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3,118,846

COMPOSITION COMPRISING TETRAFLUOROETHYLENE POLYMER AND CELLULOSE ESTER AND PROCESS FOR PREPARING SHAPED ARTICLES THEREFROM

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The present invention relates to the formation of shaped articles, films, fibers and the like, from particularly highly intractable, heat fusible polymers. Specifically, the invention is directed to a process of making continuous structures from polytetrafluoroethylene.

A fiber having the desirable properties of polytetrafluoroethylene, e.g., chemical inertness, high temperature stability, non-adhesiveness, low modulus, low wettability with water and organic liquids, low coefficient of friction and unique electrical properties, has promising utility for many industrial purposes. However, the chemical inertness of polytetrafluoroethylene (apparent from its low solubility) and its high temperature stability (apparent from its high melting point) has made the processing of this polymer difficult. It is therefore obvious that polytetrafluoroethylene cannot be spun into fibers by conventional spinning methods, e.g., by wet or dry spinning from solution or by melt extrusion. A newer method involving the spinning of polytetrafluoroethylene in the form of a lubricated paste, requires enormous pressures, and yields only coarse fibers of uneven denier before the sintering which is involved in the making of the desired product. The high pressure, the unadaptability of the polymer to the spinning of multifilament yarns composed of low denier fibers, and the necessity of using the batch process in the lubricated paste method impose serious limitations on the use of this process. Other known techniques for forming continuous structures of polytetrafluoroethylene have resulted in very weak filaments of no practical value; the filaments were not well-formed and the filament weakness before they were subjected to the sintering step prevented handling by conventional methods. An approach to the problem of dry spinning of polytetrafluoroethylene dispersions by transferring the aqueous polytetrafluoroethylene dispersion into an organic liquid, or discrete mechanical dispersion of dry polytetrafluoroethylene powder in an organic liquid has hitherto been unsuccessful; this attempt resulted in the formation of a coagulated non-filterable paste which could not be diluted with additional dispersant. Similar difficulties have arisen with respect to some polymers other than polytetrafluoroethylene, in connection with their conversion into filaments and other shaped products, due to their general intractability towards conventional spinning and shaping processes.

It is, accordingly, an object of the present invention to provide a process for making shaped articles from polytetrafluoroethylene and similarly intractable 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 polytetrafluoroethylene. A still further object is to provide a process for making textile filaments of adequate strength from the aforesaid polymer. Other objects will appear hereinafter.

The objects of this invention are accomplished, in one form, by forming a spinning composition comprising an aqueous dispersion of discrete particles of polytetrafluoroethylene and a water-miscible organic solvent in which is dissolved a different polymeric material serving as a matrix for the polytetrafluoroethylene, shaping the resulting mixture by extruding it through an orifice into a setting

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medium, such as air or coagulating liquids, which promotes spontaneous coalescence of the matrix material, and then coalescing the polytetrafluoroethylene by fusing it in the presence of the matrix without destroying the shape of the extruded article. In the sintering step, the matrix materials used in practicing the present invention are preferably destroyed by decomposition and flash off, thus leaving the shaped article substantially free of matrix material.

Contrary to known processes, the process of this invention starts with discrete particles of polytetrafluoroethylene dispersed in an aqueous medium which are converted into a shaped article and does not involve the usual steps of dissolving or melting and resolidification of the polymer in order to form the desired shape. Instead, the shaped polytetrafluoroethylene-containing article is conveyed into a region where the polymer is coagulated and is simultaneously or subsequently coalesced. The coalescing action is so regulated that it serves to partially fuse or sinter the polytetrafluoroethylene particles. This feature, in conjunction with the use of the matrix-forming material, defines a process which is distinctly different from, and is faster, simpler, and therefore more economical than, previous processes. The matrix material supporting the discrete polytetrafluoroethylene particles in the spinning process of the present invention must comply with certain rigid requirements in order to be effective. The matrix should be soluble in an organic water-miscible liquid and its solution in this water-miscible organic solvent must be compatible with a polytetrafluoroethylene dispersion (or dispersion of other intractable polymer) in water. Furthermore, a moderately low concentration of this matrix material must be capable of producing a self-supporting fiber or film which can easily be handled and further processed; this characteristic is readily determined by casting a solution of the matrix polymer (in relatively low concentration) on a plate and removing the solvent with the production of a self-sustaining sheet or, alternatively, a solution of the matrix polymer can be spun with removal of solvent to form a coherent filament which can be handled readily. Also, the matrix polymer should, in the sintering process, decompose to relatively volatile products which flash off. The matrix polymer, is, preferably, commercially available at a low price and capable of being dissolved in substantial amounts. A polymeric material having the required properties has been found, in accordance with the present invention, to comprise the class of cellulose esters.

The present invention is illustrated in the following examples, which are not intended to be limitative of the invention. Parts, proportions and percentages are to be understood as by weight throughout the examples and elsewhere in the specification unless otherwise indicated. All processes of these examples were carried out at room temperature (about 25° C.) unless otherwise stated.

Example 1

100 grams of a 60% aqueous polytetrafluoroethylene dispersion (i.e., polymer is 60% of the dispersion) were mixed with 100 grams of dimethylformamide containing 10 grams of an alkyl aryl polyether alcohol prepared by condensing 10 moles of ethylene oxide per mole of octyl phenol to provide $p\text{-C}_8\text{H}_{17}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_n\text{OH}$ where C_8H_{17} is diisobutyl, and which is marketed under the trade name "Triton X-100" by Rohm & Haas Co. To this was added with stirring 100 grams of a spinning solution consisting of 25% cellulose acetate (54.5% combined acetic acid) and 75% acetone, until thorough emulsification took place. The smooth pasty dope was extruded vertically through a spinneret having one spinning orifice of 8 mil diameter, into a hot air spinning

cell such as may be used for the dry-spinning of cellulose acetate filaments, to yield a white fiber which supported two feet of its length. This filament was wound up under very low tension and rewound by leading it successively over and in contact with two hot rollers at 380° C. with a total contact time of 7 to 10 seconds. The sintered fiber was brown from a small charred residue of the matrix cellulose acetate material and possibly the emulsifying agent, but had otherwise the typical desirable high qualities of polytetrafluoroethylene fibers.

Example II

In another experiment the spin-mix of Example I was extruded through the same spinneret into a hot water bath (wet spinning). The filament was immediately sintered by leading it through a salt bath at 400° C. A tough brown filament was obtained.

Example III

To 40 grams of a commercial 60% polytetrafluoroethylene dispersion was added first 5 grams "Triton X-100" alkyl aryl polyether and subsequently there was added with stirring 75 grams of a cellulose acetate spin-dope solution consisting of 26% cellulose acetate, 7.4% "Triton X-100" alkyl aryl polyether and 66.2% acetone to form a mixture with a ratio of 6:5 of polytetrafluoroethylene to cellulose acetate. This mixture was extruded through a 5-hole spinneret of 0.020 inch hole diameter into water at room temperature at the speed of ten yards per minute. The flexible dry fibers were withdrawn from the water bath, were dried and sintered for a short time to a brown flexible filament. Long exposure of this fiber to the sintering temperature yielded a white filament which can be drawn at room temperature to four times its undrawn length (300% draw or 4×).

Example IV

Although acetone is a coagulant for polytetrafluoroethylene dispersed in water, this is a time-dependent phenomenon. By adding acetone to a polytetrafluoroethylene dispersion and then quickly increasing the viscosity of the system by adding a solution containing 25% cellulose acetate dissolved in acetone, a viscous non-coagulated dope results. The increased viscosity of the system greatly reduces the rate of agglomeration. Such a mixture was prepared having the following composition:

	Percent
Polytetrafluoroethylene	16
Cellulose acetate	12
Water	11
Acetone	57
"Triton X-100" polyether	4

This material was dry-spun in a conventional cellulose acetate dry-spinning cell with filtration of the spinning solution in the spinneret through a 200 mesh screen at a back pressure 150 p.s.i. (pounds per square inch gage pressure). The threadline supported its weight, but the sintered product was weak, reflecting the large quantity of matrix material in the above composition. A similar filament was obtained by wet-spinning the composition into warm water. Greater strength in the sintered product would result with a smaller amount of cellulose acetate matrix, or alternatively, by prolonged sintering to remove substantially all the matrix material.

Example V

One of the materials which can be added to a dispersion of polytetrafluoroethylene in water without immediately coagulating it is dimethylformamide. By adding dimethylformamide to the dispersion followed by the addition of the cellulose acetate spin-dope of the preceding examples, a spinnable mixture can be achieved.

Such a mixture was made, having the following composition:

	Percent
Polytetrafluoroethylene	15
Cellulose acetate	14
Water	9
Dimethylformamide	19
"Triton X-100"	2
Acetone	41

Mixtures such as this are stable and show no tendency for the polytetrafluoroethylene to agglomerate. A filament about 2 feet in length was spun from this composition by dry-spinning as in the previous examples and then sintered to give a polytetrafluoroethylene filament of poor drawability.

A combined wet-spinning dry-spinning operation was also carried out with the above mixture. The filament was spun into air for a length of about 1 foot and then submerged into hot water to complete the coagulation. The resulting filament was stronger in its unsintered stage than in the aforesaid dry-spun example.

The compositions of Examples IV and V have a very low content of combined solids which is reflected in the weak resulting fiber. Wet-spinning, however, permits operation at a lower solids content, by virtue of the supporting nature of the bath and the lower speeds used.

From the above examples it can be seen that novel fibers and films comprising the water-insoluble synthetic polymer and the water-insoluble self-coalescing matrix material are produced. It is surprising that these shaped products can be led through long paths in an unsupported fashion, particularly when it is realized that the synthetic polymer particles constituting the major portion of the filament solids are in an uncoalesced form.

The above process can also be employed to convert polymers other than tetrafluoroethylene polymers into shaped structures from an aqueous dispersion comprising also a water-soluble organic liquid containing the matrix polymer. Other materials which can be used as the primary polymers in the present invention are any polymers which are water-dispersable, non-self-coalescable but coalescable by heat or a liquid treatment, and insoluble in the organic liquid which is used to dissolve the matrix polymer, for instance, polytrifluorochloroethylene, acrylonitrile polymers, containing a high percentage, e.g., 85%, of combined acrylonitrile in the polymer, copolymers of the above, and other polymers and copolymers which are insoluble in the matrix solvent. The term "copolymer" is intended to include all types of copolymers, such as random, ordered, segmented, block, and graft copolymers.

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. Many suitable heating media, such as molten salt or metal baths, heated rollers, plates, hot air, or radiant heat may be used. 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.

Suitable tensile properties for commercial application

are obtained by drawing the filaments after sintering, preferably at temperatures between the melting point (327° C.) and the decomposition temperature (430° C.) of the tetrafluoroethylene 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. Where drawing is performed as a separate operation from sintering, it is preferably carried out at temperatures between 330° C. and 400° C.

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

While the particle size of the tetrafluoroethylene 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 range for the tetrafluoroethylene polymer is 8,000 or higher.

An important selection has to be made concerning the composition of solids in the new composition of matter. The ratio of polytetrafluoroethylene to matrix polymer is from 1:1 to about 10:1, the preferred range being from 1:1 to about 3:1. Too low a polytetrafluoroethylene content yields poor fibers after sintering. A higher ratio produces a weaker thread line for obvious reasons. A high solids ratio of polytetrafluoroethylene polymer to matrix polymer in the dispersion can readily be obtained by the addition of sufficient surfactant (surface-active agent). A great many surfactants, particularly those that are nonionic or anionic, traded as emulsifiers, have been tried and found very satisfactory; among these are polyethylene glycol esters of fatty alcohols, diaryl sulfonates, alkyl aryl polyether alcohols, polyglycol esters, fatty alkylol amide condensates, aliphatic ester sulfates, glycerol monoesters from fatty acids, polyoxyethylene alkyl ethers, soya lecithin, phosphates of fatty alcohols, tertiary amine salts, etc. An addition of one to ten percent (by weight of the combined weight of solids in the dispersion) of such a surfactant allows a combined solid weight in the dispersion up to about 60%.

The strength providing matrix materials particularly useful in practicing the present invention are polymers meeting the following requirements: (1) they should be soluble in an organic solvent miscible with water at a pH of somewhere between 1 and 14 and temperatures somewhere between 0 and 100° C., and (2) their organic solution has to be compatible with the aqueous dispersion of the insoluble main polymer; "compatibility" signifies that the organic solution of the matrix polymer does not precipitate the dispersed particles of the main polymer, and that the matrix polymer is not precipitated by the addition of the aqueous dispersion of the main polymer. By the addition of an emulsifier from one of the classes mentioned hereinbefore, the dissolved particles of the matrix polymer and dispersed particles of the main polymer can be kept from precipitating. The preferred matrix materials for practicing the invention have a decomposition temperature at least 20° C. below the melt temperature of the main polymer and flash off at such a temperature without leaving charred remains. Examples

of matrix materials are cellulose esters, such as cellulose acetate, cellulose propionate, cellulose butyrate, and nitro cellulose, particularly those cellulose esters which are completely or nearly completely acetylated or nitrated. It will be understood that the cellulose ester may be any of the well-known cellulose esters capable of being spun from solution into filaments, particularly those now commercially used in dry spinning processes, e.g., cellulose triacetate saponified to 54-57% combined acetic acid.

The new compositions of matter of the present invention distinguish clearly from the formerly known dispersion spinning mixtures. In the case of these new compositions, non-water-soluble organic polymers can be used as matrix materials. Many of these matrices, in contrast to water-soluble polymers, decompose into volatile materials at sintering temperatures of the intractable polymer. A volatile matrix material has a valuable and desirable characteristic of flashing off during sintering without leaving any great amount of charred residue, thus yielding white or almost white continuous polymer structures which are not obtainable by using polymeric water-soluble matrices. The compositions of the present invention can be kept for long periods without agglomeration, they can be filtered, they are fiber forming with about the same ease as cellulose acetate spin-dope, and they are readily dry spun. Also, shaped articles can be obtained by extruding the new composition into a liquid coagulant for the matrix material which does not contain a surface-active agent such as an emulsifier. This wet process is particularly attractive for polymer dispersions having a relatively low content of solids, for example, less than 30%.

A surprising feature of the present invention is the fact that the organic solvent does not precipitate the polytetrafluoroethylene from its dispersion and that the water does not precipitate the cellulose ester from its solution in the organic solvent. This is accomplished by the addition of an inert, highly active emulsifier which keeps the dispersed particles in suspension, and by increasing the viscosity of the mixture. Without this emulsifier, the organic solvent is a strong coagulant for the polytetrafluoroethylene dispersion.

A great advantage of the present invention is the possibility of producing shaped articles from the polytetrafluoroethylene dispersion without separating it from its preparation mixture. This invention, therefore, offers a great improvement for the process described in U.S. 2,413,498 to Hill, issued 1946, according to which the said dry polymer has to be comminuted first and can only be shaped in this form with the use of a matrix material.

For convenience, much of the foregoing discussion has been limited to the preparation of filaments. It should be readily apparent, however, that this new invention applies equally well to the formation of fibers, threads, film, tapes, ribbons, bristles, rods, and the like.

Any departure from the above description which conforms to the spirit of the present invention is also intended to be included within the scope of the claims.

I claim:

1. A composition capable of being formed directly into a self-supporting shaped article comprising a non-ionic emulsifier and an aqueous dispersion of a water-insoluble polyhalogenated ethylene polymer selected from the group consisting of polytetrafluoroethylene and polytrifluorochloroethylene intimately admixed with a water-soluble organic liquid containing dissolved therein a water-insoluble cellulose ester, the ratio of polyhalogenated ethylene polymer to cellulose ester being from about 1:1 to about 10:1 respectively.

2. A composition capable of being formed directly into a self-supporting filamentary structure comprising a non-ionic emulsifier and an aqueous dispersion of polytetrafluoroethylene intimately admixed with a water-soluble organic liquid containing dissolved therein a water-insoluble cellulose ester, the ratio of polytetra-

fluoroethylene polymer to cellulose ester being from about 1:1 to about 10:1 respectively.

3. A composition capable of being formed directly into a self-supporting filamentary structure comprising a non-ionic emulsifier and an aqueous dispersion of polytetrafluoroethylene intimately admixed with a water-soluble organic liquid containing dissolved therein a water-insoluble cellulose acetate, the ratio of polytetrafluoroethylene polymer to cellulose acetate being from about 1:1 to about 10:1 respectively.

4. A composition capable of being formed directly into a self-supporting filamentary structure comprising a non-ionic emulsifier and an aqueous dispersion of polytetrafluoroethylene intimately admixed with acetone containing dissolved therein a water-insoluble cellulose acetate the ratio of polytetrafluoroethylene polymer to cellulose acetate being from about 1:1 to about 10:1 respectively.

5. The process which comprises forming a self-supporting shaped article from an aqueous dispersion of a water-insoluble polyfluoroethylene polymer selected from the group consisting of polytetrafluoroethylene and polytrifluorochloroethylene containing a non-ionic emulsifier intimately admixed with a water-soluble organic liquid containing dissolved therein a water-insoluble cellulose ester, and coagulating said cellulose ester whereby to form a matrix for the said polymer, the ratio of said water-insoluble polyfluoroethylene polymer to the cellulose ester in said aqueous dispersion being from about 1:1 to about 10:1 respectively.

6. The process which comprises forming a self-supporting filament from an aqueous dispersion of a water-insoluble polyfluoroethylene polymer selected from the group consisting of polytetrafluoroethylene and polytrifluorochloroethylene containing a non-ionic emulsifier intimately admixed with a water-soluble organic liquid containing dissolved therein a water-insoluble cellulose ester, and coagulating said cellulose ester whereby to form a matrix for the said polymer, the ratio of said water-insoluble polyfluoroethylene polymer to the cellulose ester in said aqueous dispersion being from about 1:1 to about 10:1 respectively.

7. The process which comprises forming a self-supporting filament from an aqueous dispersion of a water-insoluble polyfluoroethylene polymer selected from the group consisting of polytetrafluoroethylene and polytrifluorochloroethylene containing a non-ionic emulsifier intimately admixed with a water-soluble organic liquid containing dissolved therein a water-insoluble cellulose ester, and coagulating said cellulose ester whereby to form a matrix for the said polymer, the ratio of said water-insoluble polyfluoroethylene polymer to the cellulose ester in said aqueous dispersion being from about 1:1

to about 10:1 respectively and thereafter subjecting said filament to a temperature which sinters said polymer.

8. The process which comprises forming a self-supporting filament from an aqueous dispersion of a water-insoluble polyfluoroethylene polymer selected from the group consisting of polytetrafluoroethylene and polytrifluorochloroethylene intimately admixed with a water-soluble organic liquid containing dissolved therein a non-ionic emulsifier and a water-insoluble cellulose ester, and coagulating said cellulose ester whereby to form a matrix for the said polymer, the ratio of said water-insoluble polyfluoroethylene polymer to cellulose ester being from about 1:1 to about 10:1 respectively.

9. The process which comprises forming a self-supporting filament from an aqueous dispersion of a water-insoluble polyfluoroethylene polymer selected from the group consisting of polytetrafluoroethylene and polytrifluorochloroethylene containing a non-ionic emulsifier and being intimately admixed with a water-soluble organic liquid containing dissolved therein a water-insoluble cellulose acetate and a non-ionic emulsifier, and coagulating said cellulose acetate whereby to form a matrix for the said polymer, the ratio of said water-insoluble polyfluoroethylene polymer to cellulose acetate being from about 1:1 to about 10:1 respectively.

10. The process which comprises forming a self-supporting filament from an aqueous dispersion of polytetrafluoroethylene, said dispersion containing an alkyl aryl polyether alcohol emulsifier and being intimately admixed with acetone containing dissolved therein a water-insoluble cellulose acetate, and coagulating said cellulose acetate whereby to form a matrix for the said polymer, the ratio of tetrafluoroethylene polymer to cellulose acetate being from about 1:1 to about 10:1 respectively.

11. A composition comprising a non-ionic emulsifier and an aqueous dispersion of polytetrafluoroethylene intimately admixed with an organic solvent containing dissolved therein a water insoluble cellulose ester selected from the group consisting of cellulose acetate, cellulose propionate and cellulose nitrate, the ratio of polytetrafluoroethylene to cellulose ester being from about 1:1 to about 10:1, respectively.

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