Evaluation of Crosslinking Co-Agents in HCR Silicone

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ABSTRACT: Evaluate the use of crosslinking co-agents in HCR Silicone. TAC, TAIC, and TMPTMA will be evaluated individually in DBPH, DCP, and DCBP peroxide systems. Comparative rheology and physical property analysis will be performed to evaluate the effects of the co-agents.

Peroxide	MW	% Active oxygen	1 hour half-life (°C)
Dicumyl	270.3	5.9	137
DBPH	290.44	5.5	139
DCBP	380.07	4.21	55

Introduction

HCR silicones unique properties allow it to be used in many niche ways. These unique properties include temperature stability, weatherability, compatibility, and processing ease. Silicone has a very low starting durometer in its raw state. High levels of reinforcing filler are typically needed to obtain high durometer specifications. Additionally, physical properties of silicone are generally lower than most other elastomers. This can often cause difficulties in meeting tear, modulus, compression set, or dynamic property application requirements. Application segments for silicone include automotive, wire & cable, architectural, aerospace, consumer products, and medical devices.

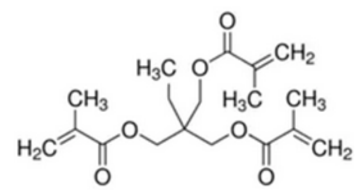
Three different crosslinking coagents were studied TAC, TAIC and TMPTMA. The general degree of crosslinking of common coagent crosslinkers is: TAIC = TAC > DVB => TMPTMA = DAP = EGDM > None

The main factors in theory affecting the increase in state of elastomer cure with the use of multifunctional coagents are the reactivity of the elastomer towards hydrogen abstraction and direct vinyl addition, the coagent compatibility with the elastomer, the stability of radical species formed, and the microstructure of the elastomer being cured. The effects of polarity differences between the coagent and elastomer may result in a broad distribution of crosslink densities due to microdomains of thermoset homopolymerized coagent.

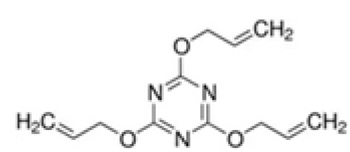
Peroxides Evaluated

This study also investigated diacyl peroxide di(1,4-dichlorobenzoyl) peroxide (DCBP), and aliphatic peroxides dicumyl peroxide and 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (DBPH).

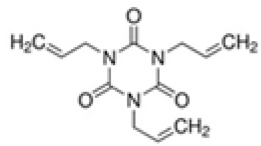
Crosslinkers Evaluated



Trimethylolpropane trimethacrylate (TMPTMA) is known to increase the rate of cure (T2 delta torque) and the extent of cure (T90, final torque) which correlates to crosslink density. Scorch time typically decreases with the addition of TMPTMA which rapidly propagate reactive radicals by addition at the double bonds. Scorch retarders may be used and with a slight increase in peroxide level, crosslink density can be maintained. TMPTMA can homopolymerize in the absence of inhibitors, while the propagating macroradical species graft to polymer chains via direct addition and abstraction mechanisms.



Triallyl cyanurate (TAC) (2,4,6-Triallyloxy-1,3,5-triazine) curing agent for rubber compounds, such as CM, EPDM, FKM and silicone. TAC is believed to increase crosslink density not only by increasing the concentrations of vinylic addition sites, but also by reducing polymer chain scission during the curing process.



Triallyl isocyanurate (TAIC) (1,3,5-Triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione) (1,3,5-Triallylisocyanuric acid) is another type II curing agent advantageously used with low-unsaturated- or saturated thermoplastics (e.g. PE, EVA, EPDM, FKM, TPV, HNBR, PMMA and PS typically under peroxide or E-beam curing.

TAIC as a Type II coagent generally exhibits greater scorch safety. TAIC as with TAC exhibits a relatively higher crosslink density (MDR delta torque) in polymers with low/no unsaturation.

Evaluation in Dicumyl Peroxide
Dicumyl peroxide is commonly used in HCR silicone molding formulations. It can also be used as a secondary peroxide in extrusion applications to enhance the crosslink density. The Dicumyl peroxide used for this evaluation was pre-dispersed in a silicone binder at a 40% activity. DCP is a vinyl specific peroxide.

Table 1 – Dicumyl Peroxide Formulations

Material	TAC	TAIC	TMPTMA	Control
40 Duro GP Silicone Base	100	100	100	100
Ground Quartz	20	20	20	20
Si-DCP(40)	1.25	1.25	1.25	1.25
TAC	5.00	0	0	0
TAIC	0	5.00	0	0
TMPTMA	0	0	5.00	0

The coagents provided a substantial boost in durometer. The TAIC increased durometer by 15.6 points without the addition of any reinforcing fillers. This increase in durometer allows for the raw compound to maintain lower viscosity, resulting in better processing ease, while reaching higher durometer targets. There was a noticeable improvement in modulus values with the addition of TAIC.

Table 2 – Dicumyl Peroxide Physical Properties

Dicumyl Peroxide Evaluation - Physical Properties				
	Durometer	**Tensile (MPA)**	**Elongation**	**300% Modulus**
TAC	56.8	7.28	443%	4.52
TAIC	63.7	6.37	315%	6.02
TMPTMA	61.9	6.19	451%	5.09
Control	48.1	6.79	484%	4.13

The compression set of the control compound was good by industry standards to begin with. There were slight losses on compression set with the addition of the co-agents, most notably with the TMPTMA. Tear strength by comparison was within typical deviation with no noticeable improvement.

Table 3 – Dicumyl Peroxide Compression and Tear

Dicumyl Peroxide Evaluation - C/S & Tear		
	Compression Set	**Tear Die B**
TAC	6.56	19.55
TAIC	6.78	18.40
TMPTMA	7.71	20.88
Control	5.27	19.51

MDR analysis was performed on the Dicumyl compounds at 177°C for 15 minutes.

The addition of the coagents did increase the MH (max torque) when evaluated on the MDR. Higher MH, more torque resistance in test, has been often correlated to crosslink density.

The ML (minimum torque) has often been correlated to flow of the raw compound or viscosity. The TAC and TMPTMA has slight increases however all values remained low.

The scorch (Ts2) sped up slightly with the TMPTMA and lengthened slightly with the TAC. None of the scorch differences were substantial. The cure time (Tc90) did increase substantially with the TAC and TMPTMA coagents. The TAIC had a slight increase in cure time over the control compound.

Dicumyl Peroxide Evaluation – Rheology (MDR)				
	MH	**ML**	**Ts2** (min.)	**TC90** (min.)
TAC	14.92	0.70	0.66	2.50
TAIC	20.28	0.52	0.52	1.80
TMPTMA	18.16	0.70	0.44	2.83
Control	11.39	0.55	0.54	1.57

The TAIC coagent provided the best overall benefit in the Dicumyl evaluation. It provided a large boost in durometer and modulus properties with the smallest impact on cure time.

Evaluation of Aliphatic Dialkyl peroxide (DBPH)

2,5-dimethyl-2,5-di(t-butylperoxy) hexane, also referred to as (DBPH), is commonly used in HCR silicone molding formulations. It can also be used in dual peroxide sponge formulations. The DBPH used in this evaluation was pre-dispersed in a silicone binder at a 50% activity. DBPH is a vinyl specific peroxide.

Material	TAC	TAIC	TMPTMA	Control
40 Duro GP Silicone Base	100	100	100	100
Ground Quartz	20	20	20	20
Si-DBPH(50)	1.25	1.25	1.25	1.25
TAC	5.00	0	0	0
TAIC	0	5.00	0	0
TMPTMA	0	0	5.00	0

As in the Dicumyl evaluation, the TAIC provided the largest increase in durometer. However, in the DBPH evaluation it had more of a negative impact on tensile, elongation and modulus. The TMPTMA provided 13.9-point increase in durometer along with a slight improvement in elongation, and a noticeable improvement in modulus.

DBPH Peroxide Evaluation - Physical Properties				
	Durometer	Tensile (MPA)	Elongation	300% Modulus
TAC	55.8	6.93	425%	4.77
TAIC	62.8	6.10	289%	-
TMPTMA	61.9	7.15	398%	5.37
Control	48.0	6.99	522%	3.63

Compression set properties were negatively impacted with the addition of the co-agent however the impact was small. Tear properties remained within standard deviation ranges.

DBPH Peroxide Evaluation - C/S & Tear		
	Compression Set	Tear Die B
TAC	6.56	19.55
TAIC	6.78	18.40
TMPTMA	7.71	20.88
Control	5.27	19.51

MDR analysis was performed on the DBPH compounds at 177°C for 15 minutes.

The max torque (MH) increased by more than double with the TAIC and had a similar increase with the addition of the TMPTMA. There were no dramatic swings in the minimum torque values and the low viscosity remained despite the large increase in durometer on the TAIC and TMPTMA.

There was a slight reduction in scorch safety with the addition of the TMPTMA however the total cure time nearly doubled.

DBPH Peroxide Evaluation – Rheology (MDR)				
	MH	ML	Ts2 (min.)	TC90 (min.)
TAC	15.18	0.68	0.70	2.51
TAIC	22.09	0.55	0.52	1.89
TMPTMA	19.44	0.74	0.40	2.53
Control	10.99	0.56	0.59	1.39

The TMPTMA coagent provided durometer and modulus increases. It did however have a large increase in total cure time. One solution could be to increase processing temperatures when adding TMPTMA to a DBPH cured HCR silicone. TMPTA would be expected to lower cure time as it is known for faster cure kinetics than the methacrylate analogue.

The TAIC did not exhibit a relative increase in cure time in comparison to the other coagents. It provided the largest durometer increase however did not perform as well with tensile, elongation and modulus. Alternative loading levels of TAIC should be evaluated to determine the amount of durometer gain that is obtainable without impacting physical properties.

Evaluation in DCBP Peroxide

Bis(2,4-dichlorobenzoyl) peroxide, also known as DCBP, is commonly used in HCR extrusion applications. It’s low decomposition temperature and short half life are ideal for continuous profile extrusion applications. The DCBP used in this evaluation was pre-dispersed in a silicone oil at a 50% activity. DCBP is considered a general-purpose peroxide and is not vinyl specific.

Material	TAC	TAIC	TMPTMA	Control
40 Duro GP Silicone Base	100	100	100	100
Ground Quartz	20	20	20	20
PD-50S-PS	1.25	1.25	1.25	1.25
TAC	5.00	0	0	0
TAIC	0	5.00	0	0
TMPTMA	0	0	5.00	0

Overall, the durometer increases obtained with the DCBP were lower than the Dicumyl and DBPH compounds. The TAIC acted adversely with the polarity of the compound resulting in plasticization effect. The durometer, tensile and modulus properties dropped considerably. The plasticization resulted in an increased elongation.

TMPTMA provided an 8.9-point durometer increase while maintaining tensile and elongation performance. Unlike the other peroxides evaluated, the DCBP control compound yielded the best modulus results.

DCBP Peroxide Evaluation - Physical Properties				
	Durometer	**Tensile (MPA)**	**Elongation**	**300% Modulus**
TAC	54.7	7.47	569%	3.33
TAIC	39.0	6.85	760%	2.32
TMPTMA	56.0	7.92	585%	3.55
Control	47.1	7.59	505%	4.23

Overall compression set of the control formulation was low. There were slight reductions in compression set performance with the addition of the coagents. Tear properties remained within standard deviation ranges.

DCBP Peroxide Evaluation - C/S & Tear		
	Compression Set	**Tear Die B**
TAC	6.56	19.55
TAIC	6.78	18.40
TMPTMA	7.71	20.88
Control	5.27	19.51

Max torque (MH) values increased with the addition of the TAC and TMPTMA. Like what was observed with physical properties performance, the TAIC had a reduction in crosslinking. All the coagents exhibited slight reductions in minimum torque (ML) properties. The DCBP evaluation was the only analysis this reduction in minimum torque was observed in.

Scorch times (Ts2) were close in-line with the TAIC compound being a slight outlier. Similar to all evaluations, the total cure time (Tc90) was increased with the addition of the co-agents.

MDR analysis was performed on the DCBP compounds at 100°C for 15 minutes.

DCBP Peroxide Evaluation – Rheology (MDR)				
	MH	**ML**	**Ts2**	**TC90**
TAC	11.58	0.73	1.01	5.00
TAIC	6.67	0.77	1.89	4.09
TMPTMA	12.70	0.65	0.99	5.60
Control	9.54	0.89	1.16	3.43

The TAIC did not respond well in the DCBP evaluation. The addition of the TAIC resulted in lower physical properties, a plasticization effect, and a weaker crosslink density.

The TMPTMA provided benefits in durometer increase and remained neutral on other physical properties measured. The TMPTMA slightly reduced scorch safety however it increased total cure time. TMPTMA could be used in DCBP systems to increase durometer without the addition of additional structural filler. Process cure temperatures may need adjusted with the addition of the TMPTMA to maintain operational efficiencies.

Dynamic Property Evaluation

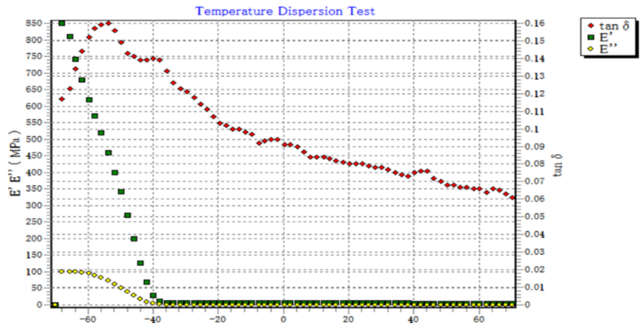
Dynamic mechanical analysis (DMA) was performed on the Dicumyl evaluations to determine comparative differences in modulus values and Tg.

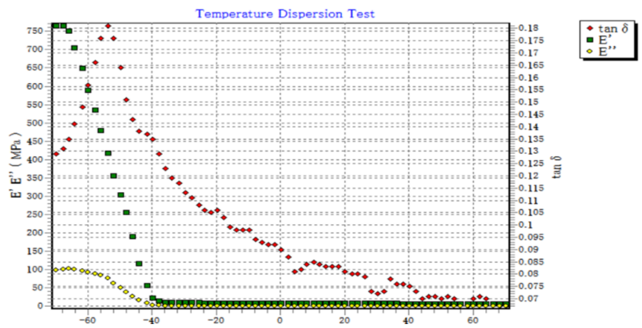
All the coagents yielded much higher storage modulus values at elevated temperatures, room temperature and zero degrees Celsius. Once reaching lower temperatures the TAC and TAIC fell behind the control while the TMPTMA maintained a slightly higher storage modulus.

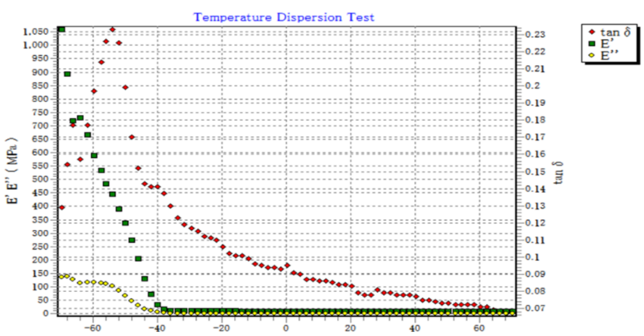
The control compound displayed a double Tg peak in the tan δ while the TAIC and TMPTMA displayed a crisper singular Tg peak. Initial Tg peak range temperatures were similar.

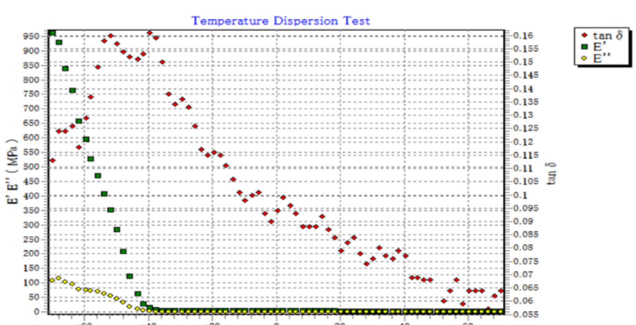
The TAIC compound has the lowest torsional stiffness rate by comparison to the control and other coagents.

Dicumyl Peroxide Evaluation – Storage Modulus (Mpa)				
Temp C	-70	0	23	70
TAC	855.88	6.24	5.81	5.01
TAIC	771.01	8.39	7.78	6.63
TMPTMA	1059.08	9.52	8.81	7.59
Control	968.35	4.2	3.98	3.69









Conclusions

In nearly all evaluations the additions of co-agents did provide durometer increases. The ability to dramatically increase durometer without the addition of structural filler can prove beneficial for mixing and downstream processing of the compounds. In some instances, tensile and 300% modulus was also improved with the addition of the co-agent. For these evaluations the addition of the coagents did not provide much positive impacts on compression set or tear properties.

TAIC proved to be the most beneficial coagent with the two vinyl specific peroxides. TMPTMA provided the best overall performance in the general purpose DCBP.

DMA analysis of the Dicumyl compounds showed improvements in storage modulus at elevated and room temperature. The TAIC showed improvements in torsional stiffness performance. Further evaluation of this effect would be worthwhile.

Further analysis and variants would be beneficial to help determine the effects of coagents. Variables to explore included highly extended compounds, dual peroxide compounds, and various loading levels of the coagents.

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