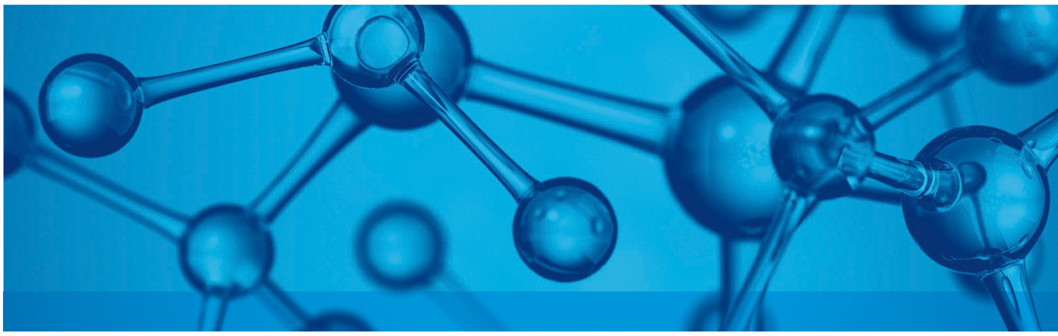


Ryton® PPS Compression Molding and Free Sintering

Ryton® PPS (polyphenylene sulfide) is a unique engineering thermoplastic developed to meet the requirements of demanding industries. It is successfully being used in injection molding, coating, compression molding, extrusion, and free sintering processes. PPS has outstanding resistance to heat and can be used at temperatures as high as 260 °C (500 °F). PPS polymers have been rated V-0 by the Underwriters Laboratories UL94 test, and are classified as non-burning and non-dripping when tested in accordance with ASTM D635. There is no known solvent for PPS below 204 °C (400 °F). Additional information on its outstanding chemical resistance is available in the Ryton® PPS Chemical Resistance Guide.

Unlike most other thermoplastics, heating PPS in the presence of oxygen induces chain extension and crosslinking processes that increase the molecular weight and melt viscosity of the polymer. The degree of this "precuring" can be controlled with time and temperature, and makes possible the molding of large, heavy-walled parts as opposed to the thin-walled, intricate parts typically produced by injection molding. The technique for molding large, heavy-walled parts is referred to in this memorandum as "compression molding."

In combination with polytetrafluoroethylene (PTFE), PPS can also be free sintered (the term "sinter" refers to a fused conglomerate of heated non-metallic powders) using techniques very similar to those used to sinter PTFE compounds. PPS improves the physical properties of PTFE without appreciably reducing the chemical resistance or thermal stability of PTFE. Unlike compression molding, sintering does not require applying pressure to the part during the sintering or cooling stages, and therefore does not require handling hot molds.

These methods provide an alternative to injection molding for producing heavy walled parts (not possible by injection molding), and for reducing tooling costs for smaller production quantities. Rods, sheets, and hollow forms produced by these methods can be easily machined into other useful shapes. Typical operations such as turning, milling, drilling, and tapping are quite facile, however carbide tools are recommended because high loadings of hard fillers can result in severe wear of machining tools. Optical finishes are possible with grinding and lapping.

Blending

Ryton® PPS polymers have a high affinity for a variety of fillers. Thermally stable materials have been successfully used to modify various physical properties of the polymer such as rigidity, electrical or thermal conductivity, coefficient of friction, and flexibility. Fillers such as glass, minerals, metal powders, fluorocarbons, molybdenum disulfide, carbon, and graphite have all been successfully used in various applications. One advantage of PPS as a matrix is that it can bond 80–90 % filler levels, however this requires less precuring of the polymer (precuring is discussed in a later section). There are also commercially available low flow rate PPS polymers that can be used to bond high filler levels without the need for precuring.

Thorough blending of the various fillers with the PPS powder is an important factor in obtaining good results in the compression molding or sintering of the material. Any intensive mixer (such as a Henschel mill) that can homogeneously mix the filler and powders may be employed. The most important consideration in blending is that the filler be thoroughly coated with PPS powder. Blending chopped strand glass fiber with PPS powder requires special consideration due to the difficulty of breaking up the individual glass bundles. Milled glass fillers, however, may typically be incorporated in much the same manner as other fillers. The bulk density of a PPS compound is affected by the type and percentage of filler added (the bulk density of Ryton® PR11 powder is approximately 0.4 gm/cm^3 (0.014 lb/in^3). Compounds having higher bulk densities will have higher compaction ratios and increased rates of precuring. If necessary, Ryton® PPS powders may be milled to smaller particle sizes using various common methods such as air mills or cryogenic grinding.

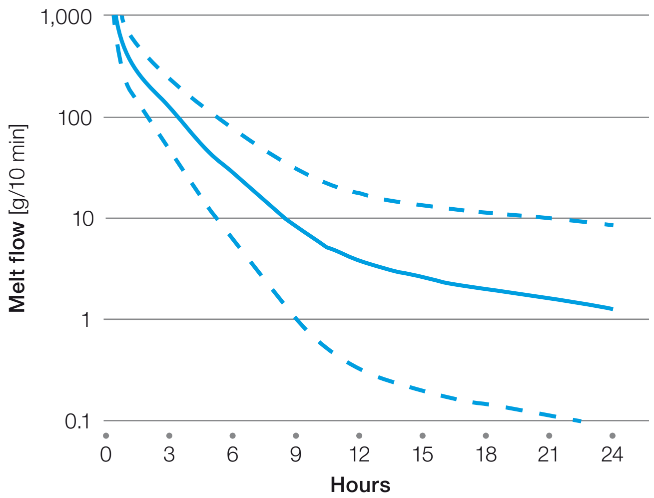
Ryton® PPS sintering compounds generally contain molding grade PTFE. Homogeneous blending of the PPS and PTFE powders is essential for high quality void-free sintered parts. One way to obtain homogeneous blends is to use PPS and PTFE grades of matching particle size (the median particle size of Ryton® PR11 powder is about 40 µm). Because compounds are usually tailored to specific applications, we do not specify any particular combinations of PPS and PTFE. However, experience has shown that at least 35 % PTFE and no more than 50 % PPS must be present in the compound to obtain a good dimensionally stable sintered part.

Precuring

Heating Ryton® PPS above its glass transition temperature in the presence of oxygen causes chain extension and cross-linking reactions commonly referred to as "precuring" the polymer. It is necessary to precure the PPS prior to compression molding or sintering to increase the melt viscosity and melt strength of the polymer, as well as to partially degas the polymer to prevent voids from forming during the compression molding or sintering processes. The degree of precuring can be controlled with time and temperature of the precure cycle. For instance, temperatures close to the melt point of PPS (285 °C, 545 °F) cause a faster curing rate than lower temperatures. Precuring may be done before or after compounding with PTFE and other fillers, but precuring higher bulk density blends of PPS and fillers generally requires significantly less time.

Precuring of Ryton® PPS (either neat or blended with fillers) may be done in open pans at depths of up to 5 cm (2 inches), depending on the bulk density of the blend, in air circulating ovens at 271 °C (520 °F). Heated ribbon blenders can be used for precuring, but care must be taken to ensure the uniform and sufficient oxygen contact necessary to achieve an even cure throughout the material. Precuring generally requires a minimum of about 12–16 hours at 271 °C (520 °F), depending on the bulk density of the material. Ending the precure at this stage would be sufficient for compression molding small, thin walled and flat section parts, and compounds with a high filler content. At least 16–24 hours at 271 °C (520 °F) is generally required to provide a satisfactory melt strength for compression molding large, thick-walled parts or for free sintering. Figure 1 illustrates the variable cure rate that may be observed when precuring Ryton® PR11 powder at 271 °C (520 °F).

Figure 1: Variable cure rate of Ryton® PR11 at 271 °C (520 °F)



If necessary, additional precuring may be achieved more rapidly at temperatures above the melt temperature of PPS. Mixtures which have been precured as described above, may be "melt cured" up to two hours at 343–377 °C (650–710 °F) to further increase the melt viscosity of the polymer and more thoroughly degas the mixture. Melt cured material usually forms a sheet or solid mass, slightly smaller than the curing pan, which requires granulating prior to its use as a compression molding resin. Granulation can be accomplished with a variety of choppers and blenders. For optimum results the particle size should be no larger than 3 mm (1/8 inch) pellets and preferably as small as finely divided powder. Melt cured compounds are not suitable for free sintering operations.

Compression Molding

The precured Ryton® PPS compounds and blends described above may be compression molded in clean steel molds of the positive pressure type at 315–399 °C (600–750 °F) with 14–69 MPa (2,000–10,000 psi) pressure. Part length and diameter should be considered when applying pressure. As a general rule, the longer the part and smaller the cross section, the higher the pressure required. Ryton® PPS injection molding compounds are generally not suitable for compression molding without precuring and milling.

A typical approach to the compression molding of PPS compounds is as follows:

1. Filling and cold pressing

The mold should be thoroughly cleaned and dried, and the inside surface should then be sprayed or otherwise coated with a suitable mold release agent such as high temperature fluorocarbons, silicones, or stearate dusts. The mold may then be filled with the precured molding compound and cold pressed ("preformed") by applying approximately 14–69 MPa (2,000–10,000 psi) pressure, depending on the length and configuration of the part.

2. Heating

Heat the filled mold in an oven or with heater bands to 315–399 °C (600–750 °F) until the contents are thoroughly melted to complete proper fusion. When using "melt cured" mixtures, molding temperatures should be held 11–22 °C (20–40 °F) below the "melt curing" temperature to prevent any additional volatilization. This is especially important in thick sections and rods. Heating times required for compression molding may vary as much as from 1 to 8 hours or more, depending on the mold construction, the part diameter, and the part length. Molds with heavy walls and large diameters will require considerably more heating time than thin-walled, small diameter molds.

3. Cooling

Apply approximately 14–69 MPa (2,000–10,000 psi) pressure to the hot mold for a period of 3–5 minutes, or until the outer portion of the part reaches approximately 204 °C (400 °F). To prevent seizing, tube stock moldings should have the mandrel removed when the temperature reaches 232–260 °C (450–500 °F). To ensure good quality moldings, an insulating jacket or other device should be used to control the rate of cooling from molding temperatures down to 149–204 °C (300–400 °F). The cooling rate should be maintained at approximately 2 °C (4 °F) per minute to avoid formation of cracks and voids. Thermally conductive fillers, such as carbon powder, generally reduce the possibility of cracking and may speed the cooling process. The part may be removed from the mold when the temperature reaches approximately 149 °C (300 °F).

Free Sintering

Precured blends of Ryton® PPS and PTFE, prepared as described above, may be free sintered using techniques very similar to those used to sinter PTFE compounds. Experience has shown that at least 35 % PTFE and no more than 50 % PPS must be present in the compound to obtain a good quality, dimensionally stable, sintered part. "Melt cured" compounds and Ryton® PPS injection molding compounds are not suitable for free sintering.

Since PPS and PTFE have different transition temperatures and thermal expansion rates, sintering cycles are somewhat slower than for comparable PTFE compounds. The goal should be to minimize the temperature gradient across the part during the entire cycle.

A typical approach to free sintering PPS/PTFE compounds is as follows:

1. Filling the mold

Loading molds for preforming PPS/PTFE compounds follows standard practices used for filled PTFE compositions. The compaction ratio of most PPS/PTFE sintering compounds is about 4 to 1. If difficulty is encountered in adding the charge, the powder may be settled by shaking or tapping the mold. It is important to add the full charge of powder to the mold before applying any compressive force. Successively compressing partial charges may leave flaws that are difficult to heal on free sintering. If excess volume in the preforming press is limited, hand pressure may be used to partially compress the powder.

2. Preforming

After filling the mold, the preform is made by applying pressure to the powder. Pressure requirements may vary from 34.5 to 69 MPa (5,000 to 10,000 psi), according to the PPS/PTFE ratio. For preforming parts no larger than 5.1 cm (2 inches) in diameter, 34.5 MPa (5,000 psi) should be adequate pressure for most compounds. At this preform pressure, optimum dimensional stability and density increases of the sintered part are usually achieved. Pressures below 34.5 MPa (5,000 psi) usually result in sintered parts with low density. Preforms should be inspected for porosity or cracks before sintering. A properly pressed preform should have a smooth, close-textured surface and should be strong enough to remove from the mold and move to the oven. Material may be reclaimed from improperly pressed preforms by grinding the preforms and reusing the powder.

3. Sintering

Preforms of PPS/PTFE compounds are usually sintered in circulating air ovens at 360–371 °C (680–700 °F). To obtain reproducible results, the time and temperature of the sintering cycle must be carefully controlled, because those factors affect the degree of fusion, and thus the final dimensions and physical properties of the part. To avoid cracking, especially in larger parts, it is important to maintain a slow heating rate. Initial oven temperature should be no more than 93 °C (200 °F), and should be increased to the sintering temperature at about 33 °C (60 °F) per hour. Preforms of less than 19 mm (0.75 inches) thickness do not require this controlled heating and may be placed directly in a 371 °C (700 °F) oven for sintering. The sintering temperature is usually maintained for one hour per inch of part thickness.

4. Cooling

The rate of cooling should also be carefully controlled, especially for thicker parts, to control dimensions and prevent formation of cracks in the sintered part. A 5.1 cm (2 inch) diameter part should be cooled at a rate of about 33 °C (60 °F) per hour until the temperature is below 177 °C (350 °F), at which point no further control of the cooling rate is necessary. Small or thin parts may be cooled at faster rates. Parts may be cooled under pressure or in fixtures to maintain flatness in sheet moldings (the method known as "coining" in PTFE sintering) or to control a desired dimension. The use of thermally conductive fillers such as MoS_2, graphite, or carbon powders generally allows a faster rate of cooling once the temperature is below 177 °C (350 °F).

Dimensional changes should be primarily transverse to the direction of compression. For example, a 5.1 cm (2 inches) diameter part of 40 % PTFE, 30 % PPS, and 20 % fiberglass preformed at 34.5 MPa (5,000 psi), showed a 6 % decrease in diameter, a 4 % decrease in length, and had a density of 1.42 g/cm^3. Taller and larger parts with diameters greater than 50.8 mm (2 inches) are more susceptible to fracturing and may require lower preform pressures than described above. If growth occurs in the sintered part, excessive pressure was used to compress the preform.

The properties of compression molded Ryton® PPS compounds may vary greatly depending on the combination of fillers used. Unlike injection molded parts, the mechanical properties of compression molded parts are generally more isotropic due to a more random filler distribution and fiber alignment. Table 1 shows the variety of mechanical properties that might be expected when using several different filler systems. Results may still vary, however, due to differences in part geometry, precuring methods, and molding conditions. Furthermore, surface defects from machining operations may act as crack propagators and compromise the mechanical strength of a part.

PPS/PTFE sintered parts exhibit some very unique properties compared to filled PTFE compounds. At high strains, PPS/PTFE mixtures exhibited a compressive modulus two to three times as great as bronze filled PTFE. It was also reported that this high compressive modulus provides for 30 times lower wear rate of the PPS/PTFE surface and mating surface when compared with glass filled PTFE. (See Lubrication Engineering – Volume 33, 1, pp. 33–38.) Shore D hardness for PPS/PTFE compounds is usually 85 or higher compared to 60–75 for PTFE compounds. Other physical properties vary according to the ratio of PPS to PTFE and other fillers.

Properties

Table 1: Typical properties of Ryton® PPS composites

Property	Unit	Unfilled	40 % Milled Glass	40 % Glass Fiber	33 % Glass Fiber 33 % Mineral	20 % Milled Glass 40 % PTFE (free sintered)
Tensile strength	MPa	62.05	55.16	103.42	68.95	9.65
	psi	9,000	8,000	15,000	10,000	1,400
Elongation	%	1.5	1.0	1.0	0.5	
Flexural strength	MPa	89.63	89.63	124.11	124.11	
	psi	13,000	13,000	18,000	18,000	
Flexural modulus	MPa	3,447.4	6,894.8	10,342.2	17,237	1,034.22
	psi	500,000	1,000,000	1,500,000	2,500,000	150,000
Notched Izod	J/m	16	16	53	43	
	ft·lb/in	0.3	0.3	1.0	0.8	
Unnotched Izod	J/m	96	53	80	80	
	ft·lb/in	1.8	1.0	1.5	1.5	
Compressive strength	MPa	110.32	117.21	144.79	158.58	
	psi	16,000	17,000	21,000	23,000	
Rockwell hardness		R120	R120	R120	R120	
Shore D hardness		85	90	90	90	85
Heat deflection temperature	°C	135	121.1	260	260	
at 1.82 MPa (264 psi)	°F	275	250	> 500	> 500	
Coefficient of linear thermal expansion						
x10^{-6} in/in/°C –15.6 to 51.7 °C		54	36	36	27	
x10^{-6} in/in/°F, –60 to 125 °F		30	20	20	15	
x10^{-6} in/in/°C, 51.7 to 204.4 °C		126	54	54	45	
x10^{-6} in/in/°F, 125 to 400 °F		70	30	30	25	
Thermal conductivity	W/m/K	0.3	0.3	0.3	0.6	
	BTU·in/hr·ft^2·°F	2.0	2.0	2.0	4.2	
UL 94 Flammability rating		V-0	V-0	V-0	V-0	V-0
Density	g/cc	1.35	1.65	1.65	1.9–2.0	1.70

Applications

Ryton® PPS compounds provide the end user an attractive combination of high use temperature and outstanding chemical resistance. There are many successful applications using compression molded PPS parts, such as pump impellers, pump packing, housings, bushings, gas and air compressor pistons, piston rings, seals and balls for ball valves, to mention a few.

Where sintered PTFE compounds are now used, sintered PPS/PTFE compounds can give improved performance. PPS improves the physical properties of PTFE without appreciably reducing the chemical resistance or thermal stability of PTFE. Sintered PPS/PTFE composites also offer better dimensional stability under load than PTFE compounds. Physical properties and bearing tests indicate the utility of these materials where low maintenance and long life are important. Bearings, piston rings, gaskets, valve seats, seals, and packing are just a few of the applications in which PPS/PTFE composites can be utilized.

Where an application calls for performance at high temperatures and/or in chemically corrosive environments, Ryton® PPS has the capability to meet the most demanding requirements.

www.solvay.com

SpecialtyPolymers.EMEA@solvay.com | Europe, Middle East and Africa
SpecialtyPolymers.Americas@solvay.com | Americas
SpecialtyPolymers.Asia@solvay.com | Asia Pacific

SOLVAY
asking more from chemistry®