Silicone Reclaim for HCR Compounds

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ABSTRACT: Evaluation of reclaimed silicone polymer in HCR silicone compounds. Factors evaluated in this experiment include part level of reclaim, types of reclaim and types of formulations. Measured variables in this study are rheology properties, physical properties and processability.

Given the current market conditions for silicone polymer, users are looking for new technologies to reduce their demand and curve the cost implications. Partial polymer offsets and extenders are being widely evaluated.

Silicone reclaim technology has been around for decades. Until recently there has not been a large justification for using it nor much effort put into perfecting its uses. This study shows the capabilities for using silicone reclaim in HCR compounds.

Introduction

The reclaim evaluated in this study is cured HCR silicone compound that has been devulcanized using a unique and innovative process. The reclaim in this study is not a mesh dry powder forms of vulcanized silicone compounds.

This study looks at the physical property differences at various loadings of silicone reclaim. Peroxide technologies are evaluated to determine the best approach to linking the reclaimed material back into the HCR compound. Additionally, it reviews the performance differences when using reclaim from a higher quality compound. Lastly, we evaluate options for modifying the reclaim to better interact with the compound chemistry. Variables are evaluated for rheology, physical properties, heat age, processability and dispersion.

All processing and testing was performed at ACE Products & Consulting's independent laboratory in Ravenna, Ohio. Mixing of all formulations was done on a 1.7 liter tilt style lab mixer. Testing was performed under the following conditions.

- Slab Curing: 6' at 177°C (350°F)
- Pellet Curing: 10' at 177°C (350°F)
- Compression Set: 22 hours at 177°C (350°F)
- Heat Age: 70 Hours at 232°C (450°F)
- Tear Method: Die B
- Compression Set Method: Pellet
- Rebound Resilience Method: Pellet
- Sample Conditioning: 72°F / 22% RH

Reclaim Material

The reclaim for this study was obtained from a molding operation. Two different grades of HCR molding compounds were used in this study. The initial material was flash and fabricated components that did not meet the dimensional specification of the end customer. This material was then ground down. The smaller and more uniformed chunks allow the material to be reclaimed more easily. The chunked material is then place in an autoclave utilizing proprietary handling containers. Utilizing a combination or temperature, pressure and moisture the material is devulcanized. The times and temperatures are modified according to the type of compound being reclaimed. When the material is removed from the autoclave it is often still in its original form. While looking unchanged, it can be plied into another form with your fingers. The moisture levels are high due to the steam used during the devulcanization. This moisture must be mostly removed before the reclaim can be used in HCR compounds. Typically, it is flashed off during a heating process following the devulcanization. The material is then refined. Refining the material into a paste form improves the dispersion and breakdown of the reclaim into the HCR compound.

Part Level Evaluation

The purpose of the part level evaluation was to determine at what level of substitution, reclaim for polymer, do the physical properties start to fall off.

Table 1: Part Level Evaluation Formulation

Material	PHR
40 duro silicone base	100 / 90 / 80 / 70 / 50
Silicone reclaim	0 / 10 / 20 / 30 / 50
Ground Quartz Filler	50
Precipitated Silica	15
Pigment	1
DBPH-50	1.2

For the part level evaluation raw reclaim silicone was used. The raw reclaim is tacky and requires some additional handling. As a result, on the batches with reclaim material present the mixer rotors were coated with some of the precipitated silica before starting the mix.

Table 2: Part Level Evaluation Mix Procedure

Addition	Time
Base, Reclaim, Pigment & DBPH-50	30 Seconds
Precipitated Silica	90 Seconds
Ground Quartz	90 Seconds

The 30 PHR and 50 PHR batches had more material hang up on the mixer. The 10 PHR and 20 PHR batches mixed and milled similar to the control compound.

Picture 1: Reclaim Silicone

Rheology data showed a slow reduction in cure rate as the level of reclaim increased. The MH value dropped off on the 50 PHR compound. This is a good indicator of a lower crosslink density.

Table 3: Part Level Evaluation Rheology Data

	MH	ML	Tc90	Ts1
Control	88.47	8.54	1.33	0.57
10 PHR	89.14	9.48	1.26	0.54
20 PHR	89.06	10.38	1.26	0.54
30 PHR	83.39	10.62	1.19	0.51
50 PHR	73.31	15.53	1.19	0.53

The physical property testing corresponded with the rheology results. The 30 PHR and 50 PHR compounds had noticeable property drops. All the reclaim batches had an increase in in durometer. The increase corelated with the amount of reclaim.

The 10 PHR and 20 PHR batches had improved tensile results over the control. The tensile started a sharp drop off at 30 PHR. Elongation and tear had a downward trend in correlation with reclaim loadings. Compression set of the 10 PHR and 20 PHR did not differ much from the control, while there was a sharp drop offer on the 30 PHR and 50 PHR. The rebound did not drop off until the 50 PHR compound. Heat age results as a percentage remained similar on most properties. There was a noticeably lower percentage of drop off on the 50 PHR for tensile however that is likely due to the low initial value.

Table 4: Part Level Evaluation Basic Physicals

Test	Control	10 PHR	20 PHR	30 PHR	50 PHR
Duro	72.8	75.1	74.8	77.4	77.8
Tensile	676.3	725.9	705.3	662	559.3
Elongation	126.3	112.3	100	86.3	61.7
Tear Die B	27.8	25.8	25.4	22.8	19
Comp Set	22.22	25.37	26.92	36.57	51.88
Rebound	49.60	47.70	48.20	48.20	38

Table 5: Part Level Evaluation Heat Age Physicals

Test	Control	10 PHR	20 PHR	30 PHR	50 PHR
Duro	79	81	82	81.6	88.5
Duro %	8.52%	7.86%	9.63%	5.43%	13.75%
Tensile	593.5	620.6	618.4	576.8	537.5
Tensile %	-12.25%	-14.51%	-12.32%	-12.86%	-3.89%
Elongation	84.1	76.47	67.8	61.2	41.8
Elongation %	-33.4%	-31.9%	-32.1%	-29%	-32.2%

It was determined that the optimum substitution level for reclaim is between 10 PHR and 20 PHR.

Cure System Evaluation

The initial test formulation uses DBPH as the curative peroxide. DBPH is vinyl specific, therefore an evaluation was done adding a non-vinyl specific peroxide to the formulation. Most the vinyl groups on the reclaim are gone so it would not link in as well with a vinyl specific peroxide.

Table 6: Peroxide Evaluation Formulation

Material	PHR
40 duro silicone base	100 / 80

Silicone reclaim	0 / 20
Ground Quartz Filler	50
Precipitated Silica	15
Pigment	1
DBPH-50	1.2
VCP-40	0 / 1.2

The same mixing procedure was used as the part level evaluation. There were no processing differences observed with the peroxide addition.

Both the control compound and 20 PHR reclaim compound had improved physical properties with the addition of the VulCup peroxide.

Table 7: Peroxide Evaluation Basic Physicals

Test	Control	Control VCP	20 PHR	20 PHR VCP
Duro	72.8	74	74.8	77
Tensile	676.3	701.1	705.3	726.8
Elongation	126.3	116.1	100	69.8
Tear Die B	27.79	27.22	25.43	25.33
Comp Set	22.22	26.12	26.92	31.3
Rebound	49.6	51.9	48.2	49

Table 8: Peroxide Evaluation Heat Age Physicals

Test	Control	Control VCP	20 PHR	20 PHR VCP
Duro	79	77	82	80
Duro %	8.52%	4.05%	9.63%	3.90%
Tensile	593.5	646	618.4	617.4
Tensile %	-12.25%	-7.86%	-12.32%	-15%
Elongation	84.1	68.3	61.1	54.7
Elongation %	-33.4%	-41.2%	-38.8%	-21.6%

The addition of the non-vinyl specific VulCup peroxide did show some minor improvements on physical properties.

Reclaimed Compound Quality Evaluation

The reclaim used in the initial studies was a general purpose 50 durometer molding compound. It did not have very high specification. An evaluation was done to determine how much effect the quality of the reclaimed compound has on the end compound using the reclaim. A polymer rich 55 durometer molding compound was used in comparison. This compound has higher tear and heat age specifications. In this evaluation we ran a control, a batch with 20 PHR of the original GP reclaim and a batch with 20 PHR or the more polymer rich reclaim (HS).

Both the 20 PHR GP and 20 PHR HS processed equally. The durometer increased even more with the HS reclaim then the GP. Basic physical properties did not change much between the GP compound and the HS compound other then the durometer. Tensile, elongation, tear, compression set and rebound were almost identical. There was a noticeable improvement in heat age property loss for the HS reclaim.

Table 9: Quality of Reclaim Evaluation Basic Physicals

Test	Control	20 PHR GP	20 PHR HS
Duro	72.8	74.8	78
Tensile	676.3	705.3	705.6
Elongation	126.3	100	100.4
Tear Die B	27.8	25.4	26.3
Comp Set	22.22	26.92	26.7
Rebound	49.6	48.2	47.6

Table 10: Quality of Reclaim Evaluation Heat Aged Physicals

Test	Control	20 PHR GP	20 PHR HS
Duro	79	82	77
Duro %	8.52%	9.63%	-1.82%
Tensile	593.5	618.4	646
Tensile %	-12.25%	-12.32%	-8.45%
Elongation	84.1	61.2	68.3
Elongation %	-33.4%	-38.8%	-31.91

The quality of reclaim evaluation was repeated with the addition of the VulCup peroxide. In the previous study the non-vinyl VulCup showed small improvement on the physical properties. The same mixing procedure and formulation was used for this study. A Control with VCP, 20 PHR GP reclaim with VCP and 20 PHR HS reclaim with VCP was mixed for comparison. There were no differences observed in processing.

With the addition of the VCP the 20 PHR HS reclaim showed improvements over the GP reclaim.

Table 11: Quality of Reclaim with VCP Evaluation Basic Physicals

Test	Control	20 PHR GP	20 PHR HS
Duro	74	77	79
Tensile	701.1	726.8	749.1
Elongation	116.1	69.8	93.9
Tear Die B	27.2	25.3	25.9
Comp Set	26.12	31.30	27.48
Rebound	51.9	49	48.7

Table 12: Quality of Reclaim with VCP Evaluation Heat Aged Physicals

Test	Control	20 PHR GP	20 PHR HS
Duro	77	80	82
Duro %	4.05%	3.90%	3.80%
Tensile	646	617.4	627
Tensile %	-7.86%	-15.05%	-16.4%
Elongation	68.4	54.7	52.3
Elongation %	-41.15%	-21.6%	-44.3%

Modified Reclaim Evaluation

In this evaluation the raw reclaim was modified to improve compatibility with the chemistry of the HCR compound. A modified reclaim was made using a 50/50 blend of raw reclaim and 40 durometer silicone base. A proprietary blend of oligomers was added with a small amount of structural filler. This was done to try and provide additional site on the reclaim for it to cure into the system. This was done with a hot mix process. The modified reclaim was then compared against a control compound with no reclaim. The modified reclaim was added as a 50 PHR replacement. The modified reclaim has 50% raw reclaim in it therefore the total substitution of base to reclaim is 25%. The 20 PHR GP with VCP reclaim information was added to this evaluation for comparison.

Table 13: Modified Reclaim 50/50 Evaluation Formulation

Material	PHR
40 duro silicone base	100 / 50
Silicone reclaim 50/50	0 / 50
Ground Quartz Filler	50
Precipitated Silica	15
Pigment	1
DBPH-50	1.2
VCP-40	1.2

The modified reclaim showed superior results in basic physical properties over the 20 PHR GP / VCP reclaim. It did have an adverse effect on compression set and heat age properties however.

Table 14: Modified Reclaim 50/50 Evaluation Basic Physicals

Test	Control	20 PHR GP VCP	50 /50 Modified
Duro	74	77	80
Tensile	701.1	726.8	779.4
Elongation	116.1	69.8	88.0
Tear Die B	27.2	25.3	23.5
Comp Set	26.12	31.30	48.12
Rebound	51.9	49	46.3

Table 15: Modified Reclaim 50/50 Evaluation Heat Aged Physicals

Test	Control	20 PHR GP VCP	50 / 50 Modified
Duro	77	80	85
Duro %	4.05%	3.90%	6.25%
Tensile	646	617.4	620.0
Tensile %	-7.86%	-15.05%	-20.45%
Elongation	68.4	54.7	51.0
Elongation %	-41.15%	-21.6%	-42.05%

An additional modified reclaim was made doing a 90 /10 blend of GP reclaim with 40 durometer silicone base. A blend of proprietary oligomers and precipitated silica was used to help treat the material in a heated mix cycle. This material was evaluated as a 25 PHR offset for silicone base which equates to around 22 PHR of GP reclaim.

Table 16: Modified Reclaim 90/10 Evaluation Formulation

Material	PHR
40 duro silicone base	100 / 75
Silicone reclaim 90/10	0 / 25
Ground Quartz Filler	50
Precipitated Silica	15
Pigment	1
DBPH-50	1.2
VCP-40	1.2

The 90/10 reclaim had similar improvements as the 50/50 over the GP reclaim at 20 PHR. Like the 50/50 it also had more swing in heat age testing. The compression set was better on the 50/50 than the 90/10 however both were a higher percentage than the 20 PHR GP.

Table 17: Modified Reclaim 90/10 Evaluation Basic Physicals

Test	Control	20 PHR GP VCP	50/50 Modified
Duro	74	77	79
Tensile	701.1	726.8	738
Elongation	116.1	69.8	88.5
Tear Die B	27.2	25.3	24.95
Comp Set	26.12	31.30	35.8
Rebound	51.9	49	45.6

Table 18: Modified Reclaim 90/10 Evaluation Heat Aged Physicals

Test	Control	20 PHR GP VCP	50 / 50 Modified
Duro	77	80	84
Duro %	4.05%	3.90%	6.33%
Tensile	646	617.4	626.6
Tensile %	-7.86%	-15.05%	-15.09%
Elongation	68.4	54.7	48.2
Elongation %	-41.15%	-21.6%	-45.58%

Conclusions

Reclaim can be used as a partial substitution for silicone depending on the specification of the final compound. The quality of the material being reclaimed does have an influence on the end compound using the reclaim. A maximum of 20 PHR substitution is recommended based on the PHR evaluation. A non-vinyl VulCup peroxide can provide additional improvement to physical properties and crosslink density. Treated and modified reclaim provides improved physical properties over standard GP reclaim.

Types of compound used for reclaim and additional treatments should be explored. Depending upon the end application the reclaim source or treatment might vary. Reclaim processing parameters could be evaluated as well.