Low-temperature cure LSR technology enables processing improvements

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Liquid silicone rubber has emerged as a preferred elastomeric material due to a combination of ease of processing and physical properties. Traditional processing conditions utilize liquid injection molding at high temperature, typically 160-220°C, to produce complex articles while allowing short cycle time and parts consistency.

Executive summary

A new breakthrough technology, low temperature cure (LTC) liquid silicone rubber, has been developed to enable improved process efficiency and greater design freedom. With ever-increasing industry focus on innovation and quality, and with heightened consumer awareness of sustainability, LSRs have emerged as the performance material of choice for automotive components and consumer goods. LTC LSRs greatly expand on the properties of silicone rubber. While traditional LSRs typically require temperatures between 160 and 220°C, LTC LSR can cure quickly at conditions as low as 100°C.

At lower temperatures, the ability to vulcanize LTC LSR in the 100-120°C range provides design flexibility and maximum process efficiency to the LSR portfolio. At standard cure temperatures, the LTC technology translates to lower sensitivity to temperature gradients during cure, which allows for fast deep-section cure of thick-walled articles.

Another benefit is the option to add a cure accelerator to the LTC LSR, which can further reduce the processing temperature to 80°C. This new innovation greatly enhances cycle time reduction and speeds up deep-section cure, all while maintaining physical properties. This technology also enables co-molding of LSR with low-melting plastics or other temperature-sensitive components, opening new markets for 2K silicone molding.

Overall, LTC LSR is a step-change in silicone rubber. The freedom to reduce curing temperatures, create thicker parts, co-mold with a broader range of substrates or simply reduce cycle times results in new levels of efficiency and quality.

TECHNICAL NOTEBOOK

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The introduction of a novel low temperature cure (LTC) technology can greatly expand the benefits of LSR products. This new class of LSRs allows for fast curing speeds at temperatures as low as 100°C, enabling both optimized processing as well as new innovative process and product designs.

The benefits of LTC technology have been demonstrated in consumer, electronic and automotive applications. At higher temperatures, LTC technology affords improved cycle times and fast deep-section cure. At lower temperatures, the ability to vulcanize LTC LSR in the 100-120°C range provides design flexibility and maximum process efficiency to the LSR portfolio.

Injection molding process studies and mold flow simulations both highlight the broad processing range of this new class of materials. Furthermore, this technology also enables co-molding of LSR with low-melting plastics, opening new markets for 2K silicone molding. Another benefit is the option to add a cure accelerator to the LTC LSR, which can further reduce the processing temperature to 80°C, greatly enhance cycle time reduction and speed up deep-section cure, all while maintaining physical properties

Fig. 1: Addition-curing reaction of LSR (platinum-catalyzed hydrosilylation reaction).

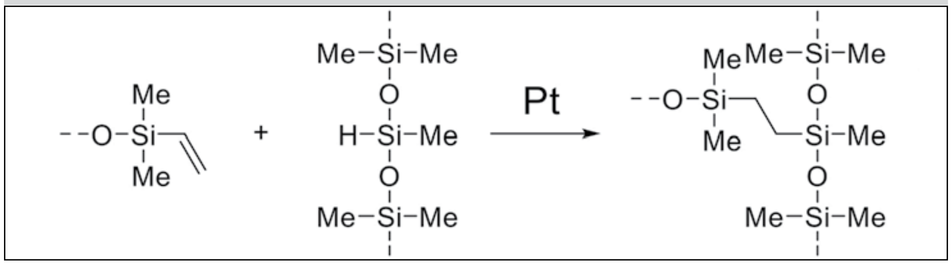


Fig. 2: DSC cure curve for a standard LSR. Heating rate 10°C/min. The temperature activation profile is characterized by its onset temperature (T_{onset}) and peak temperature (T_{peak}).

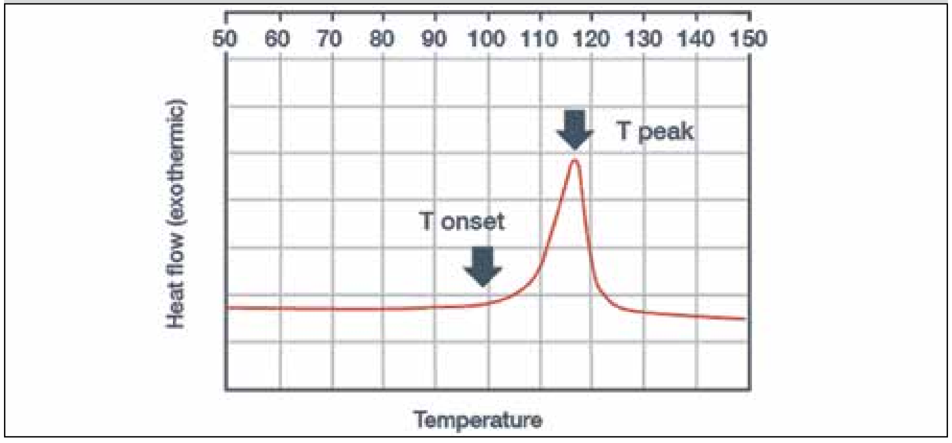
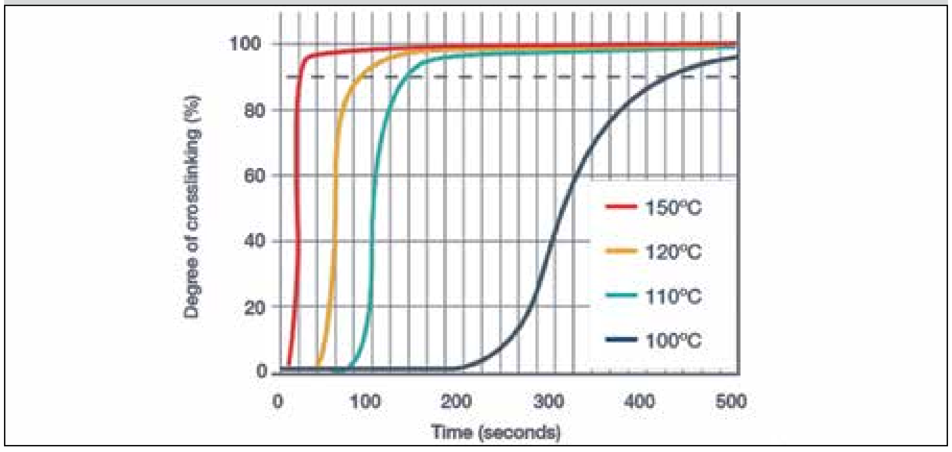


Fig. 3: Isothermal cure curves of a standard LSR as tested by MDR. The dotted line denotes a degree of crosslinking of 90 percent, taken as an estimate to derive cure times.



Maximizing cure rates

Silicone elastomers are polydimethylsiloxane (PDMS) rubbers, ubiquitous in both consumer and specialty markets, characterized by their chemical resistance, weatherability, resistance to thermal and photo degradation, low surface energy and low glass transition temperatures, which allows for fewer changes in physical properties over a wide temperature range.[1,2]

In particular, liquid silicone rubber is known for its fast cure rate, lower production cost and excellent performance, which result from hydrosilylation, a platinum-catalyzed addition reaction.[3,4] To maximize the cure rates, LSR is typically cured at high temperatures ranging from 160°C to 220 °C to enable curing times in the order of seconds.

Hydrosilylation is a robust vulcanization chemistry. In LSRs, hydride-functional PDMS polymers readily combine with vinyl-functional PDMS in the presence of platinum (**Fig. 1**).[5]

Due to its inherent high reactivity, an inhibitor is usually added to suppress the cure at room temperature and allows for a workable time or pot life. A pot life of 72 hours or greater is critical to allow for a stable injection molding process and avoid undesired curing in the injection unit. To reverse this inhibition and resume the cure process, LSR needs to be cured at high temperatures above its activation temperature, generally around 100°C (**Fig. 2**).

Processing LSR materials at higher temperatures well above this activation threshold gives fast cure rates, with heating times in the range of seconds (**Fig. 3**). Conversely, lowering the cure temperature toward the activation temperature significantly slows the cure rates. This slow cure significantly impacts productivity at the lower temperature range, and thus limits co-molding applications and new material combinations of LSRs.

A recent trend in evolution of LSR applications is to create LSR composite articles.[6]

In co-molding applications, LSR can provide reliable sealing, moisture protection, soft elastomeric elements or encapsulation of sensitive components. Examples include overmolding of electrical devices used in consumer electronics, automotive electrification and automation, or the en-

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The authors

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Wang

Wang grew up in and earned his bachelor's in chemistry from Washington University in St. Louis in 2011, and his doctorate in organic chemistry from Northwestern University in 2016.

Craig Gross joined Dow Corning in 1996 and became part of Dow through the acquisition in 2016. During his career, he has held various roles in process engineering, manufacturing, development, and TS&D within North America. His expertise includes formulation and application of LSR, HCR and FSR materials, and he has knowledge in a wide range of materials and fabrication processes used in both the plastics and rubber industries.

Gross

In his current position, Gross leads a variety of initiatives focused on delivering silicone elastomer solutions to customers. He graduated from Ferris State University with a bachelor's in plastics engineering and has four patents.

Patrick Beyer studied chemistry at the University of Mainz, Germany, where he obtained his doctorate in 2007 in polymer chemistry with a thesis on "Liquid Crystalline Elastomers." In 2007 he joined Dow Silicones Deutschland GmbH in Germany, where he is working as a research scientist in the field of liquid silicone rubber.

Beyer

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capsulation of functional additives in consumer and hygiene applications.

In these cases, conventional high-cure temperatures would lead to thermal decomposition of the encapsulated component. In overmolding applications, LSR is combined with thermoplastic substrates to produce hard-soft composites. Here the cure temperature is limited by the softening temperature of the thermoplastic. The use of conventional, high-temperature curing LSR technology would lead to deformation of the plastic during molding, or to unacceptably long curing times and inefficient processes when cured at reduced temperatures.

The activation temperature of LSR cure is a function of many factors, including amount and type of platinum catalyst and inhibitor. Kinetic studies allowed us to derive key structure-property relations and enabled development of the new low temperature cure LSR series. In this new generation of LSR materials, the temperature activation threshold is shifted to below 100°C, with an onset temperature of 85°C. A new class of LTC LSR is presented for use in a wide range of process temperatures.

Experimental

The standard LSR used as a point of comparison was Silastic-brand RBL-9200-50 liquid silicone rubber from Dow, as the LTC LSR was Silastic LTC 9400-50 liquid silicone rubber and Silastic LTC 9400 acceleration additive.

The LSRs come in two parts and were mixed in a 1:1 ratio using DAC 150 FVZ SpeedMixer. The LSR was mixed three times at 2,000 rpm for 20 seconds, with manual hand mixing in between machine mixing steps.

Cure curves and cure times were measured using an Alpha Technologies MDR 2000 moving die rheometer. Temperatures were set at various ranges and cure curves were recorded for 1° arc for 10 minutes. Samples were prepared with 4-7 grams of mixed LSR material. Activation temperature profile was measured by differential scanning calorimetry (DSC) on Mettler-Toledo DSC 1 equipped with HSS8 sensor using a 10°C/min heat rate.

Injection molding trials used Engel eMac 100 equipped with CC300 digital control unit interface. The shutoff nozzle valve was supplied by Fluid Automation with Nexus Servomix pail pump. Injection screw was 30 mm in diameter and molds were made of stainless steel with surface polish.

LSR was injected between 5-160 cm^3/s into molds at 120-160°C with 1,000 kN clamping force. The mold was 180 mm by 132 mm by 2 mm, and the shot weight was 44.2 grams.

For modeling, heat distribution was simulated using octave software, and mold flow analysis was completed by Sigma Engineering.

Results

Standard LSR materials generally cure at elevated temperatures, about 160°C and above. Once the curing temperature was lowered to 100°C, the Tc90 (time to reach a degree of 90 percent of maximum cure) was greatly lengthened to 420 seconds (**Fig. 4**). Even at 120°C, the LSR showed 90 seconds Tc90, compared to 20 seconds at 150°C, which is much closer to typical curing conditions.

LTC LSR demonstrates increased cure rates at low temperatures. Initial DSC results demonstrated that LTC had a significantly lower onset temperature of T_{onset} = 85°C This shift in (**Fig. 5**) activation temperature significantly increases the reactivity in the targeted low temperature range 100-120°C as measured by Tc90 (**Fig. 6**). For example, at 100°C LTC LSR demonstrated a reduction of the cure time from 418 seconds to 245 seconds, a greater than 40 percent reduction of cure time.

Next, injection molding tests were done to validate the previous results. For evaluation, rectangular test sheets of 2 mm thickness and a shot weight of 44 grams were created. Molding tests were done in direct comparison to a standard LSR. The minimum heating time to obtain fully cured parts was recorded as a function of mold temperature (**Fig. 7**).

In good agreement with laboratory studies, the heating time at low temperatures is significantly reduced for the LTC LSR. As predicted, the relative benefits (shorter cure time) tend to decrease at higher temperature, away from the activation temperature range. This was a result of carefully balancing

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Fig. 4: Cure time (90 percent cure) of a standard LSR at varying temperatures, derived from cure curves of Fig. 3.

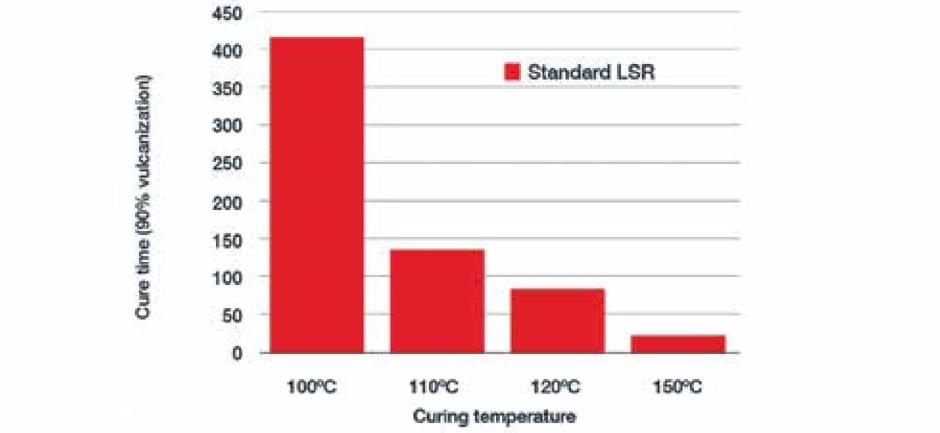


Fig. 5: DSC cure curve for a standard LSR (right curve, red), and Silastic LTC 9400-50 LSR (left curve, blue). Heating rate 10°C/min. T_{onset} is shifted from $T_{onset, strd}$=101°C to $T_{onset, LTC}$=85°C (see arrows).

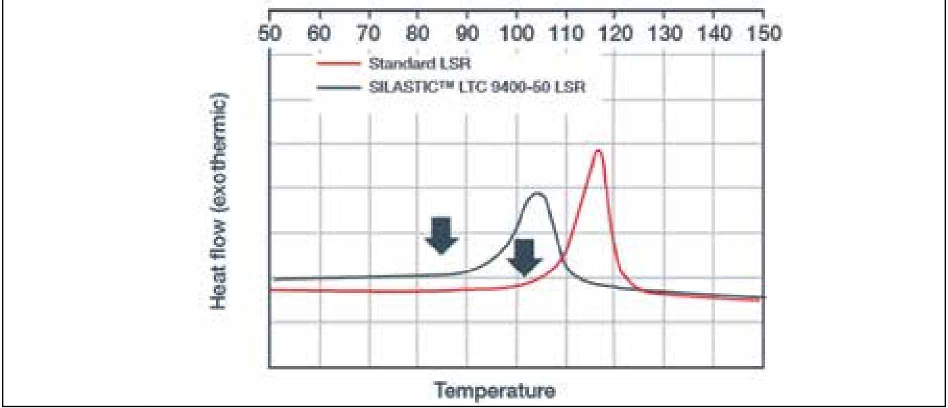


Fig. 6: Comparison of cure times (90 percent vulcanization) between Silastic LTC 9400-50 and a standard LSR.

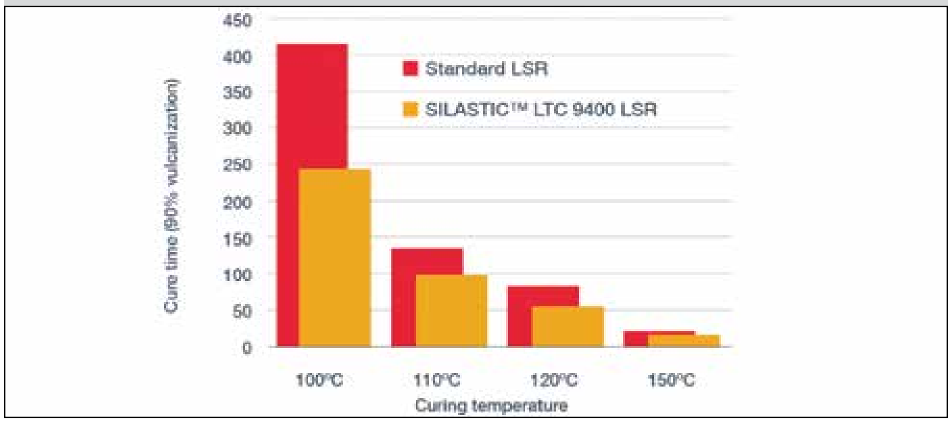


Fig. 7: Injection molding validation. Heating times as a function of temperature for conventional and low temperature cure (LTC) technology.

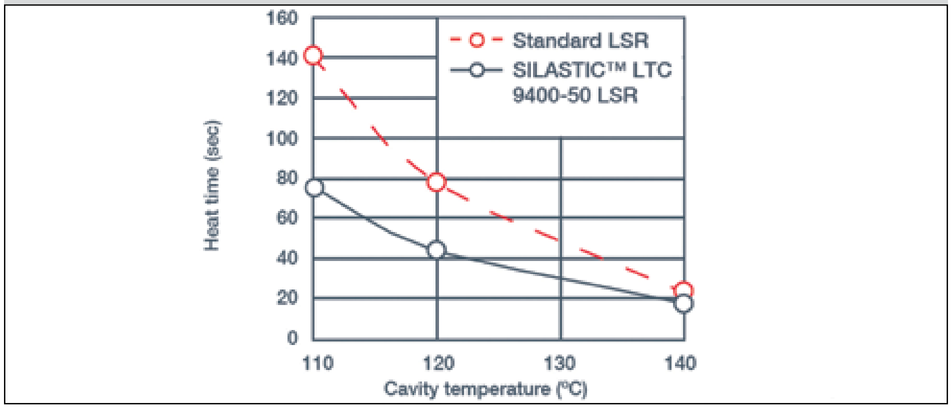


Fig. 8: Schematic representation of the computational heat flow simulation. A sphere of diameter r with initial temperature T_0=25°C is exposed to an outside temperature T_{mold}. The temperature distribution in the sphere is then modeled as function of time t and cross-section r.

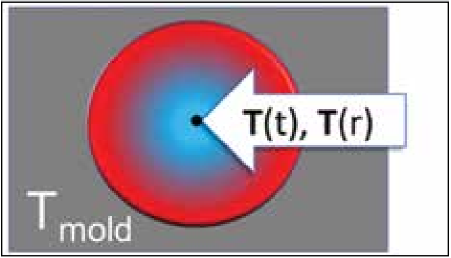


Fig. 9: Simulation of heat transfer in an LSR sphere of varying radii r=1-3mm. At t=0 a temperature of T_{mold}= 175°C is applied to the outside of the sphere. Graphs show the temperature at the center point (core temperature) as function of time.

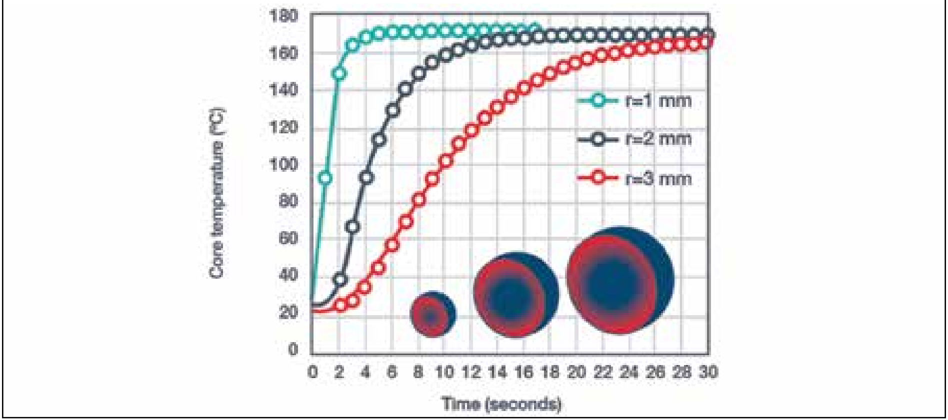
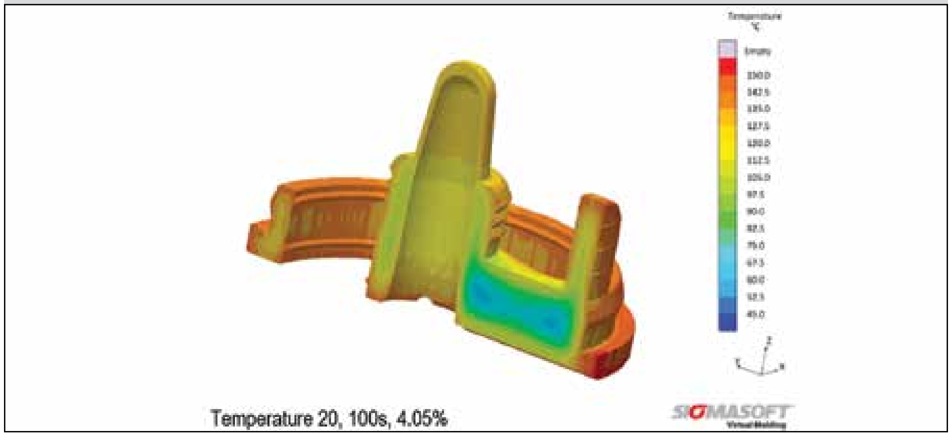


Fig. 10: Temperature distribution in a bottle ventilation valve 20 seconds after injection. Simulation done by Sigma Engineering.



LSR

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reactivity to maintain an activation threshold well above room temperature, leading to enough room temperature stability.

The reduced sensitivity of LTC technology to temperature distributions and thermal gradients, which are unavoidable in practical injection molding, demonstrate an opportunity for significant productivity gains of thick-walled parts. To initiate cure, thermal energy heat needs to be transported into the bulk of the molded part. Silicones typically show low thermal conductivities λ in the range of ~0.22 W/mK.[7] Thermal conductivity is thus a key property of the vulcanization process.

A computational simulation was performed to understand this important factor. LSR spheres of varying diameters were modeled with an initial temperature of $T_0 = 25°C$. At time t_0, a constant external temperature was applied to simulate reflecting the mold temperature, $T_{mold}=175°C$ (**Fig. 8**).

The temperature profile T(r,t) was then modeled as a function of cross-section, r, and time, t. To understand the behavior of the bulk, the temperature at the core of the sphere was plotted as a function of time for different spheres of 1-3 mm radii (**Fig. 9**).

At 1 mm radius, a uniform heat distribution was obtained after five seconds. Doubling the sphere dimensions to 2 mm showed a significantly longer time of 15 seconds to reach a temperature equilibrium. Finally, at 3 mm, the sphere requires more than 30 seconds to come to uniform temperature.

As these simulations have shown, large temperature gradients during molding are unavoidable, especially when producing thick-walled articles, and thus heat transfer is the limiting factor for the overall curing time. Considering the temperature dependence of LSR vulcanization, a temperature gradient directly translates into a reactivity gradient within the molded part: while the outer areas will be cured instantaneously, the curing time of the bulk is limited by the thermal conductivity of silicone, resulting in slow heat transfer. The slow bulk vulcanization is thus the primary limiting factor for fast curing of thick-walled parts, even at high molding temperatures.

LTC LSR technology uses PDMS as its primary polymer and likewise also shows the inherent low thermal conductivity. While a similar temperature gradient exists upon heating, the lower T_{onset} of LTC LSR allows for earlier thermal activation in these cold areas, and consequently a faster bulk vulcanization. This reduced sensitivity to variations in temperature also can minimize effects of temperature gradients in the tool and contribute to more uniform cure and improved part quality.

This hypothesis also was tested by modeling. The temperature distribution in a bottle ventilation valve made of LTC LSR was investigated using Sigmasoft virtual molding in a molding simulation (**Fig. 10**). In agreement with previous results, large temperature gradients were found specifically in the thick-walled sections, which were up to 8 mm in diameter. In these areas, the bulk temperature did not exceed 100°C, even 20 seconds after mold filling.

As expected, fast bulk activation and short cycle times could be demonstrated on that part using LTC LSR. Other examples of thick-walled articles include electrical connectors in automotive applications, where larger part dimensions are necessary for increasingly higher voltages in electric vehicles. For these applications, an oil-bleeding low compression set LSR based on LTC technology has been added to the product portfolio.

To further enhance reactivity at low temperatures, a complementary material, Silastic LTC acceleration additive, was developed. The additive has low viscosity and can be added at one-to-three-weight percent during a process through the third-stream injector (**Fig. 11**). Dosing of the acceleration additive leads to a further reduction of the cure activation temperature (**Fig. 12**). DSC analysis showed that after the addition of 1 percent acceleration additive, cure onset can be further reduced from T_{onset} 85°C to 70°C.

The impact of the acceleration additive was then evaluated on the cure time of LTC LSR. The additive had a significant effect on heating times as a function of temperature and dosing levels (**Fig. 13** and **Table 1**). At 100°C, the curing times of LTC LSR can be further reduced from 245 seconds down to 66 seconds at 3 percent additive loading, a reduction of cure time of 73 percent.

For reference, a standard LSR will need greater than 400 seconds to cure at this temperature. Furthermore, this enhanced reactivity after additive addition expands the temperature range down to 90°C. At this extreme temperature, a standard LSR would need more than 20 minutes to cure, whereas Silastic LTC 9400-50 LSR was cured in 127 seconds using 3 percent additive.

Addition of accelerant also impacts the pot life. While the LTC LSR technology is designed to provide a pot life of >72 hours, use of the cure acceleration additive incrementally reduces it (**Table 1**). Consequently, the acceleration additive is to be applied temporarily during the molding process to maximize reactivity in running molding operations.

At the end of molding, the addition is terminated to restore the original 72-hour pot life. The enhanced reactivity can help to minimize sensitivity to temperature gradients, both at low and conventional high molding temperatures. It should be considered as an optional component when complex part designs, thick-walled parts or new thermosensitive material combinations are needed to further push the boundaries of reactivity.

For LSR plastic-composite materials, molding conditions are particularly important to avoid deformation, haze and thermal stress on the plastic substrates. LSRs have been successfully co-molded and overmolded with engineering plastics, due to their high heat-deflection temperature (HDT). However, other thermoplastics, including polycarbonate and polypropylene, have significantly lower HDT, with polyethylene typically below 100°C.

As demonstrated, standard LSR materials can cure at such temperatures, and while possible, the very long cycle times would be commercially infeasible. LTC LSR displays great performance at these low-temperature extremes, especially with the inclusion of an accelerant, enabling co-molding of LSR with low-melting plastics and opening new markets for 2K silicone molding.

Conclusions

Low-temperature cure is a novel technology platform for LSR pioneered by Dow Silicones, enabling a step-change reduction in curing temperatures and resulting process cycle times. It enables new design options by allowing co-molding of LSR onto thermosensitive substrates and components in consumer, electronics and automotive applications.

At conventional high temperatures, Silastic LTC LSR allows for a fast bulk activation, resulting in enhanced efficiency and quality. A complementary additive approach allows manufacturers to further maximize reactivity, and to lower the application range to temperatures as low as 90°C.

The LTC LSR technology is considered a key trend in 2K applications, where self-adhesive LTC grades can open new performance levels in the co-molding of low-melting plastics, such as polycarbonates or polyolefins. For high-melting engineering plastics widely used in automotive and consumer applications, this new class of materials can enable increased robustness and process efficiency, by allowing for fast-bulk vulcanization and reduced sensitivity to interfacial temperature gradients inherent to 2K co-molding applications. These developments are covered in subsequent extensions of the Silastic LTC LSR material portfolio.

Acknowledgment

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Fig. 11: Schematic representation of the injection molding process. Components A + B of the low-temperature cure LSR are mixed in a 1:1 mixing ratio. Silastic LTC 9400 acceleration additive can be added to the process as an optional component.

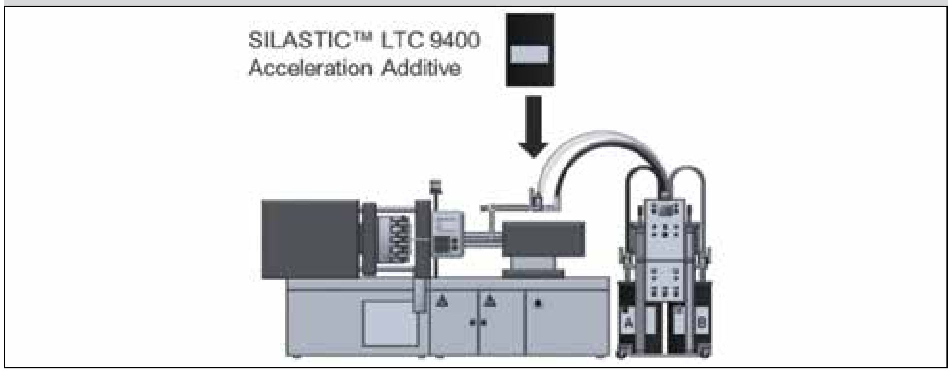

Fig. 12: DSC cure curves (from right to left): standard LSR, Silastic LTC 9400-50 LSR, and Silastic LTC 9400-50 LSR + 1 percent Silastic LTC 9400 acceleration additive. Heating rate 10°C/min.

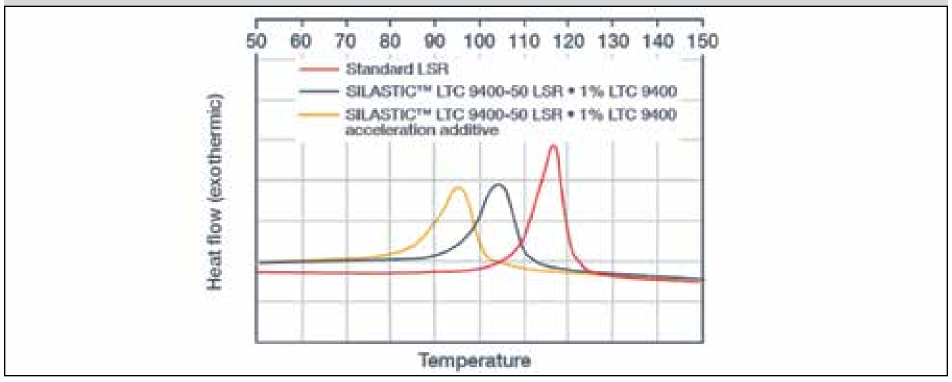

Fig. 13: Cure time of Silastic LTC 9400-50 LSR as a function of temperature, and Silastic LTC 9400 acceleration additive loading.

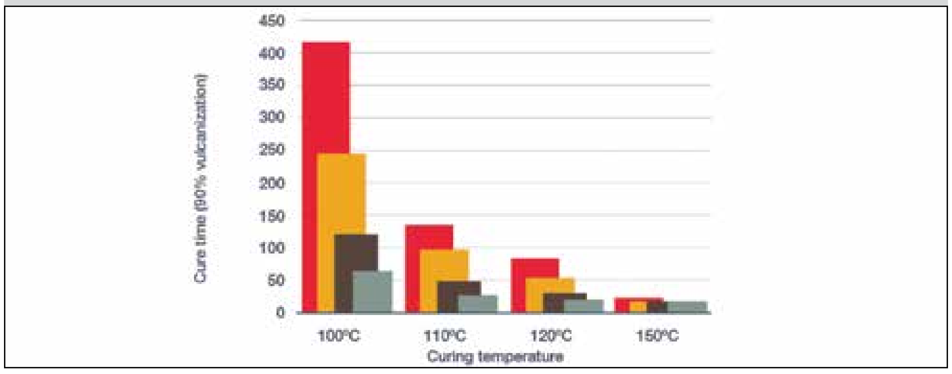

Table 1: Curing times (90 percent vulcanization) of Silastic LTC 9400-50 LSR at different concentrations of acceleration additive. For comparison, curing times for standard LSR are included.

		Curing temperature, °C					
		90	100	110	120	150	
Material	SILASTIC™ LTC 9400 Acceleration Additive, wt%	Curing times, s					Pot life at 25 °C, h
Standard LSR	-	1500	418	137	86	23	>72
SILASTIC™ LTC 9400-50 LSR	-	427	245	101	57	18	>72
SILASTIC™ LTC 9400-50 LSR	1%	268	125	51	33	18	>24
SILASTIC™ LTC 9400-50 LSR	2%	180	85	38	26	18	>15
SILASTIC™ LTC 9400-50 LSR	3%	127	66	31	23	18	>9