Technetics
PTFE & POLYMER SOLUTIONS

Fine Powder PTFE Resins

Characteristics and Applications

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Contents

In this third article about PTFE in its various forms, we will approach PTFE resins commercially known as **Fine Powders**. Previous articles discussed the basics of Polytetrafluoroethylene (PTFE) and the resins commercially known as granular powders.

Fine Powder PTFE Processing

Fine powder PTFE resins are produced in a range of very high molecular weights (10^6 – $3x10^7$). The powder is processed by forming a paste by the addition of a petroleum-based hydrocarbon lubricant. This paste is then extruded into tubing, wire insulation, tape, or film. Typically, the extruded shape is dried in an oven to remove the lubricant. In the final step, the dried extrudate is sintered in an oven. The process of paste extrusion and sintering is usually continuous.

As discussed in the first article of this series, PTFE is the polymer made by the polymerization of the TFE (tetrafluoroethylene) monomer. An emulsion or dispersion polymerization is the method by which fine powder PTFE resins are manufactured. Fine powder resins are also called coagulated dispersion resins, which is descriptive of their production method. In general, the key characteristics of the emulsion polymerization regime include ample surfactant and mild agitation at elevated temperature and pressure. The dispersion recovered from the reactor is finished by two different processes depending on whether a dispersion or a dry powder (fine powder) is the desired final product, as illustrated in Fig. 1.

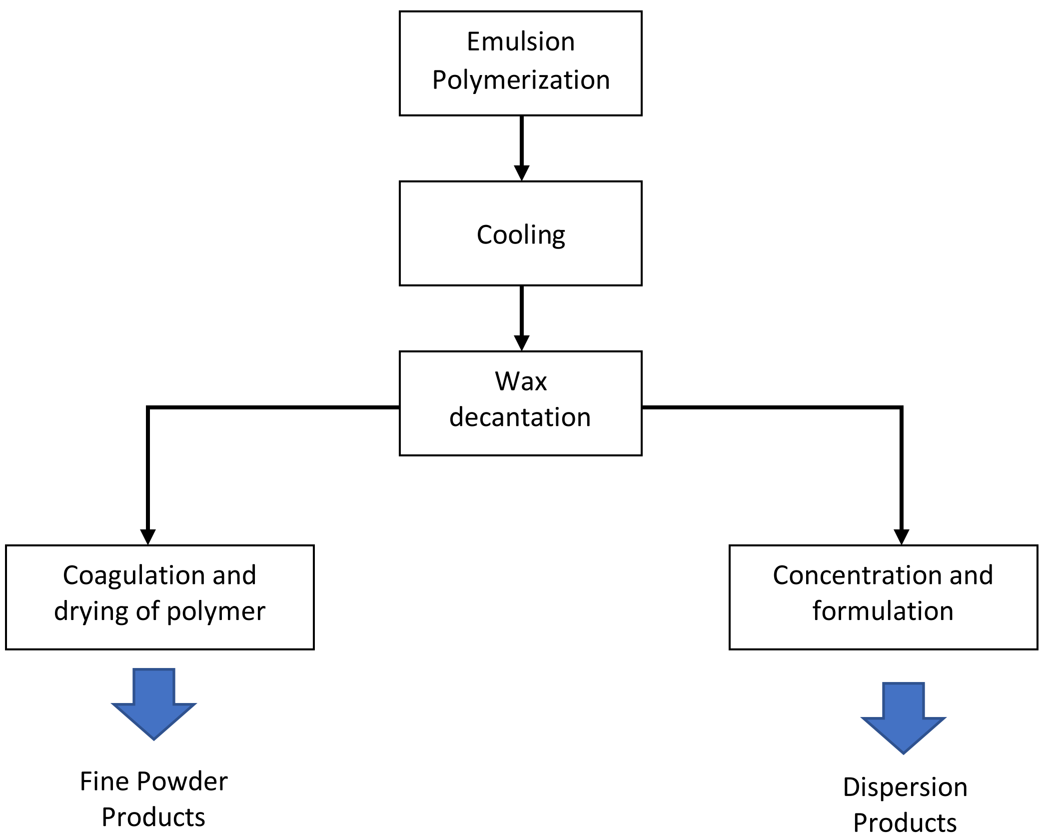

Figure 1 - Emulsion polymerization of TFE and product finishing processes.

Evolution of the Polymerization Process

The emulsion polymerization process has evolved significantly since the discovery of PTFE. Many manufacturers use small amounts of modifiers to improve specific properties and allow very thin-wall products to be produced by the paste extrusion process. Before this development, moderately high molecular weight fine powder PTFE was available, which could not be used to create thin parts such as wire coating, tubing, and thin films.

Excessive paste extrusion pressure and flaws developed when extremely high molecular weight resins were converted to parts less than 500μm in thickness. The addition of modifiers – or comonomers during the polymerization process – initially aimed to improve the thermal stability of the dispersion. Researchers soon discovered that the addition of specific modifiers allowed them to control the molecular weight of the polymerized particles. The advantage of these polymers is the possibility of paste extrusion of their fine powders at a high reduction ratio without the complication of the high extrusion pressure and flaws in the extruded parts such as tubing or wire insulation. The introduction of the comonomer improved the paste extrudability of the resin or the properties of the final product. Copolymers tend to improve the transparency of the sintered part, such as tubing. However, occasionally the modifier improves the extrudability but deteriorates properties of the sintered part.

Production of Fine Powder Resins from the Dispersion

To produce fine powder from the polymerization dispersion, three processing steps have to take place.

1. Coagulation of the colloidal particles
2. Separation of the agglomerates from the aqueous phase
3. Drying the agglomerates

Coagulation of the colloidal particles

The coagulation of the particles consists of a dilution step with the addition of coagulating agents such as a water-soluble organic compound or inorganic salt or acid. The diluted dispersion is then agitated vigorously.

Separation of the agglomerates

The separation of agglomerates from the aqueous phase is done by skimming or filtration. Drying of the PTFE agglomerates is carried out by vacuum, high frequency, or heated air such that the wet powder is not excessively fluidized.

Drying the agglomerates

Individual particles of PTFE, usually referred to as primary particles, are in the 0.2 – 0.5 microns range. These particles form agglomerates (in the coagulation step) that are roundish and average several hundred microns in size. Figure 2 shows agglomerates of a typical PTFE fine powder. Closer examination at higher magnifications reveals that agglomerates are composed of many small particles.

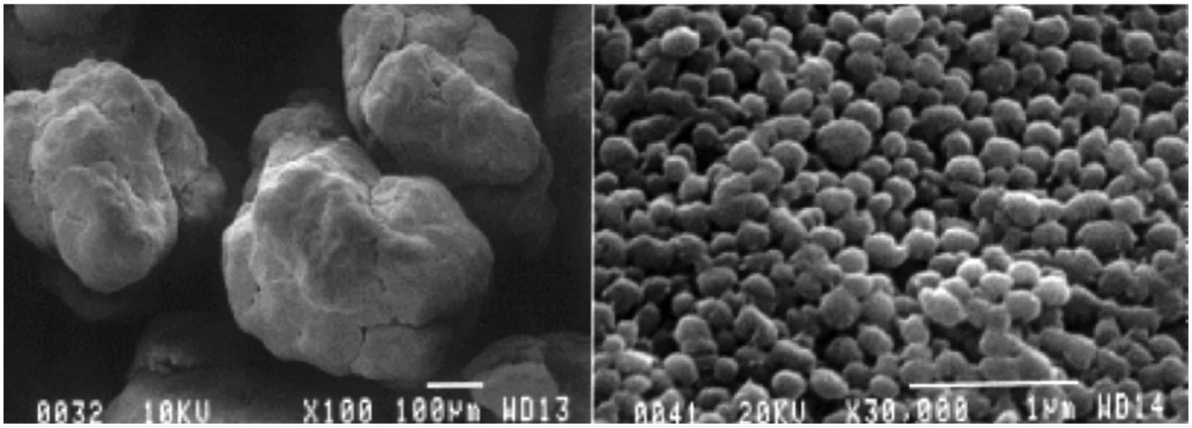

Figure 2 - Agglomerates of a typical fine powder and 100X and 30,000X magnification.

Processing of Fine Powder PTFE resins

Fine powder PTFE is unique; it is highly crystalline (96% – 98%) and has a high molecular weight. The crystalline form of PTFE changes from a triclinic to a hexagonal lattice at 19°C. Above this temperature, fine powder PTFE becomes softer and more deformable, which is vital to its processing.

Because it does not melt and flow, fine powder PTFE is fabricated by a technology adopted from ceramic processing called paste extrusion. PTFE powder is first blended with a hydrocarbon lubricant (hence the term paste), which acts as an extrusion aid. It is then formed into a cylindrical preform at low pressure. Finally, it is placed inside the barrel of a ram extruder where it is forced through a die at a constant ram rate.

Fine powder PTFE is susceptible to shear damage, particularly above its transition point (19°C). Handling and transportation of the containers could easily subject the powder to enough shear rate to spoil it if the resin temperature is above the transition point.

A phenomenon called fibrillation occurs when particles rub against a surface or other particles. Fibrils are pulled out of the surface of PTFE particles. Uncontrolled fibrillation must be prevented to ensure high-quality products from the powder. Premature fibrillation leads to the formation of lumps, which cannot be completely broken up. The resin should be cooled below its transition temperature to avoid fibrillation.

Paste Extrusion and the Fibrillation Mechanism

In a single particle of PTFE, almost all the polymer chains are packed in a crystalline lattice (Figure 3). The orderly packing of completely linear polymer chains takes place during the polymerization, monomer by monomer, or brick by brick. This effect of polymerization is precisely the reason that nearly perfect crystallinity is achieved despite very high molecular weights.

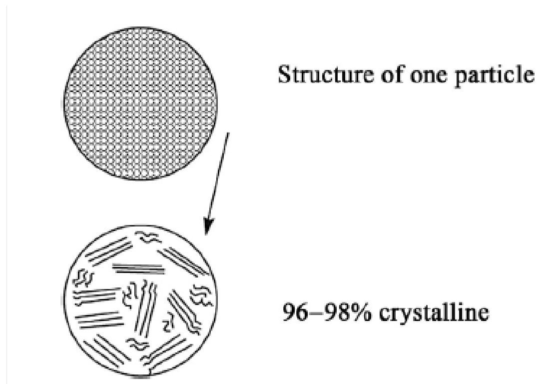

Figure 3 - Structure of one polytetrafluoroethylene fine powder particle

One of the characteristics of PTFE crystals is that they are loosely packed because of the relatively low Van der Waals attraction forces between the chains in contrast to other polymers such as polyethylene. Chains can thus be removed from the surface of particles by the application of a small force above the transition temperature. The chains abstracted from the particle are called ***fibrils***. The ease with which chains can be pulled out at higher temperatures is the main reason that fine powder PTFE is handled, stored, and transported below its transition point

During the extrusion process, preformed resin particles going through the die are highly compressed due to the reduction in the cross-sectional area. Figure 4 shows a schematic of particles being pushed through a conical die. The neighboring particles begin to mechanically interlock, as they rub against one another while competing for an exit out of the die. This compression results in the interconnection of adjacent particles. At the exit of the die, the connected particles are accelerated, causing the particles to separate. Still, because they had been interconnected, chains are pulled out from the particle – the fibrils. Now particles are connected through the fibrils. The quality and number of fibrils generated during extrusion are responsible for the strength of the extrudate. The die design has a significant impact on the quality of the extruded material. Figure 5 shows the SEM micrographs of PTFE particles once mixed with the lubricant, preformed, and extruded.

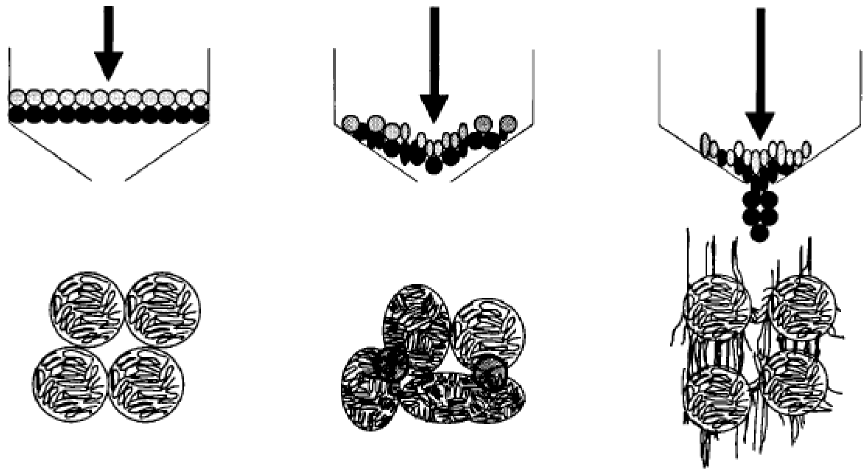

Figure 4 – Illustration of PTFE particles traveling through an extrusion die generating the fibrils connecting them

PTFE pastes can be extruded as tubes, solid rods, or beads, as a coating over conductors/wires or as sheets/films. In all cases, once extruded, the material must go through one or more steps before it becomes the desired finished product. Regardless of the extrudate shape, a standard step post-extrusion is the drying of the lubricant used as an extrusion aid. The lubricants used in the extrusion process are typically highly flammable hydrocarbons, which must be evaporated from the PTFE before performing the sintering process.

Post-extrusion steps

Besides drying, common post-extrusion steps include:

- **Calendering**: usually employed to reduce or control thickness when the desired finished product is thin films or tapes
- **Expansion or stretching:** used to reduce density, improve or manage porosity and mechanical properties
- **Sintering**: most extruded tubes are sintered to achieve the desired physical and mechanical properties
- **Slitting**: slitting is usually performed after drying and can be done with unexpanded or expanded PTFE. Wide films (or webs) are usually slit to narrow widths commonly used for wire insulation or yarns used in sealing and medical applications;

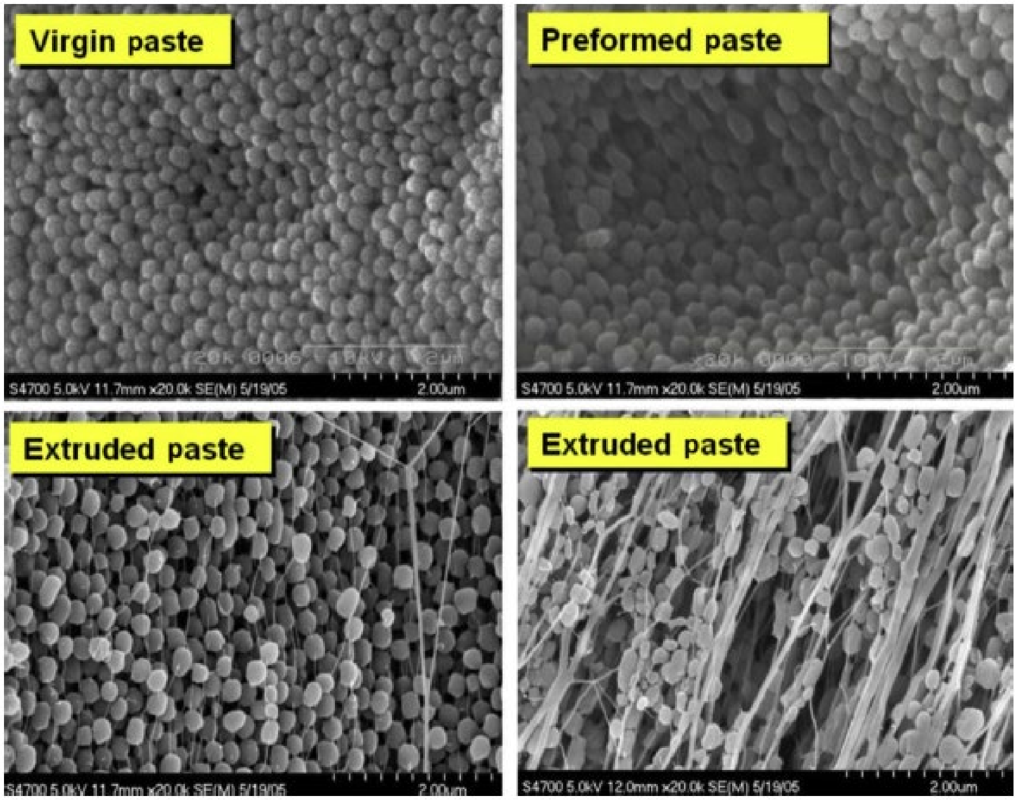

Figure 5 – SEM micrographs showing the changes to the PTFE from virgin to extruded paste

Typical Applications for Parts Made of Fine Powder PTFE Resin

Tubing

The majority of tubes made from PTFE by paste extrusion have relatively thin walls (<8 mm). They are produced in a wide size range from a fraction of millimeter to several centimeters in diameter. Applications where PTFE tubes are used range from fluid transfer in healthcare to fuel and hydraulic transfer in jet engines. Tubing is divided into three categories based on the size and wall thickness for various applications:

1. Spaghetti tubing
2. Pressure hose
3. Pipe liner

Wire Coating

One of the critical applications of fine powder polytetrafluoroethylene is wire insulation. It is found primarily in automotive, aerospace, and industrial applications, where a high-temperature rating (>250°C) and resistance to chemicals are required. Coaxial cable is another application where PTFE is used as the dielectric material between the two concentric conductors.

Unsintered Tapes and Films

Unsintered tapes and films are the most versatile form of product that can be produced using fine powder PTFE resins. Narrow widths of unsintered tapes and films are primarily used in the wire and cable industry as the primary insulation or as an outer jacket of wire bundles. One advantage of using tape wrapped insulation instead of extrusion over wire is that tape wrap machines enable the application of several layers of PTFE or other insulating materials simultaneously.

Applications Requiring Unsintered Tapes and Films

This unsintered manufacturing method creates insulation systems capable of withstanding high temperatures of operation (up to 260°C), chemical attacks, arcing events, and abrasion while simultaneously providing light-weight insulation, which is desirable, especially in aerospace applications. Due to its low dielectric constant, expanded PTFE (ePTFE) tapes (also known as Low-Density Tapes) and films are highly used in coaxial and data cables to reduce signal loss. PTFE tapes are used to make convoluted pressure hoses for chemical transfer. They are also used to make yarns for industrial sealing and medical applications.

The Perfect PTFE Solution

Whether you are looking for a standard PTFE film or need assistance developing a solution that meets specific and strict requirements, our team of specialists will promptly assist you in material selection and properties definition to supply the appropriate parts for your application. Our knowledge of raw materials and additives, along with our process capabilities, enable us to create the perfect solution for your specific requirements. Visit our website www.techneticsptfe.com for more information or contact us at PTFE@technetics.com.

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