United States Patent

McMahon et al.

[54] PROCESS FOR PREPARING COMPOSITE ARTICLES FROM COMPOSITE FIBER BLENDS

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[58] Field of Search ............... 264/136, 29.2, 103, 264/324, DIG. 75, 257; 57/908, 350, 351; 425/112

[56] References Cited

U.S. PATENT DOCUMENTS

2,964,900 12/1960 Hicks ........................................ 47/140
3,073,005 1/1963 Tiede ........................................ 28/32
3,175,331 3/1965 Bloch ........................................ 57/157
3,252,484 5/1966 Meyer ........................................ 139/426
3,358,436 12/1967 Niina et al. .............................. 57/162
3,436,797 4/1969 Graf et al. ................................. 264/121
3,619,448 11/1971 Palfreyman et al. ...................... 264/103
3,873,289 4/1975 Daniels ...................................... 156/181
3,978,267 8/1976 Selwood .................................... 428/360
4,021,660 10/1977 Griset, Jr. ................................ 57/140
4,084,399 4/1978 Kanemaru et al. ........................... 57/140 C
4,159,618 7/1980 Sokaris ...................................... 57/251

FOREIGN PATENT DOCUMENTS

894875 11/1982 Belgium ........................................
0033244 1/1981 European Pat. Off. ...........................
7901172 1/1979 France ....................................... 264/29.2
47-3861 2/1972 Japan ........................................
41-85356 1/1973 Japan ......................................
51-10871 1/1976 Japan ...................................... 264/29.2
1238573 4/1971 United Kingdom ...........................
2093768 2/1982 United Kingdom ...........................
2090882 7/1982 United Kingdom ...........................
2102487 3/1983 United Kingdom ...........................

OTHER PUBLICATIONS

CSA Slater, Research Disclosure 20239, 2/81.

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ABSTRACT

A composite article is prepared by forming a continuous tow of continuous carbon fibers, forming a continuous tow of thermoplastic polymer fibers, uniformly and continuously spreading the thermoplastic polymer fibers to a selected width, uniformly and continuously spreading the carbon fiber tow to a width that is essentially the same as the selected width for the thermoplastic polymer fiber tow, intermixing the tows intimately, uniformly and continuously, in a relatively tension-free state, continuously withdrawing the intermixed tow and applying the tow to a mold and heating the tow.

23 Claims, 2 Drawing Sheets
ARTICLES FROM COMPOSITE FIBER BLENDS

This invention was made with government support under contract No. NAS1-15749 awarded by the National Aeronautics and Space Administration (NASA). The Government has certain rights in this invention.

This is a continuation of co-pending application Ser. No. 06/589,823 filed on Mar. 15, 1984, now abandoned.

The preparation of thermosetting materials from composite fiber blends which are useful in preparing composite articles is well known in the art. In general, the process involves the impregnation of a fabric with a solution and/or low viscosity melt of a thermosetting material which was then cured. The second process involved the extrusion of carbon fiber tapes impregnated with high melting, thermoplastic polymers. These tapes or fabrics were then used in forming the composite. However, the prepregs formed by both of these processes were somewhat difficult to handle. Specifically, prior art thermoplastic tapes were stiff and "boardy" and could not be draped across intricately shaped molds. While thermoset prepregs were somewhat more flexible, they were often quite tacky and difficult to handle. As a result, the use of both types of tapes was limited.

Accordingly, it is an object of this invention to prepare fibrous blends which are useful in forming thermoplastic carbon fiber composites.

It is another object of this invention to prepare materials, e.g., fabrics, which may be formed into fiber composites.

These and other objectives are obtained by employing the process of the instant invention.

SUMMARY OF INVENTION

Basically, the process of this invention involves (a) forming a carbon fiber tow from a multitude of carbon fibers; (b) forming a thermoplastic polymeric fiber tow; (c) intermixing the two tows; and (d) withdrawing the intermixed tow for use. The intermixed tows may then be employed in forming various carbon fiber-containing composites.

The fiber blends prepared according to the instant invention are flexible and handleable and have good draping properties, so that they can be used to form intricately shaped articles. In addition, because of the intermixing of the two fibers, good wetting of the carbon fiber by the thermoplastic material is obtained when appropriate heat and pressure are applied to the mold. Good wetting is obtained in large measure because of the substantially uniform distribution of the thermoplastic fiber and the carbon fiber within the fiber blend. Specifically, the products of the instant invention find particular utility in end use applications where a small radius of curvature in the final product is desired. For example, using the prior art tapes, it was not possible in many instances to prepare articles which had 90° bend, because the tapes would crack or deform at the bend line. However, the processes of the instant invention may be employed with radii of curvature as low as 0.002 in.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagramatic view of the various devices used in carrying out one of the processes of the instant invention.

FIG. 2 is a diagramatic view of the various devices used in carrying out another version of the processes of the instant invention.

FIG. 3 is a perspective view of the gas spreading means used in carrying out a part of the the process of the instant invention.

FIG. 4 is a perspective view of the same device with the top removed.

DETAILED DESCRIPTION OF INVENTION

The thermoplastic polymers which are useful in carrying out the instant invention constitute virtually any type of relatively high molecular weight thermoplastic polymer, including polyethylene, polypropylene, polyester, the various polyamides, polyimides, polyamide-
ring systems in which the individual rings are joined by equimolar amounts; R1, R2 wherein units I and I1, if present, are present in substantial amounts. Higher melting temperatures insure that there will be no undue sticking or binding of the spun fibers prior to use. In addition to one component polymer systems, mixtures of various thermoplastic polymers may also be employed to advantage where specific combinations of properties are desired.

Of particular importance are the liquid crystal polymers or LCPs. Examples of these polymers include the wholly aromatic polyester resins which are discussed in the following publications: (a) *Polyesters of Hydroxybenzoic Acids*, by Russell Gilkey and John R. Caldwel, J. of Applied Polymer Sci., Vol. II, Pages 198 to 202 (1959), (b) *Polyarylates (Polyesters From Aromatic Dicarboxylic Acids and Bisphenols)*, by G. Bier, Polymer, Vol. 15, Pages 527 to 535 (August 1974), (c) *Aromatic Polyester Plastics*, by S. G. Cottis, Modern Plastics, Pages 62 to 63 (July 1975); and (d) *Poly-Oxybenzoyl Systems: Homopolymer and Copolymer Systems for Compression and Injection Molding*, by Roger S. Storm and Steven G. Cottis, Coatings Plast. Preprint, Vol. 34, No. 1, Pages 194 to 197 (April 1974). See also, U.S. Pat. Nos. 3,039,994; 3,169,121; 3,221,437; 3,553,167; 3,637,595; 3,651,014; 3,723,388; 3,759,870; 3,767,621; 3,778,410; 3,787,370; 3,790,528; 3,829,406; 3,890,256; and 3,975,487.

Other polyesters are disclosed, for instance, (a) Polyester X7G-A Self Reinforced Thermoplastic, by W. J. Jackson, Jr., H. F. Kuhfuss, and T. F. Gray, Jr., 30th Anniversary Technical Conference, 1975 Reinforced Plastics/Composites Institute, The Society of the Plastics Industry, Inc., Section 17-D, Pages 1 to 4, (b) Belgian Pat. Nos. 838,935 and 828,936, (c) Japanese Pat. Nos. 3,975,487; 3,787,370; 3,790,528; 3,829,406; 3,890,256; and 3,975,487. The foregoing ring systems, except for R2, as indicated below are also intended to include one or more substituents, e.g., chloro, bromo, fluoro, or lower alkyl (1-4 carbon atoms) on the ring or rings. The R2 aromatic ring systems should preferably be unsubstituted because of thermal or hydrolytic instability and/or cost of the R2 ring-substituting polymers. Preferred group (2) radicals are two-ring systems. Illustrative of (1) are

The polyesters and copolyesters which are preferred contain essentially of structural units having recurring groups of the formula

\[ +O-R_1-O+ \] and

\[ +OC-R_2-CO+ \] or

\[ +O-R_3-CO+ \]

wherein units I and II, if present, are present in substantially equimolar amounts; R1, R2 and R3 are radicals selected from the group of (1) single and fused six-membered aromatic carbocyclic rings wherein the chain-extending bonds of the ring system if attached to the same ring, are positioned 1,3- or 1,4- (preferably 1,4-) to each other, and if attached to different rings, are preferably in positions parallel and oppositely directed, and (2) multiple six-membered aromatic carbocyclic ring systems in which the individual rings are joined by a chemical bond or a trans-vinylene group and in which the chain extending bonds of each ring are in the 1,3- or 1,4- (preferably 1,4-) positions; R2 may also be

\[ \text{or} \]

wherein A is a divalent radical containing one or two bicyclic in-chain atoms; and R3 may also be

\[ \text{and of (2) are} \]

\[ \text{and} \]

The following ring systems, except for R2, are intended to include one or more substituents, e.g., chloro, bromo, fluoro, or lower alkyl (1-4 carbon atoms) on the ring or rings. The R2 aromatic ring systems should preferably be unsubstituted when only one kind of unit I and one kind of unit II are used, i.e., when a homopolymer is formed to insure obtaining oriented fibers. In the case of copolymers, it is preferred that the R2 aromatic ring systems be unsubstituted because of thermal or hydrolytic instability and/or cost of the R2-ring-substituting copolymer.

Also included are those (co)polymers wherein up to 25 mol %, preferably up to 5 mol %, based on the total I, II and III units, are aromatic polymer-forming units (i.e., units wherein the chain extending functional groups are attached to aromatic rings) not conforming to those described above and which do not interfere with the anisotropic melt forming capability of the polymers. A non-limiting list of these units includes
The (co)polyesters, as mentioned above, may comprise units I and II in substantially equimolar amounts or may comprise unit III or may comprise a combination of units I, II, and III and, of course, more than one kind of unit (I, II and/or III) can be present in the polymer.

Preferred (co)polyesters of the invention consist essentially of units I and II. In such polymers, it is preferred that R₁ is selected from the group of 1,4-phenylene; chloro-, dichloro-, bromo-, dibromo-, methyl-, dimethyl- and fluoro-1,4-phenylene; 4,4'-biphenylene; 3,3',5,5'-tetramethyl-4,4'-biphenylene and R₂ is selected from the group of trans-1,4-cyclohexylene; trans-2,5-dimethyl-1,4-cyclohexylene; trans-vinylenebis(1,4-phenylene); 4,4'-biphenylene; 2,6-naphthylene; and 1,4-phenylene and with the proviso that more than one kind of unit I or II are present. Of such copolyesters, two types are particularly preferred because of properties and cost. In the first type, the polymers consist essentially of the recurring units

\[
\text{(1,4-benzoate unit)}
\]

wherein X is selected from the group of chloro-, bromo-, fluoro-, and methyl radicals; n is 1 or 2; and Y is selected from the group of 4,4'-biphenylene and 2,6-naphthylene, the ratio of units being within the range of 4:1 to 1:4. In the second type, the polymers consist essentially of the recurring units

\[
\text{(4,4'-benzoate unit)}
\]

wherein Z is selected from the group of 4,4'-biphenylene, 2,6-naphthylene, and 1,4-phenylene, the ratio of units being within the range of 4:1 to 3:2. With each type of polymer, up to 25 mol percent of non-conforming units may be present as described above.

A list of useful dicarboxylic acids includes terephthalic acid, 4,4'-biphenylic acid, 4,4'-oxydibenzoic acid, 4,4'-thiodibenzoic acid, 4-carboxyphenoxoacetic acid, 4,4'-transstilbenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, ethyleneoxy-4,4'-dibenzoic acid, isophthalic acid, the halogen and methyl substituted derivatives of the foregoing dicarboxylic acids, 1,4-trans-cyclohexanedicarboxylic acid, 2,5-dimethyl-1,4-trans-cyclohexanedicarboxylic acid, and the like.

A nonlimiting list of phenolic carboxylic acids includes 6-hydroxy-2-naphthoic acid, 4-hydroxy-4'-carboxy azobenzene, ferulic acid, 4-hydroxybenzoic acid, 4-(4'-hydroxyphenoxo)-benzoic acid and 4-hydroxycinamic acid and the alkyl, alkoxy and halogen substituted versions of these compounds.

Of the (co)polyesters containing only type III units, the polymers consisting essentially of the recurring units
are preferred.

The (co)polymers are prepared preferably by melt polycondensation of derivatives of dihydric phenols and aromatic-aliphatic, aromatic and cycloaliphatic dicarboxylic acids or their derivatives. A convenient preparative method is the melt polycondensation of the diacete of a dihydric phenol with a dicarboxylic acid. Alternatively, phenolic carboxylic acids or their derivatives may be used as coreactants in the preparation of polymers and copolymers.

A list of useful dihydric phenols preferably in the form of their diacetate derivatives includes hydroquinone, chlorohydroquinone, bromohydroquinone, methyldihydroquinone, dimethyldihydroquinone, dichlorohydroquinone, dibromohydroquinone, 4,4'-oxydiphenol, 4,4'-isopropylidenediphenol, 4,4'-thiodiphenol, 4,5,5',5'-tetramethyl-4,4'-bisphenol, 3,5,5',5'-tetrachloro-4,4'-biphenyl, 2,6-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, and 4,4'-methylene diphenol and the like.

In addition, it is possible to prepare anisotropic polyesters by polymerizing methylacryloxy benzoic acid utilizing an alkali metal hydroxide and free radical initiators as described in U.S. Pat. Nos. 4,112,212, 4,130,702 and 4,160,755.

Useful phenolic-carboxylic acid derivatives include p-acetoxybenzoic acid and p-acetoxycinnamic acid and the like.

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Useful phenolic-carboxylic acid derivatives include p-acetoxybenzoic acid and p-acetoxycinnamic acid and the like.

A nonlimiting list of various polymers and copolymers includes; poly(methyl-1,4-phenylene 2,5-dihydroxyterephthalate); copoly(methyl-1,4-phenylene trans-hexahydroterephthalate/terephthalate) (8/2); copoly(chloro-1,4-phenylene trans-hexahydroterephthalate/isophthalate) (9/1) and (8/2); copoly(ethyl-1,4-phenylene terephthalate/2,6-naphthalate) (7/3); copoly(tert. butyl-1,4-phenylene/3,3',5,5'-tetramethyl-4,4'-biphenyl/tereephthalate) (7/3); copoly(chloro-1,4-phenylene/3,3',5,5'-tetrachloro-4,4'-biphenyl/tereephthalate) (7/3).

The liquid crystal polymers including wholly aromatic polymers and poly(ester-amides) which are suitable for use in the present invention may be formed by a variety of ester forming techniques whereby organic monomer compounds possessing functional groups which, upon condensation, form the requisite recurring moieties are reacted. For instance, the functional groups of the organic monomer compounds may be carboxylic acid groups, hydroxyl groups, ester groups, acryoxy groups, acid halides, amine groups, etc. The organic monomer compounds may be reacted in the absence of a heat exchange fluid via a melt acidolysis procedure. They, accordingly, may be heated initially to form a melt solution of the reactants with the reaction continuing as said polymer particles are suspended therein. A vacuum may be applied to facilitate removal of volatiles formed during the final state of the condensation (e.g., acetic acid or water).

Commonly-assigned U.S. Pat. No. 4,083,829, entitled "Melt Processable Thermotropic Wholly Aromatic Polyester," describes a slurry polymerization process which may be employed to form the wholly aromatic polyesters which are preferred for use in the present invention. According to such a process, the solid product is suspended in a heat exchange medium. The disclosure of this patent has previously been incorporated herein by reference in its entirety. Although that patent is directed to the preparation of wholly aromatic polyesters, the process may also be employed to form poly(ester-amide)s.

When employing either the melt acidolysis procedure or the slurry procedure of U.S. Pat. No. 4,083,829, the organic monomer reactants from which the wholly aromatic polyesters are derived may be initially provided in a modified form whereby the usual hydroxy groups of such monomers are esterified (i.e., they are provided as lower acyl esters). The lower acyl groups preferably have from about two to about four carbon atoms. Preferably, the acyl esters of the organic monomer reactants are provided. When poly(ester-amide)s are to be formed, an amine group may be provided as a lower acyl amide.

Representative catalysts which optionally may be employed in either the melt acidolysis procedure or in the slurry procedure of U.S. Pat. No. 4,083,829 include dialkyl tin oxide (e.g., dibutyl tin oxide), dialkyl tin oxide, titanium dioxide, antimony trioxide, alkoxyl titanium silicates, titanium alkoxides, alkali and alkaline earth metal salts of carboxylic acids (e.g., zinc acetate), the gaseous acid catalysts such as Lewis acids (e.g., BF₃), hydrogen halides (e.g., HCl), etc. The quantity of catalyst utilized typically is about 0.001 to 1 percent by weight based upon the total monomer weight, and most commonly about 0.01 to 0.2 percent by weight.

The wholly aromatic polyesters and poly(ester-amide)s suitable for use in the present invention tend to be substantially insoluble in common polyester solvents and accordingly are not susceptible to solution processing. As discussed previously, they can be readily processed by common melt processing techniques. Most suitable wholly aromatic polyesters are soluble in pentfluorophenol to a limited extent.

The wholly aromatic polyesters which are preferred for use in the present invention commonly exhibit a weight average molecular weight of about 2,000 to 200,000, and preferably about 10,000 to 50,000, and most preferably about 20,000 to 25,000. The wholly aromatic poly(ester-amides) which are preferred for use in the present invention commonly exhibit a molecular weight of about 5,000 to 50,000, and preferably about 10,000 to 30,000; e.g., 15,000 to 17,000. Such molecular weight may be determined by gel permeation chromatography and other standard techniques not involving the solutioning of the polymer, e.g., by end group determination via infrared spectroscopy or compression molded films. Alternatively, light scattering techniques in a pentfluorophenol solution may be employed to determine the molecular weight.

The wholly aromatic polyesters and poly(ester-amide)s additionally commonly exhibit an inherent viscosity (I.V.) of at least approximately 2.0 dl./g., e.g., approximately 2.0 to 10.0 dl./g., as determined at a concentration of 0.1 percent by weight in pentfluorophenol at 60°C.
For the purposes of the present invention, the aromatic rings which are included in the polymer backbone of the polymer components may include substituents, preferably of the hydrogen atoms present upon an aromatic ring. Such substituents include alkyl groups of from one to four carbon atoms; alkoxy groups having up to four carbon atoms; halogens; and additional aromatic rings, such as phenyl and substituted phenyl. Preferred halogens include fluorine, chlorine and bromine. Although bromine atoms tend to be released from organic compounds at high temperatures, bromine is more stable on aromatic rings than on aliphatic chains, and therefore is suitable for inclusion as a possible substituent on the aromatic rings.

The fibers useful herein are basically carbon fibers which may be prepared by a variety of methods. Virtually any of the prior art methods of carbon preparation may be employed in this invention. The preparation of carbon fibers has been well known in the art for many years. Basically, there are two methods for preparing these fibers, which differ with respect to the starting materials employed. One method starts with a natural or synthetic fiber, which is then carbonized. In the other process, petroleum pitch or coal tar pitch is used as the starting material. The preparation of carbon fibers involves a first heating step in the range of about 800°-3000° F., with sparging to form a mesophase pitch. Following this step, the pitch is converted into a fiber, thermoset, and carbonized.

Included among the fibers which may be formed into graphite or carbon fibers and are useful in this invention are those materials where the polymeric precursor is, for example, cellulose, acrylic derivatives, and, in particular, polyacrylonitriles. Specifically, the acrylic polymer may contain not less than about 85 mol percent of acrylonitrile units, and not more than about 15 mol percent of monovinyl compound which is copolymerizable with acrylonitrile, such as styrene, methylacrylate, methylmethacrylate, vinyl acetate, vinyl chloride, vinylidene chloride, vinyl pyridine and the like. Other copolymerizable monomers include the various types of fiberglasses and ceramic fibers. In the event additional reinforcing fibers are added, it is possible to reduce the amount of the carbon fiber which is used to as low as approximately 10 volume percent. However, the maximum combined amount of the added reinforcing fiber plus the amount of the carbon fiber which is employed should not exceed the upper limit specified above for the carbon fiber alone.

In FIG. 1 of the instant invention, a carbon fiber tow (1) is obtained having the properties specified above. The fibers from the carbon fiber tow are passed through a fiber guide (3) and onto a first Godet roll (4). The first Godet roll is synchronized with a second Godet roll (11) at rates of speed such that the second Godet roll revolves slightly slower than the first Godet roll. Hence, the fibers between the two Godet rolls, which are subsequently spread and intermixed during the process of the invention, remains in a low tensioned (approaching tension-free) state which provides for effective fiber intermixing. Individual thermoplastic polymer fibers, such as polyethylene terephthalate fibers, are mounted on a bobbin rack (2) and the fibers are fed through a fiber guide (3) onto the first Godet roll (4). A tension comb may be employed after the fibers leave the bobbin and before they are brought into contact. Rather, both are wrapped separately around the Godet roll. This tension comb serves to improve the contact of the fiber with the Godet roll and to increase the width of the fiber tow.

At this point in the process neither the carbon fibers nor the thermoplastic fibers are intermixed or are in contact. Rather, both are wrapped separately around the first Godet roll (4) to provide tension control. After leaving the Godet roll, the individual fibers separately pass through a fiber guide (5) to maintain directional...
The mixed fibers are then wrapped around a second Godet roll (11) which, as pointed out above, serves in conjunction with the first Godet roll to provide a relatively tension-free zone to allow fiber intermixing. The fibers are then taken up by a takeup roll (12) for storage. Of course, it is possible to impart false-twisting or actual twisting or to wrap the fiber tow with another fiber either before or after the Godet roll. In addition, the intermixed fibers may be made stable by application of an appropriate fiber finish which serves to hold the intermixed fibers together and enable easier handling in subsequent operations, such as weaving.

FIG. 2 is similar to FIG. 1 but is the process most preferred when a liquid crystal type polymer or other higher melting point polymer is used. In FIG. 2 a carbon fiber roll (21) feeds carbon fiber through tension comb (22) and Godets (25). Liquid crystal fibers from a roll (23) are fed through a guide (24) and onto the same Godet roll (25). Separation is maintained between both fibers on the Godet roll. As pointed out above, the first Godet roll (25), when used in combination with the optional second Godet roll (35), serves to maintain the fibers in a relatively tension-free state during the intermixing process. High tension during intermixing must be avoided to assure that complete intermixing occurs.

After the carbon fibers and the liquid crystal fibers leave the first Godet roll they are both fed into gas banding jets (26) and (27) through guides (28) and (29), respectively. In the gas banding jet the fibers are spread to a uniform width. The fibers then pass through a second set of fiber guides (30) and (31) and are intermixed using the stationary, longitudinally extended bars shown at (32). In general, intermixing occurs as the thermoplastic bundle is fed onto the same bar in the same area as is the fiber. At this point in the processing, the width of both tows is the same, and as they are brought simultaneously into contact with the same area of a second Godet roll (35) and onto Godet roll (25). Separation is maintained between both fibers on the Godet roll. As pointed out above, the first Godet roll (25), when used in combination with the optional second Godet roll (35), serves to maintain the fibers in a relatively tension-free state during the intermixing process. High tension during intermixing must be avoided to assure that complete intermixing occurs.

Following intermixing, the fibers are fed through twist guides (33) to add at least a half-twist per yard to the fiber to ensure dimensional stability. Fibers then pass through a guide (34) onto a second Godet roll (35) and from there onto an either-up roll (36).

In use, the intermixed fibers can be filament wound, or otherwise assembled and placed on a mold, and heated under pressure to the flow temperature of the thermoplastic polymer to form composite articles which are useful in a variety of end uses where high strength, high stiffness and low weight are essential. For example, the composites formed from products prepared according to this invention may be used in forming spacecraft, airplane or automobile structural components. In addition, the carbon fiber blends of the instant invention find particular utility in those end uses where there is a small radius of curvature requiring substantial bending and shaping of the compositions of the instant invention.
The only limiting factor in forming carbon fiber shaped articles using the compositions of the instant invention is the “bendability” of the carbon fiber itself. Therefore, utilizing the compositions of the instant invention, it is possible to prepare materials having a minimum radius of curvature of about 0.002 in., preferably as low as 0.003 in. However, with prior art thermoplastic tapes, the minimum radius of curvature is about 0.005 in. (Even then fiber directionality or alignment is distorted.) As structural elements formed from the fiber tows of this invention are heated under pressure above the melting point of the thermoplastic fiber, these fibers will melt and fuse the carbon fibers together forming a consolidated composite product containing well-dispersed reinforcing fibers. Using the fiber blends of the instant invention, it is possible to prepare recreational articles, such as tennis racquet frames, racquetball racquet frames, hockey sticks, ski poles, fishing rods, golf club shafts and the like.

The fibers of the instant invention find particular utility in filament winding applications. As pointed out above, in the prior art it was extremely difficult to prepare composite articles utilizing the prior art fiber tapes. These tapes, which are prepared on extremely large scale, are difficult to handle on a small scale, and it is particularly difficult to form them into intricately shaped articles. While the prior art employed the filament winding process, this process was limited to use of carbon fibers in combination with thermosetting resins if long, thin rods were to be prepared. In the prior art process, the graphite was wound onto a mandrel either by a layer of thermoplastic film, followed by another layer of graphite, etc. Now the materials can be combined in a solid woven layer and much more readily applied to a mold. After the composite is formed, it is then heated under pressure above the flow point of the thermoplastic polymer and a composite having good mechanical strength and stiffness properties results. The strength and stiffness enhancement can occur in one or more directions, i.e., those directions along which carbon fiber is aligned parallel to the defining vector.

EXAMPLE 1

A liquid crystal polymeric (LCP) fiber tow based upon a copolymer prepared from 6-hydroxy-2-naphthoic acid and p-hydroxy benzoic acid was obtained. The LCP had a density of 1.4 g/cc, and the tow itself was formed of 660 filaments (2.25 denier per filament). The tow had an initial modulus of 3570 gms, a tenacity of 10.5 g/denier, and an elongation of 2%. The second fiber jet was used for intermixing with carbon fiber/thermoplastic fiber tow to form a composite containing the 25 fused layers was placed in a pressure mold after applying a thermosetting coating or coated with the thermosetting material after winding. As a result, however, it was often difficult for the thermosetting material actually to penetrate and/or achieve good wetting of closely wound products.

Utilizing the process of the instant invention in a modified filament winding procedure, it is possible to prepare intricately shaped articles when the fiber blends are oriented in directions not parallel to the long axis of the article, utilizing thermoplastic polymers in conjunction with carbon fiber reinforcements. This modified filament winding process begins with the use of the intermixed tows of the instant invention. These tows may be fed directly to a filament winder. As the filament winder moves around or up and down the mandrel or form, the carbon fiber/thermoplastic fiber tow is applied directly to the mold and heated using a radiant heater or other suitable means for immediately melting and fusing the thermoplastic polymeric fibers within the carbon fiber tow. In other words, the carbon fiber/thermoplastic fiber tow should be heated under pressure as soon as or soon after it meets the mandrel. After full melting and resolidification occurs, the mandrel either may be dissolved using a suitable solvent, may be pulled from the product, or the mandrel may actually become a part of the product.

Another unique use for the fiber blends prepared according to the instant invention is in forming woven fabrics utilizing standard techniques. According to this process, the tow of the instant invention is used either alone or in combination with other tows or fibers to form a woven mat. The woven fabrics prepared according to the process of this invention may be applied to the desired mold or otherwise used in forming a composite. The previous method of choice of forming such materials involved laying down a layer of graphite, followed by a layer of thermoplastic film, followed by another

Utilizing the same process, an eight ply 34 x 10” composite panel was prepared having a carbon fiber
volume of 60.3%, a panel thickness of 0.035". The composites were evaluated for tensile, flexural and compression properties with the following results:

**TABLE I**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Test</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0° Tensile(*)</td>
<td>Strength (ksi)</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td>Modulus (Msi)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Strength (ksi)</td>
<td>200° F.</td>
</tr>
<tr>
<td></td>
<td>Modulus (Msi)</td>
<td></td>
</tr>
<tr>
<td>0° Flexural(1)</td>
<td>Strength (ksi)</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td>Modulus (Msi)</td>
<td></td>
</tr>
<tr>
<td>0° Compression(1)</td>
<td>Strength (ksi)</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td>Modulus (Msi)</td>
<td></td>
</tr>
<tr>
<td>90° Flexural</td>
<td>Strength (ksi)</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td>Modulus (Msi)</td>
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</tbody>
</table>

(1) Fiber volume normalized to 62%.
(2) Performed on 8 ply. Remainder of tests performed on 25 ply.

**EXAMPLE 2**

Utilizing the same carbon fiber as described in Example 1, an approximate 50% by volume polybutylene terephthalate (PBT)/carbon fiber blend was prepared. The polybutylene terephthalate material had a density of 1.34 g/cc and a denier of 1520 g/9000 m. The polybutylene terephthalate had a draw ratio of 2.5–1, an initial modulus of 24 g, a tenacity of 5.3 g/denier, an elongation of 28%, a melting point of 227° C. and a denier per filament of 2.7. Seventeen packages of 33 filament count yarn were employed on a creel, and all packages were merged into a single polybutylene terephthalate fiber tow on a Godet roll. Maintained separately, but on the same Godet roll, was one package of 3000 filament count carbon fiber to provide a total approximate blend of 50/50 by volume carbon fiber/PBT.

The polybutylene terephthalate tow was fed through a fiber comb having approximately 30 teeth, while the carbon fiber tow was fed through a gas banding jet operating as described in Example 1, at a pressure of about 24–34 psi. The tow was then intermixed over and under parallel extended rods by feeding both tows into the same area on the bars. Intermixing was aided by the use of a second gas banding jet of the type described in Example 1, operating at 24–34 psi. After leaving the banding jet, the fibers were then wound through a second fiber comb which was arranged parallel to the direction of flow of the fiber, so as to provide a tensioning path to aid in intermixing. After leaving the comb, the fibers were then wound into a single polybutylene terephthalate fiber tow on a Godet roll. Maintained separately, but on the same Godet roll, was one package of 3000 filament count carbon fiber to provide a total approximate blend of 50/50 by volume carbon fiber/PBT.

A 6" wide fabric was then woven on a modified Draper XD loom, using a plain weave pattern. The resulting woven product had dimensions of 16 ends per inch × 15 picks per inch and weighed 16 oz./yd². The fabric was 35 mils in thickness, was soft but compact, and exhibited good dimensional stability. Satisfactory fiber composites having irregular shapes are prepared from the resulting fabric.

**PROPERTIES FOR CARBON/PBT MATRIX LAMINATES (Example 2)**

<table>
<thead>
<tr>
<th>Process History</th>
<th>Test (Room Temp)</th>
<th>MPa (ksi)</th>
<th>GPa (Msi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22-ply at 468° F., 300 psi for 5 min., and reprocessed at 468° F., 300 psi for 20 min.</td>
<td>0° Flex</td>
<td>598 ± 34 (156 ± 2)</td>
<td>83.5 ± 2.1 (115.2 ± 0.3)</td>
</tr>
<tr>
<td>8-ply at 468° F., 300 psi for 10 min. and reprocessed at 468° F., 300 psi for 2 min.</td>
<td>0° Compression</td>
<td>659 ± 83 (95.6 ± 12)</td>
<td>130.4 ± 7.6 (18.9 ± 1.1)</td>
</tr>
<tr>
<td>Fiber volume was 49.5%, and thickness was 0.0415&quot;.</td>
<td>Short Beam Shear</td>
<td>39.9 ± 2.1 (5.2 ± 0.3)</td>
<td>—</td>
</tr>
<tr>
<td>Processed three times:</td>
<td>0° Tensile</td>
<td>1518 ± 34 (220 ± 5)</td>
<td>130.4 ± 4.8 (18.9 ± 0.7)</td>
</tr>
<tr>
<td>1. 300 psi for 30 min at 471° F.</td>
<td>0° Tensile</td>
<td>1525 ± 34 (221 ± 12)</td>
<td>164.9 ± 4.1 (21.9 ± 0.6)</td>
</tr>
<tr>
<td>2. 500 psi for 15 min at 471° F.</td>
<td>0° Tensile</td>
<td>1525 ± 34 (221 ± 12)</td>
<td>164.9 ± 4.1 (21.9 ± 0.6)</td>
</tr>
<tr>
<td>3. 500 psi for 15 min at 469° F.</td>
<td>0° Tensile</td>
<td>1525 ± 34 (221 ± 12)</td>
<td>164.9 ± 4.1 (21.9 ± 0.6)</td>
</tr>
<tr>
<td>Fiber volume was 61.4%, and panel thickness was 0.0402&quot; (8-ply panel).</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
EXAMPLE 3

An approximate 50/50% by volume blend was prepared based upon the carbon fiber described in Example 1 and a polyether ether ketone (PEEK) thermoplastic polymer. The fiber prepared from the PEEK had a density of 1.3 g/cc, a melting point of 338° C., an elongation of 63%, and in 10 filaments per package tow a ddf of 367 (g/9000 m). Four (10 filaments per package) tows were placed on a creel and the fibers were blended together on a Godet roll, but maintained separately from the carbon fiber which was also wrapped around the Godet roll. The PEEK fiber was then directed through a fiber comb as described in Example 2 and into a gas banding jet. The carbon fiber after leaving the Godet roll also entered a gas banding jet. Both jets were operating at a pressure of about 3 psi. After leaving the jets the fibers were intermixed above and below two parallel, longitudinally extended rods and fed through a second parallel fiber comb, twisted to maintain dimensional stability, fed over a second Godet roll and taken up at a speed of 7-10 m/min. A satisfactory composition resulted.

What is claimed is:

1. A process for preparing a composite article which comprises:
   (a) forming a continuous tow of continuous carbon fibers;
   (b) forming a continuous tow of continuous thermoplastic polymer fibers having a melting point of at least about 50° C.;
   (c) uniformly and continuously spreading the thermoplastic polymer fiber tow to a selected width to preserve the separation of the individual fibers;
   (d) uniformly and continuously spreading the carbon fiber tow to a width that is essentially the same as the selected width for the thermoplastic polymer fiber tow;
   (e) intimately, uniformly and continuously intermixing the spread carbon fiber tow and the spread thermoplastic polymer fiber tow in a relatively tension-free state by bringing the tows into simultaneous contact with each other in substantially the same area such that there is provided a substantially uniform distribution of the thermoplastic fibers and the carbon fibers within an intimately intermixed tow;
   (f) continuously withdrawing the intimately intermixed tow;
   (g) applying the intimately intermixed tow to a mold; and
   (h) heating the intermixed tow to a temperature above the melting point of the thermoplastic fibers.

2. The process of claim 1 wherein the carbon fibers are formed from polyacrylonitrile polymers and copolymers.

3. The process of claim 1 wherein the carbon fibers are formed from pitch blends.

4. The process of claim 1 wherein the carbon fiber tow has a bundle denier of about 300 to 100,000.

5. The process of claim 1 wherein the carbon fiber tow has a bundle denier of about 1,000 to 16,000.

6. The process of claim 1 wherein the carbon fiber tow contains from about 300 to 300,000 filaments.

7. The process of claim 1 wherein the carbon fiber tow contains about 3,000 to 24,000 filaments.

8. The process of claim 1 wherein the thermoplastic polymer fibers are selected from the group consisting of polyethylene, polypropylene, polyesters, polyamides, polyetherimides, polysulfones, polyether ether ketones and wholly aromatic polyester resins.

9. The process of claim 1 wherein the thermoplastic polymer fibers are liquid crystal polymer fibers.

10. The process of claim 1 wherein the thermoplastic polymer fibers are wholly aromatic polyester fibers.

11. The process of claim 1 wherein the denier of the individual thermoplastic polymer fibers is in the range of about 1 to about 50 and wherein the thermoplastic polymer fiber tow contains from about 10 to about 150,000 filaments.

12. The process of claim 1 wherein the carbon fibers are prepared by a first heating step in the range of about 200° C. to about 400° C., followed by a second heating step in the range of about 800° C. to about 3000° C. and are based upon polyacrylonitrile polymers and copolymers.

13. The process of claim 1 wherein the intimately intermixed fiber tow contains a mixture of about 90 to about 70 percent by volume, based on the total fiber content, of the thermoplastic polymer fibers and about 10 to about 70 percent by volume of the carbon fibers, based upon the total fiber content.

14. The process of claim 13 wherein the intimately intermixed tow contains about 20 to about 60 percent by volume of carbon fibers.

15. The process of claim 13 wherein the intimately intermixed tow contains about 60 percent by volume of carbon fibers.

16. The process of claim 1 wherein the intimately intermixed fiber tow is continuously applied to a mold employing a filament winding process.

17. The process of claim 1 wherein the fiber tow is applied to the mold in the form of a woven fabric.

18. The process of claim 1 wherein the composite article is a recreational article.

19. The process of claim 18 wherein the composite article is a tennis racquet frame.

20. A process for preparing a composite article which comprises:
   (a) forming a continuous tow of continuous carbon fibers;
   (b) forming a continuous tow of continuous thermoplastic polymer fibers having a melting point of at least about 50° C.;
   (c) uniformly and continuously spreading the thermoplastic polymer fiber tow to a selected width to preserve the separation of the individual fibers;
   (d) uniformly and continuously spreading the carbon fiber tow to a width that is essentially the same as the selected width for the thermoplastic polymer fiber tow;
   (e) intimately, uniformly and continuously intermixing the spread carbon fiber tow and the spread thermoplastic polymer fiber tow in a relatively tension-free state by employing a gas intermixing means which directs a generally perpendicular gas flow onto the fibers and by bringing the tows into simultaneous contact with each other in substantially the same area such that there is provided a substantially uniform distribution of the thermoplastic fibers and the carbon fibers within an intimately intermixed tow;
   (f) continuously withdrawing the intimately intermixed tow;
(g) applying the intimately intermixed tow to a mold; and
(h) heating the intermixed tow to a temperature above the melting point of the thermoplastic fibers.
21. A process for preparing a composite article which comprises:
(a) forming a continuous tow of continuous carbon fibers;
(b) forming a continuous tow of continuous thermoplastic polymer fibers having a melting point of at least about 50° C.;
(c) uniformly and continuously spreading the thermoplastic polymer fiber tow to a selected width to preserve the separation of the individual fibers;
(d) uniformly and continuously spreading the carbon fiber tow to a width that is essentially the same as the selected width for the thermoplastic polymer fiber tow;
(e) intimately, uniformly and continuously intermixing the spread carbon fiber tow and the spread thermoplastic polymer fiber tow in a relatively tension-free state by bringing the tows into simultaneous contact with each other in substantially the same area such that there is provided a substantially uniform distribution of the thermoplastic fibers and the carbon fibers within an intimately intermixed tow;
(f) continuously withdrawing the intimately intermixed tow;
(g) applying the intimately intermixed tow to a mold; and
(h) heating the intermixed tow to a temperature above the melting point of the thermoplastic fibers.
22. A process for preparing a composite article which comprises:
(a) forming a continuous tow of continuous carbon fibers;
(b) forming a continuous tow of continuous thermoplastic polymer fibers having a melting point of at least about 50° C.;
(c) uniformly and continuously spreading the thermoplastic polymer fiber tow to a selected width to preserve the separation of the individual fibers;
(d) uniformly and continuously spreading the carbon fiber tow to a width that is essentially the same as the selected width for the thermoplastic polymer fiber tow;
(e) intimately, uniformly and continuously intermixing the spread carbon fiber tow and the spread thermoplastic polymer fiber tow in a relatively tension-free state by bringing the tows into simultaneous contact with each other in substantially the same area of a longitudinally extended, substantially horizontal, non-drawing rod such that there is provided a substantially uniform distribution of the thermoplastic fibers and the carbon fibers within an intimately intermixed tow;
(f) continuously withdrawing the intimately intermixed tow;
(g) applying the intimately intermixed tow to a mold; and
(h) heating the intermixed tow to a temperature above the melting point of the thermoplastic fibers.
23. The process of claim 22 wherein a second non-drawing rod is employed.

* * * * *