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 times and parts consistency.

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. 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 applications.

Overall, LTC LSR is a step-change in silicone rubber technology. 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.

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.

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. This new class of LSRs allows for fast deep-section cure of thick-walled articles.

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 wider temperature range.1

In particular, liquid silicone rubber is known for its fast cure rate, lower production cost and excellent performance, which result from hydrolysislation, a platinum-catalyzed addition reaction.2,3 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.4

Hydrolysilation is a robust vulcanization chemistry. In LSRs, hydroly-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 high 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 of materials. Furthermore, this technology also enables molding of LSR with low-melting plastics or other temperature-sensitive components, opening new markets for 2K silicone molding applications.

Fig. 4: Addition-curing reaction of LSR (platinum-catalyzed hydrosilylation reaction).

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Michael Wang is a product development chemist at Dow Performance Silicones. He specializes in formulation research, optimization, polymer synthesis, material science and quantitative analysis. As part of the HTF Elastomers team, he has had the opportunity to explore new technology for a range of silicone elastomer products, including LSRs, F-LSRs, HCRs and FSRs.

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 of Hexion 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.

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 now working as a research scientist in the field of liquid silicone rubber.

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LSR

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capsulation of functional additives in con-
sumer and hygiene applications.

In these cases, conventional high-cure
temperatures would lead to thermal de-
composition of the encapsulated compo-
nent. 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 thermoplas-
tic. The use of conventional, high-tem-
perature 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, in-
cluding amount and type of platinum
catalyst and inhibitor. Kinetic studies
allowed us to derive key structure-prop-
erty 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 Si-
lastic LTC 9400 acceleration additive.

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

Cure times and cure times were
measured using an Alpha Technologies
MDR 2000 moving die rheometer. Tem-
peratures 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 calo-
rimetry (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. Injec-
tion screw was 30 mm in diameter and
molds were made of stainless steel with
surface polish.

LSR was injected between 5-160 cm/s
into molds at 120-160°C with 1,000 kN
clamping force. The mold was 180 mm
into molds at 120-160°C with 1,000 kN
clamping force. The mold was 180 mm
x 132 mm by 2 mm, and the shot weight
was 44.2 grams. Molding tests were
done in direct comparison to a standard
LSR.

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In good agreement with laboratory
studies, the heating time at low tem-
peratures is significantly reduced for
the LTC LSR. As predicted, the relative
benefits (shorter cure time) tend to de-
crease at higher temperature, away
from the activation temperature range.
This was a result of carefully balancing
the activation temperature significantly in-
duced to 420 seconds (Fig. 4). Even at 120°C,
the LSR showed 90 seconds Tc90, com-
pared 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 tempera-
ture of T onset = 85°C This shift in (Fig. 5)
activation temperature significantly in-
creases the reactive time in the targeted
low temperature range 100-120°C as
measured by Tc90 (Fig. 6). For example,
at 100°C LTC LSR demonstrated a re-
duction of the cure time from 418 sec-
onds 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 ob-
tain fully cured parts was recorded as a
function of mold temperature (Fig. 7).

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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 distribution 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 needs to be transported into the bulk of the molded part. Silicomates typically show low thermal conductivities in the range of ~0.22 W/mK. 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 $T_0 = 25^\circ C$. At time $t_0$, a constant external temperature was applied to simulate reflecting the mold temperature, $T_{mold} = 175^\circ C$ (Fig. 8).

The temperature profile $T(t,r)$ 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 simulated as a function of time for different spheres of 1-3 mm radius (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 within the mold temperature. Consequently, the curing time of the bulk is increased as the bulk temperature at the core of the sphere is simulated as a function of time for different spheres of 1-3 mm radius (Fig. 9).

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 is 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 has a significant effect on heating times as a function of temperature and dosing levels (Fig. 13 and Table 1). At 100°C, the curing time 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 71 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 acceleration also impacts the pot life. While the LTC LSR technology is designed to provide a pot life of >72 hours, use of the curing acceleration 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 and thermal gradients, both local and conventional high melting temperatur -ures. 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 LTC applications.

For LSR plastic-composite materials, molding conditions are particularly important to avoid deformation, hazy and thermal stresses 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 accelerator, 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 Silicomates, 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 polyurethane 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 as well as increased reactivity 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

The authors would like to thank Pierre DESCAMPS for help with simulating heat distribution using octave software.

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.

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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.