Technical

Transforming regular LSR into self-bonding LSR

By Paul Wheeler
Parker Lord

Liquid silicone rubber is used to produce a wide range of parts across various markets, with presence in segments like medical devices, cookware, electronics and personal electronic devices.

Silicone polymers exhibit many unique properties that other materials cannot achieve, combining rubbery flexibility with excellent thermal stability, durability, low surface energy, biocompatibility and soft feel.

TECHNICAL NOTEBOOK
Edited by John Dick

Because of its unique performance and manufacturing ease, the global LSR market has grown rapidly, and that trend is expected to continue. As the market need for LSR expands, product designs are becoming more sophisticated and require bonding of silicone to other substrates, which can be challenging due to its ultra-low surface energy and chemical resistance.

The current technology on the market requires the use of primers or special self-bonding LSRs when bonding to plastics or metal, but there are significant drawbacks to both methods. Primers require extra process steps, specialized application equipment and management of volatile solvents, while self-bonding LSRs suffer from high price, short shelf life and limited availability. To combat these market challenges and expand the bonding technology for LSR, a new adhesion-promoting additive technology, Chemlok-brand 3Stream, imparts self-bonding properties to non-self-bonding LSRs.

Developed by Parker Lord (previously Lord Corp.), Chemlok 3Stream is designed to be third-streamed into an injection molding process, just prior to the static mixer, by means of a standard dosing pump, like colorant dosing systems. (**Fig. 1**)

With an adhesion additive, molders can eliminate the need for expensive self-bonding LSRs, with a cost savings of up to 50 percent by utilizing standard and readily available LSR grades. In addition, molders can remove the application of primers, along with their associated volatile organic compounds, significantly decreasing manufacturing time and increasing plant safety.

Based on extensive trials, Chemlok 3Stream is proven to bond at levels as low as 0.5 wt-percent in LSR. However, optimal loading levels will depend on the substrate, process parameters and specific application. At 1.0 wt-percent of Chemlok 3Stream in LSR, excellent bonding can be achieved with various thermoplastics (PBT, PA-6, PA-66) and metal (aluminum, steel, nickel) substrates.

Bonding performance

Chemlok 3Stream was benchmarked at 1 wt-percent in two standard grades of LSR versus two commercially available self-bonding LSRs. This study was completed at Parker Lord's Erie, Pa., laboratory on a Wittmann Battenfeld EcoPower 110 injection molding machine equipped with model 622-1A Graco Fluid Automation LSR feeding system. Chemlok 3Stream additive was loaded into 6-ounce Semco cartridges and fed with the model 622-1As pneumatically-actuated pumping system. Test specimens consist of a plastic coupon over-molded with silicone.

Testing was conducted at a rate of 300 mm/minute on an MTS Criterion Model 45 using a sled fixture such that 90 degrees peel angle is maintained for the entire test. Peel strength is calculated from an average value of force across a large elongation range. After peel testing, failure mode is reported as cohesive, boundary layer, or adhesive. Cohesive failure means a significant thickness of rubber is retained on the substrate, meaning that the adhesive strength exceeded the strength of the rubber. Adhesive failure occurs when the rubber is cleanly removed from the substrate, leaving little-to-no residue. Boundary layer is in between these two failure modes and is evidenced by thin rubber and/or residue remaining on the substrate.

For this benchmarking study, fully molded test specimens were post-baked at 150°C for 60 minutes. Post-baking is dependent on specific applications and bonding performance requirements. After molding, parts were tested as-is, and also after exposure to two environments: 150°C for three days, and 85°C/85 percent RH for three days.

The data shows that, in most cases, the bond strength of standard LSR modified with Chemlok 3Stream gives adhesion values that are equivalent to, or greater than, the two self-bonding silicone grades (**Fig.2**) In many cases, the performance of Chemlok 3Stream-modified silicones show superior adhesion and more robust strength retention when exposed to hot and hot/humid environments.

Primary bonding measures the bond strength immediately after molding and post-baking and is a good initial representation of adhesion. On PBT, Chemlok 3Stream-modified silicones greatly exceeded performance of commercial self-bonders, in terms of both peel strength values and failure mode. Similarly good performance was observed on PA6, in which both Chemlok 3Stream-modified silicones gave nearly 100 percent cohesive failure, which slightly exceeded the performance of the self-bonders.

To measure bond retention in a high-heat environment, coupons were exposed to 150°C for three days. In most cases, Chemlok 3Stream-modified systems out-performed self-bonders. Notably on PBT, Chemlok 3Stream systems gave more than double the peel strength as well as perfect failure modes of 100 percent cohesive failure, compared to both self-bonders, which failed around 90 percent adhesively.

On PA6, Chemlok 3Stream systems gave excellent peel strength with nearly 100 percent cohesive failure, as did Competitor A, while Competitor B failed adhesively and gave a relatively low peel strength. Good bonding also was achieved on PA66, although somewhat less than PA6, with generally lower peel strength and lower levels of cohesive failure.

In a final evaluation of bond strength retention, coupons were exposed to 85°C/85 percent RH environment for three days. Interestingly, Chemlok 3Stream-modified systems exceeded the performance of self-bonders in most instances and showed improved adhesion compared to primary results. This shows that the hot and humid condition causes additional curing of the Chemlok 3Stream additive at the silicone/plastic interphase, leading to improved adhesion.

Curing performance

To study curing performance, MDR cure curves were generated (**Fig. 3**) and T90 values were tabulated (**Table 1**). As shown in the data, adding Chemlok 3Stream to standard LSR gives a modest decrease in curing speed. For example, at 160°C, T90 cure time of Xiameter RBL2004-40 and Silopren 2660 were extended by 5 to 6 seconds. The two commercial self-bonders showed dra-

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The author

Paul Wheeler is a staff scientist at Parker Lord, where he develops innovative adhesive and bonding solutions. Much of his career has focused on generating bonding solutions for silicone elastomers.

Wheeler received a bachelor's in plastics engineering technology from Penn State Erie, and a doctorate in polymer science from the University of Southern Mississippi.

Prior to joining Lord, he held several technology leadership positions, primarily around nylon 66 compounds for the automotive market and nanotechnology for thermoplastic and thermoset materials.

Fig. 1: Parker Lord's Chemlok 3Stream in an injection molding process.

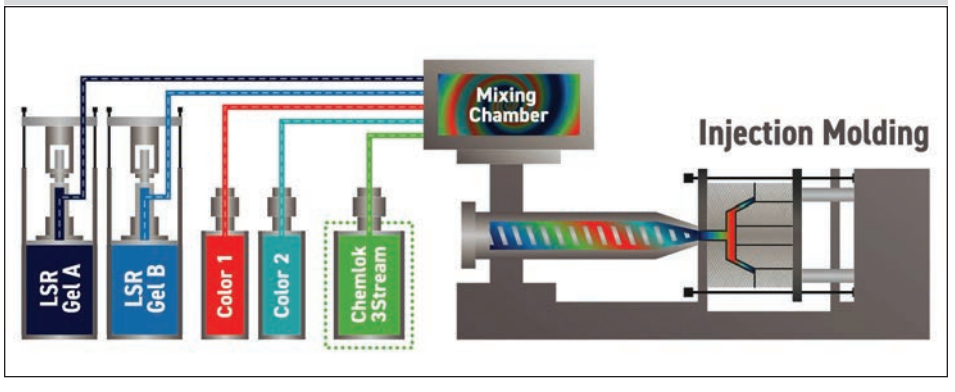


Fig. 2: Failure modes of LSR modified with Chemlok 3Stream additive compared to self-bonding grades. PBT coupons were post-baked.

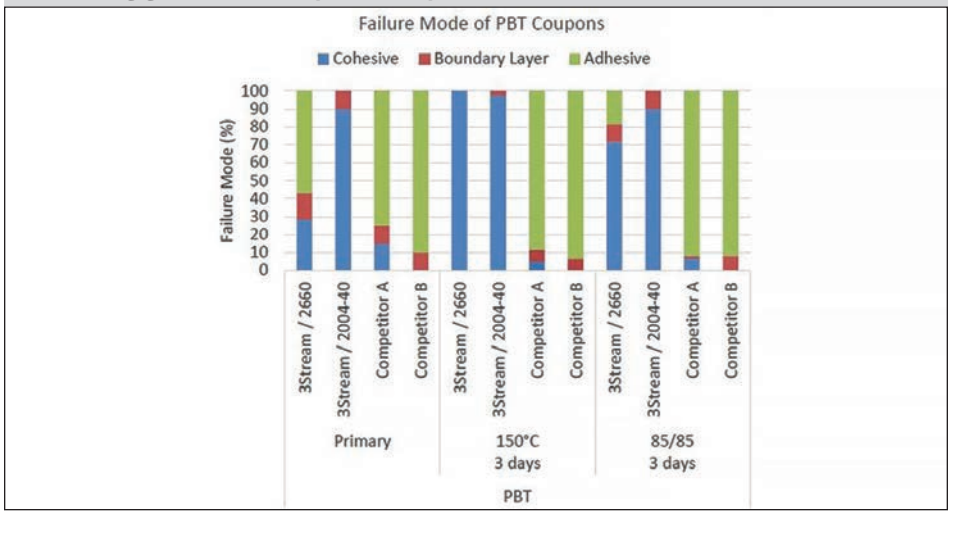
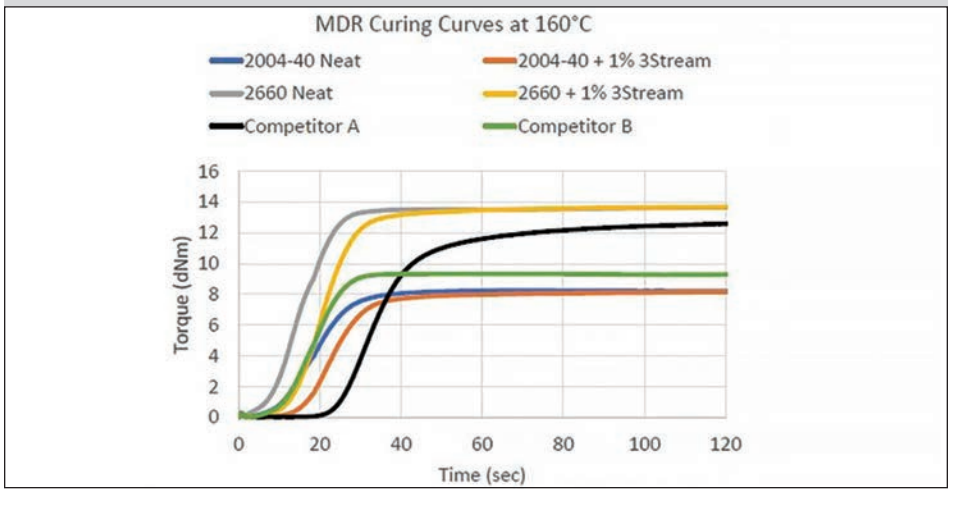


Fig. 3: Cure curves of elevated standard LSR, LSR modified with Chemlok 3Stream additive and self-bonding grades at 160°C.



Commerce places duties on S. Korean ESBR imports

Rubber & Plastics News Staff

WASHINGTON—South Korean exporters dumped emulsion SBR in the U.S. from September 2018 to August 2019, the U.S. Department of Commerce ruled.

The decision means the companies now are subject to import duties of 44.3 percent.

The Enforcement and Compliance unit of the International Trade Administration in the DOC issued a final ruling Oct. 23 in the case after coming out with preliminary findings July 1.

A total of seven South Korean companies are impacted by the ruling, including LG Chem Ltd., Daewoo International Corp., Hyundai Glovis Co., Kukje Trading Corp., Kumho Petrochemical Co. Ltd., Sungsan International Co. Ltd. and WE International Co. Ltd.

LG Chem, after the initial ruling this summer, told the Commerce Department it would not participate in a review of the case. No one submitted comments following the preliminary results, the administration said.

At issue is the price of cold-polymerized ESB rubber in primary forms, bales, granules, crumbs, pellets, powders, plats and sheets strip, the federal government said. ESB rubber includes non-pigmented rubbers and oil-extended non-pigmented rubbers that contain at least 1 percent organic acids from the emulsion polymerization process.

Not included in the ruling is the blending of ESB rubbers with other polymers, high-styrene resin master batch, carbon black master batch and latex.

Commerce officials determined that there was a dumping margin of 44.3 percent during the period in question. This means all the companies will be required to provide a cash deposit of 44.3 percent, equal to the dumping margin established in the final results, on imports of the material.

"The following cash deposit requirements will be effective for all shipments of ESB rubber from Korea entered, or withdrawn from warehouse, for consumption on or after the publication date of the final results of this administrative review," according to a notice in the Federal Register.

This is the second time Commerce has levied import duties on the material being imported from South Korea.

The ITA determined in 2017 the U.S. synthetic rubber industry was injured by imports of emulsion styrene-butadiene rubber from Brazil, South Korea, Mexico and Poland being sold at less than fair value. Antidumping duty orders ranged from 9.66 to 44.3 percent in that case.

ESBR is used predominately in car and light truck tires and truck tire retread compounds, according to the federal government. The material also is used in a variety of other products, including conveyor belts, shoes, hoses, roller coverings and flooring.

The Department of Commerce has levied duties on imports of South Korean ESBR.

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matic differences in cure speed, with Competitor B giving a T90 of 26 seconds compared to Competitor A giving 58 seconds. Overall, the data indicates that Chemlok 3Stream modified systems retain curing performance within a normal expected range for LSR.

As demonstrated by this data, Chemlok 3Stream can convert standard LSR to self-bonding LSR.

Through other experiments, excellent bonding performance has been demonstrated on PBT, PA6, PA66, PPA, PPS, and plasma-treated PC, showing comparable, and in many cases better, adhesion than can be achieved with commercial self-bonding LSR grades. Chemlok 3Stream enables molders to utilize standard LSR grades that are dramatically less expensive and more widely available, while offering shorter lead times and a longer shelf life. Molders now have an expanded supply chain by utilizing regular LSR, as well as increased design flexibility, while achieving significant cost savings.

Parker Lord is continuing to innovate additional LSR adhesion additive solutions to expand the substrate and processing temperatures to meet varying customer demands.

Table 1: T90 values obtained from MDR.

Product	T90 Values (seconds)
Xiameter RBL2004-40	29
Xiameter RBL2004-40 + 1% 3Stream	34
Silopren 2660	25
Silopren 2660 + 1% 3Stream	31
Competitor A	58
Competitor B	26

At 160°C curing temperature