The modification and application of PTFE

Polytetrafluoroethylene (PTFE) resin was invented by Dr. Champlain Kate (Plankett) in 1938 and formally put into industrial production by Du Pont in 1950. PTFE has excellent, special physical and chemical characteristics, being widely used in the chemical industry and other related industries. However, due to some inherent defects of PTFE, especially its large cold flow performance and poor processing performance, its application is limited. Therefore, it has become the main research and development direction of PTFE to further study the properties of PTFE, improve its processing performance and develop new PTFE composites.

Composition, structure and physical and chemical properties of PTFE

As for the high crystalline polymer of tetrafluoroethylene (TEF) monomer, PTEF is a white waxy feel thermoplastic. In PTFE, the fluorine substituted hydrogen atoms in polyethylene, because the radius (0.064nm) of the fluorine atom is larger than the hydrogen atom's (0.028nm), which makes the carbon - carbon chain polyethylene by fully extended planar, zigzag conformation to gradually reverse helical conformation of PTFE. The helical conformation just surrounded outside the carbon chain skeleton, susceptible to chemical attack in PTFE, to form a close completely fluorinated protective layer, which makes the polymer backbone without any outside agent invasion, endowing PTFE with unique solvent resistance, chemical stability and low cohesive energy density; at the same time, the Carbon fluorine bond is very strong, the bond can reach 460.2kJ/mol, far more than the carbon hydrogen bonds (410kJ/mol) and carbon carbon bond (372kJ/mol), making PTFE has better thermal stability and chemical inertness; In addition, the electronegativity of the fluorine atom, and TFE monomers with perfect symmetry and PTFE intermolecular attraction and low surface energy, so that the PTFE has very low surface friction coefficient and good ductility at low temperature, also makes the PTFE creep resistant ability poor, prone to cold flow phenomenon; PTFE's non branched symmetric backbone structure also makes it a high degree of crystallinity, making the processing of PTFE more difficult . PTFE's composition and structure decide it has the following characteristics:

(1) High degree of chemical stability. In addition to the molten, alkali metal, fluoride and high fluoride medium (e.g. three chlorine fluoride), the PTFE can withstand the effect of the other all strong acid (including aqua regia, hydrofluoric acid, hydrochloric acid, nitric acid, fuming sulfuric acid and organic acid), alkali and oxidant, reductant and all kinds of organic solvents, which are lower than the sodium hydroxide at 300 degrees Celsius.

(2) Widely use temperature range. PTFE can be used in a wide range of -190 degrees Celsius to 260 degrees Celsius, even in the ultra -low temperature of -260 degrees Celsius ， it is still not brittle, but also can maintain a certain degree of flexibility.

(3) Outstanding function is nonstick. PTFE is a solid material with the lowest surface tension at present, only 0.019N/m, almost all solid materials are not adhered on its surface, only the liquid with a surface tension within 0.02N/m can completely infiltrate the surface.

(4) Abnormal lubrication. Because of the small gravitational attraction between PTFE molecules and the attraction of other molecules on the surface is very small, the friction coefficient is very small, generally only 0.04. With the increasing of load, the friction coefficient will decrease in a certain range. Usually ,PTFE's coefficient of static friction (f) and load (W) in the presence of =0.178w F - 0.5 relationship, such as in the high speed, high pressure conditions, the coefficient of friction can be less than 0.01, which conforms it is a very excellent self- lubrication material.
(5) Excellent electrical insulation properties. PTFE is a highly nonpolar material, having excellent dielectric properties, and the breakdown voltage is 25 ~ 40kV/mm; maximum resistance, volume resistivity at 200 degrees Celsius is still as high as 1016 psi - cm.
(6) Excellent aging resistance and radiation resistance. PTFE not only can keep size being stable in low temperature and high temperature, retain the same performance under harsh environment, stay away from the invasion from microorganisms under the wet condition, but also possess a high protection to a variety of rays to radiation.
(7)Excellent thermal stability. The melting point of PTFE is 327 degrees Celsius, higher than other general polymer. At 260 degrees Celsius, its fracture strength still maintains at 5MPa (about 1/5 at room temperature), and the bending strength is up to 1.4MPa. It has a very valuable non-flammable prosperty, and its limited oxygen index (L0I) is more than 95, which means it can only be molten in the flame, do not generate droplets, and only can be carbonated ultimately.
(8)Minimal water absorption. The water absorption rate of PTFE is generally 0.005% ~ 0.001%, and its permeability is low.

PTFE has the advantages of the above, which makes it an alternative to other materials can not be anti-corrosion and friction materials. At the same time, the composition and structure of PTFE also have some disadvantages:
(1) Poor mechanical performance. The mechanical strength of TFE is low, only 14 ~ Pa 25M (hard polyvinyl chloride is 35.2 ~ Pa 50M), and it has no back elasticity, its hardness is low either, but the elongation rate is bigger.
(2) Larger linear expansion coefficient. Between -50 ~ 250 degrees Celsius, PTFE linear expansion coefficient of 1.13 * 10-4 ~ 2.16 * 10 -5/ degrees Celsius, which is 13 times of the steel's, so deformation, cracking and other phenomena are easy to happen when PTFE composites with other materials.
(3) Molding and two processing difficulties. The molding shrinkage rate of PTFE is large, with molding method, it can reach 1% ~ 5% (the rigid poly's is 0.1% ~ 0.6%), PTFE cannot use the injection molding of plastic used, two processing molding etc.
(4) Small creep resistance, easy to creep, and easy to cold flow. Under the long-term load, the creep of PTFE is larger, and the phenomenon of cold flow is easy to occur. The cold flow phenomenon of PTFE is one of the main reasons that limit its wide application.
(5) Poor wear resistance. PTFE has low hardness, high abrasion, when the load (P) and sliding velocity (V) exceeds a certain condition, the friction loss will be very large, so the application

value of PV have certain limitations, such as being bearing when the PV value is no more than 10kg/ (CM - s).

(6) Poor thermal conductivity. The thermal conductivity of PTFE is only 0.24kcal/ (m • h • ℃), and it is easy to cause thermal expansion, thermal fatigue and thermal deformation.

(7) Prices are more expensive than other plastic.

These defects of PTFE limit its wide range of applications to a certain extent. At present, the research focus on PTFE in the world is to find the appropriate method to modify it, in order to improve its performance to a certain extent, so as to expand the application in various aspects.

The modification of PTFE

Proper modification of pure PTFE can improve its comprehensive performance and expand its application in various fields. At present, the modification of PTFE mainly uses the composite principle, which is combined with other materials to make up its own defects. The methods of modification include: surface modification, filling modification, blending modification and so on.

The surface modification

PTFE's very low surface activity and non adhesion limit the bonding with other materials, especially the bond between PTFE thin film and other skeleton materials. Therefore, it is necessary to modify the surface of PTFE material to improve its surface activity. PTFE commonly used surface modification technology:

Surface activation technique

(1)Radiation grafting method. By irradiation of high energy radiation, the surface of the film can be grafted with other materials under certain conditions, and a layer of PTFE film which is tightly combined with the framework material is formed.

(2)Plasma activation method. With an inert gas such as argon, helium plasma treatment of PTFE material, the surface etching, and carbon fluorine bonds and carbon carbon bonds fracturing, generating a large number of free radicals, but also can be introduced into the active groups, greatly increase the surface free energy of PTFE, improve the wettability and adhesion, which can be formed the adhesive layer on the surface of the surface activation. In general, the stick relay can be 10 times larger than before treatment.

(3)Potassium acetate activation method. Immersing the PTFE in the molten potassium acetate, and the active layer could be formed after a certain amount of time to be treated at a proper temperature.

(4)Mixed liquor activation treatment. PTFE in a certain proportion of sodium hydroxide, two propylene based melamine mixture to heat treatment for a certain period of time can improve the surface activity.

(5) Corona discharge activation. The PTFE can be formed into adhesive bonded active layer by the corona treatment of the proper time and a certain atmosphere.
(6) Tesla transformer discharge activation treatment. The transformer is used to discharge the PTFE, and the surface of the transformer is activated.

Chemical modification
The surface corrosion of PTFE mainly includes:
(1) The ammonia solution of sodium metal can be treated with a certain concentration of sodium ammonia solution for a certain period of time, so that the contact angle of PTFE can be reduced from 108 to 52 degrees, which can be used as a composite of epoxy resin and other materials.
(2) Sodium naphthalene solution in tetrahydrofuran. PTFE with a certain concentration of sodium, naphthalene, tetrahydrofuran solution processing can achieve the goal of modification.
(3) Alkali metal amalgam .The use of alkali metal amalgam corrosion of PTFE, which makes the surface carbonized and easy to be wetted and bonded.
(4) Osmic acid corrosion. The use of osmium acid corrosion can increase the hydrophilicity of PTFE, which contributes to the composite molding.
(5) The corrosion of iron pentacarbonyl. Using iron pentacarbonyl solution impregnates PTFE, which can improve its the surface corrosion and activity.

Surface deposition modification
Impregnating the PTFE in the colloidal solution of some metal hydroxide, which makes the colloidal particles deposited on the surface of PTFE, increasing the wetting angle, and improving the surface activity, which is easy to be combined with other materials.

The above surface modification methods are mainly applied to PTFE thin films. Usually, when the PTFE film is treated properly, it can be combined with other materials, and can be widely used in the design and manufacture of chemical anti-corrosion lining, sealing products and lubricating device. The basic design ideas of these methods, such as the introduction of polar groups, increase the interface bonding force; or to eliminate the weak interface layer, forming a strengthened surface layer; or to adjust the surface roughness, to give anchor effect. In short, various methods have their advantages and disadvantages, reasonable application or to find a new surface activation treatment is the main way to expand the application of PTFE thin film.

Filling modification of PTFE
Filling modification is adding filler to the PTFE, so as to improve and overcome the defects of pure PTFE, while maintaining its original advantages on the basis of the composite effect, improve the comprehensive performance. The filler can make the PTFE wear resistance increased about 1000 times; creep resistance increased 1.5 ~ 4.5 times at room temperature, 1.5 times at high temperature; flexural modulus increased 2 ~ 3 times; the hardness increased by

10% ~ 30%; the highest thermal conductivity increased 2 times; linear expansion coefficient reduced by about 1/2.

The filling properties of PTFE are closely related with the filler's properties, content and technology, the basic principle for the general choices of filler include: (1)The filler can withstand the sintering temperature of PTFE. (2) The filler can improve PTFE's abrasion resistance, mechanical strength, or increase the thermal conductivity coefficient, reduce the linear expansion etc.(3) When in use, the filler will not effect other contact metals or fluid. The current commonly used fillers can be divided into 3 categories: inorganic materials, organic materials and metal materials.

(1) Inorganic filler materials. The commonly used inorganic filler are mainly glass fiber, graphite, MoS2, carbon fiber etc.
Filled PTFE glass fiber is generally no alkali glass fiber, the filling amount is generally 15% ~ 25%, the ratio of length to diameter of 5 ~ 10. The hardness of the PTFE composited by the glass fiber can be generally increased by 10%, wear resistance can be increased by more than 500 times, creep resistance and resistance to cold flow properties have a greater degree of improvement and improvement.
Adding MoS2 helps to increase the rigidity and hardness of PTFE products, reduce the wear of the early start. In general, there's little dosage of MoS2 in filling PTFE, and it often combines with other fillers.
The graphite can be used alone, and can be used in conjunction with the glass fiber or carbon black. Graphite filled PTFE has excellent chemical resistance, compression creep and better thermal conductivity, but its wear resistance worse than glass fiber filled PTFE difference. Only a small amount of carbon fiber filled PTFE can achieve carbon and graphite filling efficiency, but also has a very superior tensile properties. The wear resistance of the products in air and water can be greatly improved, and it has good creep resistance at room temperature and high temperature, but the biggest limitation to the application of this kind of material is the high cost.

(2) Metal filling material. In order to improve the mechanical properties, thermal conductivity and dimensional stability of PTFE, it's common to fill PTFE with iron, copper, lead, molybdenum, tungsten, silver and other metals, especially with copper and its alloys.
The copper filled PTFE can improve the creep resistance, compressive strength, hardness and dimensional stability of products, but the corrosion resistance and dielectric properties decrease. The suitable dosage of copper powder is 60%, at the moment, the limit value of PV can reach 29000, higher than that of other general materials.

Blending modification of PTFE

The blending modification of PTFE are familiar with the basic principle of filling modification generally, often refers to blend with other organic polymers, in order to improve its processing performance and use performance. In the blending modification, the PTFE is usually used only as a filling agent, and the processing method of the main material is usually used as the processing method of the blending material. The use of blending modification with PTFE has the following advantages:(1)The existing material and the existing process can be used to develop new varieties, and the investment is small, and the effect is fast; (2) Many varieties can be developed and the range is wide, such as the thermoplastic plastics, rubber, thermosetting resins, coatings, sealant, etc.;(3) The method of injection, molding curing, coating solidification and other methods of the main body material can be processed more efficiently and less energy consumption than the PTFE molding and sintering process;(4) Other polymers can improve the processing performance and use performance, such as heat resistance, chemical resistance, in particular, friction, wear resistance can be greatly improved.

The basic principle of blending is the principle of similar compatibility, solubility parameter and surface tension. PTFE blending modification engineering plastics mainly have polycarbonate (PC), poly formaldehyde (POM), nylon 66 (PA6), etc.. Modified engineering plastics not only maintain its original characteristics, especially the processing performance, but also improve its wear resistance, and improve the critical value of PV.

The rubber of PTFE modification is mainly silicone rubber, fluorine rubber. The wear resistance of the modified rubber is greatly improved. In some synthetic rubber and its coating, the blending of PTFE will greatly improve the chemical stability, oil resistance and solvent resistance of the rubber.

PTFE modified thermosetting resins are less. Often using a small amount of low molecular weight PTFE modifies the resin, and its wear performance is greatly improved; in addition, adding PTFE in curing type sealant, without reducing the sealing characteristics, can improve the use of temperature and chemical stability, while increasing lubrication.

In addition to the above modification method, introducing a small amount of non fluorine group into the PTFE chain, and the block is grafted to destroy the symmetry, so the modified PTFE is obtained by the method of thermoplastic processing. The performance of this product is similar to that of PTFE, but the performance of this product is greatly improved, so it is being paid more and more attention.

In addition, PTFE dispersion, paste and PTFE powder and expanded PTFE (EPTFE) are widely used in various industries because of its good processing performance.

The processing and forming of PTFE

PTFE has high melting point, high melt viscosity, and the shear in the amorphous state is very sensitive, prone to melt fracture, therefore it cannot be used to melt extrusion and injection molding of plastic molding process of conventional thermoplastic, can only use similar methods for powder metallurgy sintering molding. The manufacturing of the filling PTFE is equal to the molding of PTFE , which can be used for pre molding, free sintering process, and can also be used in plunger extrusion molding. The PTFE particles are sintered at a certain temperature, and then being cooled at a certain temperature after pressure forming and pressing forming. This process is relatively simple, but only for a certain thickness of the product, not suitable for processing PTFE thin film. Because PTFE thin film material has the characteristics of less material consumption, simple application and wide adaptability, people have been exploring the production and processing methods of PTFE thin films in recent years. At present, the more mature processing methods are:

(1) Rolling processing of PTFE thin films. This processing method is only applicable to dispersed resin. Making the use of low cohesion and fibrotic properties of this resin, and adding the PTFE emulsion to the powder system, stirring time, PTFE fiber can live complex powder, and then compress it, making the powder becomes solid, then the solid rolling can be obtained PTFE films filled with modified. Different powders give different properties to PTFE film.

(2) Turning of PTFE thin film. This kind of processing method actually belongs to the two processing method of plastics. It mainly uses the low hardness of PTFE sintering products, and good toughness of the characteristics, therefore, the PTFE film can be processed by the method of metal turning. Special lathe is usually used for turning, also can be used for metal processing lathe and woodworking lathe. The thickness of PTFE thin films processed by turning method is up to 0.04mm, and its mechanical properties is good, without any material when processing, and low impurities, non-toxic, also can be used for medicine.

(3) Extrusion processing of PTFE thin films. This process is actually the synthesis of a conventional extrusion and calendaring, the only difference is, resin without melting, but raw material processing in the processing. In this method, the residual deformation can be produced by using PTFE under the action of compressive force, and the residual deformation can be increased by adding a certain additive. Usually the PTFE material is added to help squeeze agent pressed into the ring with certain density, then put it in the extruder for proper heating, extruding strips, and finally put it into the calendering roll rolled into thin films, and then remove the squeeze agent.

In addition to the above one processing technology of PTFE processing, there are a lot of two processing methods. PTFE two processing refers to the PTFE semi-finished products: PTFE board, film, tube, rod, etc., using hot deformation, welding, turning, compositing and other processing technology into a variety of specifications and shapes of PTFE products. At present, a number of new technologies have emerged in the process of the two processing in addition to the above methods.

(1) Vacuum forming technology of PTFE. The technology is to preheat the PTFE film in vacuum conditions into the desired shape. The structure of complex parts by this method can be made less than 100 μm, and the surface of the product without further processing, especially suitable for production of composite parts together with other materials.

(2) Hot press molding and hot blow molding of PTFE. The technology uses PTFE semi-finished products under the heat can be deformed, after cooling can be made of the required shape of the basic principles of products. PTFE container for hot blow molding possesses the performances including high temperature, stable size, uniform thickness, light weight, good transparency and so on, and it is a promising processing method for the preparation of PTFE containers. This technology can also be processed PTFE corrugated pipe and other complex shape of the cylinder.

(3) Pressure molding process. This technology is a new processing technology developed in 70s. Applying this technique can process different specifications of the PTFE board, rods, tubes, shaped body and a variety of complex shapes of PTFE lining. Isobaric molding technology is based on the Pascal principle, the pressure of a liquid or gas in a sealed container along the direction of uniform transfer to PTFE powder layer to isobaric compression molding, and sintering to obtain the desired shape of PTFE products.

The application of PTFE

PTFE is the preferred material for corrosion resistant pipe, pipe fittings, corrugated pipe, pump body, valve, tank, tower and various types of standard equipment corrosion resistant lining. In addition, as a sealing material, lubricating materials in mechanical, petrochemical, transportation, medicine, food, light industry, textile, construction and other industries, PTFE is widely used.

(1) Anti-corrosion lining. Anti-corrosion lining is one of the biggest applications of PTFE in chemical engineering. Especially in the working conditions that traditional materials can not be resolved by the strong corrosion, low temperature, anti - adhesive, high - purity and other harsh , PTFE is an ideal anti-corrosion equipment lining material.

(2) Sealing material. Another application of PTFE in the chemical industry is the sealing material. The PTFE film composite on the rubber sealing material surface, can improve the rubber sealing parts of the solvent resistance and resistance to medium, the price is relatively low, which has been used for a variety of demanding occasions, sealing requirements. High and low temperature properties of PTFE filled with sealing material is excellent, and it is the main alternative to replace the traditional asbestos gasket materials at present; Carbon fiber reinforced PTFE sealing material has high strength, high modulus, fatigue resistance, creep resistance and high thermal conductivity, small thermal expansion coefficient and friction coefficient etc.. These properties are not comparable to any kind of sealing material, which is the ideal high sealing material.

(3)Other aspects of the application. PTFE and modified PTFE can also be used as a valve, chemical bearings, piston rings, gaskets, sliding blocks, rails and other requirements of corrosion resistance and low friction components. In addition, the PTFE film can be used as separation material and selectively through gas or liquid according to the choice of the treatment. The porous membrane can also be used for gas liquid separation, gas separation and liquid separation, and can also be used for filtering corrosive liquid. In addition, PTFE in medicine, electronics, construction and other industries also has a wide range of applications, such as PTFE film can be used as human organs, artificial blood vessels, heart valves, and so on.