The research progress of PTFE fiber preparation technology

Polytetrafluoroethylene (PTFE) fiber is PTFE as raw material, after spinning or made of thin film after cutting or fibrillation of a synthetic fiber. Industrial production of PTFE fiber began in 1954, developed by DuPont, was the first industrialized special synthetic fiber. Austrian Lenzing has successfully developed PTFE membrane crack fiber in the 1970s which strength can also reached the level of emulsion spinning fiber, high production efficiency, but not the exact linear density. Moreover, in Russia, in the development of a variety of PTFE fiber is quite effective. The current main methods of preparation of PTFE fiber spinning of carrier spinning, paste extrusion spinning, melt spinning, cutting film crack method, etc. PTFE because of its excellent chemical properties and thermal stability, low friction factor, good biocompatibility, and is widely used in national defense, aerospace, instrument machinery, petrochemical, building, textile, electronics, medicine, and many other industries and fields.

1. Structure and performance of PTFE fiber

1.1 The molecular structure of PTFE fiber

PTFE is linear polymer fluoride, it is a kind of highly symmetric nonpolar polymer compound, its structure is linear macromolecule structure, spiral and molecular chain conformation. According to the apparent color different, PTFE fiber can be divided into the brown and white fiber two kinds. Brown PTFE fiber carrier usually in spinning, the fabric is very soft, and low friction factor, widely used in machinery industry, oil free, dynamic and static anti-wear areas. White PTFE fiber is generally by membrane crack cutting method, the fiber filter material can improve filtering section, so as to improve the accuracy of filtering.

1.2 The performance of PTFE fiber

1. 2. 1 Chemical resistance

The key of "C - F" in PTFE molecules has a very high bonding energy, molecular chain appear conformation which is spiral, nonpolar and crystal structure, This makes the PTFE has very excellent chemical resistance. In addition to the strong element fluoride and fluoride medium (such as trifluoride chloride), molten alkali metals and 300 ℃ of sodium hydroxide, corrosion of PTFE almost without any chemical reagent, all of the strong acid, strong alkali, strong oxidizing agents, salt for PTFE are no effect, even in aqua regia boil, its quality and performance are also don't have any change. For organic compounds, in addition to aromatic hydrocarbons and halide amine on the slight swelling, other organic solvent has no effect on PTFE, so is known as "plastics king".

1.2. 2 Thermal properties

PTFE has very excellent high and low temperature resistance, can be used in - 190 ~ 260 ℃ temperature for long time. It can not only bear the instant high temperature of up to 290 ℃, but is

not brittle below -260 ℃, still can keep a deflection. So in some poor conditions, PTFE products are often used.

1 .2 .3 Mechanical properties

Because PTFE is nonpolar molecular chain, the mutual attraction between macromolecules is very small; Combined with the molecular chain is not branched chain of high rigidity, entanglement is very small, leading to poor mechanical properties of PTFE. Under long-term load, PTFE will have large creep, prone to cold flow phenomenon. But its fatigue resistance is excellent, general won't appear permanent fatigue damage.

In addition to the above excellent performance, PTFE also has a good flame retardant performance, excellent lubricity, water repellency and electrical insulating properties, resist ultraviolet ageing resistance, etc.

2. Preparation technology of PTFE fiber

2. 1 Carrier spinning method

2. 1. 1 Wet spinning

Wet spinning of PTFE usually in viscose or polyvinyl alcohol (PVA) as the carrier, mix with PTFE powder or emulsion dispersion, and add a small amount of boric acid, make spinning solution , perform wet spinning, spinning head placed in sodium sulfate and ammonium sulfate coagulation bath, dope from the nozzle in the coagulation bath solidified into fiber, fiber after leaching roller soft water leaching, again after oil roller and drying roller respectively, in 380 ~ 400 ℃ high temperature sintering, remove PVA carrier carbide, stretch to make PTFE fiber under 350 ℃. This method of spinning spend process cumbersome, high processing cost and energy consumption and time-consuming.Guo Yu-hai and others invented a highly efficient rapid method of preparation of PTFE fiber. This method will first evenly mix low relative molecular mass of volatile organic solvent with water, in under the condition of stir with PVA, continue to stir until completely dissolved, mixture of PVA water solution. Then the PVA water solution and persulfate, PTFE dispersion mixing uniformity, dope. Then borate or boric acid dissolved in water, with alkaline pH adjustment as alkaline, mixture coagulation bath. Finally adopt the wet spinning equipment of conventional , the spinning fluid conveying to the nozzle, through metering pump metering, direct spinning in the coagulation bath, then drying, sintering and stretch, the PTFE fiber is made.

2.1.2 Dry spinning

This method is PTFE gel realized by dry spinning. PTFE is first concentrated dispersion and PVA blended, add gel regulator boric acid or Borate salts and alkalis adjust the pH to alkaline, whisking to a sudden increase in the viscosity and gel formation, are spinning solution. And then dry them using conventional spinning equipment, gas pressure or screw spinning liquid to the

spinning head, measured in metering pumps, dry spinning, and then dried, prepared mixture of PTFE and PVA fiber. Finally using conventional sintering and stretching equipment, will be mixed sintering to remove PVA fiber, finally after stretching process stretching, PTFE fiber preparation.

Carrier spinning method is the most mature method of preparing PTFE fiber, and has been one of the few companies to realize industrialization. Among them, Japan toray company USES mass fraction 60%, the average particle size was 0. 3 microns of PTFE, and the mass fraction of 2% sodium alginic acid aqueous solution of the emulsoid mixed spinning, the fiber by coagulation, bath again after washing, drying, and under 380 ℃ hot stretching, removal of alginic acid sodium, gain PTFE fiber, its monofilament linear density of 0. 67 dtex and fracture strength of l. 25 cN/dtex, elongation at break of up to 59%, the method of spinning dope spinnability better than with viscose as carrier of PTFE dope spinnability. Showa industries, the use of the 114 mass fraction of 60% PT - 100 FE dispersed emulsion and cellulose of mass fraction of 8.9% viscose spinning solution spinning, after solidification of the nascent fibers by water, squeeze liquid, with 0. 05 mol/L Na0H processing, and the fiber heat treatment under 280 ℃ and hot stretching under 320 ℃, the final heat treatment 72 h under 320 ℃, the fiber's breaking strength for 1. 16 cN/dtex elongation at break was 16.1%. In addition, Beijing demonstration plant will be 60% mass fraction of PTFE emulsion and 10% mass fraction of PVA solution in proportion of 1:1.5 the spinning solution spinning, after solidification of the fiber by acetal, washing, drying, sintering and stretch to PTFE fiber system.

2. 2 Cutting film splitting method

Cutting film crack method in the early 1970 s by the Austrian Lenzing company development and industrialization, in the preparation of PTFE fiber, need to make PTFE powder sinter cylindrical PTFE parison, cutting it up with a certain thickness of the film, and then by serrated tool divided into silk, above the melting point (327 ℃) sintering, then through stretching and end up with PTFE fiber heat treatment. This method can get the fiber with microporous structure, and high strength. Multifilament can be used as the sealing filler material, short fibers, can be used in the needle felt.

In addition, the PTFE film or sheet can also be cut into tiny width, and then direct tensile narrow fabric made of high strength PTFE fibers. But it is difficult to maintain uniform obtained by cutting along the longitudinal direction through the narrow width of the fabric, and narrow fabric tends to end part of fibril, so much stretch in narrow fabric PTFE fibers easily broken or through partial cutting in the longitudinal direction of the film are filament PTFE membrane orientation. Along the membranes of the longitudinal direction and in the transverse direction of the film with a z shape or linear-convex shape embossed and cut, the resulting filament including individual fibrils partially broken rule the network structure. PTFE fibers produced this way the individual fibrils with small average size and uniform size.

Japan Asahi of into Corporation through cutting film crack legal into has high stretch strength, and resistance chemical performance excellent of PTFE yarn. will containing hole rate 48% of PTFE film tear into 222 dtex of fiber, again on its added twist to 750 twist/m, in 440 ℃ and 1 000 m/min Xia stretch, get of fiber line density for 55 dtex, and containing hole rate 1%, modulus up to 294 cN/dtex.

2.3 Paste extrusion spinning method

Paste extrusion spinning usually PTFE powder 16% ~ 25% with mass fraction of volatile lubricants mixes, tune into a paste, made of shaped prefabricated embryos, and under certain pressure through a spinneret with a strip of die extrusion spinning, and then by drying, sintering, high stretch under high temperature, non-uniform white yarn. In addition, can also squeeze film extrusion equipment or thin strips, then by a rolling process to remove additives, and longitudinal cutting, drawing and fluffy after processing, are PTFE fibers were made by paste extrusion of thin wall, small diameter and permeability of PTFE hollow fiber. PTFE powder in conditions below its melting point made of PTFE hollow fiber, and then fired 10 min at 350 ℃, 250 ℃ under 400%, was 0.76 mm inner diameter and wall thickness of 0.10 mm, diameter of less than 0.15 mm hollow fibers.

In 1997, M. Shimizu proposes a method for preparing high strength and PTFE fibers by paste extrusion. Added to the PTFE powder mass fraction 20% of lubricants, embryo, extrusion, gained single wire, heated treatment and then 350 ℃ 1.5h, and 387 ℃ to 50 mm/min of speed stretching 10 times, received strength as much as 1.56 ~ 2.82 GPa PTFE fibers.

The PTFE powder was mixed with a lubricant (isoparaffin oil Isopar-E) to form a paste, standing at 0 ℃ 180 h at 40 ℃ cure 30 h, make the mix full wetting and swelling, then press embryo and extrusion , handle 2 h under 340 ℃, and then to 0. 5 c/min speed down to room temperature, finally stretching to get in a 370 c PTFE fiber, 3.5 ~ 4.0 cN/dtex the fracture strength, elongation at break is 22%.

2. 4 Melt spinning method

Melt spinning is PTFE content to 4% ~5% of perfluorinated ethylene copolymer of perfluoro-n-propyl ether mixed spinning melt, after spinning by screw extrusion machines pump quantitative pressure injection hole, making it into a fine stream into the air, and cooling in the spinning channel into the wire. PTFE fibers high strength of this method, but PTFE supermolecular structure changes after melting, leading to its ductility disappeared and molecular chain orientation stretch is blocked, together with PTFE high viscosity and apparent flexibility, PTFE melt fiber prepared by screw extruder for direct comparison difficult, difficult to achieve industrialization. Plunger extrusion method can overcome this difficulty. The plunger in the extrusion process, due to extremely low surface energy of PTFE and wall-slip phenomenon,

reduce unnecessary shear in the flow process, so they can be on PTFE melt spinning. Li Min and other person in Donghua university, are prepared by the PTFE fibre with high molecular weight. Tervoort by high relative molecular mass such as PTFE and PTFE mixed with low relative molecular mass, melt processing, preparing PTFE filament. Properties of PTFE fibers produced this way worse than that of pure PTFE fiber with high molecular weight.

Comparison of advantages and disadvantages of these different spinning methods are shown in table 1.

Table 1 Advantages and disadvantages of PTFE spinning method

Textile method	Advantage	Disadvantage
Wet spinning	Linear density of fibers have exact can be obtained by linear low density fibers	Process cumbersome, higher processing costs, pollution of the environment; solidifying Groove is long, low manufacturing efficiency; sintering takes energy, and PVA carbides in high temperature will reduce the fiber strength
Each part spinning		
Dry spinning	Simple, low cost, no pollution, good fiber quality, without washing, can be linear low density fiber	Sinter process energy consumption, and PVA carbides in high temperature will reduce the fiber strength
Cutting film crack	Fracture strength of fiber high	Complex process, higher equipment requirements, higher costs; with coarse fibers, no exact linear density
Paste extrusion spinning	Fracture strength of fiber high	PTFE powder raw materials are bulked, expensive linear density of fibers do not have the exact
Melt spinning	Fracture strength of fiber high	Equipment fiber difficult

3. The application of PTFE fiber

3. 1 Filtering material

PTFE fiber has an important role in high temperature flue gas filtration. With PTFE fiber or PTFE fibers mixed with other high-temperature resistant fibers, can be made from high-temperature composite filter carpet, this filter has good corrosion resistance, heat resistance, friction-resistant properties, suitable for high temperature, high humidity, high viscous powder with acid or alkali, corrosive chemicals industrial fume purification, is unmatched by other filtering materials.

3.2 Medical materials

In recent years, PTFE fibers are widely used in medicine, such as can be used in artificial blood vessels, heart valves and artificial heart assist device, artificial ligaments and esophagus. In addition, PTFE fibers can also be used in general surgery and plastic surgery, surgical suture, such as the more common cosmetic surgery rhinoplasty and plastic jaw PTFE is used as fill material.

3.3 Textile industry

PTFE fibers used in the manufacture of high-performance sewing thread, heat resistance and chemical resistance and high performance requirements of other textile products, as well as bruising spelled resistance of medical textiles and wearing apparel. For example, with PTFE fibers rub sports socks in cycling and other sports, can prevent athlete's foot, blisters.

3.4 Other applications

PTFE fibers also have a wide range of applications in other areas, such as can be used for bearings with low friction rate components, ion-exchange, packing, etc. In addition, due to their inherent low-loss dielectric constant, PTFE fibers can also be used to prepare the insulation of wires and cables, and so on.

4. Conclusion

PTFE due to its excellent performance in the fields of petrochemical and other widely used, its main carrier spinning, spinning o f cutting split method, paste extrusion spinning, melt spinning, and so on. Large manufacturers in the world such as the United States, DuPont Corporation, United Kingdom the ICI company, Japan Daikin company and Germany's Hoechst company has mastered the technology of PTFE fibers.