

Description

The present invention relates to reinforcing filament bundles in the form of elongated granules and to their use in dispersing fibers in thermoplastic resins during injection molding processes.

BACKGROUND OF THE INVENTION

Fiber filled plastic compounds suitable for injection molding have become widely used. The fibers impart many valuable characteristics to the injection molded articles, foremost of which are high dimensional stability, high modulus of elasticity, high resistance to distortion by heat, high tensile strength, unusually high flexural modulus and low shrinkage during curing. Glass-reinforced thermoplastic injection molding compounds and injection molding processes employing them are described in Bradt, U.S. 2,877,501. The technology of the Bradt patent has subsequently been extended. In addition to the styrene resins, styrene-acrylonitrile copolymer resins and styrene-butadiene copolymer resins described therein, numerous other injection-moldable thermoplastic resins, such as polycarbonate resins, acrylonitrile-butadiene-styrene terpolymer resins, poly (ethylene terephthalate) resins, polysulfone resins, polyphenylene ether resins, nylon resins, and the like, are effectively reinforced by glass fibers. Moreover, instead of glass fibers, subsequently developed commercial products are reinforced with filaments of carbon fibers, graphite fibers, aramid fibers, stainless steel filaments and others, as well as mixtures of any of the foregoing, many such products stemming directly from the technology disclosed in the above-mentioned U.S. 2,877,501. Such technology involves providing elongated granules, each of the granules containing a bundle of elongated reinforcing filaments extending generally parallel to each other longitudinally of the granule and a thermoplastic molding composition surrounding and permeating the bundle. In the process of injection molding, such granules are forced into a mold, wherein the filaments will be dispersed and produce molded articles with improved properties in comparison with the molded thermoplastic alone.

The above-mentioned U.S. 2,877,501, discloses pellets comprising 15-80 wt. % glass in thermoplastic resin, e.g., polystyrene. This corresponds to 8.1%-42.9% of filaments by volume and correspondingly 91.9-57.1% by volume of resin. Current processes for making such prior art filament-filled granules require a compounding/pelletizing step, in which the thermoplastic material is mixed with filaments, usually chopped bundles of filaments, and usually in an extruder, then the extrudate is chopped into molding granules. Such equipment is not readily available to the molder, and a number of specialty compounders have established businesses in which fibers from one source, and thermoplastics from another source are formulated into granules in drums or truckloads for sale to molders. It would be desirable to by-pass such compounders and permit molders to feed mixtures of thermoplastics and fibers directly into the molding press hopper achieving fiber dispersion by shear forces at the screw, nozzle, check valve, runners, gates, etc. in the injection molding machine. It would also be desirable to use, in comparison with the prior art, much less resin in the pellets, e.g., 2.5-32.5% by volume (instead of 57.1-91.9%) and much higher filament loadings, e.g., 67.5-97.5% by volume (instead of 8.1-42.9% by volume). However, until the present invention, this has not been possible because the fiber or filament bundles separate during chopping and tumbling with the reduced volume fractions of resin. There is also a tendency for the resin to degrade if the temperature is raised to lower viscosity and enhance dispersion. Moreover, individual fibers can become airborne and cause problems in handling.

The above-mentioned patent application discloses improved elongated granules which solve such problems by substituting for the thermoplastic matrix separating and coating the fiber bundles, as in the prior art, a much thinner layer of an efficient thermoplastic adhesive, which acts as a binder. However, although the polyvinyl acetate or polyester binder used in the above-mentioned application holds the fiber bundle together sufficiently to prevent broken bundles during chopping into elongated pellets and tumbling with the resin to be reinforced and then readily breaks down in the presence of molten resin and thereafter does not interfere with fiber dispersion, or degrade the resin properties, or constitute an environmental hazard, one drawback has developed and this is a tendency to prematurely break apart or "bird's nest" when high speed aggressive blending equipment is used.

Because the molding process itself is used to disperse the fibers uniformly throughout the molded part and the melt-blending compounding/pelletizing step is to be strictly avoided, it is obviously important to maintain fiber bundle integrity prior to the dispersion step.

The present invention has, as its principal object, the provision of a means to keep the bundles together during dryblending in high speed production machinery. As a result, when using electrically conductive fibers, such as nickel coated graphite fibers, superior electromagnetic shielding can be provided at vastly increased rates of production at equal load levels (compared with compounded pellets), providing better

shielding at one-half the cost, and, in comparison with the use of conductive, e.g., silver, paint there is much less or no secondary finishing with equivalent or better shielding, far superior physical properties, and superior long-term reliability.

5 DESCRIPTION OF THE DRAWING

In the drawing,

- FIG. 1 is a somewhat idealized isometric view, on an enlarged scale, of a molding granule of the prior art;
 10 FIG. 2 is a somewhat idealized, fragmental cross-section of a molding granule of the prior art on a still further enlarged scale;
 FIG. 3 is a somewhat idealized isometric view, on an enlarged scale, of a molding granule according to this invention, showing closer packing and no overcoat;
 FIG. 4 is a somewhat idealized, fragmental cross-section of a molding granule of this invention on a still
 15 further enlarged scale;
 FIG. 5a is a semi-schematic diagram showing a preferred way of making the elongated molding pellets of this invention; and
 FIG. 5b is a semi-schematic drawing illustrating the way in which the pellets of this invention are mixed and molded into shaped articles.

20 SUMMARY OF THE INVENTION

In accordance with the invention there is provided injection molding compound in the form of elongated granules, each of said granules containing a bundle of elongated reinforcing filaments extending generally
 25 parallel to each other longitudinally of the granule and substantially uniformly dispersed throughout said granule in a thermally stable, film forming thermoplastic adhesive comprising

(a) a poly(C₂-C₆ alkyl oxazoline), the monomeric unit of which is



whereby R = C₂-C₆ alkyl, in combination with

(b) a poly(vinylpyrrolidone),

35 wherein component (b) comprises from 7.5 to 75 percent by weight of component (a) and component (b) combined, said reinforcing filaments comprising from 67.5 to 97.5 percent by volume and the thermally stable, film forming adhesive comprising correspondingly from 2.5 to 32.5 percent by volume, the amount of thermoplastic adhesive not being substantially in excess of that which maintains fiber bundle integrity handling, said adhesive substantially surrounding each said filament.

40 Also contemplated by the invention are mixed injection molding compositions comprising:

(i) thermoplastic resin molding pellets; and

(ii) elongated granules comprising 67.5-97.5% by volume of reinforcing filaments extending generally parallel to each other longitudinally of each of the granules and substantially uniformly dispersed throughout the granule in from 2.5 to 32.5% by volume of a thermally stable, film forming thermoplastic
 45 adhesive comprising

(a) a poly(C₂-C₆ alkyl oxazoline) as defined above: in combination with

(b) a poly(vinylpyrrolidone), the amount of component (ii) in the composition being sufficient to provide 1-60% by weight of the filaments per 100% by weight of (i) plus (ii).

It is a further feature of the invention to provide a method of manufacturing an injection molding
 50 compound comprising the steps of continuously passing reinforcing filaments through one or more baths of a thermally stable, film forming thermoplastic adhesive in a liquid medium, e.g., water, to impregnate the filaments, passing the impregnated filaments through means such as a sized opening or over grooved rollers to remove any excess adhesive, passing the impregnated filaments into a heating zone first to evaporate the liquid medium and then to flux the thermoplastic adhesive, and withdrawing the treated
 55 filaments from the heating zone and thereafter chopping them into elongated granules, whereby there are produced granules comprising 67.5-97.5% by volume of reinforcing filaments extending generally parallel to each other longitudinally of the granule, substantially uniformly dispersed throughout said granule in from 2.5-32.5% by volume of the thermally stable, film forming thermoplastic adhesive combination as above

defined which substantially surrounds each said filament.

In still another aspect, the present invention contemplates, as an improvement in the process of injection molding, the step of forcing into a mold an injection molding composition comprising a blend of:

- (i) thermoplastic molding pellets; and
- 5 (ii) an amount effective to provide reinforcement of elongated granules, each of the granules as above defined: containing a bundle of reinforcing filaments extending generally parallel to each other longitudinally of the granule substantially uniformly dispersed in a thermally stable, film forming thermoplastic adhesive comprising
 - (a) a poly(C₂-C₆ alkyloxazoline) as defined above in combination with
 - 10 (b) a poly(vinylpyrrolidone), said adhesive substantially surrounding each said filament.

DETAILED DESCRIPTION OF THE INVENTION

Referring to the drawing, FIGS. 3 and 4, each filament contained in the injection molding granule is 15 surrounded by and the bundle is impregnated by the thermally stable, film-forming thermoplastic adhesive combination. The pellet itself may be of cylindrical or rectangular or any other cross-sectional configuration, but preferably is cylindrical. The length of the granules can vary, but for most uses 3.17 mm to 19.0 mm, (1/8 inch - 3/4 inch) will be acceptable and 3.17 to 6.35 mm (1/8 inch - 1/4 inch) will be preferred. The differences between the pellets of this invention and those of the prior art can be seen by comparison of 20 FIG. 1 with FIG. 3 and FIG. 2 with FIG. 4, respectively. Unlike the prior art (FIGS. 1 and 2) the pellets of this invention have close-packed filaments and the thermoplastic adhesive jacket is substantially dispersed upon contact with hot molten thermoplastic in the present invention. On the other hand, the prior art pellets will not readily separate into reinforcing filaments because of interference by the relatively thick jacket of thermoplastic resin.

25 Instead of using a lot of resin to impregnate the fiber bundle and surround it, as is done in the prior art, it is essential to use an adhesive efficient for the purposes of the invention, and that is to bind a high proportion of filaments into each elongated granule and maintain them throughout the chopping process and any subsequent blending steps in high speed, high throughput machines. The adhesive preferably will be used also in an amount which is not substantially in excess of that which maintains the fiber bundle integrity 30 during chopping. This amount will vary depending on the nature of the fibers, the number of fibers in the bundle, the fiber surface area, and the efficiency of the adhesive, but generally will vary from 2.5 to 32.5% and preferably from 5 to 15% by volume of the granule.

For uniform adhesive pick up on the fibers in the bundle it is preferred to use a small, but effective amount of a conventional surface active agent, which facilitates wetting and bonding to numerous different 35 substrates. Anionic, cationic and non-ionic surfactants are suitable for this purpose, the only requirement being that they be miscible with any solvent system used for impregnation and compatible with the thermoplastic film forming adhesive combination. Preferred surfactants, especially when graphite, or metal coated carbon fiber substrates are used, comprise anionic surfactants especially sodium salts of alkyl sulfuric acids. Particularly useful is sodium heptadecyl sulfate, sold by Union Carbide Co., under the 40 Trademark NIACET® No. 7.

Careful consideration should be given to selection of the film forming thermoplastic adhesive combination, subject to the above-mentioned parameters. Some adhesives are more efficient than others, and some, which are suggested for use as fiber sizings in the prior art will not work. For example, poly(vinyl acetate) and poly(vinyl alcohol), the former being suggested by Bradt in U.S. 2,877,501, as a sizing, do not work 45 herein because, it is believed, thermo-setting or cross linking occurs and this operates to prevent rapid melting and complete dispersion in the injection molding machine. While such materials are suitable for the resin rich compounded granules used in the Bradt patent, they are unsuitable herein.

The binder for use herein is a combination comprising poly (C₂-C₆ alkyl oxazolines) and poly (vinylpyrrolidone). The former is somewhat structurally related to N,N-dimethylformamide (DMF) and have 50 many of its miscibility properties. A readily available such polymer is poly(2-ethyl oxazoline), Dow Chemical Co. PEOx. This can also be made by techniques known to those skilled in this art. Poly(2-ethyl oxazoline) is thermoplastic, low viscosity, water-soluble adhesive. It can be used in the form of amber-colored and transparent pellets 4.74 mm (3/16") long and 3.17 mm (1/8") diameter. Typical molecular weights are 50,000 (low); 200,000 (medium) and 500,000 (high). Being water soluble, it is environmentally acceptable for 55 deposition from aqueous media. It also wets the fibers well because of low viscosity. It is thermally stable up to 380°C. (680°F.) in air at 500,000 molecular weight. Poly(vinylpyrrolidone) is an item of commerce, being widely available from a number of sources, and varying in molecular weight, as desired. While the poly(oxazoline) appears to provide dispersibility to the elongated bundles, the poly(vinylpyrrolidone) is

useful for high temperature resistance. Like the oxazoline, poly(vinylpyrrolidone) works well in water based impregnation media. Typical molecular weight ranges readily available can be used, for example 10,000; 24,000; 40,000; and 220,000. The higher molecular weight material tends to provide bundles which are more difficult to disperse. On the other hand, the lowest molecular weight causes some loss in heat resistance.

5 However, within the foregoing parameters, the adhesive combination on fiber bundles does not fracture appreciably during chopping to minimize free filaments from flying about, which can be a safety hazard. When blended with pellets of a thermoplastic resin system, the adhesive combination will melt readily allowing complete dispersion of the fibers throughout the resin melt while in a molding machine. However, pellets bound with this thermoplastic adhesive combination are indefinitely stable with the resin pellets
10 during blending, and don't break apart prematurely.

As a result of a number of trials, the invention as currently practiced provides optimum results when the following guidelines are adhered to:

The fiber type can vary, any fiber being known to be useful as a filler or reinforcement in a resin system can be used. Preferred fibers are carbon or graphite fibers, glass fibers, aramid fibers, stainless
15 steel fibers, metal coated graphite fibers, or a mixture of any of the foregoing.

The preferred thermoplastic adhesive component (a) comprises poly(ethyloxazoline), having a molecular weight in the range of 25,000 to 1,000,000, preferably 50,000-500,000, most preferably about 50,000.

The preferred thermoplastic adhesive component (b) comprises poly(vinylpyrrolidone), having a molecular weight in the range of from 10,000 to 220,000, preferably from 24,000 to 40,000 and most preferably
20 about 24,000.

It is preferred that the adhesive be deposited onto the filaments from a solvent system which can comprise any polar organic solvent, e.g., methanol, or mixture of such solvents, or water, alone, or in admixture. Acceptable bath concentrations for the thermoplastic adhesive can vary but is generally for component (a) it is in the range of 2.5-12% by weight, preferably 2.5-8%, and especially preferably 4-8%
25 by weight and, for component (b), in the range of 1-8% by weight, preferably 1-6% by weight, and, especially preferably, 1-4% by weight.

If a surface active agent is used, this too can vary in type and amount, but generally if an anionic alkyl sulfate is used, such as sodium heptadecyl sulfate, bath concentrations can range from 0.0005-0.5% by weight, preferably from 0.0005 to 0.05%, and most preferably, 0.0005-0.005%, by weight.

30 The amount of non-filament material in the filament-containing granules of the invention will vary, but, in general, will range from 2.5 to 32.5% by volume with any fiber, preferably from 5 to 15% by volume.

The amount of component (b) will be from about 7.5 to about 75% by weight based on the combined weights of (a) and (b) preferably from about 15% to about 50%.

The length of the elongated granule will generally range from 3.17 to 19.0 mm (1/8 to 3/4 inch),
35 preferably from 3.17 to 6.35 mm (1/8 to 1/4 inch). The diameters of each elongated granule can vary, depending primarily on the number of filaments and the thicknesses will vary from 0.53 to 4.76 mm one-forty eighth to three-sixteenths inch in diameter. Preferably, the diameter will be in the range of from 0.79 to 3.17 mm (one-thirty-second to one-eighth inches).

Numerous thermoplastic resins can be employed with the elongated granules of the present invention.
40 In general any resin that can be injection molded and that can benefit from a uniform dispersion of fibers can be used. For example polystyrene, styrene/acrylic acid copolymer, styrene/acrylonitrile copolymer, polycarbonate, poly (methyl methacrylate) poly(acrylonitrile/butadiene/styrene), polyphenylene ether, nylon, poly(1,4-butylene terephthalate), mixtures of any of the foregoing, and the like, can be used.

It is preferred to manufacture the injection molding composition of this invention by a continuous
45 process. A suitable apparatus is shown in FIG. 5a. Typically, bundles of filaments, such as graphite fiber tows or metal coated graphite fiber tows, 3,000 to 12,000 filaments per bundle, glass yarns, 240 filaments to a strand, or stainless steel tow, 1159 filaments per bundle, are drawn from storage roller 2 and passed through one or more baths 4, containing the thermally stable, film forming thermoplastic adhesive in a liquid medium, e.g., water, to impregnate the filaments, then through means such as die 6, to control pick up. The
50 impregnated filaments thereafter are passed into a heating zone, e.g., oven 8, to evaporate the liquid medium, e.g., water and then to flux the thermoplastic adhesive. The treated filaments 10 are withdrawn from the heated zone, transported to chopper 12 and cut into fiber granules illustratively varying between 3.17 to 6.35 mm (1/8-1/4") according to the requirements of the particular apparatus. The granules are then stored in a suitable container 14 for subsequent use. Any surfactant conveniently is included in a single
55 bath with the adhesive. It will be observed that this procedure results in the orientation of the reinforcing fibers along one axis of the granule.

To carry out the molding method of the present invention, a flow diagram in the general form illustrated in FIG. 5b is preferably employed. Fiber granules 16 are mixed with resin pellets 18 to produce a blended

mixture 20. This is added to conventional hopper 22 on molding press 24. When passing through cylinder 26, prior to being forced into mold 28 a uniform dispersion of the fibers is accomplished. Removal of molded article 30 provides a fiber reinforced item produced according to this invention.

It is understood that other plasticizers, mold lubricants, coloring agents, and the like, can be included, and that the amount of reinforcement in the components can be varied according to well understood techniques in this art.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following are examples of the present invention but are not to be construed to limit the claims in any manner whatsoever. The electrical measurements (Shielding effectiveness (SE) values in decibels) are averages usually of four samples.

EXAMPLE 1

Using an apparatus of the type generally shown in FIG. 5a a bath comprising the following is formulated:

Component	% by weight
poly(ethyl oxazoline), MW 50,000	6.0
poly(N-vinylpyrrolidone), MW 24,000	4.0
sodium heptadecyl sulfate*	0.001%
water	89.899

* NIACET® No. 7 surfactant

A tow of continuous graphite fibers (12,000 count) each of which has an electroplated nickel coating thereon is led through the bath. The graphite filaments each average about 7 μ m in diameter. The nickel-coating thereon is approximately 0.5 μ m in thickness. The nickel coated graphite tows are prepared by continuous electroplating in accordance with the procedure described in European Patent Application No. 0088884 (published September 21, 1983). After passing out of the coating bath the treated fibers are passed over grooved rollers to remove excess adhesive then passed through an oven at about 149°C (300°F). The impregnated filaments then are chopped to 6.35 mm (1/4") lengths and there are produced elongated granules of approximately 1.58 mm (1/16") in diameter of cylindrical shape and form. The non-filament material content is 9% by volume.

EXAMPLES 2-3

The procedure of Example 1 is repeated, adjusting the poly(vinylpyrrolidone) content in the bath to 2% and 6% by weight, respectively, and elongated granules according to this invention are produced.

EXAMPLES 4-6

Using the process generally shown in FIG. 5b, sufficient of the elongated pellets produced in Examples 1, 2 and 3, respectively, are blended with pellets of a thermoplastic molding resin composition comprising poly(bisphenol A carbonate) (Mobay Co. MERLON® 6560) to provide 5 weight percent of nickel-coated graphite filaments in the blend. The blended mixture is molded in an injection molding press into work pieces suitable for physical and electrical testing. The electromagnetic shielding effectiveness (SE) and EMI attenuation are measured to determine dispersion efficiency.

The Electro-Metrics Dual Chamber test fixture is used according to ASTM E57-83 to measure the shielding effectiveness (SE) of the compositions of Examples 4-6 of this invention. The results are set forth in Table I:

TABLE 1**Shielding Effectiveness Poly(bisphenol-A Carbonate) Containing Nickel-Plated Graphite Filaments**

EXAMPLE	4	5	6
Composition (parts by weight)			
Poly(bisphenol A carbonate)	95	95	95
Elongated film bonded bundles (Examples 1-3)	5	5	5
Shielding Effectiveness, decibels @			
30 MHz	20	13	15
100 MHz	17	12	13
300 MHz	33	31	31
1000 MHz	12	10	11
* Controls			

These data demonstrate that the fibers are uniformly and efficiently dispersed.

EXAMPLE 7

The procedure of Examples 4-6 is repeated substituting for the thermoplastic resin pellets, pellets comprising poly(acrylonitrile/butadiene/styrene) (Borg Warner CYCOLAC® KJB) resin and plaques suitable for measuring SE effect are molded.

EXAMPLE 8

The procedure of Example 4-6 is repeated but poly(2,6-dimethyl-1,4-phenylene ether)-high impact strength rubber modified polystyrene resin pellets (General Electric NORYL® N-190) are substituted, and plaques suitable for measuring SE are prepared.

EXAMPLES 9-11

The procedure of Example 1 is repeated, substituting for the nickel coated graphite tows, tows of uncoated graphite fibers (Example 9), glass fibers, 240 filaments/ strand (Example 10), and stainless steel fiber tows comprising 1159 count filaments each measuring about 7 μ m in diameter (Example 11). Elongated granules according to this invention are prepared, comprising about 85 to 95% by volume of the respective filaments.

EXAMPLES 12-14

The procedure of Examples 1-3 and 4-6 are repeated but poly(N-vinyl pyrrolidone), MW 40,000 is substituted for the 24,000 molecular weight PVP. Plaques for measuring SE properties and test pieces for strength testing are prepared.

The Shielding Effectiveness of the compositions molded from the mixtures of Examples 12, 13 and 14 are measured by ASTM E87-83 as described above and the data are set forth in Table 2:

TABLE 2

**Shielding Effectiveness of Polycarbonate Resins
Containing Nickel Coated Graphite Fibers**

<u>EXAMPLE</u>	<u>12</u>	<u>13</u>	<u>14</u>
<u>Composition (parts by weight)</u>			
Poly(bisphenol A carbonate)	95	95	95
Nickel coated graphite elongated film bonded bundles (4%, 2%, 6% PVP)	5	5	5
Shielding Effectiveness, decibels @			
30 MHz	16	18	17
100 MHz	14	15	15
300 MHz	38	36	39
1000 MHz	11	11	11

Again, significant shielding effectiveness is obtained after using the elongated granules of this invention.

In making the elongated pellets of this invention, other fibers can be substituted, e.g., aramid fiber, e.g., KEVLAR® fiber, ceramic fiber, or combinations of any of the foregoing such fibers. Aramid fiber is particularly interesting because it is virtually impossible to chop and blend with thermoplastic resins because it frays and birdnests. When prepared in the form of coated bundles herein, aramid fiber chops very well and mixes easily.

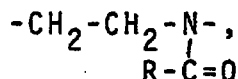
The foregoing examples show that poly(vinylpyrrolidone) (PVP) alloyed with poly(ethyloxazoline) is very useful to provide elongated granules according to this invention. Experiments have shown that various molecular weights can be used. Experiments also have shown that PVP is useful to reduce tack at elevated temperatures, while at the same time aiding significantly in the preservation of bundle integrity. It has also been observed that toughness increases as the molecular weight of the PVP increases. This property is useful when compounding at high temperature, with rapid drying, or under aggressive handling conditions.

Many variations of the present invention will suggest themselves to those skilled in the art in light of the foregoing detailed description. All such obvious variations are within the full intended scope of the appended claims.

Claims

1. An injection molding compound in the form of elongated granules, each of said granules containing a bundle of elongated reinforcing filaments extending generally parallel to each other longitudinally of the granule and substantially uniformly dispersed throughout said granule in a thermally stable, film forming thermoplastic adhesive comprising

(a) a poly(C₂-C₆ alkyl oxazoline), the monomeric unit of which is



whereby R = C₂-C₆ alkyl, in combination with

(b) a poly(vinylpyrrolidone),

wherein component (b) comprises from 7.5 to 75 percent by weight of component (a) and component (b) combined, said reinforcing filaments comprising from 67.5 to 97.5 percent by volume and the thermally stable, film forming adhesive comprising correspondingly from 2.5 to 32.5 percent by volume,



TABLE 2

Shielding Effectiveness of Polycarbonate Resins
Containing Nickel Coated Graphite Fibers

EXAMPLE	12	13	14
<u>Composition (parts by weight)</u>			
Poly(bisphenol A carbonate)	95	95	95
Nickel coated graphite elongated film bonded bundles (4%, 2%, 6% PVP)	5	5	5
<u>Shielding Effectiveness,</u> decibels @			
30 MHz	16	18	17
100 MHz	14	15	15
300 MHz	38	36	39
1000 MHz	11	11	11

Again, significant shielding effectiveness is obtained after using the elongated granules of this invention.

In making the elongated pellets of this invention, other fibers can be substituted, e.g., aramid fiber, e.g., KEVLAR® fiber, ceramic fiber, or combinations of any of the foregoing such fibers. Aramid fiber is particularly interesting because it is virtually impossible to chop and blend with thermoplastic resins because it frays and birdnests. When prepared in the form of coated bundles herein, aramid fiber chops very well and mixes easily.

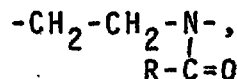
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Many variations of the present invention will suggest themselves to those skilled in the art in light of the foregoing detailed description. All such obvious variations are within the full intended scope of the appended claims.

Claims

1. An injection molding compound in the form of elongated granules, each of said granules containing a bundle of elongated reinforcing filaments extending generally parallel to each other longitudinally of the granule and substantially uniformly dispersed throughout said granule in a thermally stable, film forming thermoplastic adhesive comprising

(a) a poly(C₂-C₆ alkyl oxazoline), the monomeric unit of which is



whereby R = C₂-C₆ alkyl, in combination with

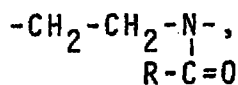
(b) a poly(vinylpyrrolidone),

wherein component (b) comprises from 7.5 to 75 percent by weight of component (a) and component (b) combined, said reinforcing filaments comprising from 67.5 to 97.5 percent by volume and the thermally stable, film forming adhesive comprising correspondingly from 2.5 to 32.5 percent by volume,



the amount of thermoplastic adhesive not being substantially in excess of that which maintains fiber bundle integrity handling, said adhesive substantially surrounding each said filament.

2. An injection molding compound as defined in claim 1 wherein said granules are from 0.53 to 4.76 mm (one-forty eighth to three-sixteenths inches) in diameter.
3. An injection molding compound as defined in claim 2 wherein said granules are from 0.79 to 3.17 mm (one-thirty second to one-eighth inches) in diameter.
4. An injection molding compound as defined in claim 1 wherein the reinforcing filaments comprise from 85 to 95 % by volume and the thermally stable, film forming adhesive comprises correspondingly from 5 - 15 % by volume.
5. An injection molding compound as defined in claim 1 wherein said reinforcing filaments comprise graphite fibers, glass fibers, aramid fibers, stainless steel fibers, metal coated graphite fibers or a mixture of any of the foregoing.
6. An injection molding compound as defined in claim 5 wherein the reinforcing filaments comprise graphite fibers.
7. An injection molding compound as defined in claim 6 wherein the reinforcing filaments comprise nickel coated graphite fibers.
8. An injection molding compound as defined in claim 1 wherein the thermoplastic adhesive comprises poly(ethyl oxazoline).
9. An injection molding compound as defined in claim 8 wherein the poly(ethyl oxazoline) has a molecular weight in the range of from 50,000 to 500,000.
10. An injection molding compound as defined in claim 1 wherein the thermoplastic adhesive comprises poly(ethyl oxazoline) and poly(vinylpyrrolidone).
11. An injection molding compound as defined in claim 10 wherein the poly(vinylpyrrolidone) has a molecular weight in the range of from 10,000 to 220,000.
12. An injection molding composition comprising:
 - (i) thermoplastic resin molding pellets;
 - and
 - (ii) elongated granules as defined in claim 1,
 the amount of component (ii) in said composition being sufficient to provide 1-60 % by weight of said filaments per 100 % by weight of (i) plus (ii).
13. A method for manufacturing an injection molding compound comprising the steps of continuously passing reinforcing filaments to at least one bath of thermally stable film forming thermoplastic adhesive in a liquid medium to impregnate the filaments, passing the impregnated filaments through means to remove any excess adhesive, passing the treated filaments into a heating zone first to evaporate the liquid medium and then to flux the thermoplastic adhesive, and withdrawing the treated filaments from said zone and thereafter chopping them into elongated granules, characterized in that the thermally stable, film forming thermoplastic adhesive comprises
 - (a) a poly(C₂-C₆ alkyl oxazoline), the monomeric unit of which is



whereby R = C₂-C₆ alkyl, in combination with

(b) a poly(vinylpyrrolidone), whereby granules according to claim 1 are produced.



14. In the process of injection molding the step of forcing into a mold an injection molding composition comprising a mixture of
 (i) thermoplastic molding pellets
 and
 5 (ii) an amount effective to provide reinforcement of elongated granules according to claim 1.

Revendications

1. Matériau moulable par injection sous la forme de granulés allongés, chaque granulé contenant un faisceau de filaments de renforcement allongés, s'étendant à peu près parallèlement les uns par rapport aux autres, selon la longueur du granulé, en étant à peu près uniformément dispersés à l'intérieur du granulé, dans un adhésif thermoplastique filmogène stable à la chaleur, comprenant :

(a) une poly(alkyl en C₂-C₆)oxazoline dont le motif monomère est



R représentant un groupe alkyle en C₂ à C₆, associée avec :

- 20 (b) une poly(vinylpyrrolidone) ;

le composant (b) représentant de 7,5 à 75 % du poids du composant (a) et du composant (b) réunis, ces filaments de renforcement représentant de 67,5 à 97,5 % en volume, et l'adhésif filmogène stable à la chaleur, représentant, de manière correspondante, de 2,5 à 32,5 % en volume, et la quantité d'adhésif thermoplastique n'étant pratiquement pas supérieure à celle suffisante pour maintenir l'intégrité des faisceaux de fibres en cours de manutention, l'adhésif enrobant à peu près chaque filament.

2. Matériau moulable par injection selon la revendication 1, les granulés ayant un diamètre de 0,53 à 4,76 mm.
- 30 3. Matériau moulable par injection selon la revendication 2, les granulés ayant un diamètre de 0,79 à 3,17 mm.
4. Matériau moulable par injection selon la revendication 1, les filaments de renforcement représentant de 85 à 95 % en volume, et l'adhésif filmogène stable à la chaleur, représentant, de manière correspondante, de 5 à 15 % en volume.
- 35 5. Matériau moulable par injection selon la revendication 1, les filaments de renforcement, comprenant des fibres de graphite, des fibres de verre, des fibres d'aramide, des fibres d'acier inoxydable, des fibres de graphite revêtues de métal, ou des mélanges de celles-ci.
- 40 6. Matériau moulable par injection selon la revendication 5, les filaments de renforcement comprenant des fibres de verre.
7. Matériau moulable par injection selon la revendication 6, les filaments de renforcement comprenant des fibres de graphite revêtues de nickel.
- 45 8. Matériau moulable par injection selon la revendication 1, l'adhésif thermoplastique comprenant de la poly(éthyl oxazoline).
9. Matériau moulable par injection selon la revendication 8, la poly(éthyl oxazoline) ayant un poids moléculaire de 50 000 à 500 000.
- 50 10. Matériau moulable par injection selon la revendication 1, l'adhésif thermoplastique comprenant de la poly(éthyl oxazoline) et de la poly(vinylpyrrolidone).
- 55 11. Matériau moulable par injection selon la revendication 10, la poly(vinylpyrrolidone) ayant un poids moléculaire de 10 000 à 220 000.



12. Composition moulable par injection, comprenant :
- (i) des pastilles de résine thermoplastique moulables ; et
 - (ii) des granulés allongés selon la revendication 1, la quantité du composant (ii) dans la composition, étant suffisante pour procurer de 1 à 60 % en poids des filaments pour 100 % en poids des composants (i) et (ii).
13. Procédé de fabrication d'un matériau moulable par injection, selon lequel on fait passer de manière continue des filaments de renforcement à l'intérieur d'au moins un bain d'adhésif thermoplastique filmogène stable à la chaleur dans un milieu liquide, afin d'imprégner les filaments, on fait passer les filaments imprégnés à travers des moyens destinés à éliminer l'adhésif en excès, on fait passer les filaments traités dans une zone de chauffage afin d'évaporer d'abord le milieu liquide, et de fondre ensuite l'adhésif thermoplastique, et on retire les filaments traités de ladite zone, et on les hâche ensuite sous la forme de granulés allongés, caractérisé en ce que l'adhésif thermoplastique filmogène stable à la chaleur, comprend :
- (a) une poly(alkyl en C₂-C₆)oxazoline dont le motif monomère est
- $$\begin{array}{c} -\text{CH}_2-\text{CH}_2-\text{N}- \\ | \\ \text{R}-\text{C}=\text{O} \end{array},$$
- R représentant un groupe alkyle en C₂ à C₆, associée avec :
- (b) une poly(vinylpyrrolidone), de sorte que l'on obtient des granulés selon la revendication 1.
14. Procédé de moulage par injection, selon lequel on introduit à force dans un moule, une composition moulable par injection, comprenant un mélange :
- (i) de pastilles thermoplastiques moulables, et
 - (ii) d'une quantité de granulés allongés selon la revendication 1, efficace pour renforcer.

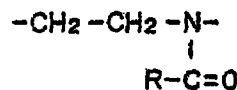
Patentansprüche

1. Formbares Material für Spritzguß in der Form von länglichen Granulat Körnern, wobei jedes der Granulat Körner ein Bündel von länglichen verstärkenden Filamenten enthält, die sich im allgemeinen parallel zueinander in Längsrichtung des Granulat korns erstrecken und im wesentlichen einförmig in dem Granulat korn dispergiert sind in einem thermisch stabilen, filmbildenden thermoplastischen Klebstoff, umfassend
- (a) ein Poly(C₂-C₆-alkyloxazolin), dessen Monomereinheit
- $$\begin{array}{c} -\text{CH}_2-\text{CH}_2-\text{N}- \\ | \\ \text{R}-\text{C}=\text{O} \end{array}$$
- ist, wobei R C₂-C₆-Alkyl ist, in Kombination mit
- (b) einem Poly(vinylpyrrolidon),
- wobei die Komponente (b) von 7,5 bis 75 Gew.% von Komponente (a) und Komponente (b) kombiniert, ausmacht, die erwähnten verstärkenden Filamente von 67,5 bis 97,5 Vol.% ausmachen und der thermisch stabile, filmbildende Klebstoff entsprechend von 2,5 bis 32,5 Vol.% ausmacht, wobei die Menge des thermoplastischen Klebstoffs nicht wesentlich größer ist als diejenige Menge, mit der die Integrität des Faserbündels bewahrt bleibt, wobei der Klebstoff im wesentlichen jedes Filament umgibt.
2. Formbares Material gemäß Anspruch 1, wobei die Granulat Körner einen Durchmesser von 0,53 bis 4,76 mm (1/48 bis 3/16 Zoll) aufweisen.
3. Formbares Material gemäß Anspruch 2, wobei die Granulat Körner einen Durchmesser von 0,79 bis 3,17 mm (1/32 bis 1/8 Zoll) aufweisen.
4. Formbares Material gemäß Anspruch 1, wobei die verstärkenden Filamente von 85 bis 95 Vol.% ausmachen und der thermisch stabile filmbildende Klebstoff entsprechend von 5 - 15 Vol.% ausma-



chen.

5. Formbares Material gemäß Anspruch 1, wobei die verstärkenden Filamente Graphitfasern, Glasfasern, Aramidfasern, Edelstahlfasern, metallbeschichtete Graphitfasern oder ein Gemisch beliebiger der vorstehenden Fasern umfassen.
6. Formbares Material gemäß Anspruch 5, wobei die verstärkenden Filamente Graphitfasern umfassen.
7. Formbares Material gemäß Anspruch 6, wobei die verstärkenden Filamente mit Nickel beschichtete Graphitfasern umfassen.
8. Formbares Material gemäß Anspruch 1, wobei der thermoplastische Klebstoff Poly(ethyloxazolin) umfaßt.
9. Formbares Material gemäß Anspruch 8, wobei das Poly-(ethyloxazolin) ein Molekulargewicht im Bereich von 50 000 bis 500 000 aufweist.
10. Formbares Material gemäß Anspruch 1, wobei der thermoplastische Klebstoff Poly(Ethyloxazolin) und Poly(vinylpyrrolidon) umfaßt.
11. Formbares Material gemäß Anspruch 10, wobei das Poly-(vinylpyrrolidon) ein Molekulargewicht im Bereich von 10 000 bis 220 000 hat.
12. Formbare Masse für Spritzgußzwecke, umfassend
- (i) formbare Pellets aus thermoplastischem Harz;
- und
- (ii) längliche Granulatkörner, wie sie in Anspruch 1 definiert sind,
- wobei die Menge der Komponente (ii) in der Masse ausreicht zur Schaffung von 1 bis 60 Gew.% der erwähnten Filamente pro 100 Gew.% von (i) plus (ii).
13. Verfahren zur Herstellung eines formbaren Materials für Spritzgußzwecke, umfassend die Stufen des kontinuierlichen Durchleitens von verstärkenden Fasern durch mindestens ein Bad von thermisch stabilem filmbildendem thermoplastischem Klebstoff in einem flüssigen Medium, um die Filamente zu imprägnieren, das Leiten der imprägnierten Filamente durch Mittel, um etwaigen überschüssigen Klebstoff zu entfernen, das Leiten der behandelten Fasern in eine Heizzone, um zunächst das flüssige Medium zu verdampfen und anschließend den thermoplastischen Klebstoff zu verflüssigen, und das Abziehen der behandelten Filamente aus der Zone, und anschließend das Zerkleinern derselben in längliche Granulatkörner, dadurch gekennzeichnet, daß der thermisch stabile, filmbildende thermoplastische Klebstoff
- (a) ein Poly(C₂-C₆-alkyloxazolin) umfaßt, dessen monomere Einheit



ist, wobei R für C₂-C₆-Alkyl steht in Kombination mit

(b) einem Poly(vinylpyrrolidon), wobei Granulatkörner gemäß Anspruch 1 hergestellt werden.

14. Im Spritzgußverfahren die Verfahrensstufe, bei der in eine Form eine formbare Masse für Spritzgußzwecke eingebracht wird, umfassend ein Gemisch von
- (i) thermoplastischen formbaren Pellets
- und
- (ii) längliche Granulatkörner gemäß Anspruch 1 in einer Menge, die wirksam ist zur Erzielung von Verstärkung.