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3,074,901

COMPOSITION COMPRISING POLYTETRAFLUOROETHYLENE PARTICLES ADMIXED WITH POLYSTYRENE CONTAINING DIMETHYL PHTHALATE

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The present invention relates to a method of preparing filaments and fibers from intractable polymers, more explicitly to a melt-spinning process for polymers which are ordinarily not melt shapable either because of instability at temperatures of their respective melting points or which have too high a melt viscosity, or which have too high a melting point or do not melt.

It is well known that polymers of high-melting point and little or no solubility in known solvents for other polymers, as for instance polytetrafluoroethylene, could not be melt spun and methods to shape these polymers into textile denier filaments have been sought for some time. Certain high-melting or non-melting polymers, e.g., acrylonitrile polymers, which have been found to dissolve in certain specific solvents, have already been proven to be of immense commercial value because of their high melting point and their resistance to common solvents and chemicals. Great demand has developed for such polymers in coating compositions and as filaments, bristles, rods, fabrics, felts, films, and other shaped articles. However, the use of solvents involves an expense not involved in melt spinning, requires rigid controls in removal of and recovery of solvent, and places limitations on the spinning process, e.g., with respect to allowable concentration of fiber-forming material in the spinning solution, the time required for coagulating and the concomitant restrictions on spinning speed.

Moreover, in spite of the obvious valuable characteristics of certain classes of polymers, as outlined above, certain of these polymers, for example, acrylonitrile polymers, of very high molecular weight, are either insoluble or their solutions cannot be spun, in a practical way, into useful filaments or shaped into other articles because of too high a solution viscosity or inability to conform to known methods used for the production of such articles. As to polytetrafluoroethylene, this polymer can, by known techniques, be shaped only into very weak filaments of no practical use before sintering and the freshly formed filaments are rather crude with the further disadvantage that their weakness before sintering prevents handling by conventional normal and relatively inexpensive methods. Methods involving extrusion of a lubricated paste of the intractable polymer have been used in the preparation of heavy denier monofilaments, but textile denier filaments and multifilament yarns containing them have not been obtainable by this method because no stretching during spinning is possible.

It is, accordingly, an object of the present invention to provide a melt-spinning process for making shaped articles from intractable, non-melt-shapable polymers. A further object is to provide new compositions of matter for use in the preparation of shaped articles such as fibers or filaments of these polymers. A still further object is to provide a process for making strong textile filaments from the aforesaid class of polymers. Other objects appear hereinafter.

These objects are accomplished by intimately mixing, preferably by aqueous dispersion procedure, a non-melt-shapable, intractable polymer with a melt-spinnable matrix polymer, the mixture being then melt-spun into non-tacky, relatively strong filaments, or melt-shaped into

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other articles, the shaped articles being then, if and when desired, sintered with coalescence of the intractable polymer and, preferably with simultaneous elimination of the matrix polymer as gaseous combustion or disintegration products so as to yield orientable fibers of the intractable polymer essentially free of the matrix polymer.

The invention will be more clearly understood by reference to the examples and the discussion which follows, in which parts, percentages and proportions are by weight unless otherwise indicated. These examples are given for illustration only and are not limitative.

EXAMPLE I

An aqueous dispersion of polystyrene (molecular weight of 250,000) sold as "Polystyrene Latex R" by the Koppers Company and a 60% polytetrafluoroethylene dispersion in water (i.e., the dispersion contains 60% of the polymer) were mixed to give a weight ratio of 2:1 polytetrafluoroethylene/polystyrene in the mixture. The mixed dispersion was then coagulated by adding acetone mixed with a saturated aqueous alum solution and vigorously stirring. The coagulum was filtered, washed with water, and dried. The mixture was readily melt-spun at 250° to 280° C. and 4,000 p.s.i. (pounds per square inch gage pressure) through a 9-mil spinneret hole. A spin stretch ratio of 10:1 was easily attained by drawing the solidified filaments to 10 times the undrawn length of the filament, with the obtaining of a smooth, white drawn filament. This was sintered over a hot plate at 375° C. to a light tan drawable polytetrafluoroethylene filament with the polystyrene matrix being decomposed and removing as gases at the sintering temperature. The drawn filament was 10 d.p.f. (denier per filament).

EXAMPLE II

To 222 cc. of the 60% aqueous polytetrafluoroethylene dispersion of Example I was added 95 cc. of the "Polystyrene Latex R" composition of Example I and the mixture stirred until smooth. 500 g. acetone and 150 g. of a saturated aqueous alum solution were mixed and added to the above smooth co-dispersion, completely precipitating the discrete particles in an intimate mixture. The solids were filtered, flushed with hot water, filtered again, and dried. The composition of this mixture was 5 parts polytetrafluoroethylene to 1 part polystyrene.

Of this mixture, 27 g. were screened through a 14-mesh screen. After adding 4 cc. dimethyl phthalate, the mass was heated 45 minutes to 65° C. under vacuum, left at room temperature for 24 hours, and finally extruded at 275° C. through a single hole spinneret comprising an inner 45° tapered conical entrance terminating in a 10 mil extrusion orifice. At a pressure of 14–15,000 p.s.i. (gage), a wind-up speed of 50 y.p.m. (yards per minute) was obtained. The dry tenacity of this monofilament before sintering was 0.36 g.p.d.; its dry elongation was 31%.

EXAMPLE III

A composition containing approximately a 9:1 weight ratio of polytetrafluoroethylene/polyvinyl acetate was prepared by adding 36.3 g. of a 55% aqueous polyvinyl acetate dispersion to 333 g. of a 60% polytetrafluoroethylene aqueous dispersion with vigorous stirring to form a smooth mixture which was coagulated, with stirring, by the addition of acetone in excess of that required to complete the coagulation. The polyvinyl acetate used was a commercial product sold as "Elvacet 80–90" by E. I. du Pont de Nemours and Company and had a molecular weight of 100,000. The coagulated mass was dried and subsequently melt-spun at 150–170° C. and 20,000 p.s.i. (pounds per square inch gage pressure). The filament was sintered in a salt bath at 375° C., washed, and drawn to 4×(300% increase in length) at 370° C.

EXAMPLE IV

A composition containing a 10:1 ratio of polytetrafluoroethylene/polyisobutylene (molecular weight of 150,000) was prepared by simultaneously coagulating a mixture of the two aqueous dispersions with acetone similarly to Example III. The aqueous dispersion of polyisobutylene was that sold as "Vistanex Type S" by Enjay Company, Inc. After filtration, washing and drying, the mixture was spun through a 8-mil tapered entrance spinneret at 180° C. and 18,000 p.s.i. (gage). The fiber was sintered at 370° C. in a salt bath and was drawn to 4× over a hot plate at 370° C., the sintered and drawn fiber having a dry tenacity of 1.58 g. per denier and a dry elongation of 15%.

EXAMPLE V

A composition containing a 2:7 ratio of high molecular weight polyacrylonitrile (mol. wt. of about 1,000,000)/polyisobutylene (of Example IV) was prepared by simultaneous coagulation of a mixture of the two aqueous dispersions with a saturated alum solution followed by filtration, washing and drying. The mixture was extruded at 180° C. and 5,500 p.s.i. (gage) through a 9-mil spinneret hole and gave a white fiber drawable to yield an elastic fiber, i.e., a fiber which could be highly stretched under tension with return, on release of tension, to the original length. This fiber was placed in an aqueous 60% calcium thiocyanate bath for one hour at 130° C. The resulting swollen fiber was washed with water and was drawn to 3× to yield a fiber of good strength. The purpose of the thiocyanate bath was to coalesce the polyacrylonitrile particles to produce the polyacrylonitrile fiber.

EXAMPLE VI

A composition containing a 2:1 ratio of polyacrylonitrile/polyethylene was made by grinding together the micropulverized polymers in a ball mill. The polyacrylonitrile had a molecular weight of about 1,000,000 and the polyethylene had a molecular weight of about 150,000. The mixture was extruded at 200° C. and at 5,500 p.s.i. (gage) to give a white fiber. The polyacrylonitrile was coalesced in an aqueous 60% calcium thiocyanate bath for 15 minutes at 130° C.

EXAMPLE VII

The experiment of Example I was repeated, using a 10:1 ratio of polytetrafluoroethylene/polystyrene solids. This mixture was melt-spun at 275° C. and 20,000 p.s.i. (gage), sintered in a salt bath at 375° C., washed with water, and dried. The filament was drawn 4× at 370° C. to give a dry tenacity of 1.4 g.p.d. and 20% dry elongation. Some yarn was drawn as high as 7×.

EXAMPLE VIII

In this example, the influence of lubricants and plasticizers were investigated with the objective of reducing pressures and increasing spinning speeds. The results are shown in the following Table A. White, high-viscosity mineral oil sold as "Primol D" by Enjay Company, Inc. was incorporated into a finely-ground solid spin mix containing 10 parts by weight of polytetrafluoroethylene and 1 part of polystyrene, and prepared by stirring the mix into a pentane solution of the oil and then evaporating the solvent (pentane). The mix was then melt-spun into a filament. Although the melt was considerably more fluid than that not containing the white oil, the threadline was weak and non-homogenous. If the material added is a good plasticizer for the support material instead of merely a lubricating medium, lower melt viscosities result and higher spinning speeds are thereby obtained. Dimethyl phthalate was sprayed with stirring into a spin mix powder of polytetrafluoroethylene/polystyrene and was permitted to soak at 60° C. for three hours. With a spin mix of 5 parts polytetrafluoroethylene, 1 part polystyrene, and 1 part plasticizer, it was possible to wind up the good

quality threadline at 50 y.p.m. and 17,000 p.s.i. (gage) approximately the pressures attained at lower spinning speeds (2 to 20 y.p.m.) with unplasticized mixtures. At comparable deliveries, pressures were about ½ those previously obtained from unplasticized mixtures. Doubling the amount of polytetrafluoroethylene and holding constant the ratio of plasticizer to the matrix polystyrene, reduced spinnability considerably due apparently to uneven plasticizing. Plasticizing was hindered by the added material and the less homogeneous spin mixture was formed. When more dimethyl phthalate was added, the spinning pressure was lowered considerably but uneven jetting and severe fibrillation of the threadline took place. Tensile properties of plasticized dispersion spun polytetrafluoroethylene were somewhat poorer than comparably drawn samples spun without plasticizer.

Table A

Ratio—Primary Polymer/Matrix Polymer/Plasticizer	Spinning Results
"Primol D" white oil: 10:1:2-----	18,000 p.s.i., weak spots and splitting, causing breakdown.
Dimethyl Phthalate: 5:1:1-----	15,000 to 17,000 p.s.i., wind-up at 35 and 50 y.p.m., good continuity, some fibrillation.
10:1:1-----	15,000 p.s.i., dry spots in threadline.
10:1:2-----	10,000 p.s.i., severe fibrillation, uneven jetting.

On measuring the strength of unsintered fibers of this invention as compared with previously known polytetrafluoroethylene fibers, it has been noted that the new fibers were extremely strong compared to the earlier-known filaments. The melt-spun filaments were, for example, 30 to 130 times as strong as the best lubricated paste-spun polytetrafluoroethylene yarn. This high tenacity for unsintered material is a strong indication that a considerable portion of the strength must come from the polytetrafluoroethylene since, for example, an undrawn polystyrene filament of one-eleventh the denier of the composite fiber would have to develop a tenacity of 4.4 g.p.d. if no contribution was being made by the polytetrafluoroethylene.

From the above examples, it is seen that dispersions of a heat-stable, solvent-resistant, intractable polymer and a low-melting, relatively volatile or a readily soluble matrix polymer were mixed and the mixture extruded through ordinary spinnerets at the melt-spinning temperature of the matrix polymer to form a shaped structure in which the matrix supports the freshly-extruded discrete particles of the intractable polymer. These composite filaments may be used directly in the manufacture of woven and knitted textile products from which the matrix material may be removed by suitable treatment, e.g., sintering. Subsequent sintering or coalescing of the intractable polymer eliminates the matrix material and leaves the filament free or almost free of matrix material. The matrix material evaporates by way of a cracking process, that is, it reverts to volatile, low-molecular weight materials.

The pressure employed to melt-spin the intractable polymer dispersed in the melt of the low-melting matrix polymer depends in large part, as demonstrated in the examples, on the ratio of the polymers in this melt. The higher the content of intractable polymer, the higher pressure has to be used to extrude the self-supporting filament. This means that if the melt contains a high percentage of melt-spinnable polymer, the composition can be extruded at low pressure; however, a compromise should be made as to the proportions since the higher the proportion of matrix material, the greater the difficulty of adequately removing the greater amount of matrix material by evaporation or by the other means discussed hereinafter. It means also, that the process is usually more economical at higher pressures because less matrix polymer has to be wasted or recovered.

Under "self-support," a term used in the specification

of the present invention, is meant that the matrix polymer, when spun into a filament, is strong enough to support itself for at least a foot without breaking, when held up vertically. Self-supporting lengths of over seven feet have been produced. Fibers spun from a matrix polymer, satisfying this requirement, can be wound up, stored or treated in package form in subsequent steps such as washing, sintering or coalescing.

The method of the present invention is applicable to all high-melting or non-melting polymers, but applicable mainly to polymers which cannot be spun from the melt and for which a practical and economical method of solution spinning has not been discovered yet. The only requirement for the intractable polymer is that it can be coalesced by either heat application or by the use of a near-solvent. A near-solvent is an inorganic or organic liquid which, at the temperature of contacting it with the shaped polymer, makes the polymer particles sufficiently tacky to form the continuous structure but without dissolving the polymer to a substantial extent to avoid losses. Among these polymers are polytetrafluoroethylene, polytrifluorochloroethylene, very high molecular weight polyacrylonitrile and its copolymers, the piperazine polyamides, such as piperazine terephthalate or 2,5-dimethylpiperazine isophthalate polymers, piperazine polyurethanes, cross-linked polymers, etc.

The matrix polymers used in practicing the invention must be capable of producing a self-supporting fiber or film when spun or cast from the molten state. Such materials are known in the art, and their ability to form such fibers and films is readily determined by melt-spinning or melt-casting filaments and films and observing the self-supporting characteristics in the solidified product.

These matrix materials used in the practice of the invention should ordinarily decompose at least about 20° below the sintering temperature of the intractable polymer, and should preferably be capable of ready elimination from the threadline. In the preferred embodiment of the invention, the matrix material is eliminated in the same step in which the intractable polymer is sintered or coalesced, e.g., by evaporation of the decomposed matrix polymer at the sintering temperature of the intractable polymer as demonstrated hereinbefore. Another method, also demonstrated hereinbefore, consists in dissolving out the matrix polymer by an inorganic or organic liquid which is a solvent for it, and a near-solvent for the intractable polymer. This latter method, however, is applicable only to that limited number of cases where a solvent of this characteristic can be found, whereas the first method can be widely employed. A third method consists of wet coalescing of the intractable polymer by an organic or inorganic liquid which constitutes a near-solvent for the intractable polymer at the temperature of the treatment, and thereafter treating the so-formed continuous filament of the intractable polymer, still containing the matrix polymer, with the solvent for the latter, thus yielding a polymer fiber essentially free of matrix material. By the wording "essentially free" is meant a content of 0% to 5% of the matrix polymer in the final structure of the intractable polymer. Still another variation consists in just coalescing the intractable polymer without destruction of the matrix material, thus yielding a fiber containing both polymers. Thus, in certain cases, a matrix polymer can be selected for at least partial retention in the final fiber so as to impart certain desirable properties to the final shaped article, such as better dyeability, flameproofness, the self-bonding characteristic required in the manufacture of felts, e.g., as by partial fusion, without the addition of adhesives, etc.

The following matrix polymers, suitable for supporting the intractable polymer can be named: polystyrene, polyisobutylene, polyvinyl acetate, polyethylene, and the like, having a molecular weight high enough for fiber-forming

properties and preferably within the range of 50,000 to 250,000.

It can be seen from the examples that complete coalescence of the polytetrafluoroethylene particles is achieved by sintering. Development of optimum mechanical properties is dependent in part upon the sintering conditions, since incomplete sintering results in weak spots with attendant poor mechanical properties. The optimum temperature for the developing of maximum properties for polytetrafluoroethylene fibers and films appears to be approximately 350 to 400° C. At this temperature, yarns have to be sintered about 7 seconds before maximum physical properties can be developed. While higher sintering temperatures naturally require shorter sintering times (and sintering temperatures up to 430° C. have been used successfully), at temperatures below about 375° C. the contact times required to develop maximum properties become excessive. Other polymers can be sintered by a similar method or they can be coalesced by other means, i.e., polyacrylonitrile coalesces by a treatment with calcium thiocyanate solution.

The sintering of the intractable polymer can be done by a number of ways, but is generally done by the application of heat in one way or another. Heat for the sintering step may be provided by hot liquid media such as molten Woods metal, fused salt-baths or hot inert hydrocarbons which are liquid at the desired temperature; hot gaseous media such as air, inert gases, and vaporized non-solvent liquids; radiant heat such as is provided by infrared lamps; and heated surfaces such as wheels, rods, bars, rollers and plates. Combination of these media may also be used. For example, the tetrafluoroethylene polymer particles in a matrix filament obtained by the melt-spinning method of the present invention may be coalesced by lifting through a stream of hot air onto a wheel heated to 380° C. The particles sinter on this wheel to produce a strong, drawable continuous filament.

Suitable tensile properties for commercial application are obtained by drawing the filaments after sintering, preferably at temperatures between the melting point and the decomposition temperature of the polymer. Polymer temperatures of approximately 430° C. represent the practical upper limit for polytetrafluoroethylene, since polymer degradation begins to become appreciable at this temperature. The melting point for polytetrafluoroethylene is a lower limit for sintering this polymer. When sintering and drawing are combined into a single operation, temperatures of approximately 400° C. represent about the best balance between sintering rate, drawability, decomposition, and the yarn properties for polytetrafluoroethylene. Where drawing is performed as a separate operation, it is preferably carried out at temperatures between 330° C. and 400° C. for polytetrafluoroethylene.

While the production of the tetrafluoroethylene polymer dispersions is not a part of the present invention, they may be prepared by any suitable process described in the prior art, for example, according to the procedures of Llewellyn and Lontz U.S. Patent No. 2,685,707, issued August 10, 1954; Berry U.S. Pat. No. 2,559,750, issued July 10, 1951; Renfrew U.S. Pat. No. 2,534,058, issued December 12, 1950, or Berry U.S. Pat. No. 2,478,229, issued August 9, 1949.

While the particle size of the tetrafluoroethylene polymer and the matrix polymer in a dispersion may vary over a wide range it is preferred that the polymer particles be of a size sufficiently small to pass through the holes of a spinneret; normally a polymer, the particles of which are included within the range of 0.05 to 5 microns and preferably within the range of 0.1 to 2 microns, is suitable for the practice of the invention.

The primary polymers can vary widely as to molecular weight. Generally speaking the preferred molecular

weight for the tetrafluoroethylene polymer is 8000 or higher. Several processes for preparing satisfactory polymers are described in Lontz U.S. Pat. No. 2,685,707.

The advantages of the present invention are of great technical interest. Thus, for example, the melt-spinning of polytetrafluoroethylene, to which part of the invention is directed, has heretofore not been solved satisfactorily. An older technique, known as lubricated paste spinning, has only produced very coarse fibers of non-uniform denier. In addition, the dispersion spinning of Berry U.S. 2,559,750 and Hill U.S. 2,413,498, have not produced continuous filaments at economically attractive speeds or have required procedures much too complicated for commercial satisfaction.

The present invention, therefore, describes for the first time a simple melt-spinning process for polytetrafluoroethylene, yielding at commercially acceptable speeds, a fiber of this polymer, substantially free of matrix material. As demonstrated in the above examples, a spin-stretch factor as high as 10:1 or higher can be attained producing a drawable filament of a uniform denier showing the free shear in filaments obtained by this method. It is also an important feature of this invention that the freshly-extruded shaped articles possess sufficient strength to permit handling without the necessity for mechanical support. Since the sintering of the very high melting or intractable polymer can be conveniently accomplished on a hot roll or plate, the process from spinning to a matrix-free drawn fiber is readily adaptable to continuous operation.

It is to be understood that the foregoing discussion is in no way meant to limit the invention to polytetrafluoroethylene but that the invention is applicable for all polymers for which a matrix material can be found which can be evaporated simultaneously in the sintering step for the intractable polymer, or which can be dissolved out readily after the coalescing step for the intractable polymer. Furthermore, the invention is not limited to intractable homopolymers and can also advantageously be applied to copolymers. Of course, it is understood, that the intractable polymer matrix-melt may be modified by incorporating therewith other materials of particulate size, such as fillers, dyes, or other additives which will impart desirable properties; the additive should not be undesirably modified by the subsequent treatment, e.g., it should not be decomposed to a useless state or coalesced (where the particle size should be retained as

in delustering) by solvents, by heat, or by any other treatment ordinarily applied to textile fibers or fabrics.

The present invention is not limited to the manufacture of filaments from intractable polymers. Other extruded or otherwise shaped articles such as rods, bristles, films, foils, tapes, ribbons, threads, coatings and the like are included in the scope of the invention.

Inasmuch as the invention is capable of considerable variation, it is not intended to limit the invention by the above description except as indicated by the claim.

I claim as my invention:

A melt-spinning composition comprising polytetrafluoroethylene particles admixed with polystyrene having a molecular weight within the range of about 50,000 to 250,000, the polystyrene containing dimethyl phthalate as plasticizer, the ratio of polytetrafluoroethylene to polystyrene to dimethyl phthalate being about 5:1:1.

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