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SHELL CHEMICAL CO.

PLASTICS TECHNOLOGY'S HOW-TO GUIDE

Injection Mold The New Polyketones

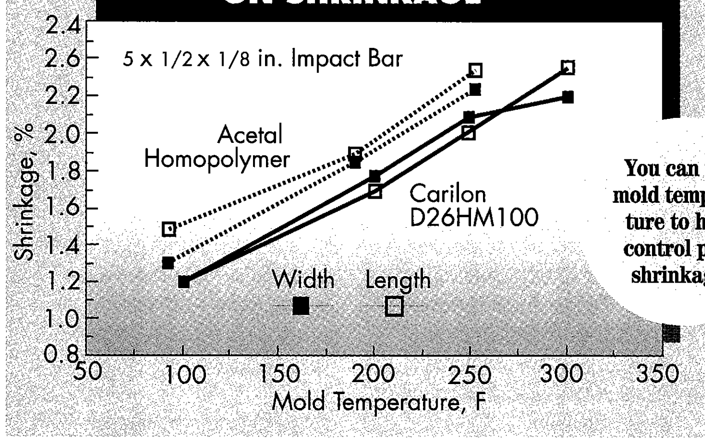
Just now available, these challengers to nylons, acetals, and polyesters set up fast and are not moisture sensitive.

The world's first aliphatic polyketones became available in commercial quantities on October 30, 1996. Carilon Thermoplastic Polymers from Shell Chemical Co. are semi-crystalline terpolymers of ethylene, carbon monoxide (CO), and small amounts of propylene. The perfectly alternating structure of CO and olefin results in a material with a unique set of properties that is easy to process in most conventional injection molding equipment.

These engineering resins offer a combination of strength, stiffness, chemical and impact resistance, and good wear and friction characteristics. Also, polyketone resins retain their performance properties over a wide temperature range. Carilon Polymers should be particularly attractive for automotive, electrical, and industrial applications, as well as business machines and consumer appliances.

Shell offers a range of CARILON Polymers, including unfilled, glass reinforced, flame retardant and lubricated tribological grades. Properties of three typical injection molding grades, D26HM100 (medium-flow, unreinforced), D26VM100 (high-flow, unreinforced) and DB6G6A10 (30% glass reinforced), appear in Table 1.

FIG. 1–EFFECT OF MOLD TEMP. ON SHRINKAGE



You can use mold temperature to help control part shrinkage.

MOLDING BASICS

Carilon Polymers generally have a wide processing window. The most important processing characteristic that molders need to be aware of is the fast set-up time. This often can result in cycle-time reductions of 15% to 40% compared with acetal or nylon 66, assuming use of properly sized sprues, runners and gates.

These polyketones are also hydrolytically stable. Thus, the presence of a small amount of water has little effect on processing or physical properties. All the same, you should take precautions to keep the polymer dry (no more than 0.2% water). Excess moisture can cause bubbles in the melt, resulting in drool, voids in parts, or surface problems such as splay.

Other thermoplastics may evolve hazardous by-products during processing upsets. But the primary by-product of Carilon Polymers, if processing degradation occurs, is water.

Table 2 outlines suggested starting-point settings for reciprocating-screw injection machines. The accompanying chart of processing tips should help you mold Carilon Polymers with minimal start-up time.

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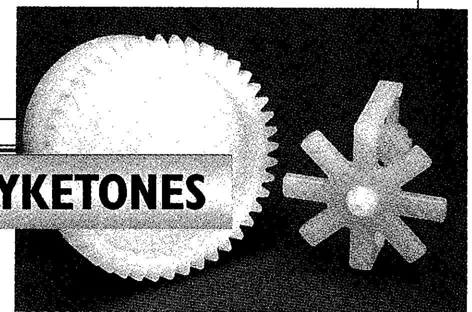
If you have any questions or encounter problems when using Carilon Polymers, technical assistance is available by phone at 1-888-Carilon (1-888-227-4566) or at Shell Chemical's World Wide Web site at www.shellchemical.com.



INJECTION MOLDING CARILON POLYKETONES

DRYING: Maximum recommended moisture content: 0.2% (measured at 285 F for approximately three minutes.) Dry 4 hr at 140 F. Resin is supplied predried. Although not moisture sensitive, Carilon Polymers should be kept dry to prevent splay, drool or voids.

Screw design: Use standard metering screws with L/D ratios from 18:1 to 22:1 and compression ratios between 2:1 and 3:1. Free-flowing check rings minimize possibility of resin overheating.

Nozzles: Use conventional or reverse-taper nozzles with polished bores and streamlined flow. Positive shut-off is not usually required. Heated nozzles are recommended to prevent freeze-off problems due to polyketone's rapid crystallization.

Melt and barrel temperatures: Balance shot size with barrel capacity to give residence times of 2-10 min. Suggested melt-temperature range is 460-490 F (see Table 2). Do not exceed 575 F. Long residence times at high end of the temperature range can cause thermal degradation and loss of physical properties. In extreme cases, crosslinking and large increases in melt viscosity can result.

Start with a flat barrel temperature profile (Table 2). Feed zone should be slightly cooler to aid removal of volatiles. A reverse profile is usually better with screw L/D's above 20:1.

Backpressure: In most cases, machine hydraulic pressure of 50 psi will achieve uniform melt temperature and consistent shot size. (This assumes a force multiplier of 10 between hydraulic and melt pressure.) When using color concentrate, 100-psi backpressure may be necessary for proper mixing. Avoid backpressures above 100 psi since they can lead to hot spots along the screw.

Screw speed: Use slow to moderate speeds as shown in Table 2.

Injection speed: Start with medium speed. Keep in mind polyketone's rapid set-up times. Increase injection rate before increasing melt temperature if lower viscosity is desired to aid part filling. See Table 2 for recommended injection pressures. Figure 2 shows shear-thinning behavior of polyketones.

Holding/packing time, pressure: Polyketone's fast set-up allows short holding times. Start with packing pressure at 50-75% of maximum injection pressure. A minimum cushion (0.25-0.50 in.) is usually sufficient

Clamp force: Use low to moderate pressure of 3-6 tons/sq in.

Mold temperature: Start at 175 F (Table 2). Parts have been molded successfully from 85 to 300 F. Rapid crystallization at elevated temperatures allows use of hot molds to improve filling, weld lines and surface finish with little effect on cycle times. As shown in Fig. 1, mold temperature can be used to help control part shrinkage.

Cycle time: Typically 10-15 sec for thin-wall moldings (0.025 to 0.060 in.), 30 sec or less for thicker sections up to 0.125 in.

Mold release: Sticking is rare in well-designed tools. If specific part geometry causes problems, light application of standard release agents may be used.

Regrind: Limit regrind content to a maximum of 25-30%. Lab tests show that Carilon Polymers can be reground several times and exhibit little loss in properties at suggested processing conditions (Table 3). However, regrind tends to pick up moisture and irregular particles can impair good flow in the hopper.

PURGING: Use a low-melt-flow HDPE (0.7-2.0) to purge Carilon Polymers before molding other resins or vice versa.

Downtime procedures: When interruptions occur in the molding cycle, do one of the following:

1. For periods up to 30 min, retract the nozzle. At start-up take a sufficient number of air shots to clear the barrel before resuming.
2. For interruptions between 30 min and 2 hr, decrease barrel temperatures by 120-212° F, take two or three air shots, leaving the screw in the forward position. At start-up, raise temperatures to proper settings and take several air shots prior to molding.
3. For interruptions greater than 2 hr, purge the barrel with HDPE as recommended above.

DESIGN MOLDS FOR FAST FILL

When you are designing gates, runners and vents, it is important for you to keep in mind that medium to high injection speeds and pressures will be required because of the rapid set-up of Carilon Polymers. Also remember that the melt-flow index for unfilled polyketone (grade D26HM100) is slightly lower than that of many acetals and is significantly lower than that of nylon 66.

Both factors point to using runner and gate systems with minimal flow restrictions in order to minimize pressure drop between the nozzle and cavities. To take full advantage of polyketones' potential to reduce cycle

TABLE 1—PROPERTIES OF DEVELOPMENTAL CARILON POLYMER GRADES

	D26HM100 Unfilled	D26VM100 Unfilled	DB6G6M10 30% glass
PHYSICAL PROPERTIES @ 73 F			
Specific Gravity	1.24	1.24	1.46
Mold Shrinkage, in./in. (flow direction, 1/8 in.)	0.018-0.022	0.018-0.022	0.001-0.003
Water Absorption @ 73 F, %			
(24-hr immersion)	0.45	0.45	0.42
(100% RH saturation)	2.1	2.2	1.8
MECHANICAL PROPERTIES @ 73 F, 50% RH			
Tensile Strength @ yield, psi	8700-9200	8700-9200	19,500
Elongation @ yield, %	22-28	22-28	–
@ break, %	300	300	3.5
Tensile Modulus, psi	230,000	230,000	1,200,000
Flexural Modulus, psi	230,000	220,000	1,050,000
Notched Izod Impact, ft-lb/in.	4.5	1.7-2.0	2.5
Gardner Impact Str., in.-lb	>400	395	–
THERMAL PROPERTIES			
Melting Point, F	428	428	–
Melt Flow Rate, g/10 min[a]	4-8	~60	9-15
Vicat Softening Point, F	410	398	419
HDT, F @ 66 psi	410	398	425
@ 264 psi	221	221	425

[a]Measured at 464 F, 2.16 kg.

TABLE 2—TYPICAL INJECTION MOLDING CONDITIONS

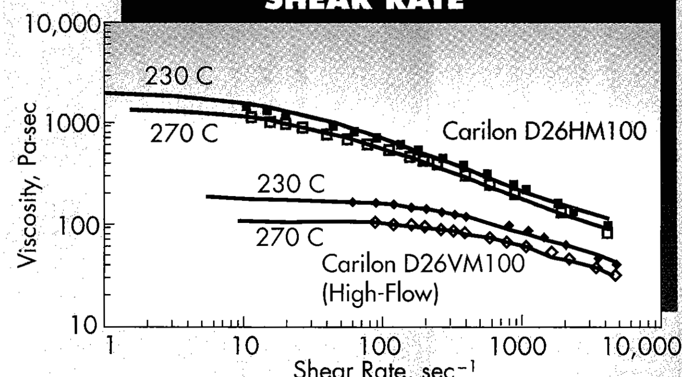
	D26HM100 (medium-flow)	D26VM100 (high-flow)
TEMPERATURE, F		
Barrel		
Rear	460	450
Middle	470	460
Front	470	460
Nozzle	470-480	460-470
Melt	470-490	460-480
Mold	175	175
Hot Runners	490-520	480-510
PRESSURE[a], psig		
Injection	700-1300	400-800
Hold/Pack	500-900	300-600
Backpressure	50	25
SCREW SPEED, rpm	50-100	40-75
TIME, sec (for 25-g to 180-g parts)		
Injection	1-3 (Medium Rate)	1-4 (Slow to Medium)
Hold	2.5-6	2-5
Cool/Clamp	6-10	4-8

[a]Approximate machine hydraulic pressure, assuming a force multiplier of 10.0.

times, pay careful attention to mold-temperature control. Ensure the proper location, sizing, and spacing of hot-water or oil channels. Separate temperature control of each mold half is best.

Figure 1 shows how mold temperature can be used to fine-tune mold shrinkage. The graph also shows the close similarity between flow-direction and transverse-direction shrinkage of Carilon in a flat, narrow test bar. Note also the similarity of shrinkage for acetal and polyketone, indicating that both can be molded in the same tools.

FIG. 2-MELT VISCOSITY VS. SHEAR RATE



Shear-thinning behavior of polyketones is not as pronounced as that of polyolefins.

An advantage of unreinforced Carilon Polymers is that very little dimensional change occurs due to shrinkage after parts cool down, unlike some other semi-crystalline plastics such as acetals. Another advantage is that no large dimensional changes occur after molding as a result of water absorption, unlike nylon 66.

For example, when parts are conditioned in air at 73 F and 50% relative humidity, the dimensional growth resulting from water absorption will stabilize at the equilibrium moisture content. For plaques of nylon 66, dimensional growth stabilizes at approximately 0.7%. For acetal plaques, that growth stabilizes at about 0.2%, and for unreinforced Carilon Polymers, the growth stabilizes at around 0.1%.

TIPS ON MOLD DESIGN

Materials: Use standard tool steels such as P-20, H-13, and S-7. Polyketones do not emit corrosive compounds during normal processing.

Gating: All common gate types—edge, fan, flash, submarine, and pinpoint/hot-tip—are suitable. Make them as large as possible—25-50% larger than for acetals and 40-75% larger than for nylon 66. Keep land length to a minimum due to polyketone's rapid set-up.

Runners, sprue bushings: Full-round runners minimize melt chilling during passage through the runner, though trapezoidal and half-round runners also can be used. Keep as short as possible, with a minimum diam. of 1/4 in. Minimize secondary runner lengths, too, and use 3/16-in. minimum diam.

Use standard sprue bushings with 2-4° draft angles. Cold wells and sprue pins used with other engineering thermoplastics also work with Carilon Polymers.

Hot runners: Externally heated manifolds and nozzles reduce the chance of material degradation due to flow stagnation. Both manifolds and nozzles should have streamlined flow channels. Nozzle tips can be used to keep the gate area from freezing. Tips should not use resistive heating but rely upon heat conduction from the nozzle to the gate. Nozzle-tip geometry should not allow flow stagnation or blockage.

Vents: Vent generously to accommodate rapid fill rates. Use vent depths of 0.0003-0.0005 in. at final fill points and areas where air traps are likely.

Shrinkage: Transverse shrinkage of unreinforced grades is usually within 10-15% of shrinkage in flow direction (see Table 1). Mold temperature can help fine-tune part dimensions (Fig. 1). Tools designed for acetal are often suitable for polyketone.

TABLE 3—REGRIND STABILITY OF CARILON POLYMERS

	Notched Izod Impact Strength, ft-lb/in.		Tensile Strength, psi		Elongation, %	
			(at yield)	(at break)	(at yield)	(at break)
	D26HM100	DB6G6A10	D26HM100	DB6G6A10	D26HM100	DB6G6A10
VIRGIN	4.0	2.4	9000	18,700	25	4
1st Regrind Pass	4.0	2.5	9000	17,000	20	4
3rd Regrind Pass	3.9	2.4	8900	15,500	20	4
5th Regrind Pass	3.8	2.3	8800	12,600	20	5

For most polyketone parts, dimensional changes due to water absorption will not be a problem. However, for parts requiring extreme accuracy in dimensions after molding—such as high-precision gears—adjustment for water absorption can be made by changing molding conditions such as mold temperature (see Fig. 1) without affecting part performance. □□

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