Granular PTFE Resins

Characteristics and Applications

TECHNETICS GROUP – PTFE & Polymer Solutions

10633 W Little York, Bldg 3, Suite 300 | Houston, TX USA 77041

www.techneticsptfe.com

Contents

In our previous article, we introduced the amazing polymer Polytetrafluoroethylene (PTFE), highlighting its main properties, structure, and the types of PTFE resins commercially available. In this article, we will focus on the granular PTFE resins.

Manufacturing PTFE Resin

As mentioned in the previous article, granular resins are produced by the process known as ***Suspension Polymerization***. This polymerization method includes little to no dispersing agent and high agitation at an elevated temperature and pressure. The first reported polymerization of PTFE was by Dr. Roy Plunkett in 1941, and it was anything but commercial. The early reports of a process suitable for the manufacturing of granular PTFE resins were reported in 1946. The polymerization of the TFE – which is a colorless and odorless gas – happens inside a reactor (also called a kettle or polykettle). The greatest challenge in the polymerization reaction is to remove the heat. That is the reason for the vigorous agitation during the reaction and the addition of water as a polymerization media. The agitation enhances the heat transfer to the cold water. If the heat is not controlled, it can result in overpressure and possible explosion of the reactor. The product of suspension polymerization is stringy shaped particles (beads). They are of variable size and shape and are elongated, resembling shreds of grated coconut, as a result of the aggressive agitation. Therefore, some finishing steps are required to give the polymer particles are more uniform particle size and allow for parts with usable properties to be manufactured. Figure 1 below shows the general steps involved in manufacturing granular PTFE resins.

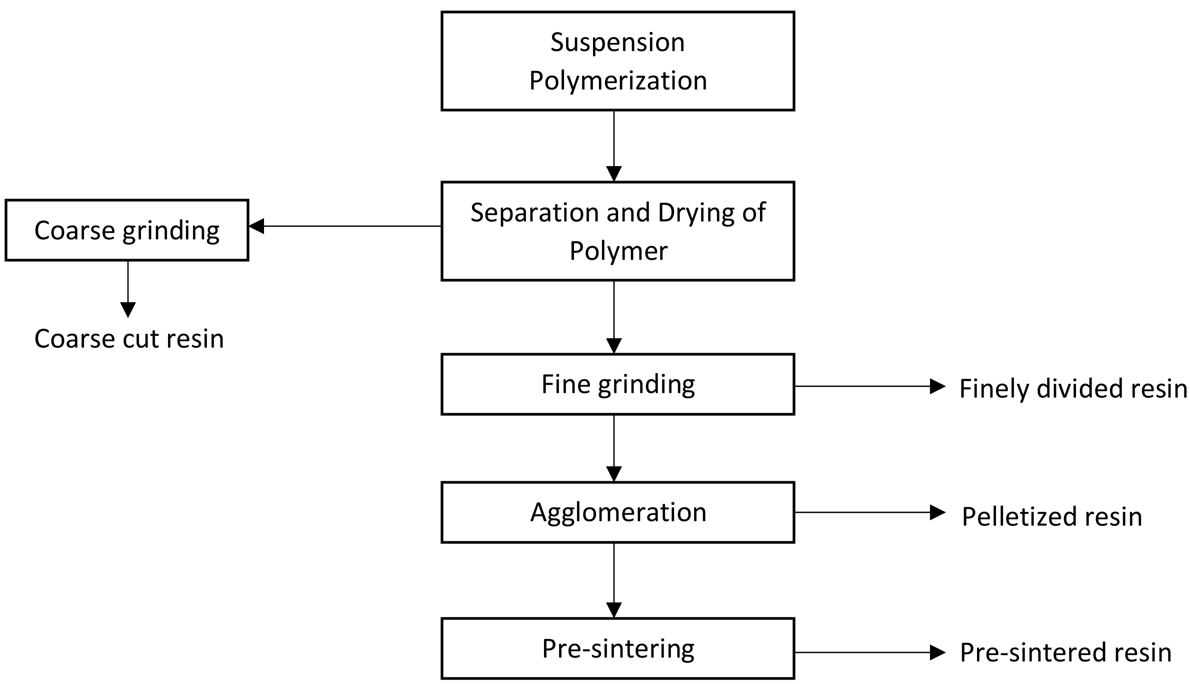

Figure 1 *– Suspension polymerization and finishing steps*

Polymer Designations

The earlier article also touched on the homopolymer/copolymer designations. The usual convention of polymer science applies the name ***copolymer*** to any fluoropolymer resin containing *more than 1% of a comonomer*. If *no comonomer* is used in the polymerization process, the fluoropolymer is called ***virgin homopolymer***. A fluoropolymer containing *less than 1% comonomer* is categorized as a ***modified homopolymer*** resin (check our video library for more details on modified PTFE).

Most commercially available grades of granular PTFE resins are either virgin or modified homopolymers, following the definition of ASTM D4894. It is essential to highlight that this ASTM standard does not cover mixtures of PTFE resin with additives such as colorants, fillers, or plasticizers. Nor does it cover reprocessed or reground resin.

Virgin and Modified granular resins are further divided into two groups: low flow (or fine cut) and free flow (or pelletized). Due to the smaller molecular weight of the comonomer, the resultant molecular weight of the modified PTFE is smaller. However, the mechanical properties of the PTFE are improved as well as the resistance to permeation. These changes occur because the modifier reduces the crystal size within the polymer structure and reduces the melt viscosity. Therefore, during melting, particles flow better, improving void closure and, consequently, porosity, increasing specific gravity.

Fine Cut Resins

Fine cut (low flow) resins have a typical average particle size in the range of 20 – 40 microns. The small particle size of fine cut PTFE resins imparts the best physical properties that are possible to obtain from granular resins to the articles made with them. These resins have “poor flow” and a relatively low apparent density (< 500 g/l). The small particle size of the resins renders them suitable for high quality skived films, large billets, and compounding with fillers such as glass fiber, carbon black, bronze, and others.

Pelletized (Free Flow) Resins

Pelletized (free flow) resins have a typical average particle size in the range of 450 – 550 microns and a bulk density above 500 g/l. Typically, mechanical and electrical properties of parts made with free-flow resins are lower than parts made with fine cut resins. Processing free flow resins can be more efficient as they make it easier to fill molds, and therefore require smaller molds.

Fabrication Methods

The most common way to produce parts from granular PTFE resins is by compression molding. In most cases, the molding process is employed to convert PTFE resins into basic, solid shapes: rods, cylinders, and sheets or blocks. Sizes can vary from diameters of a few inches up to more than 5 feet (more than 1.5m) for rods and cylinders. Sheets can be as large as 48” x 48” (1.3 x 1.3 meters), as thin as 0.063” (1.6mm) up to 8” thick (203mm).

In a compression molding process, PTFE powder is compressed inside a mold at ambient temperature. After removal from the mold, the preform is heated in an oven above its melting point and is "sintered." Sintering is a heat treatment process, primarily used in powder metallurgy and ceramics processing, for bonding particles into a coherent, solid structure via mass transport events that often occur on the atomic scale. The chemical bonding that occurs in the sintering process leads to improved strength of the PTFE and lower system energy. In powder metallurgy and ceramics processing, the sintering temperature is slightly less than the material melting point. However, when sintering PTFE molded parts, the material temperature usually surpasses its melting point of 342°C. This heat resistance is possible due to the exceptionally high melt viscosity of PTFE – the molten resin will not flow and has an appearance like gelatin. Controlling the sintering temperature, among other molding and sintering parameters, enables manufacturers to manage physical and mechanical properties of the parts produced.

When molten, PTFE has a viscosity of 10^{11} - 10^{12} poise (at 380°C)

For comparison, the viscosity of honey, at room temperature is 10^{2} poise

Post-Production Manufacturing

The molded parts can further be machined to produce more complex parts such as manifolds, endcaps, valve seats, pump bodies, and more. Films can be produced by the process known as skiving – which consists of "peeling" layers of the desired thickness from a cylinder. Skived films (also referred to as sintered films) can be as thin as 0.001" (0.025mm). Above 0.25" (6.35mm), skived parts produced are called "sheets" and can be as thick as 0.375" (9.5mm).

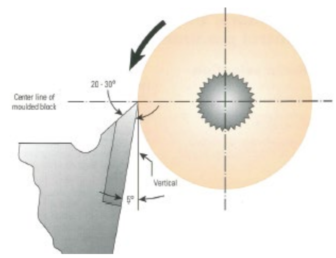

Fig. 2 *– Arrangement of a skiving knife*

The Premier Properties of PTFE

As a fully fluorinated polymer, PTFE is virtually inert to the most aggressive organic and inorganic chemicals and solvents over a wide temperature range. Chemical inertness means that PTFE can be in continuous contact with another substance with no detectable chemical reaction or degradation taking place.

Table 1 *– PTFE properties relatively independent of processing conditions*

Chemical Properties	Electrical Properties	Mechanical Properties
Resistance to corrosive reagents	Low dielectric constant	Flexibility at low temperatures
Non-solubility	Low dissipation factor	Low coefficient of friction
Long-term weatherability	High arc resistivity	Stability at high temperatures
Non-adhesiveness	High surface resistivity	
Non-flammability	High volume resistivity	

Table 1 shows the chemical, electrical and mechanical properties of PTFE relatively independent of processing conditions. In addition to the typical properties, modified granular PTFE grades offer weldability, improved resistance to deformation under load, increased permeation resistance, and higher dielectric breakdown voltage.

Five Factors that Influence PTFE Properties

Literature has pointed out that approximately 15 mechanical properties plus several electrical and chemical properties are influenced by molding and sintering conditions such as compression pressure, dwell time under pressure, sintering temperature, time, and cooling rate. The most common properties affected by these processing conditions are tensile strength and elongation, dielectric strength, permeability, flex life, resiliency, stiffness, and impact strength. Five primary factors influence these properties:

1. **Presence of Macroscopic flaws:** internal bubbles, tears, foreign impurities, shear planes, or poor charge-to-charge bonds
2. **Extent of Microporosity**: number and size of microscopically visible voids created by imperfect particle fusion
3. **Percent of Crystallinity**: a percentage based on the weight fraction of a sample consisting of polymer chains fitted in a close-packed, ordered arrangement
4. **Molecular Weight**: a measure of the average length of polymer chains
5. **Degree of orientation**: a measure of the extent of alignment of polymer chains in a given direction

Measuring PTFE Characteristics

Directly measuring these characteristics can be problematic; therefore, indirect measurement methods have been devised: dielectric strength, tensile strength, ultimate elongation, specific gravity, and heat of fusion. Dielectric strength is a function of the degree of porosity, which can be evidenced by specific gravity and voids observation at 100x magnification. Specific gravity, tensile strength, and elongation are functions of percent of crystallinity, molecular weight, and voids (microporosity and macroscopic flaws). Tensile strength and elongation also indicate the degree of orientation. For example, an increase in the degree of crystallinity leads to an increase in elongation and specific gravity but decreases tensile strength and has almost no effect on dielectric strength. As a second example, higher molecular weight resins will produce parts with higher tensile strength. Still, elongation and specific gravity may be compromised, while dielectric strength is hardly affected by molecular weight.

Typical Applications for parts made of Granular PTFE resin

Chemical Processing Industry (CPI)

In this industry, manufacturing PTFE often involves using highly corrosive fluids. PTFE's chemical inertness and broad operating temperature range help prevent corrosion and contamination, extending service life and preventing unscheduled downtime. Although sometimes more expensive initially, some PTFE components can minimize maintenance costs, in the long run, helping companies to be more competitive. .

Piping

Flanged steel piping and a variety of fittings (T's, elbows, reducers, spacers, etc.) are lined with PTFE tubes. PTFE is a standard material for gasketing due to its nearly universal chemical compatibility, good performance at temperatures from cryogenic to over 260°C, and conformability. PTFE is used alone, with fillers, with metal supports, or as a dispersion for impregnating fibers such as aramids for gasketing. In addition to excellent sealing performance, gaskets made with PTFE can be used in a broad range of applications, enabling inventory reduction and reducing the risk of misapplication.

Sealing

The almost universal chemical compatibility, the broad temperature range of operation, and the low coefficient of friction makes PTFE an excellent material for sealing purposes. PTFE is mostly used as either a complete seal or as a component part. In seats and packings, PTFE provides conformability; that is, the parts conform to mating surfaces for impeccable sealing, and low friction for ease of operation. For diaphragms, PTFE provides superb flex life. Seals for rotating or sliding shafts use elements of PTFE compounded with fillers such as graphite. PTFE is used alone, or with fillers or metal supports, or as a dispersion for impregnating fibers such as aramids for gasketing.

Semiconductor processing

In semiconductor manufacturing, wet processing equipment, fluid transport systems, and wafer handling have relied on PTFE parts because these processes are incredibly intolerant of particulate and chemical contamination. Even in trace amounts, impurities can cause a severe decrease in yields. PTFE resistance to chemical attack along with high purity are essential attributes for this application.

Bearings

Due to its inherent low friction and lubricity, PTFE is often used in bearings and bushings. It can be compounded with other materials such as bronze, graphite, and other special fillers to reduce creep and improve wear resistance or thermal conductivity, for example. In this application, PTFE is usually applied to a metal support (substrate). For PTFE to bond, it must be chemically etched – PTFE etching is discussed in another article.

If you are looking for a basic molded PTFE shape or a more complex geometry (machined part) or PTFE films or sheets, don't hesitate to contact us. Our team of specialists will promptly assist you in material selection and properties definition to supply the correct parts for your application. Visit our website www.techneticsptfe.com for more information or contact us at PTFE@technetics.com.

REFERENCES

[1] Ebnesajjad, Sina. *Fluoroplastics - Volume 1: Non-Melt Processible Fluroplastics, the Definitive User's Guide and Databook*. 2nd ed., Elsevier, 2015.

[2] Sperati, C. A., and H. W. Starkweather. "Fluorine-Containing Polymers. II. Polytetrafluoroethylene." *Fortschritte Der Hochpolymeren-Forschung Advances in Polymer Science*, 1961, 465–95.

[3] *Teflon PTFE: Compression Molding. Teflon PTFE: Compression Molding*, The Chemours Company, 2019

[4] DuPont. *DuPont Fluoropolymers: An Introduction to DuPont Fluoropolymers. DuPont Fluoropolymers: An Introduction to DuPont Fluoropolymers*, DuPont, 2012.