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Low temperature cure of liquid silicone rubber

P. Beyer, N. Gerard, H. P. Wolf

Liquid silicone rubber (LSR) is a high-performance elastomer used in many markets and applications. New application trends require enhanced design flexibility, process efficiency and co-molding using combinations of different material types. In such co-molding applications, the cure temperature of LSR is inherently limited by the thermal stability of the overmolded counterpart, and conventional high process temperatures often cannot be used. A new generation of low temperature cure (LTC) LSR materials that cure between 90 °C and 120 °C is now available to overcome those co-molding challenges and enable new designs and applications. At conventional high process temperatures and in existing applications, LTC LSR can provide for new levels of process efficiency.

1 Introduction

Liquid silicone rubber (LSR) is known for its fast vulcanization and high productivity, which result from a platinum catalyzed addition cure reaction (hydrosilylation) [1, 2]. To maximize the cure rates, LSR is typically cured at high temperatures of 160 °C up to 220 °C, enabling heating times in the range of seconds. In co-molding applications, LSR can provide reliable sealing function, moisture protection, soft elastomeric elements in hard-soft composite materials, or encapsulation of sensitive components. Examples include overmolding of electrical devices used in consumer electronics, automotive electrification and automation, or the encapsulation of functional additives and actives in the field of consumer and hygiene applications. In those cases, the application of conventional high cure temperatures would lead to thermal decomposition of the encapsulated component during heat-cure.

Another important trend is the overmolding of thermoplastic substrates by LSR to produce hard-soft composites. Here the cure temperature is limited by the softening temperatures of the thermoplastic substrate. Depending on the type of substrate, the use of conventional (i.e., 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. A new class of low temperature cure (LTC) LSR is presented for use in a wide range of process temperatures.

2 Vulcanization of liquid silicone rubber

Liquid silicone rubbers are addition-cured in a hydrosilylation reaction that involves reaction of a vinyl-functional poly(dimethylsiloxane) (PDMS) and a hydride-functional PDMS in the presence of a platinum catalyst **(fig. 1)** [2, 3]. Due to its inherent high reactivity, an inhibitor needs to be added, which suppresses the cure at room temperature and allows for a workable time (pot life) of the catalyzed mixture of 72 h or more. The pot life is critical to allow for a stable injection molding process and avoid premature curing in the injection unit. As reaction inhibitors, alkynols such as ethinyl-cyclohexanol are typically added. To overcome this inhibition, LSR needs to be cured at high temperatures.

Dr. Patrick Beyer
patrick.beyer@dow.com

Nathalie Gerard
nathalie.gerard@dow.com

Dr. Hans Peter Wolf
hans.peter.wolf@dow.com

Dow Silicones Deutschland GmbH,
Wiesbaden, Germany
www.dow.com

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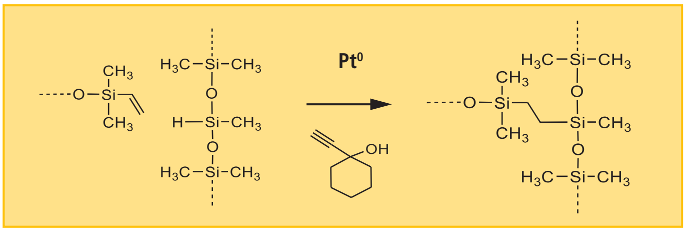


Fig. 1: Addition-curing reaction of LSR (Platinum catalyzed hydrosilylation reaction). Alkynols can be used as cure inhibitors.

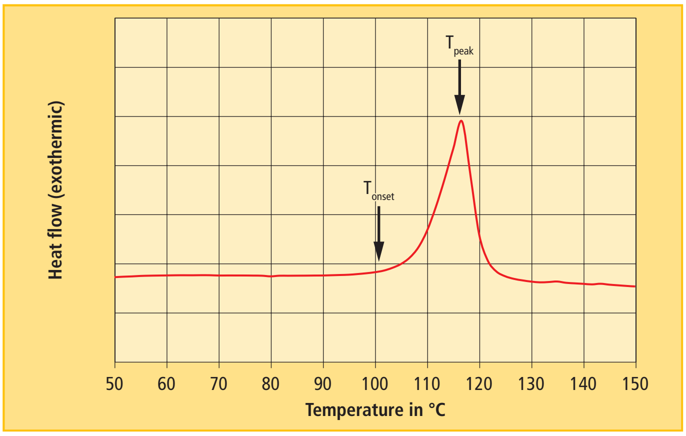


Fig. 2: DSC cure curve for a standard LSR. Heating rate 10 K/min. The temperature activation profile is characterized by its onset temperature (T_{onset}) and peak temperature (T_{peak}).

2.1 Temperature activation in a standard liquid silicone rubber

To initiate the cure, the LSR needs to be heated above its activation temperature. **Figure 2** shows the cure exotherm for a conventional LSR material, as tested by differential scanning calorimetry (DSC) [4]. In this example an onset temperature of 101 °C and a peak temperature of 116 °C are found. This high activation threshold is a direct outcome of the use of inhibitors described previously.

When processing LSR materials at high temperatures well above this activation threshold, fast cure rates can be obtained, with heating times in the range of seconds. However, when lowering the cure temperature towards the activation range, the cure rates are significantly slowed down. This is illustrated in **figure 3**, showing isothermic cure curves of a standard LSR at different temperatures. From these curves the cure times can be estimated as time to reach a degree of crosslinking of 90 %, as summarized in **figure 4.** At 150 °C a heating time of 20 s is obtained. Curing time is increased to 90 s at 120 °C (close to T_{peak}), and further to 420 s at 100 °C (close to T_{onset}). This slow cure significantly impacts productivity in the lower temperature range, and thus limits co-molding applications and new material combinations described initially.

2.2 Temperature activation in low temperature cure (LTC) liquid silicone rubber

The temperature activation of LSR 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 (LTC) LSR series. In this new generation of LSR materials the temperature activation threshold is shifted to below 100 °C, with an onset temperature of about 85 °C **(fig. 5).** This shift in activation temperature significantly increases the reactivity in the targeted low temperature range 100 °C to 120 °C.

Figure 6 shows a comparison of resulting cure times as a function of cure temperature. As an example, at 100 °C a reduction of the cure time from 418 s to 245 s was demonstrated, corresponding to a relative saving of more than 40 %. The reactivity is balanced to maintain an activation threshold well above room-temperature, leading to enough room temperature stability. At higher temperatures of more than 150 °C relative savings seem less pronounced, yet clear benefits were found in practical molding applications in this range.

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

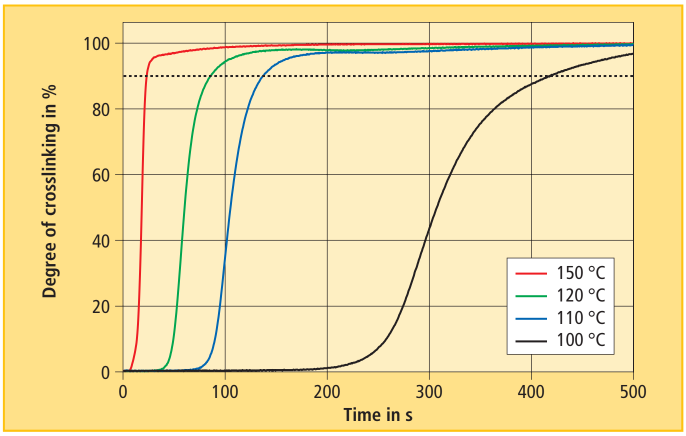


Fig. 4: Cure time (90 % vulcanization) of a standard LSR at varying temperatures, derived from cure curves of **figure 3**.

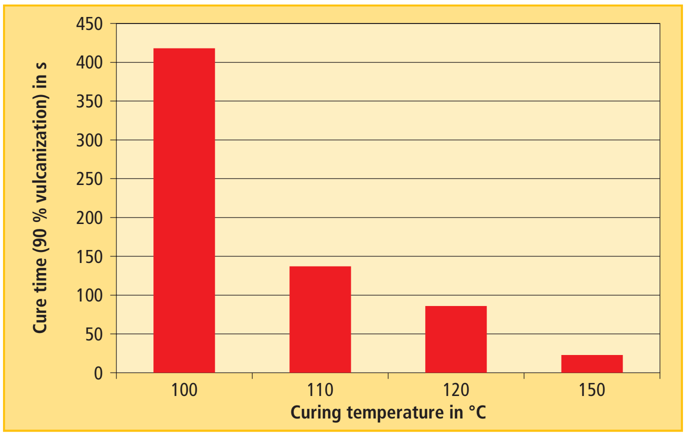


Fig. 5: DSC cure curve for a standard LSR and Silastic LTC 9400-50 LSR. Heating rate 10 K/min. T_{onset} is shifted from $T_{onset,\ strd}$ = 101 °C to $T_{onset,\ LTC}$ = 85 °C (see arrows).

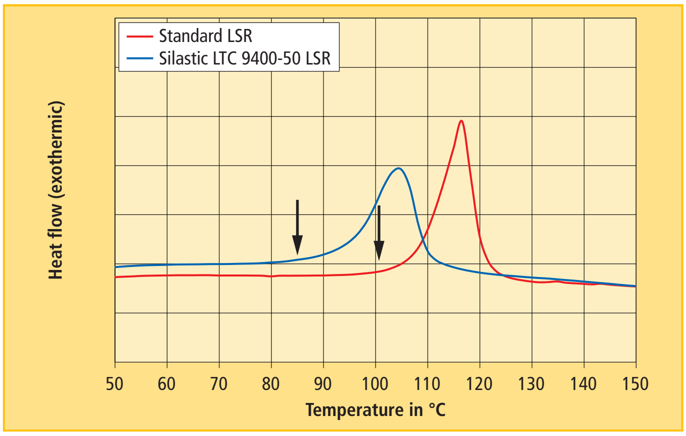
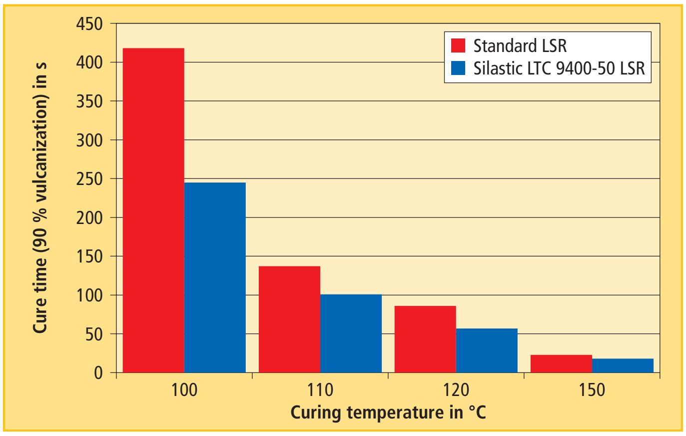


Fig. 6: Comparison of cure times (90 % vulcanization) between Silastic LTC 9400-50 LSR and a standard LSR.



2.3 Injection molding validation

Injection molding tests were done to validate the experimental results described in the previous section. For evaluation rectangular test sheets of 2 mm thickness and a shot weight of 44 g were selected. 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. **Figure 7** shows the results of this comparative molding study.

In agreement with lab studies described in the previous section, the heating time at low temperatures is significantly reduced for the Silastic LTC LSR (a trademark of The Dow Chemical Company). As predicted, the relative benefits are getting smaller at higher temperatures and further away from the activation range. In these practical molding tests, the benefits of Silastic LTC technology as compared to conventional LSR technology become even more apparent, with overall higher relative cure time savings found in the investigated temperature range. This is a result of the reduced sensitivity of LTC technology to temperature distributions and thermal gradients, which are unavoidable in practical injection molding.

3 Low temperature cure at high temperatures – a contradiction?

In both lab experiments and injection molding studies described previously, the relative cure time savings are getting smaller when moving from low temperatures (100 °C to 120 °C) to higher temperatures (more than 150 °C). Yet in complementary injection molding studies performed on thick-walled parts, significant productivity gains could be demonstrated also at higher cure temperatures above 150 °C. How can this be explained?

To activate the cure of an LSR the heat needs to be transported into the bulk of the molded part to provide for temperatures more than $T_{activation}$. Silicones, including silicone rubber, typically show low thermal conductivities λ in the range of about 0.22 W/mK [5]. Thermal conductivity is thus a key factor to consider when looking at temperature activation and its impact on overall heating time.

A computational simulation was performed to understand this relative impact. As a model system an LSR sphere of varying diameters was selected, with an initial

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

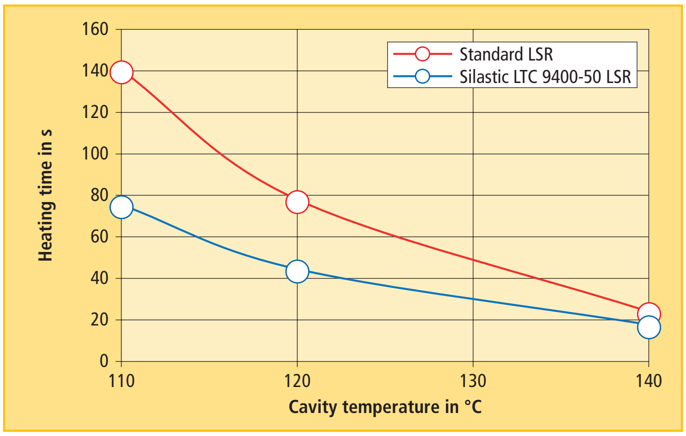


Fig. 8: Schematic representation of the computational heat flow simulation. A sphere of diameter r with initial temperature T_0 = 25 °C is exposed to an outside temperature T_{mold}. The temperature distribution in the sphere is then modelled as function of time t and cross-section r.

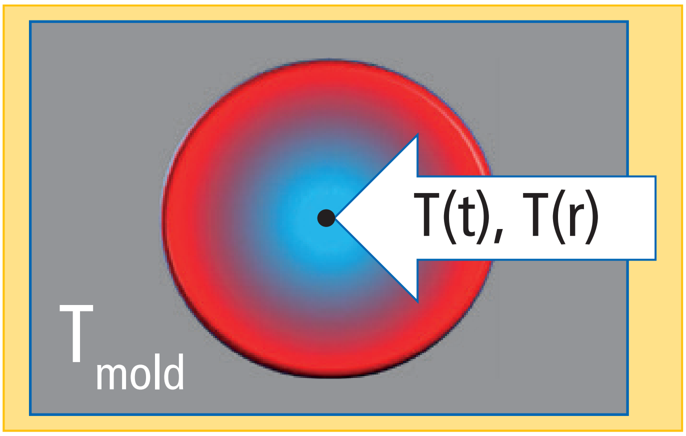


Fig. 9: Simulation of heat transfer in an LSR sphere of varying radii r = 1 mm to r = 3 mm. At t = 0 a temperature of T_{mold} = 175 °C is applied to the outside of the sphere. Graphs show the temperature at the center point (core temperature) as function of time.

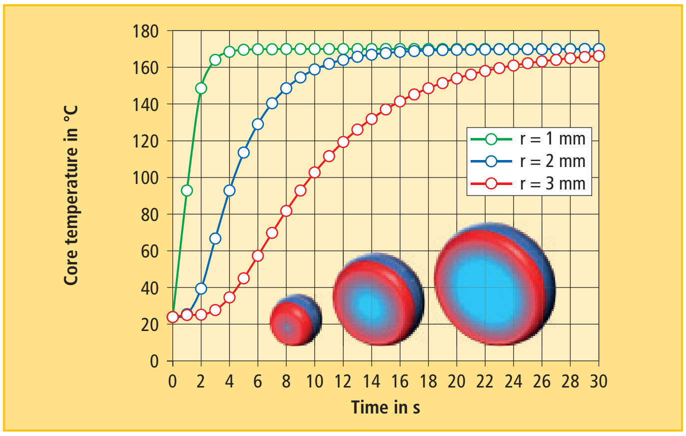
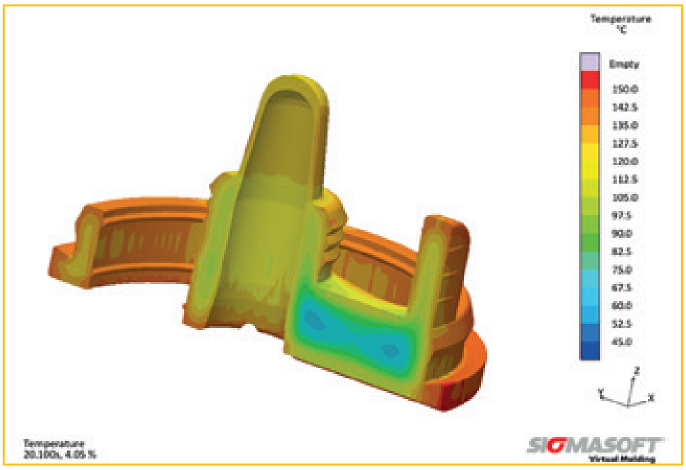


Fig. 10: Temperature distribution in a bottle ventilation valve 20 s after injection. Simulation done by Sigma Engineering.



temperature of T_0 = 25 °C. At time t_0, a constant temperature is applied to the outside of this sphere (reflecting the mold temperature T_{mold}). The temperature profile T(r,t) was then modelled as a function of cross-section r and time t. **Figure 8** gives a schematic representation of the applied model.

One key result of this simulation is shown in **figure 9**, where the temperature at the center point of the sphere (core temperature) is plotted as a function of time for different sphere radii (1 mm to 3 mm). As outside temperature T_{mold}, a conventional high molding temperature of T = 175 °C was chosen in this example. While at small radius r = 1 mm a uniform heat distribution is already obtained after about 5 s, a doubling of the sphere dimensions to r = 2 mm requires a significantly longer time of 15 s to reach a temperature equilibrium. At r = 3 mm, finally more than 30 s are required to uniformly heat the sphere. This demonstrates that large temperature gradients during molding are unavoidable, especially when producing thick-walled articles, and that the heat transfer is the limiting factor for the overall curing time.

Considering the temperature dependence of LSR vulcanization discussed in section 2, a temperature gradient directly translates into a reactivity gradient within the molded part: While the outer areas will be cured instantaneously within a couple of seconds, the curing time of the inner bulk is limited by the slow heat transfer, and the time to reach $T_{activation}$. The slow bulk vulcanization thus is the primary limiting factor for fast curing of thick-walled parts, even at high molding temperatures.

LTC LSR technology also shows the inherent low thermal conductivity λ of silicones, thus leading to similar temperature gradients as with conventional LSR materials. However, LTC LSR allows for an earlier temperature bulk activation in these cold areas, and consequently a faster bulk vulcanization. This reduced sensitivity to temperature variations can also limit effects of temperature gradients in the tool and contribute to more uniform cure and improved part quality.

A practical example showing the effect of thermal conductivity is illustrated in **figure 10.** The temperature distribution in a bottle ventilation valve made of Silastic LTC 9400-50 LSR was investigated using Sigmasoft Virtual Molding in a molding simulation. In agreement with previous results, large temperature gradients are found specifically in the thick-walled sections of up to 8 mm diameter. In these areas the bulk temperatures do not exceed 100 °C even 20 s after mold filling. As expected, fast bulk activation and short cycle times could be demonstrated on that part using Silastic LTC 9400-50 LSR.

Other examples of thick-walled articles include electrical connectors in automotive applications, where part dimensions continuously increase with higher use 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.

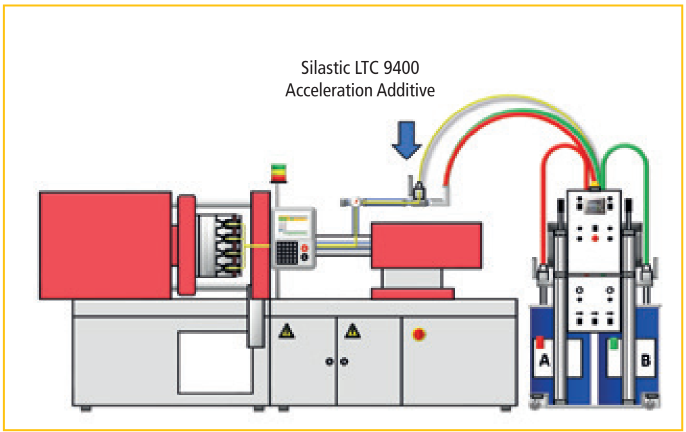


Fig. 11: Schematic representation of the injection molding process. Components A and B of the low temperature cure LSR are mixed in a 1:1 mixing ratio. Silastic LTC 9400 Acceleration Additive can be added to the process as an optional component.

4 Low temperature cure acceleration

To further enhance reactivity at low temperatures, a complementary product – the Silastic LTC Acceleration Additive – has been developed. The additive has low viscosity

Fig. 12: DSC cure curves for (from right to left) a standard LSR, Silastic LTC 9400-50 LSR, and Silastic LTC 9400-50 LSR + 1 % Silastic LTC 9400 Acceleration Additive. Heating rate 10 K/min.

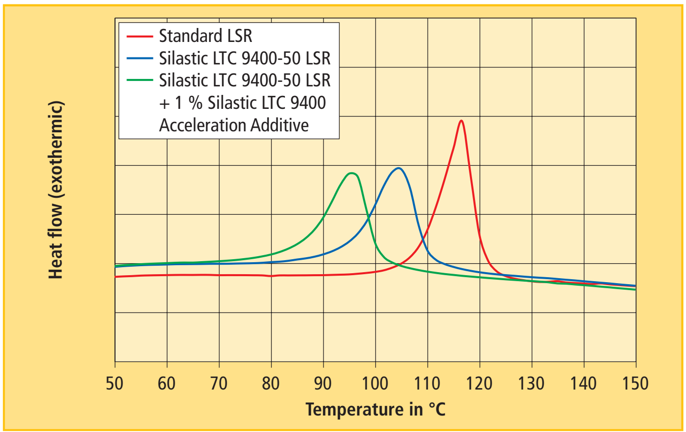
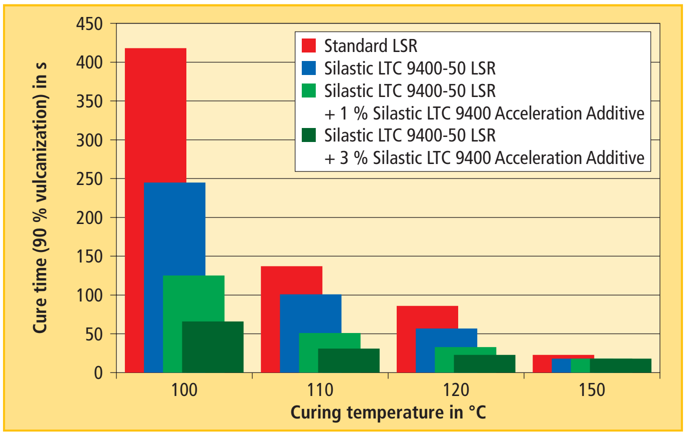


Fig. 13: Cure time of Silastic LTC 9400-50 LSR as a function of temperature, and Silastic LTC 9400 Acceleration Additive loading.



and can be added at 1 – 3 wt% one to three weight percent during the process through the third-stream injector **(fig. 11).**

Dosing of the acceleration additive leads to a further reduction of the cure activation temperature. As an example, **figure 12** shows the DSC curve for Silastic LTC 9400-50 after the addition of 1 % acceleration additive. At this dosing level the activation onset can be further reduced from a T_{onset} of about 85 °C (without additive) to an T_{onset} of about 70 °C. **Figure 13** and **table 1** summarize the resulting heating times as a function of temperature and additive dosing levels.

At 100 °C the curing times of Silastic LTC 9400-50 LSR can be further reduced from 245 s down to 66 s at 3 % additive loading, corresponding to a reduction of heating time of up to 73 %. For reference, a standard LSR will need more than 400 s to cure at this temperature. Furthermore, this enhanced reactivity after additive addition enlarges the temperature range down to 90 °C. At this temperature, a standard LSR would need over 20 min to cure, as compared to about 125 s for the accelerated (3 %) Silastic LTC 9400-50 LSR.

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.

Additivation also impacts the pot life. While the Silastic LTC LSR technology is designed to provide for a pot life of more than 72 h, use of the cure acceleration additive incrementally reduces it **(tab. 1).** Consequently, the Silastic LTC Acceleration Additive is to be applied temporarily during the molding process to maximize reactivity in running molding operations. After termination of molding, the addition is terminated to restore the initial 72 h pot life.

5 Conclusion and outlook

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.

Silastic 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 product portfolio.

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

	Curing time at 90 °C	Curing time at 100 °C	Curing time at 110 °C	Curing time at 120 °C	Curing time at 150 °C	Pot life at 25 °C
Silastic LTC 9400-50 LSR	427 s	245 s	101 s	57 s	18 s	>72 h
+1 % Silastic LTC 9400 Acceleration Additive	268 s	125 s	51 s	33 s	18	>24 h
+2 % Silastic LTC 9400 Acceleration Additive	180 s	85 s	38 s	26 s	18 s	>15 h
+3 % Silastic LTC 9400 Acceleration Additive	127 s	66 s	31 s	23 s	18 s	>9 h
Standard LSR	1,500 s	418 s	137 s	86 s	23 s	>72 h

Publication information & contacts

Publisher
Indira E. Gupta

Address
Dr. Gupta Verlags GmbH
Am Stadion 3b,
40878 Ratingen, Germany
CEO Indira E. Gupta
Amtsgericht Düsseldorf HRB 79922
VAT No. DE 314055034

Tel. +49 2102 9345-0
Fax +49 2102 9345-20

E-mail info@gupta-verlag.de

Internet www.rfp-international.com

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Editorial office
info@gupta-verlag.de
Tel. +49 2102 9345-0

Advertising
Julian Bäumer
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Max Godenrath
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Subscription
E-Mail service@gupta-verlag.de
Tel. +49 2102 9345-12

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Ulrich Gewehr
Tel. +49 2102 9345-19

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