fiber thermoplastics and that also have strength to weight and stiffness to weight ratios that are higher than those of metals. In the past twenty five years several processes have been invented wherein thermoplastic composites have been produced with continuous fibers and with fiber content as high as 70%. These materials generally have much higher strength and/or stiffness than short fiber FRP materials. In fact these composites exhibit strength and/or stiffness comparable and in many cases superior to metals, including steel. Also, generally, the density of these materials is much lower than metals. Hence their strength to weight and stiffness to weight ratios are much higher than metals, including steel. U.S. Pat. No. 4,680,224 discloses a preferred method for producing such continuous fiber thermoplastic composites.

[0011] This APC-2 thermoplastic composite manufactured by Cytec Engineering Materials, a division of Cytec, Inc. It is made with continuous unidirectional AS4 carbon fiber and PEEK thermoplastic resin. For illustration of the enhanced strength of these continuous fiber composite thermoplastics, FIG. 2 depicts selected mechanical properties at room temperature of APC-2. The fiber content in this composite is 68% by weight. Note the enhanced properties in the fiber direction as compared to the unreinforced PEEK and the FRP short fiber PEEK properties listed in FIG. 2. The
strength in the fiber direction is 9 times greater than the 150CA30 short fiber PEEK FRP and more than 20 time greater than the unreinforced 150 PEEK. The strength and stiffness perpendicular to the fibers is however, much lower. The tensile strength perpendicular to the fibers is approximately the same as the unreinforced resin while the stiffness perpendicular to the fibers is about double the unreinforced resin.

[0012] These values clearly demonstrate both the tremendous strength and stiffness of continuous fiber thermoplastic composites and the influence of fiber direction at the same time. This directional or non-isotropic nature of continuous fiber composites allows the designer much greater freedom to create optimized designs when compared to most conventional plastics and metals which have more or less isotropic or non directional properties. If the designer is desirous of more isotropic properties in the thermoplastic composite, any number of layers of this material having fibers in various directions may be combined under heat and pressure to form a more isotropic material. Most often multiples of 4 layers are used with -45°, 0°, 45°, 90° fiber orientations to produce what are termed “quasi-isotropic” material properties.

[0013] Advanced Materials engineers finally discovered how to manufacture more complex thermoplastic composites with difficult plastics. The initial process consisted of adding chemical solvents to the heated thermoplastic resin, to make the resin sufficient wetly to saturate a mass of fibers. Although this solvent had to be removed later in the process, composite manufacturers could now produce a thermoplastic composite with a relatively even distribution of plastic matrix to hold the fibers in place.

[0014] Such methods of producing short fiber reinforced thermoplastics as described above are widely practiced today with virtually all thermoplastics, but not with UHMW PE. However, is UHMW PE has a linear polyethylene structure just like high density polyethylene but its molecules are exceptionally large, having a molecular weight of from 2 to 6 million daltons. This high molecular weight provides UHMW PE with exceptional impact strength and abrasion resistance; however, it also results in special well known processing characteristics which preclude use of standard extrusion and molding techniques. In short, UHMW PE does not “flow” at high temperature as do virtually all other thermoplastics. In fact, when attempting to inject mold UHMW PE, the extreme pressures result in shear-degradation of the polymer.

[0015] Because of UHMW PE’s unusual behavior, the processes used to make UHMW PE stock materials (plate, sheet and bar being the most common forms of UHMW PE) are most akin to compression molding or sintering. The typical procedure is to fill a form or mold with UHMW PE in powder form and then apply heat and pressure to remove the air between the particles and to force the particles to soften and deform and fuse into a single mass. This ideally results in an essentially void free solid although microscopic porosity will still exist. In some special cases a lower pressure is used specifically to produce a porous structure. This porous solid form of UHMW PE is sometimes used for filtration. These processes do not require the UHMW PE to flow.

[0016] Desiring reinforced products of UHMW PE, many individuals have sought ways to successfully add short fibers to UHMW PE. U.S. Pat. Nos. 4,055,862, 5,622,767 and 5,620,770 disclose successful methods for making such “FRP” materials with UHMW PE and carbon fibers without requiring the UHMW PE or the fibers to flow wherein the carbon fibers may be up to 8 mm long. These patents disclose methods that are essentially the same as the method described above for making reinforced UHMW PE materials. In these “compression molding like” or “sintering like” methods the short carbon fibers are mechanically mixed with the particles of UHMW PE powder prior to introducing the mixture to the form or mold, and prior to melting the UHMW PE.

SUMMARY OF THE INVENTION

[0017] In one embodiment of the invention, the invention relates to composite material of continuous fibers and ultra high molecular weight polyethylene, the composite material comprising ultra high molecular weight polyethylene, and continuous high strength fibers, wherein the ultra high molecular weight polyethylene forms a continuous matrix among and surrounding the fibers.

[0018] In another embodiment of the invention, the invention relates to a composite material of continuous fibers and ultra high molecular weight polyethylene, the composite comprising ultra high molecular weight polyethylene; continuous high strength fibers, wherein the ultra high molecular weight polyethylene forms a continuous matrix among and surrounding the fibers; and at least one additive or filler.

[0019] The invention also relates to a method of manufacturing an ultra high molecular weight polyethylene composite, the method comprising selecting unidirectional and continuous high strength fibers; impregnating the fibers with ultra high molecular weight polyethylene in a fine powder to form a composite; optionally adding additives or fibers to the composite; and forming a continuous matrix of the ultra high molecular weight polyethylene surrounding the fibers.

[0020] The techniques described above, however, until the present invention, did not particularly work well with UHMW plastics. It is an object of the invention to provide a composite material of continuous fiber and ultra high molecular weight polyethylene (UHMW PE) exhibits many improved physical properties in comparison to both unreinforced and short fiber reinforced UHMW PE. Another object of the invention is to improve strength and stiffness in the fiber direction as well as thermal and electrical conductivity when a highly conductive fiber is employed. It is yet another object of the invention to provide a composite that exhibits many of the outstanding characteristics of unreinforced UHMW PE, such as excellent abrasion resistance, low coefficient of friction and high PV.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] FIG. 1 is a data table listing the properties of the prior art composites, as presented by Victrex USA Inc.

[0022] FIG. 2 is a data table listing the properties of the prior art unreinforced and reinforced composites, as manufactured by Cytec Engineering Materials.

[0023] FIG. 3 is a data table listing the properties of the prior art unreinforced composite, as manufactured by Ticona Engineering Polymers.
DESCRIPTION OF THE PREFERRED EMBODIMENT

[0024] As required, detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention, which may be embodied in various forms. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the present invention in virtually any appropriately detailed structure.

[0025] Production of a continuous fiber UHMW PE composite is expected to exhibit very high strength and stiffness, excellent toughness, exceptional abrasion resistance, excellent chemical resistance, a low coefficient of friction and high bearing (PV) capacity. Continuous fibers are well known in the art as fibers extending to a length of several feet or meters that maintain its structural strength continuously throughout the fiber when the fiber is stretched. Depending on the fiber chosen, the composite could also be highly conductive or highly resistive, both electrically and thermally, or able to absorb great amounts of energy at high speed impact. To be successful in fashioning such a composite, one would have to overcome the same peculiar properties of UHMW PE that render the extrusion and injection molding of both un reinforced and short fiber reinforced UHMW PE problematic.

[0026] In particular, all known methods of making continuous fiber thermoplastics require flow under pressure such as through film stacking methods as practiced by Ten Cate and Bond Laminates or pultrusion type methods practiced by others, including the pultrusion type method disclosed in U.S. Pat. No. 4,680,224.

[0027] In this invention, a slurry of UHMW PE powder, such as GUR 2126 made by Ticona Engineering Polymers, a division of the Celanese Corporation, having a molecular weight of approximately 2,500,000 daltons, and water is impregnated into a web of unidirectional fibers, such as AS4C carbon fibers made by Hexcel. FIG. 3 depicts selected physical properties of unreinforced GUR 2126 UHMW PE, as published by Ticona. The web impregnated with UHMW PE powder and water is then passed through a dryer to remove the water. The web impregnated with loose dry UHMW PE powder is heated and tensioned in such a way as to cause the UHMW PE to melt and fuse into a solid band under essentially no external pressure greater than atmospheric pressure. The solid band then is then pulled through a heated die to reform it into the desired cross sectional shape. This method requires no flow of the UHMW PE under high pressure and therefore the UHMW PE is not degraded by shearing.

[0028] The resultant continuous fiber UHMW PE composite produced using this method may be made in almost any cross sectional shape such as flat ribbon, sheet, flat bar, round, square, triangle, channel, angle, I-beam, etc. The composite of the chosen cross sectional shape may then be cut into lengths or coiled for shipment and/or further fabrication depending on its shape, thickness, stiffness, customer preference or other considerations.

[0029] In the process described above, the impregnation of the web of fibers with a slurry of UHMW PE powder and water may be replaced by impregnation of the web with dry UHMW PE powder in a fluidized bed. Using the fluidized bed, the dryer is unnecessary. The fluid in the fluidized bed may be any suitable gas, such as air.

[0030] Fabrication techniques well known to those skilled in the art of continuous fiber thermoplastic composites may be used to make subsequent forms of the materials, parts or structures, such as slitting, pelletizing, weaving, laminating, tape placement, thermoforming, table rolling, compression molding, bladder molding, machining, ultrasonic welding, etc. for any number of end use products.

[0031] In other embodiments of the invention, the continuous unidirectional fibers may be replaced by woven continuous fibers or randomly oriented continuous fibers, for example a felt or matted fabric of random fibers.

[0032] It should be noted that the strength and stiffness of the reinforced UHMW PE in the fiber direction are dramatically higher than the unreinforced UHMW PE, as are the thermal and electrical conductivity. The PV (sliding bearing capacity) of the reinforced UHMW PE is also significantly improved with the continuous fiber as is thermal expansion. The composite maintains the low coefficient of friction and the exceptional abrasion resistance of UHMW PE. The only loss of property of the composite relative to the unreinforced UHMW PE is in impact strength. This is typical of virtually all fiber reinforced thermoplastics; however the impact strength of reinforced UHMW PE is significantly higher than most other fiber reinforced thermoplastics.

[0033] It will be readily apparent to those skilled in the art that various changes and modifications of an obvious nature may be made, and all such changes and modifications are considered to fall within the scope of the appended claims. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims and their equivalents.

What is claimed is:

1. A composite material of continuous fibers and ultra high molecular weight polyethylene, the composite material comprising:
   (a) ultra high molecular weight polyethylene; and
   (b) continuous high strength fibers, wherein the ultra high molecular weight polyethylene forms a continuous matrix among and surrounding the fibers.

2. The composite material of claim 1, wherein the molecular weight of the ultra high molecular weight polyethylene is greater than 2,000,000 daltons.

3. The composite material of claim 1, wherein the high strength fibers comprise carbon, glass, aramid, boron, basalt, and steel.

4. The composite material of claim 1, wherein the high strength fibers may be unidirectional continuous fibers.

5. The composite material of claim 1, wherein the high strength fibers may be woven continuous fibers.

6. The composite material of claim 1, wherein the high strength fibers may be randomly oriented continuous fibers.
7. A composite material of continuous fibers and ultra high molecular weight polyethylene, the composite material comprising:
   (a) ultra high molecular weight polyethylene;
   (b) continuous high strength fibers, wherein the ultra high molecular weight polyethylene forms a continuous matrix among and surrounding the fibers; and
   (c) at least one additive or filler.
8. The composite material of claim 7, wherein the molecular weight of the ultra high molecular weight polyethylene is greater than 2,000,000 daltons.
9. The composite material of claim 7, wherein the high strength fibers comprise carbon, glass, aramid, boron, basalt, and steel.
10. The composite material of claim 7, wherein the high strength fibers may be woven continuous fibers.
11. The composite material of claim 7, wherein the high strength fibers may be unidirectional continuous fibers.
12. The composite material of claim 7, wherein the high strength fibers may be randomly oriented continuous fibers.
13. The composite material of claim 7, wherein the additive or filler comprises other polymers.
14. The composite material of claim 7, wherein the additive or filler comprises heat stabilizers.
15. A method of manufacturing an ultra high molecular weight polyethylene composite, the method comprising:
   (a) selecting unidirectional and continuous high strength fibers;
   (b) impregnating the fibers with ultra high molecular weight polyethylene in a fine powder to form a composite;
   (c) optionally adding additives or fibers to the composite; and
   (d) forming a continuous matrix of the ultra high molecular weight polyethylene surrounding the fibers.
16. The method of claim 15, wherein the molecular weight of the ultra high molecular weight polyethylene is greater than 2,000,000.
17. The method of claim 15, wherein the high strength fibers comprise carbon, glass, aramid, boron, basalt, and steel.
18. The method of claim 15, wherein the high strength fibers may be woven continuous fibers.
19. The method of claim 15, wherein the high strength fibers may be randomly oriented continuous fibers.
20. The method of claim 15, wherein the additive or filler comprises other polymers.
21. The method of claim 15, wherein the additive or filler comprises heat stabilizers.