Chemlok 3S-902 Liquid Silicone Rubber Adhesion Additive

Patent Pending

Adhesion Benchmarking Study
White Paper

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Chemlok 3S-902 Liquid Silicone Rubber Adhesion Additive

Adhesion Benchmarking Study

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Paul Wheeler, PhD., 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. Dr. Wheeler received a BS in Plastics Engineering Technology from Penn State Erie and a PhD in Polymer Science from the University of Southern Mississippi. Prior to joining LORD, Dr. Wheeler held several technology leadership positions primarily around nylon 66 compounds for the automotive market and nanotechnology for thermoplastic and thermoset materials.

Introduction

Liquid silicone rubber (LSR) is used to produce a wide range of parts for many different markets. Some notable segments include 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, soft feel, etc. Because of its unique performance and relative ease of part manufacturing, the global LSR market has seen rapid growth that 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 of around 20 mN/m and chemical resistance.

Bonding LSR to plastics and clean metals with current technology on the market requires the use of primers or special self-bonding LSRs. Both methods have significant drawbacks. 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.

This paper introduces a new additive technology, Chemlok 3Stream (3S), to impart self-bonding properties to non-self-bonding LSRs. Chemlok 3S-902 additive is fed via a standard additive pump directly into the LSR feed stream, similar to colorant dosing. In doing so, OEMs and tiers can eliminate the application of primers and their associated VOC and save significant costs gained from utilizing standard LSR grades over more expensive self-bonders.

Experiment Details

Injection Molding Description: Parts were injection molded on a Wittmann Battenfeld EcoPower 110 injection molding machine equipped with a model 622-1A Graco Fluid Automation LSR feeding system. Chemlok 3S-902 additive was loaded into 6-ounce Semco cartridges and fed with the model 622-1A's pneumatically-actuated pumping system. Test specimens consist of a plastic coupon overmolded with a strip of silicone that overhangs both edges of the coupon (Figure 1). Plastic coupons were molded on a Sumitomo SE100EV 100 ton electric injection-molding machine and immediately packaged in moisture-proof foil bags to minimize moisture absorption between plastic injection and LSR injection.

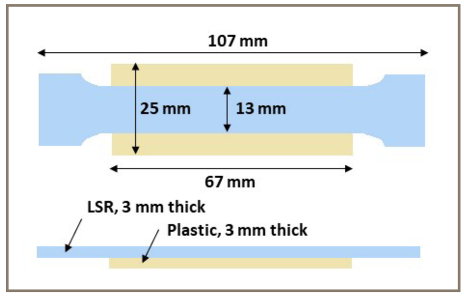

Figure 1: Test specimen used

Peel Testing: Testing was conducted on an MTS Criterion Model 45 using a sled fixture such that 90 degrees peel angle was maintained for the entire test. Peel strength was calculated from an average value of force across a large elongation range. The test was conducted at a rate of 300 mm/min.

Failure Mode: After peel testing, failure mode was 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 means that the rubber was 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.

Curing Curves: Curing profiles were measured on a Montech D-RPA 3000 at 160°C for two minutes.

Adhesion Benchmarking Test

In the following experiment, two standard LSR silicones* were converted to self-bonding grades using Chemlok 3S-902 additive and compared to commercial self-bonding LSR*. Thus, 1 wt-% of Chemlok 3S-902 was added to Momentive Silopren 2660 and Dow Xiameter RBL2004-40. These were compared to commercially available self-bonding LSR grades from two major silicone producers, referred to as Competitor A (50 Shore A durometer) and Competitor B (40 Shore A durometer). Cure temperature and time was 150°C and 80 seconds, except for Competitor A, which was cured for 100 seconds due to undercure at 80 seconds. The overmolded plastics consisted of 30% glass filled PBT (Lupox GP 2300 by LG Chem), 30% glass filled PA6 (Akulon K224-HG6 by DSM), and 35% glass filled PA66 (Zytel 70G35HSLR by DuPont).

**The liquid silicone rubbers used in this analysis were obtained on the open market by Parker Hannifin for the sole purpose of evaluating the performance of Chemlok 3S-902 adhesion promoting additive. Use of them does not imply any affiliation with or endorsement by them.*

Postbaked Performance

Previous testing has shown that maximum adhesion with Chemlok 3S-902 additive is achieved by postbaking the molded parts at an elevated temperature for several minutes. In this section, fully molded test specimens were postbaked at 150°C for 60 minutes. After molding, parts were tested as-is, and also after exposure to two environments: 150°C for 3 days, and 85°C / 85% RH for 3 days. Test results are depicted in Figure 2.

The data shows that in most cases, the bond strength of standard LSR modified with Chemlok 3S-902 additive gives adhesion values that are equivalent to, or greater than, the two self-bonding silicone grades (Figure 2 through Figure 5). In many cases, the performance of Chemlok 3S-902-modified silicones shows superior adhesion and more robust strength retention when exposed to hot and hot/humid environments.

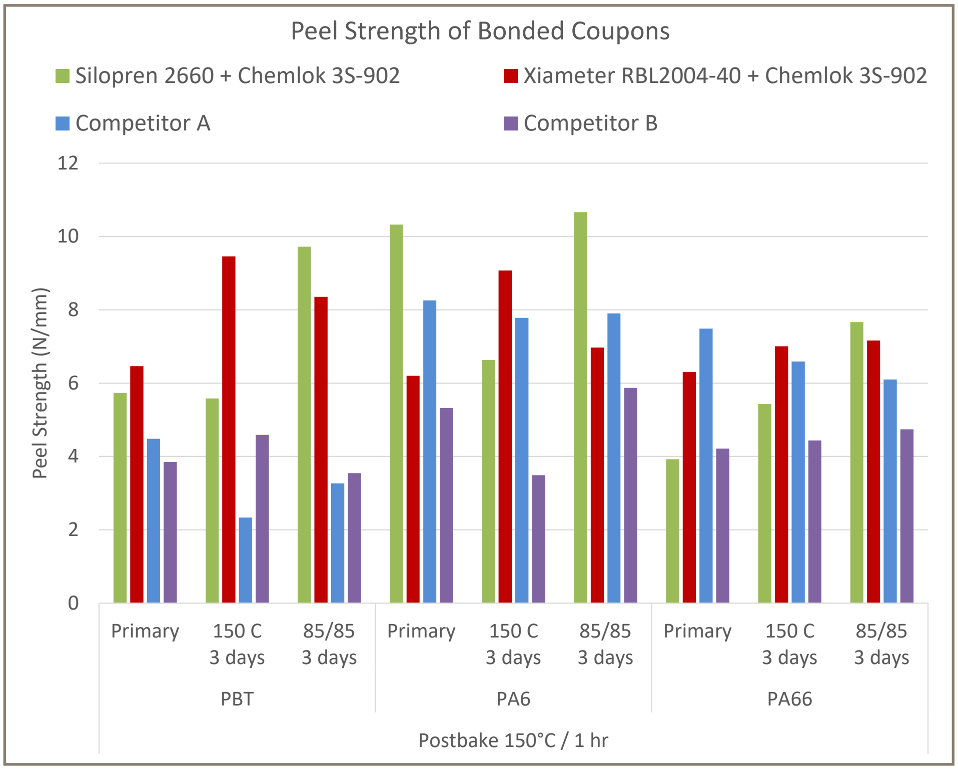

Figure 2: Average peel strength of LSR modified with Chemlok 3S-902 additive, bonded to various plastics, compared to commercially available self-bonding grades. Coupons were postbaked.

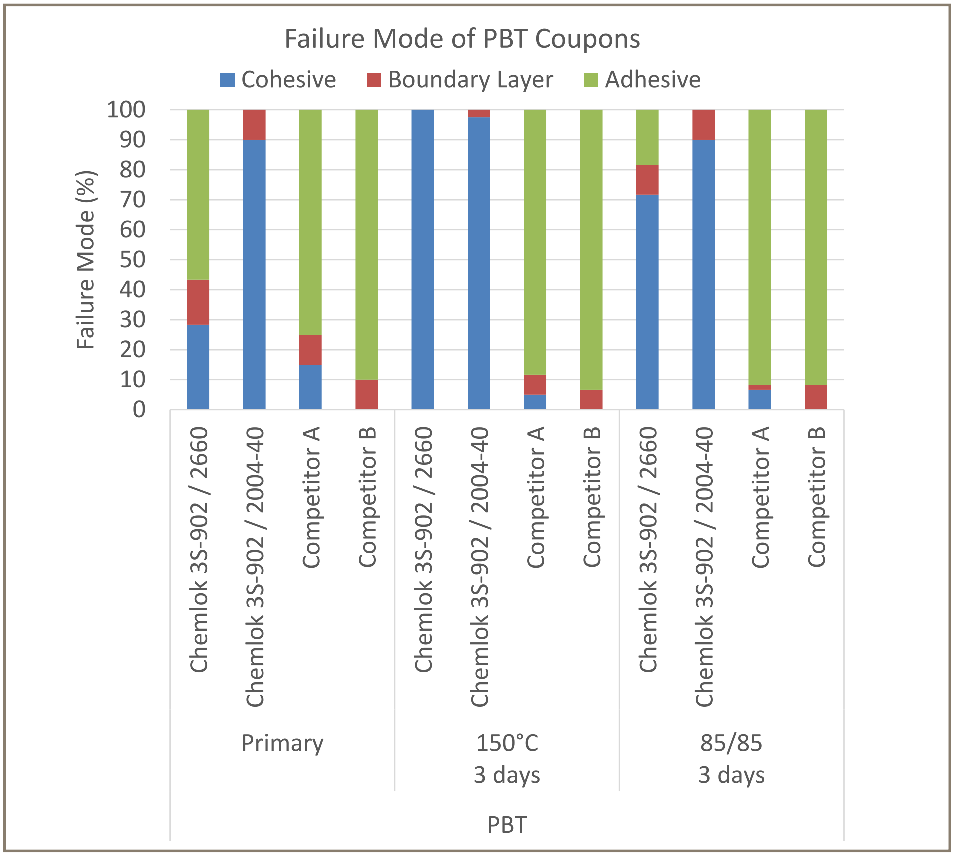

Figure 3: Failure modes of LSR modified with Chemlok 3S-902 additive compared to self-bonding grades. PBT coupons were postbaked.

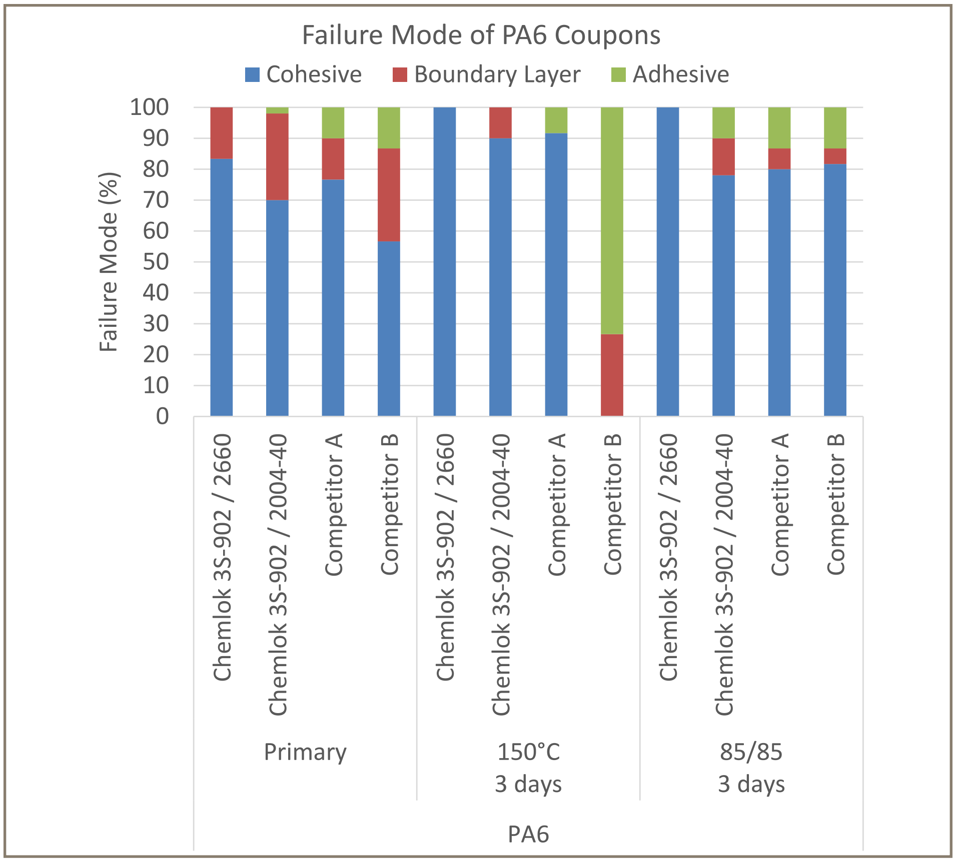

Figure 4: Failure modes of LSR modified with Chemlok 3S-902 additive compared to self-bonding grades. PA6 coupons were postbaked.

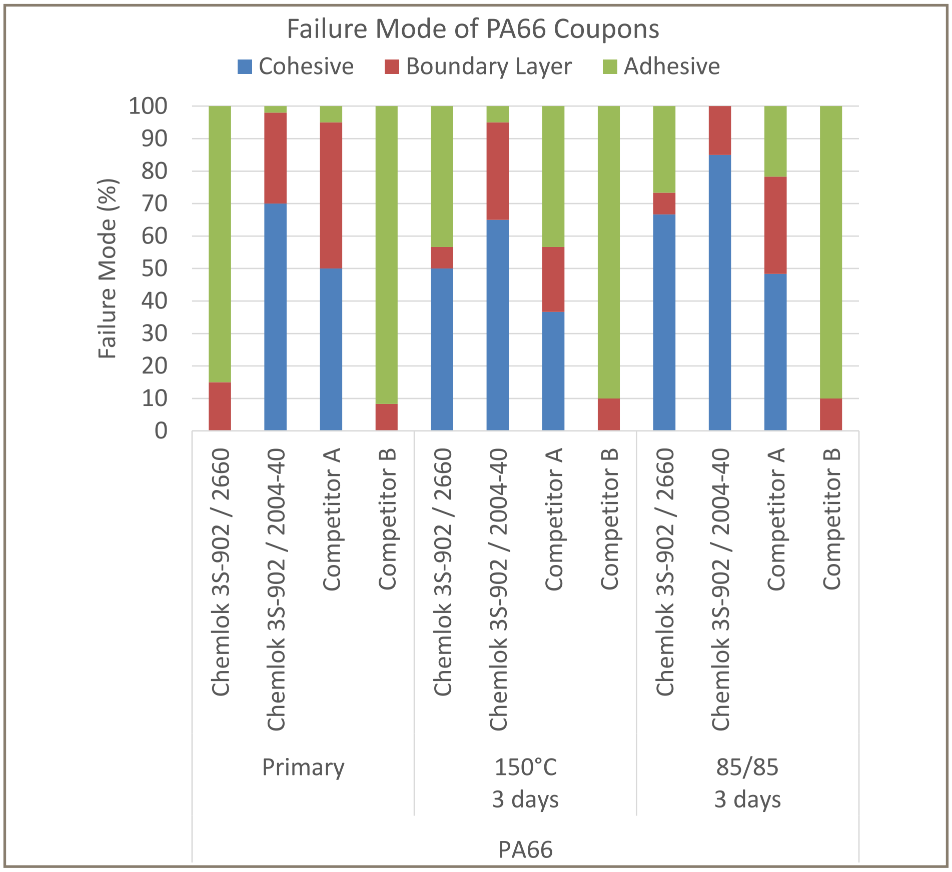

Figure 5: Failure modes of LSR modified with Chemlok 3S-902 additive compared to self-bonding grades. PA66 coupons were postbaked.

Primary bonding measures the bond strength immediately after molding and postbaking and is a good initial measure of adhesion. On PBT, Chemlok 3S-902-modified silicones greatly exceeded performance of commercial self-bonders, in terms of both peel strength values and failure mode. For example, Chemlok 3S-902-modified Xiameter RBL2004-40 gave a peel strength that exceeded the others by greater than 45% and a failure mode of nearly 100% cohesive failure. Similarly, good performance was observed on PA6, in which both Chemlok 3S-902-modified silicones gave nearly 100% cohesive failure, which slightly exceeded the performance other self-bonders. Excellent bonding was achieved on PA66 with Chemlok 3S-902-modified RBL2004-50 as well as Competitor A. Bond integrity was slightly lower with Chemlok 3S-902-modified 2660 and Competitor B.

To measure bond retention in a high heat environment, coupons were exposed to 150°C for 3 days. In most cases, Chemlok 3S-902-modified systems out-performed self-bonders. Notably on PBT, Chemlok 3S-902 systems gave more than double the peel strength as well as perfect failure modes of 100% cohesive failure, compared to both self-bonders which failed around 90% adhesively. On PA6, Chemlok 3S-902 systems gave excellent peel strength with nearly 100% cohesive failure, as did Competitor A, while Competitor B failed adhesively and gave a relatively low peel strength. Good bonding was also 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% RH environment for 3 days. Interestingly, Chemlok 3S-902-modified systems exceeded the performance of self-bonders in most instances and showed greatly improved adhesion compared to primary results. This shows that the hot and humid condition causes additional curing of the Chemlok 3S-902 additive at the silicone / plastic interface, leading to improved adhesion.

Non-Postbaked Performance

To use Chemlok 3S-902 additive, postbaking parts is recommended to achieve optimum adhesion. Postbaking is commonly carried out on silicone parts to achieve final cured properties as well as eliminate low molecular weight volatile components, so in many cases this step is already incorporated into the manufacturing process. However, in some cases postbaking is not performed nor desired, thus it is important to understand adhesion immediately after molding. Figures 6 and 7 depict bond strength and failure mode after molding, with no postbake.

As seen in Figure 6, primary bond strength of Chemlok 3S-902-modified silicones are generally lower than self-bonders, with corresponding failure modes showing mostly adhesive failure. Self-bonders demonstrate a more favorable failure mode in all cases. After exposure to 85°C / 85% RH, bond strength improved for all Chemlok 3S-902 systems but gave a mixed reaction for self-bonders. For example, on PBT, 85/85 exposure dramatically improved bonding for Chemlok 3S-902 systems but decreased strength for both self-bonders. On PA6 and PA66, Chemlok 3S-902 systems again showed a dramatic improvement in bond strength, Competitor A also improved, while Competitor B maintained performance.

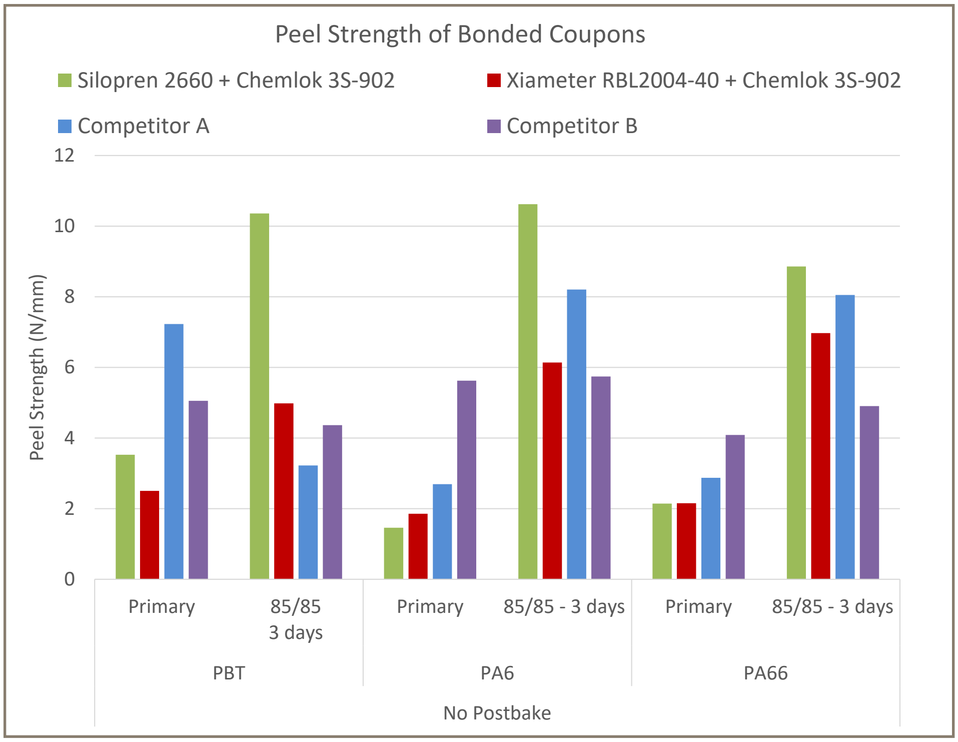

Figure 6: Average peel strength of LSR modified with Chemlok 3S-902 additive, bonded to various plastics, compared to commercially available self-bonding grades. Coupons were not postbaked.

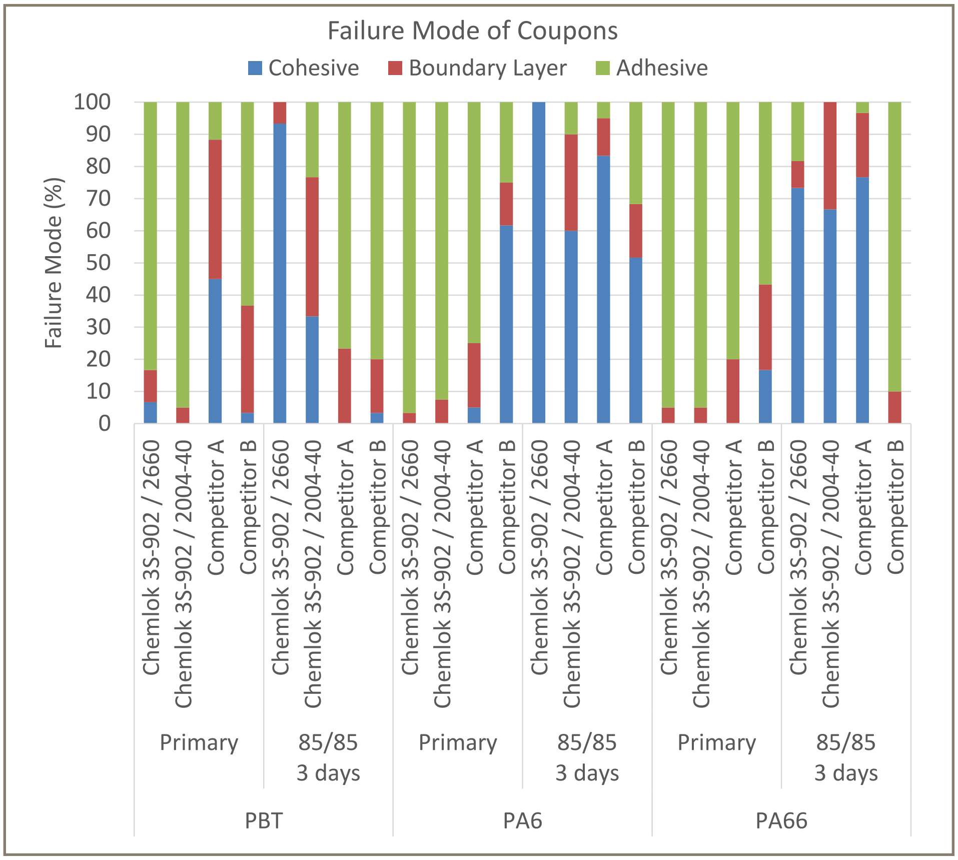

Figure 7: Failure modes of LSR modified with Chemlok 3S-902 additive compared to self-bonding grades. Coupons were not postbaked.

Curing Performance

To study curing performance, MDR cure curves were generated (Figure 8) and T90 values were tabulated (Table 1). As shown in the data, adding Chemlok 3S-902 additive to standard LSR gives a modest increase in cure time. 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 dramatic differences in cure speed, with Competitor B giving a T90 of 26 seconds compared to Competitor A giving 58 seconds. Overall, the data indicate that Chemlok 3S-902-modified systems retain curing performance within a normal expected range for LSR.

Table 1: T90 Values obtained from MDR

Product	T90 Values (seconds)
Xiameter RBL2004-40	29
Xiameter RBL2004-40 + 1% Chemlok 3S-902	34
Silopren 2660	25
Silopren 2660 + 1% Chemlok 3S-902	31
Competitor A	58
Competitor B	26

At 160°C curing temperature

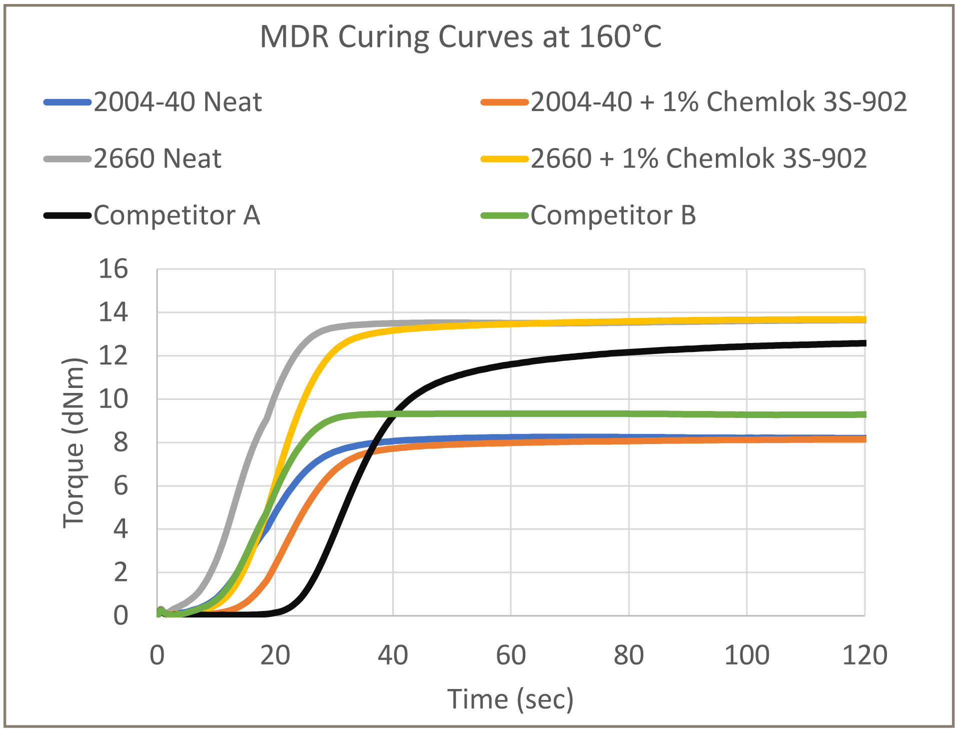

Figure 8: Cure curves of evaluated standard LSR, LSR modified with Chemlok 3S-902 additive, and self-bonding grades at 160°C.

Non-Postbake with Catalyst

Understanding the limited bonding performance of Chemlok 3S-902 additive without postbaking, an alternative approach was developed in which a catalyst is added to Chemlok 3S-902, immediately before molding, at a ratio of 100 parts Chemlok 3S-902 to 5 parts of catalyst solution. Thus, the liquid catalyst solution was mixed with Chemlok 3S-902 additive, and then fed into the injection molding machine as described above.

The first results in Figures 9 and 10 compare adhesion results of Chemlok 3S-902 additive with and without catalyst. In this study, Chemlok 3S-902 was added at 1 wt-% to Dow Silastic RBL9200-30. Coupons were overmolded with silicone at a cure temperature of 160°C and cure time of 60 seconds.

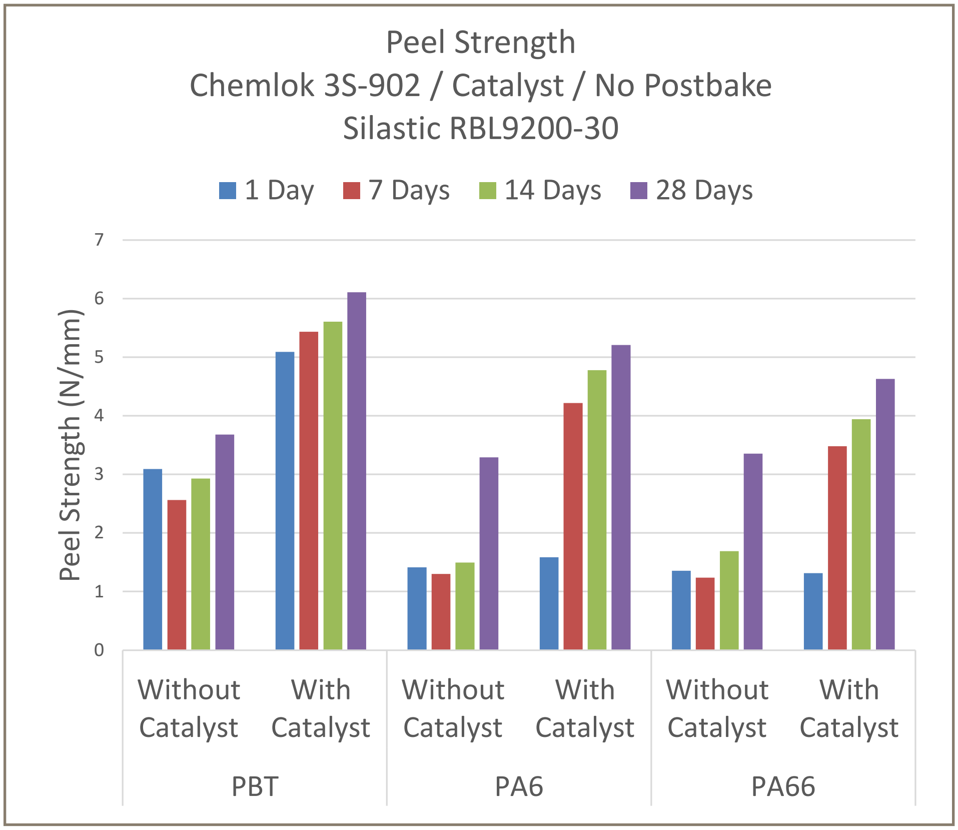

Figure 9: Peel strength of Chemlok 3S-902 additive with and without catalyst, aged at room temperature for 1, 7, 14, and 28 days after molding.

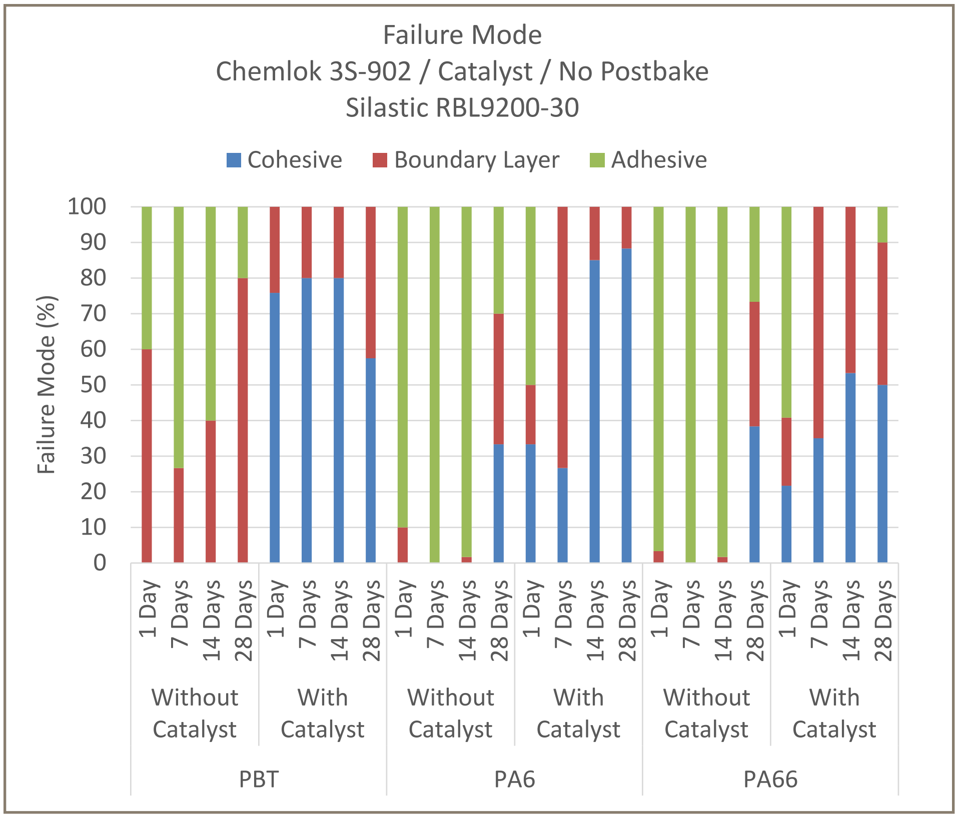

Figure 10: Failure modes of Chemlok 3S-902 additive with and without catalyst, aged at room temperature for 1, 7, 14, and 28 days after molding.

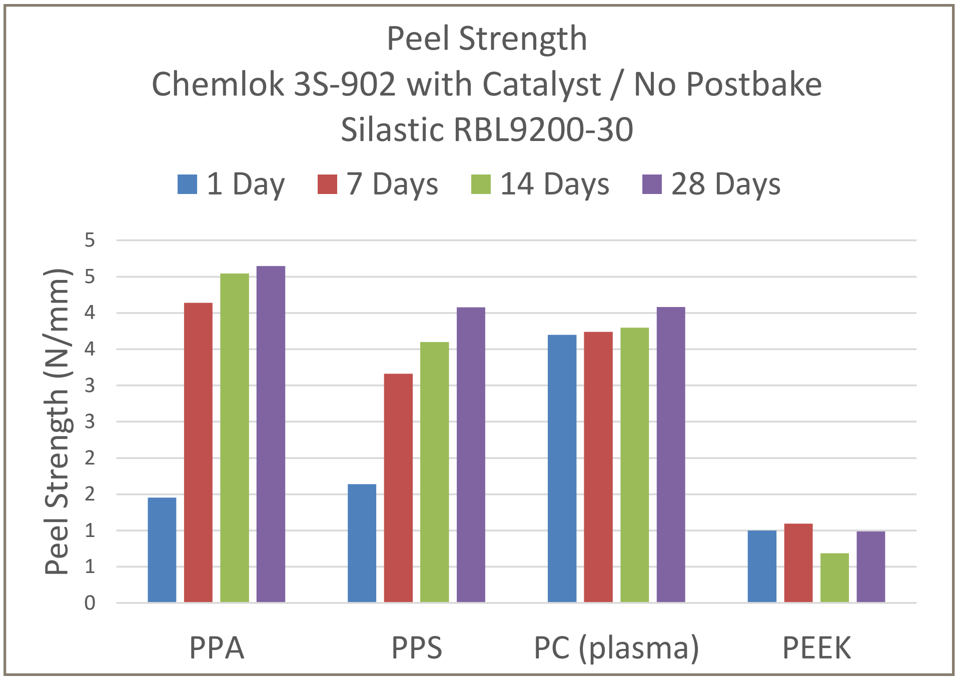

Figure 11: Peel strength of Chemlok 3S-902 additive with catalyst overmolded onto PPA, PPS, PC, and PEEK.

The molded test specimens were not postbaked. Peel tests were performed at 1, 7, 14, and 28 days after molding with the parts being stored under ambient conditions in a lab (~20°C / ~40% RH).

Coupons that used Chemlok 3S-902 additive without catalyst showed an initial decrease in bond strength after 7 days, a modest increase after 14 days, and then a dramatic increase after 28 days. This is evidence of the Chemlok 3S-902 additive blooming to the surface over time and then slowly curing by reacting with atmospheric moisture. Without catalyst or postbaking, this process is somewhat slow, occurring over several weeks.

Adhesion development speed is significantly increased by adding catalyst to Chemlok 3S-902. As shown in Figures 9 and 10, adding catalyst not only improved bonding to PBT in all instances, but also caused a dramatic shift in bond strength to occur on PA6 and PA66 seven days after molding, with strength continuing to modestly build over the 28 day test.

In a subsequent study, multiple other types of plastics were tested using Chemlok 3S-902 with catalyst, including 15% glass filled PPA (Zytel HTN51G15 HSL by DuPont), 40% glass filled PPS (Fortron 1140L4 by Celanese), unfilled PC (Lexan 121 by SABIC), and PEEK (Ketaspire KT-880NT by Solvay). Parts were overmolded with Dow Silastic RLB9200-30 using a cure temperature and time of 160°C and 60 seconds for PPA and PPS, and a cure time and temperature of 130°C and 120 seconds for PC and PEEK. Additionally, PC was pretreated with atmospheric plasma because initial screening with non-treated PC showed very poor initial adhesion.

Again, parts were molded and then aged under ambient lab conditions and tested after 1, 7, 14, and 28 days. As shown in Figures 11 and 12, excellent adhesion was achieved after 1 day on PC, and after 7 days on PPA and PPS. Good adhesion was not achieved on PEEK.

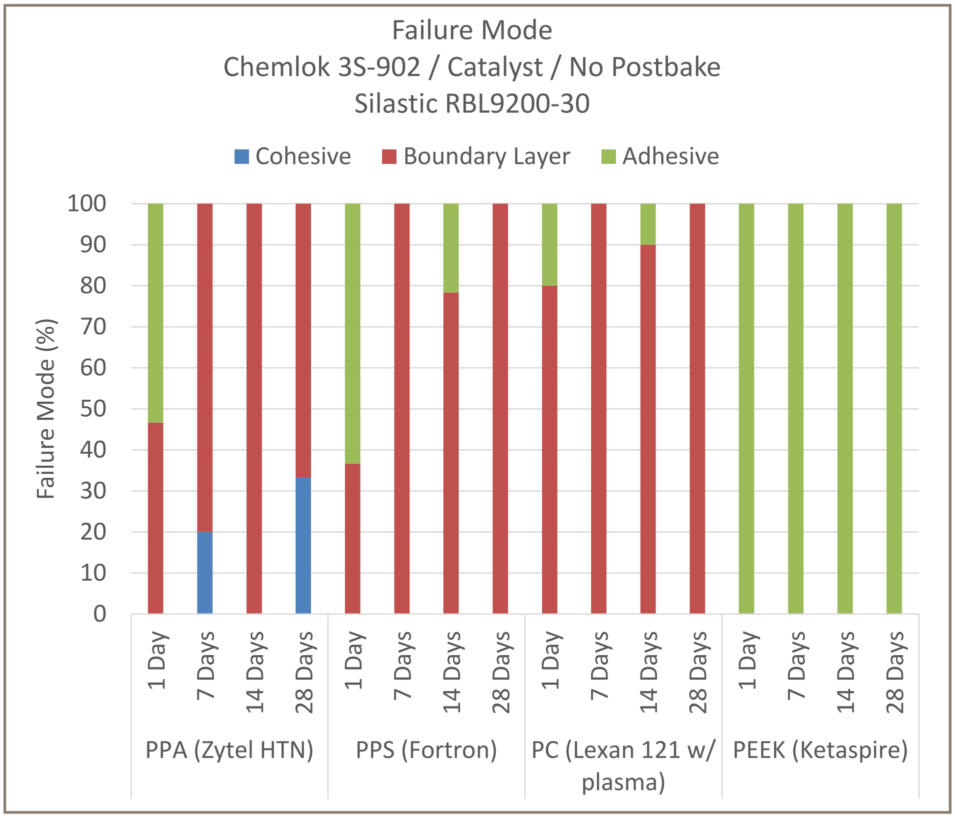

Figure 12: Failure Modes of Chemlok 3Stream Additive with Catalyst overmolded onto PPA, PPS, PC, and PEEK.

Conclusion

As demonstrated in this paper, Chemlok 3S-902 additive can convert standard LSR to self-bonding LSR. Excellent bonding performance has been demonstrated on PBT, PA6, PA66, PPA, PPS, and plasma-treated PC, giving comparable, and in many cases better, adhesion than can be achieved with commercial self-bonding LSR grades. Chemlok 3S-902 allows molders to utilize standard LSR grades that are dramatically less expensive, more widely available, have shorter lead times, and longer shelf life. This allows the molder to have much greater supply chain and design flexibility while achieving significant cost savings.

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