METHOD OF MAKING LONG FIBER-REINFORCED THERMOPLASTIC COMPOSITES UTILIZING HYBRID OR COMMINGLED YARN

A method of making a long fiber reinforced thermoplastic composite includes supplying a hybrid yarn or commingled yarn (142, 146) to a lobed die (134, 136), the yarn including both thermoplastic fibers and reinforcing fibers in intimate contact wherein the yarn is from about 10 to about 90 weight percent thermoplastic fiber and from about 90 to about 10 weight percent reinforcing fiber. The die is configured to define a tortuous conduit along the production direction and maintained at a temperature operative to melt the thermoplastic fiber of the yarn supplied thereto so that from the beginning of melting of the thermoplastic fiber the wet out of the reinforcing fiber starts and the thermoplastic matrix produced from the melted fibers substantially fully impregnates the reinforcing fibers. The process thus combining different consolidating steps - heating, impregnating, shaping and coating - within the one step of passing the hybrid or commingled yarn through the lobed pultrusion die.

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METHOD OF MAKING LONG FIBER-REINFORCED THERMOPLASTIC COMPOSITES UTILIZING HYBRID OR COMMINGLED YARN

Claim for Priority

This patent application claims the benefit of the filing date of U.S. Provisional Patent Application Serial No. 60/452,435, of the same title, filed March 6, 2003.

Technical Field

The present invention relates generally to long fiber-reinforced thermoplastic composites and more particularly to methods for making these products utilizing hybrid or commingled yarns incorporating thermoplastic fibers and reinforcing fibers and a lobed pultrusion die. Optionally included in the process is adding polymer in the pultrusion die which can be followed by adding more polymer in a coating die.

Background Art

Long fiber-reinforced thermoplastic composites are well known. There is disclosed, for example, in United States Patent No. 5,830,304 to Priesnitz et al. a method of making a core element for a communications cable. The method described in the '304 patent includes assembling mixed filaments containing glass fibers and thermoplastic fibers, heating the bundle of mixed filaments to melt the thermoplastic fibers to form a matrix with the glass fibers embedded therein, then extruding an outer covering of the desired outside diameter for the core element onto the bundle. If desired, the melted bundle can be passed through a shaping device, which is preferably heated prior to extruding the coating thereon.

So also, pultrusion processes are well known. In United States Patent No. RE 32,772 to Hawley, there is disclosed a method of making a composite pultruded structure by injection molding thermoplastic resin onto continuous glass
fibers in a lobed pultrusion die. Further, United States Patent No. 6,090,319 to Sharma et al. discloses a process including pultrusion followed by coating. The process is characterized by impregnating a plurality of continuous lengths of reinforcing fiber strands with a first thermoplastic resin material while continuously drawing the fiber strands to produce a long fiber-reinforcing composite structure followed by coating a second thermoplastic resin material containing additives onto the long fiber-reinforcing composite structure to produce a coated, long fiber-reinforcing composite structure. The coating additives may be selected from mineral reinforcing agents, lubricants, flame retardants, blowing agents, foaming agents, ultraviolet light resistant agents, heat sensitive pigments and so forth.

There are numerous publications relating to composites. As to methods and apparatus for producing composite strands, see United States Patent Nos. 5,454,846; 5,316,561; and 5,001,523. As to processes used in preparing fibrous tows which may be formed into polymeric plastic composites and a continuous tow useful in forming composite molded articles see, United States Patent Nos. 4,818,318; 4,799,985; 5,355,567; 4,871,491; and 4,874,563. As to a process for preparing fiber-reinforced thermoplastic articles see, United States Patent Nos. 4,800,113 and 4,925,729. As to reinforced pultrusion products, see United States Patent No. 6,037,056. As to composite materials comprising a thermoplastic resin and a reinforcing fiber, see United States Patent Nos. 5,076,872; 4,770,915; and 4,539,249. As to hybrid yarns containing reinforcing and thermoplastic fibers, see United States Patent Nos. 5,227,236 and 5,910,361. For a molding material for thermoplastic composites see, United States Patent No. 5,959,710.

Still yet other processes are described in United States Patent Nos. 5,626,643 and 5,451,355 as well as WO 01/81073A which describe fiber-reinforced, heat-formable material which contains thermoplastic fibers and reinforcing fibers aligned in parallel. United States Patent No. 5,626,643 is related to assembling the different fibers directly at a glass bushing. In patent
application WO 01/81073A, the following consolidating steps are necessary, after assembling a minimum of 2 sources of fibers: heating (oven), forming rolls/impregnation system, shaping and coating. See, also, WO 98/16359.

5 Despite all of the advances in the art, there exists a need for improvements in production rates and simplification of processing, especially for long fiber-reinforced thermoplastic composites, including performance resins such as polyesters, polyamides and the like as well as composites with high glass loadings.

10 **Summary of Invention**

A method of making a long fiber-reinforced thermoplastic composite includes: supplying a mixed fiber roving to a lobed pultrusion die, the mixed fiber roving comprising thermoplastic fibers and continuous reinforcing fibers; wherein the mixed fiber roving is from about 10 to about 90 weight percent thermoplastic fiber and from about 90 to about 10 weight percent reinforcing fiber; drawing the mixed fiber roving through the lobed pultrusion die along a production direction while maintaining the lobed pultrusion die at a temperature operative to melt the thermoplastic fibers of the mixed fiber roving supplied thereto and start immediately to wet out/impregnate the reinforcing fiber when melting of the thermoplastic fiber starts, optionally injecting a molten first additional thermoplastic resin composition into the pultrusion die whereby a nascent long fiber-reinforced thermoplastic composite is formed in the lobed pultrusion die including molten thermoplastic resin and continuous reinforcing fibers in intimate contact and wherein the lobed protrusion die defines a tortuous path along the production direction and is operative to knead the nascent composite as it is drawn therethrough whereby the individual reinforcing fibers are substantially wetted out with thermoplastic resin preferably such that a thermoplastic resin matrix fully impregnates the reinforcing fibers; withdrawing the long fiber reinforced thermoplastic composite from the pultrusion die; cooling the composite and optionally, cutting the long fiber reinforced thermoplastic composite into pellets.
In its many aspects, the inventive process includes: supplying a hybrid or commingled yarn of thermoplastic fibers and reinforcing fibers in intimate contact wherein the yarn includes from about 10 to about 90 weight percent thermoplastic fiber and from about 90 to about 10 weight percent reinforcing fiber to a lobed pultrusion die; maintaining the lobed pultrusion die at a temperature operative to melt the thermoplastic fiber of the yarn supplied thereto; utilizing the lobed pultrusion die such that it impregnates the reinforcing material thereof so a fully impregnated composite is formed; injecting (optionally) a molten thermoplastic resin into the lobed pultrusion die, the additional resin increasing the thermoplastic content of the hybrid reinforcing material such that a fully impregnated composite with a desired content of thermoplastic resin is formed; combining during pultrusion processing different consolidating steps — heating, impregnating, shaping and coating — within the one step of passing the yarn through the lobed pultrusion die; withdrawing the composite of intermediate resin content from the lobed pultrusion die; feeding (optionally) the composite to a coating die where the composite is coated with a molten second thermoplastic resin to further increase the polymer content of the thermoplastic composite with the same or different resins like the thermoplastic fiber, and/or additives and optionally, cutting the thermoplastic composite into pellets.

One embodiment includes utilizing from about 50 to 80 phc glass fiber, preferably from about 60 to about 70 phc glass fiber.

Another embodiment utilizes a thermoplastic fiber selected from polypropylene fibers, polyethylene fibers, polyethylene terephthalate fibers, polybutylene terephthalate fibers, nylon fibers, thermoplastic polyurethane fibers, polyacetal fibers, polyphenylene sulfide fibers, cycloolefin copolymer fibers, thermotropic polyester fibers and mixtures thereof.

The first additional thermoplastic resin may consist or consist essentially of polypropylene resin, polyethylene resin, polyethylene terephthalate resin,
polybutylene terephthalate resin, nylon resin, thermoplastic polyurethane resin, polyacetal resin, polyethylene sulfide resin, cycloolefin resin, thermotropic polyester resin and mixtures thereof.

The method sometimes includes the step of feeding the long fiber reinforced thermoplastic composite to a coating die where the composite is coated with a molten second additional thermoplastic resin composition to further increase the polymer content of the thermoplastic composite. The second additional thermoplastic resin composition is preferably the same resin as that of the fiber and may include additives such as processing aids, stabilizers and reinforcing agents. Typically, the mixed roving has a thermoplastic fiber content of from about 10 weight percent to about 50 weight percent and a reinforcing fiber content of from about 90 weight percent to about 10 weight percent. In many cases, at least about 5 phc of resin are added as first additional thermoplastic resin composition at the pultrusion die; and in many cases 5, 25, 35, 45, 60 or 75 phc are added. The first additional thermoplastic resin composition may also include the additives noted above.

Thermoplastic fiber of the mixed roving or the added thermoplastic compositions may comprise a resin selected from the group consisting of: polypropylenes, polyethylenes, polyethylene terephthalates, polybutylene terephthalates, nylons, thermoplastic polyurethanes, polyacetals, polyethylene sulfides, cycloolefin copolymers, thermotropic polyesters and mixtures thereof. Glass reinforcing fiber is preferred in many cases.

Optionally, a sizing or coupling agent such as an amino silane sizing agent is applied to the thermoplastic fiber of the mixed fiber roving.

The thermoplastic composite may be chopped into pellets having a length of from about 6 to about 50 mm; a length of from about 10 to about 25 mm is somewhat typical. The composite may have a reinforcing fiber content of at least about 50 phc in some cases or as much as 60 or 70 phc in other cases.
A line speed of at least about 100 meters per minute is preferred, while a line speed of at least about 150 meters per minute is more preferred.

In another aspect of the invention, there is provided a long fiber-reinforced thermoplastic composite in the form of a pellet having a length of from about 6 mm to about 50 mm produced by melt-fusing a hybrid fiber roving comprising from about 10 to 50 weight percent thermoplastic fiber and from about 50 to 90 weight percent reinforcing fiber in a lobed pultrusion die to form a long fiber reinforced thermoplastic composite such that the thermoplastic matrix about the reinforcing fibers is substantially continuous.

In still yet another embodiment there is provided a long fiber-reinforced thermoplastic composite in the form of a pellet having a length of from about 6 mm to about 50 mm produced by melt-impregnating a hybrid fiber roving comprising from about 10 to 50 weight percent thermoplastic fiber and from about 50 to 90 percent reinforcing fiber with at least about 10 phc of a first thermoplastic resin. Sometimes at least about 25 or 35 phc first additional resin are added in the pultrusion die and the pellets are from about 10 mm to about 25 mm in length.

Thus, this invention encompasses in preferred embodiments the use of lobed cross head dies to impregnate a plurality of continuous commingled or hybrid of thermoplastic fibers, e.g. polyester/fiberglass to form a long fiber-reinforcing composite structure. Different consolidating process steps, described in the patents mentioned above (the disclosure of which is hereby incorporated by reference) are combined within one step. The hybrid or commingled thermoplastic fibers / fiberglass rovings typically include a fiberglass weight percentage of 50-90% with the remaining parts of the composition being thermoplastic fibers. A plurality of continuous lengths of reinforced commingled fiber or hybrid yarn enter the main (lobed) die where the fibers are heated to melt the thermoplastic fibers. The heating of the fibers initiates the wetting out of the
fiberglass with the thermoplastic resin. Thermoplastic resin, such as nylon (polyamide) may optionally also be added in the lobed pultrusion die to facilitate matrix formation and increase polymer loading if so desired. The main pultrusion die has plurality of lobes projecting radially inside of the central passageway of the die which thus define a tortuous conduit, preferably with a serpentine profile as is seen in the drawings. Lobes function to allow individual reinforcing fiber strands to be thoroughly impregnated or wetted out with the thermoplastic resin. While any suitable lobed die may be used, typically upper and lower lobes are in phase as shown such that the gap therebetween is generally uniform over the length of the die. From about 2-12 lobes are employed with a gap of from about 1/16" to about 1/4" defining the tortuous conduit. The lobes may recur at a distance of from about 0.5" to about 2.5" being generally sinusoidal in nature with an amplitude of from about 1/8" to about 1.5".

The desired weight percentage (10%-90% fiberglass reinforcement) is derived from the content of thermoplastic fiber of the mixed roving or from polymer added in the pultrusion die. The amount of polymer in the composite is metered by way of sizing nibs located at the exit of the main die. The sizing nibs meter excess resin and/or additives to provide the desired weight percentage and geometry of the continuous impregnated fiberglass strands.

After treatment in the lobed die the continuous fiber rovings with a fused thermoplastic matrix can be optionally introduced to a secondary die, which introduces additional resin, which may be the same or a different thermoplastic resin, and / or additives. The additives may be selected from mineral reinforcements, color concentrates, lubricants, flame retardants, coupling agents, blowing agents, foaming agents, UV resistant agents, heat sensitive pigments, etc. The desired weight percentage (10%-90% fiberglass reinforcement) is also derived from sizing nibs located at the exit of the secondary die. Since the secondary die is separate from the main lobed die, it may be operated at different
temperatures as the main die, thus facilitating the use of the different additives listed above.

In the production of long-fiber-reinforced thermoplastics, the throughput is frequently limited by the requisite impregnation of the glass fibers. Poor impregnation results in unpredictable and sometimes unreliable processing behavior, reduction in mechanical properties as well as poor surface aesthetics of molded parts. This is the case in particular in pultrusion, but also in other long glass fiber technologies. Through the combination of glass fibers and thermoplastic fibers (such as commingled fiber or hybrid yarn), an increase in productivity is achieved. Furthermore, it should be noted that the coupling component can be already present in the thermoplastic fibers, thus good bonding between fiberglass and thermoplastic polymer is obtained without the need for adding additional coupling agents.

The standard fiberglass, non-commingled, is usually processed with twist compensation. The twist compensation reduces the twisting of the fiber tows, which facilitates impregnation and reduces surface defects (unwetted-out fiberglass swirls) in molded parts. This twist compensation is not necessary with the commingled fibers, or hybrid yarns to produce a long fiber reinforced thermoplastic composite. Eliminating twist compensation further increases production rates as will be appreciated from the discussion which follows.

Brief Description of Drawings

While the specification concludes with claims particularly pointing out and distinctly claiming the present invention, the invention may be better understood from the following description in conjunction with the accompanying drawings in which:

FIGURE 1 is a schematic view in elevation of an apparatus utilized for the production of coated, long fiber-reinforced composite structures;
FIGURE 2 is a view in elevation and cross section of a coated, long fiber-
reinforced composite structure in the form of a pellet suitable for injection
molding prepared according to the invention; and

FIGURE 3 is a partly cut away side view of a lobed pultrusion die for
producing composite reinforcing structures of the invention.

Detailed Description

The invention is described herein for purposes of illustration and
exemplification. Such discussion is not limitative of the invention which is
defined in the appended claims. One of skill in the art will readily appreciate that
the present invention simplifies composite processing and makes it possible to
greatly increase production capacity in an extrusion-limited facility. Moreover,
composite product quality is maintained or enhanced in accordance with the
invention while throughput rates are increased and down time is minimized.

Increases in capacity for extrusion-limited facilities of 100 percent or more
may be achieved by utilizing a mixed fiber roving which contains half of the final
product’s thermoplastic resin content. Process simplification is achieved by
combining heating, polymer addition and consolidation in a lobed pultrusion die.
So also, it is possible to dispense with complex twist compensation operations
which may involve rotating a spool of roving at 40-70 rpm or more, which
operations are “batchwise” in nature and thus involve periodic line shutdowns.
Here again, actual capacity is increased due to less downtime of equipment.

Without intending to be bound by any theory, it is believed that the presence of
the thermoplastic fiber in intimate contact with the reinforcing fiber over the
length of the roving provides resilience and/or favorable frictional characteristics
by ensuring good distribution of thermoplastic during processing in the lobed
pultrusion die. These and other features and advantages of the invention are
further appreciated from the discussion which follows.
As used herein, terms are given their ordinary meaning unless otherwise specifically defined.

Additives include fillers and other reinforcing agents such as calcium carbonate, glass and so forth, as well as thermal stabilizers, antioxidants, UV stabilizers and so on. Additives also include lubricants such as waxes and processing aids as are well known in the art.

Continuous reinforcing fiber or like terminology means a fiber or strand having indeterminate length and generally a continuous length over the length of the composite formed in the process of the invention. Reinforcing fiber of a roving used in connection with the invention does not melt at temperatures encountered in the lobed pultrusion die, that is, reinforcing fibers have a melting temperature above that maintained in the lobed pultrusion die.

Impregnation and like terminology refers to composites wherein individual reinforcing fibers are substantially coated by the polymer in the matrix of the composite. This condition is illustrated schematically in Figure 2.

Mixed roving includes hybrid yarn and commingled yarn as well as any related product including a continuous reinforcing fiber content and a thermoplastic fiber content. The thermoplastic fiber or thermoplastic resin in the various compositions may include a resin such as polypropylene or thermoplastic resins such as cycloolefin copolymers or thermoplastic polyesters, including polyethylene terephthalate and polybutylene terephthalate. Cycloolefin copolymers include those made from norbornene and ethylene marketed as Topas® cycloolefin copolymers by Ticona (Summit, N.J.) as well as the other resins disclosed in United States Patent No. 5,087,677 to Brekner et al. Thermotropic polyesters include polymers of 6-hydroxy-2-naphthoic acid (HNA) and copolymers of HNA and para-hydroxybenzoic acid, also marketed by Ticona.
as Vectra® thermoplastic resins. See United States Patent No. 4,161,470 to Calundann.

ppc refer to parts per hundred weight of the final composite product, that is, weight percent of the final product.

Referring to FIGURE 1, there is illustrated a schematic top view in elevation of a typical apparatus in which the process of the invention is conducted. In a preferred embodiment, the process may be characterized, in part, as a pultrusion process 10 wherein a mass of a first additional thermoplastic resin material in a flowable state without a discrete shape is extruded longitudinally through an elongated, first stationary lobed impregnation die 11 while mixed roving 12 including continuous reinforcing fiber strands as well as thermoplastic fiber are a pulled through die 11 via puller assembly 18. Die 11 may be characterized as having a continuous, fully open central passage extending longitudinally therethrough, and a plurality of lobes projecting radially inwardly into the central passage from spaced apart locations along the length of the inside, opposite side walls of said central passage in interleaving relation to each other to define a convoluted or tortuous conduit preferably having a serpentine profile as is seen in FIGURE 3 through which roving 12 is pulled and in which thermoplastic from the melted fiber and the optionally added first additional thermoplastic resin material flows. The die is maintained at an elevated temperature such that the thermoplastic fiber in the roving melts and the lobes are configured and arranged so that individual reinforcing fiber strands are passed over at least one lobe.

During this treatment, the thermoplastic from the thermoplastic fiber in the roving as well as any optionally added first additional thermoplastic resin material thoroughly impregnates the reinforcing strands and forms a reinforced fused polymer matrix therewith in one step. Die 11 is attached to extruder 13 wherein the first additional thermoplastic resin material is heated and formed into a flowable mass. Continuous lengths of mixed roving 12 are pulled through the central passage of die 11 and impregnated with the first additional thermoplastic
resin material to produce the long fiber-reinforcing composite structure 14. Optionally, while the matrix resin material is still in a flowable state, the impregnated strands are drawn through a metering device wherein the cross-sectional shape and diameter thereof may be defined to form the long fiber-reinforcing composite structure. Thereafter, the long fiber-reinforced composite structure 14 is pulled through a stationary coating die 15. Coating die 15 is attached to extruder 16 through which a second additional thermoplastic resin material and an additive material are heated and extruded through the die onto long fiber-reinforcing composite structure 14. Optionally, a second metering device may be placed after coating die 15 to define the cross-sectional diameter of the coated, long fiber-reinforcing composite structure 17 produced by the process. The coated, long fiber-reinforcing composite structure 17 is cooled and optionally cut into pellets at pelletizer 19. The first and second additional resins typically include those additives common to extrusion processing.

Referring to FIGURE 2, there is illustrated front and side views in elevation of a typical coated, long fiber-reinforced composite structure in the form of a pellet 20. Coated, long fiber-reinforced pellet 20 is characterized by a long fiber-reinforcing composite core portion 22 having a plurality of continuous fiber reinforcing strands 24 imbedded in a first fused polymer matrix and extending therethrough parallel to the longitudinal axis of the structure. Core portion 22 is composed of thermoplastic resin matrix of sufficient volume to completely impregnate and surround the continuous fiber strands 24. Coating portion 26 is illustrated schematically as a solidified, second thermoplastic fused resin matrix containing an additive material, which annularly surrounds and encloses the surface of core portion 22. An intermediate mixing zone 28, characterized as an interface of the first and second thermoplastic resin matrices where the first and second thermoplastic polymer matrices bond together to form an integral structure.
While it will be readily apparent to one skilled in the art that any suitable hybrid yarns or commingled yarns, thermoplastic resin materials, fibers and additive materials may be suitable for use in the process of the present invention to prepare coated, long fiber-reinforced composite structures, hereinafter are described some processing conditions, resins, fiber, and additive materials suitable for use in the process.

Generally, the first additional thermoplastic resin material should exhibit high flow and low viscosity when heated and extruded through the impregnation die. It should not degrade when heated to temperatures in excess of the melt temperature which may be necessary to ensure complete impregnation of the fibers therewith. The first additional thermoplastic resin material may be selected from nylon 6, nylon 66, polyethylenes, polyacetals, polyphenylene sulfide, polyurethanes, polypropylenes, cycloolefin copolymers, polycarbonates, polyesters including thermotropic polyester, acrylonitrile-butadiene-styrene, and combinations thereof.

The continuous lengths of fiber strands present in the mixed rovings necessary to provide reinforcing qualities to the composite structure may be selected from glass, amorphous carbon, graphitic carbon, aramids, stainless steel, ceramics, alumina, titanium, magnesium, metal-coated carbons, rock wool and combinations thereof. Generally, the strands, obtainable in bundles of many filaments on spools, are generally separated by the lobes within the impregnation die and impregnated with melted fiber and optionally added polymer during processing.

The second added thermoplastic resin material must be compatible with the thermoplastic material forming the matrix of the core of the composite. The two materials must exhibit compatible coefficients of thermal expansion as well as bonding forces so that the intermediate mixing zone is formed at the interface of the matrices during the process of preparing the coated, long fiber-reinforcing
composite structure. The coefficients of thermal expansion of the two matrix materials should be within the same range of each other to ensure that the core and coating of the composite will expand and contract at the same rates. Otherwise, deformation of the composite structure may occur. The second thermoplastic resin matrix material is a carrier of the additive material and should be readily mixable therewith. While the second added thermoplastic resin material may be selected from polypropylene nylon 6, nylon 66, polyethylenes, polyacetals, polyphenylene sulfide, polyurethanes, polypropylene, polycarbonates, polyesters, acrylonitrile-butadiene-styrene, and combinations thereof, it is not essential that the first and second thermoplastic resin matrix materials be identical. The second thermoplastic resin material should mix well with the additive material, bond with the first matrix material, and exhibit a relatively low melt temperature so that a coating of the mixture will not cause melting of the first thermoplastic resin matrix of the long fiber-reinforcing composite structure.

Additive materials are generally selected from components that provide enhanced molding properties as well as physical and chemical properties of shaped articles prepared therefrom. The additive materials may also be selected from components that are not suitable for incorporating into the first thermoplastic resin material due to their viscosity-increasing characteristics. It may be desirable to add pigments to the composite structure to reduce finishing labor of shaped articles, or it may be desirable to add flame retardant agents to the composite structure to enhance the flame retarding features of the shaped article. Since many additive materials are heat sensitive, an excessive amount of heat may cause them to decompose and produce volatile gases. Therefore, if a heat sensitive additive material is extruded with an impregnation resin under high heating conditions, the result may be a complete degradation of the additive material. Additive materials of the invention may be selected from mineral reinforcing agents, lubricants, flame retardants, blowing agents, foaming agents, ultraviolet light resistant agents, thermal stabilizers, pigments, and combinations thereof. The mineral reinforcing agents may be selected from calcium carbonate, silica, mica, clays, talc, calcium
silicate, graphite, wollastonite, calcium silicate, alumina trihydrate, barium ferrite, and combinations thereof.

The second added thermoplastic resin-additive material composition typically is a blend of the second thermoplastic resin and additive materials. Generally, the composition may contain from about 10 to about 90 weight percent of the additive material and from about 90 to 10 weight percent of the second thermoplastic resin material. Typically, the second thermoplastic resin-additive material composition may contain from about 15 to about 85 weight percent of the additive material and from about 85 to about 15 weight percent of the second thermoplastic resin material, and preferably, from about 25 to about 75 weight percent of the additive material and from about 75 to about 25 weight percent of the second thermoplastic resin material. The composition may be prepared by melt blending the components in an extruder to form suitable mixtures of the components prior to feeding to the coating die of the process.

Generally, the lobed die of the present invention is operated at temperatures that are sufficient to cause melting and impregnation of the thermoplastic fiber in the roving onto the long fiber-reinforcing strands in the roving. Typically, the operation temperatures of the die is higher that the melt temperature of the thermoplastic fibers and the first additional resin material, and preferably, the die is operated at temperatures of from about 400° to about 800°F. Generally, the second stationary, coating die of the invention is operated at temperatures sufficient to ensure melting of the second additional thermoplastic resin-additive material blend without degradation of the additive material in the blend. Typically, the coating die is operated at temperatures of from about 250° to about 700°F.

Generally, shaped articles are prepared from pellets of coated, long fiber-reinforcing composite structures by known injection molding processes. The pellets are placed in an extruder-die assembly and molded into the shaped articles.
Since pigments and other agents may be applied to the composite structure during the coating portion of process, there is little need for finishing or applying additives to the surface of the shaped article.

The lobed die utilized in the process of the present invention may be of any suitable configuration which defines a tortuous conduit for wetting out the reinforcing strands of a commingled or hybrid roving. FIGURE 3 shows an enlarged schematic view of a portion of one suitable die which may be used in the practice of the process of the present invention. Referring to FIGURE 3, a feed port 140 is constructed in the same way as feed port 138. It should be understood that this invention can be practiced using a plurality of identical feed ports, which may optionally be coaxial with the production direction indicated as A on Figure 3. The number of feed ports used would vary with the number of rovings to be treated in the die at one time and the feed ports may be mounted in the upper die half 134 or the lower die half 136. Feed port 138 includes a sleeve 200 mounted in upper die half 134. Feed port member 138 is slidably mounted in sleeve 200. Feed port member 138 is split into at least two pieces, here shown as pieces 202 and 204. Feed port member 138 has a bore 206 passing longitudinally therethrough. Bore 206 is preferably shaped as a right cylindrical cone opening away from the upper die half 134. Roving 142 passes through bore 206 and enters passage 210 between upper die half 134 and lower die half 136. When knots or other imperfections are encountered in roving 142, feed port member 138 may be slidably pulled from sleeve 200 along the path shown by arrow 208 to allow such knots or imperfections in roving 142 to pass through bore 206 by separating piece 202 from piece 204. When such knots or imperfections in roving 142 have passed through bore 206 and entered passage 210, feed port member 138 may be pushed back in sleeve 200 in the direction shown by arrow 208. Thus feed port 138 allows for continuous production of formed product 152 even when knots or imperfections exist in roving 142.
A series of lobes 212, 214 and 216 are formed in upper die half 134 and lower die half 136 such that passage 210 takes a convoluted route. The function of lobes 212, 214 and 216 is to cause the reinforcing fiber strands of rovings 142 and another roving 146 to be passed over at least one lobe such that thermoplastic resin material (not shown) inside passage 210 thoroughly contacts each of the reinforcing fiber strands in rovings 142 and 146. By drawing the reinforcing fiber strands of rovings 142 and 146 over the lobes 212, 214 and 216, thorough contact between molten thermoplastic resin material and the reinforcing fiber strands of rovings 142 and 146 is assured. Pressure sensor 137 measures the pressure of a thermoplastic resin material inside passage 210.
WHAT IS CLAIMED IS:

1. A method of making a long fiber-reinforced thermoplastic composite comprising:

   (a) supplying a mixed fiber roving to a lobed pultrusion die, the mixed fiber roving comprising thermoplastic fibers and continuous reinforcing fibers;

   wherein the mixed fiber roving is from about 10 to about 90 weight percent thermoplastic fiber selected from polyethylene fibers, polyethylene terephthalate fibers, polybutylene terephthalate fibers, nylon fibers, thermoplastic polyurethane fibers, polyacetal fibers, polyphenylene sulfide fibers, cycloolefin copolymer fibers, thermotropic polyester fibers and mixtures thereof and from about 90 to about 10 weight percent reinforcing fiber;

   (b) drawing the mixed fiber roving through the lobed pultrusion die along a production direction while maintaining the lobed pultrusion die at a temperature operative to melt the thermoplastic fiber of the mixed fiber roving supplied thereto and optionally injecting a molten first additional thermoplastic resin composition into the pultrusion die whereby a nascent long fiber-reinforced thermoplastic composite is formed in the lobed pultrusion die including molten thermoplastic resin and continuous reinforcing fibers in intimate contact;

   (c) wherein the lobed pultrusion die defines a tortuous path along the production direction and is operative to knead the nascent composite as it is drawn therethrough whereby the individual reinforcing fibers are substantially wetted out with thermoplastic resin such that a thermoplastic rein matrix substantially fully impregnates the reinforcing fibers;
(d) withdrawing the long fiber reinforced thermoplastic composite from the pultrusion die;

(e) cooling the long fiber reinforced thermoplastic composite; and

(f) optionally, cutting the long fiber reinforced thermoplastic composite into pellets.

2. The method according to Claim 1, further comprising the step of feeding the long fiber reinforced thermoplastic composite to a coating die where the composite is coated with a molten second additional thermoplastic resin composition to further increase the polymer content of the thermoplastic composite.

3. The method according to Claim 2, wherein the second additional thermoplastic resin composition includes at least one component selected from processing aids, stabilizers and reinforcing agents.

4. The method according to Claim 1, wherein the mixed roving has a thermoplastic fiber content of from about 10 weight percent to about 50 weight percent and a reinforcing fiber content of from about 90 weight percent to about 10 weight.

5. The method according to Claim 1, wherein at least about 5 phc of resin are added as first additional thermoplastic resin composition at the pultrusion die.

6. The method according to Claim 5, wherein at least about 25 phc of resin are added as first additional thermoplastic resin composition at the pultrusion die.

7. The method according to Claim 6, wherein at least about 35 phc of resin are added as first additional thermoplastic resin composition at the pultrusion die.
8. The method according to Claim 7, wherein at least about 45 phc of resin are added as first additional thermoplastic resin composition at the pultrusion die.

9. The method according to Claim 8, wherein at least about 60 phc of resin are added as first additional thermoplastic resin composition at the pultrusion die.

10. The method according to Claim 9, wherein at least about 75 phc of resin are added as first additional thermoplastic resin composition at the pultrusion die.

11. The method according to Claim 5, wherein the first additional resin composition includes at least one component selected from processing aids, stabilizers and reinforcing agents.

12. The method according to Claim 1, wherein the thermoplastic fiber is a polyester fiber selected from polyethylene terephthalate fibers and polybutylene terephthalate fibers.

13. The method according to Claim 1, wherein the thermoplastic fiber is nylon fiber.

14. The method according to Claim 1, wherein the thermoplastic fiber is polyphenylene sulfide fiber.

15. The method according to Claim 1, wherein the thermoplastic fiber is polyacetal fiber.

16. The method according to Claim 1, wherein the thermoplastic fiber is cycloolefin copolymer fiber.

17. The method according to Claim 1, wherein the thermoplastic fiber is thermoplastic polyurethane fiber.
18. The method according to Claim 1, wherein the thermoplastic fiber is thermotropic polyester fiber.

19. The method according to Claim 1, wherein the thermoplastic fiber is polyethylene fiber.

20. The method according to Claim 1, wherein the thermoplastic composite is chopped into pellets having a length of from about 6 to about 50 mm.

21. The method according to Claim 20, wherein the thermoplastic composite is chopped into pellets having a length of from about 10 to about 25 mm.

22. The method according to Claim 1, wherein the composite has a reinforcing fiber content of at least about 50 phc.

23. The method according to Claim 1, wherein the composite has a reinforcing fiber content of at least about 60 phc.

24. The method according to Claim 1, wherein the composite has a reinforcing fiber content of at least about 70 phc.

25. The method according to Claim 1, operated at a line speed of at least about 100 meters per minute.

26. The method according to Claim 25, operated at a line speed of at least about 150 meters per minute.

27. The method according to Claim 1, wherein the thermoplastic fiber of the mixed fiber roving has a sizing agent applied thereto.
28. The method according to Claim 27, wherein the sizing or coupling agent is an amino silane sizing agent.

29. A shaped article prepared from pellets produced according to the process of Claim 1.

30. A long fiber-reinforced thermoplastic composite in the form of a pellet having a length of from about 6 mm to about 50 mm produced by melt-fusing a hybrid fiber roving comprising from about 10 to 50 weight percent thermoplastic fiber selected from polyethylene fibers, polyethylene terephthalate fibers, polybutylene terephthalate fibers, nylon fibers, thermoplastic polyurethane fibers, polyacetal fibers, polyphenylene sulfide fibers, cycloolefin copolymer fibers, thermotropic polyester fibers and mixtures thereof and from about 50 to 90 percent reinforcing fiber in a lobed pultrusion die to form a long fiber reinforced thermoplastic composite such that the thermoplastic matrix about the reinforcing fibers is substantially continuous.

31. The long fiber-reinforced thermoplastic composite according to Claim 30, in the form of a pellet having a length of from about 10 mm to about 25 mm.

32. A long fiber-reinforced thermoplastic composite in the form of a pellet having a length of from about 6 mm to about 50 mm produced by melt-impregnating a hybrid fiber roving comprising from about 10 to 50 weight percent thermoplastic fiber and from about 50 to 90 percent reinforcing fiber with at least about 10 phc of a first additional thermoplastic resin.

33. A long fiber-reinforced thermoplastic composite in the form of a pellet having a length of from about 6 mm to about 50 mm produced by melt-impregnating a hybrid fiber roving comprising from about 10 to 50 weight percent thermoplastic fiber selected from polyethylene fibers, polyethylene terephthalate fibers, polybutylene terephthalate fibers, nylon fibers,
thermoplastic polyurethane fibers, polyacetal fibers, polyphenylene sulfide fibers, cycloolefin copolymer fibers, thermotropic polyester fibers and mixtures thereof and from about 50 to 90 percent reinforcing fiber with at least about 25 phr of a first additional thermoplastic resin.

34. A long fiber-reinforced thermoplastic composite in the form of a pellet having a length of from about 6 mm to about 50 mm produced by melt-impregnating a hybrid fiber roving comprising from about 10 to 50 weight percent thermoplastic fiber selected from polyethylene fibers, polyethylene terephthalate fibers, polybutylene terephthalate fibers, nylon fibers, thermoplastic polyurethane fibers, polyacetal fibers, polyphenylene sulfide fibers, cycloolefin copolymer fibers, thermotropic polyester fibers and mixtures thereof and from about 50 to 90 percent reinforcing fiber with at least about 35 phr of a first additional thermoplastic resin.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B29C70/52 B29B15/10

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)

IPC 7 B29C B29B

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Relevant to claim No.</th>
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<td>COMPOSITES PART A, vol. 27, no. 1, 1996, pages 3-7, XP002287330 page 1, line 1</td>
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<td>US 5 358 680 A (BOISSONNAT PHILIPPE ET AL) 25 October 1994 (1994-10-25) column 3, line 3 - line 19 column 4, line 50 - line 52; figure</td>
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* Special categories of cited documents:
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Date of the actual completion of the International search 7 July 2004

Date of mailing of the international search report 22/07/2004

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