Crosslinking of silicone rubber with peroxides

Application guide

Nouryon

Properties of silicone rubber

Silicone rubber is known for various properties

- Good chemical resistance (oil, fuel)
- Flame resistance
- Inertness
- Excellent dielectrical properties
- Applied in wide temperature range

With usage in:

- Medical, food
- Household articles, kitchen ware
- Wire & Cable
- Transportation
- Consumer goods

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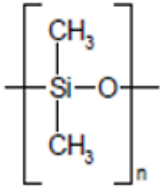
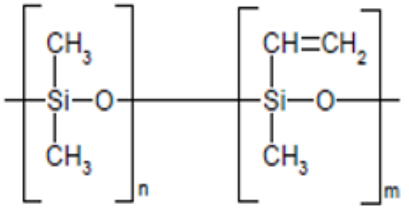
What is silicone rubber?

Silicone rubber is a polymer consisting of repeating silicone-oxygen units. Attached to this backbone, various organic groups can be attached. Typical components for silicone rubber are crosslinking agents (peroxide, platinum), fillers (reinforcing or non-reinforcing), stabilizers, colorants, other additives.
Below 4 types of silicone rubber are shown:

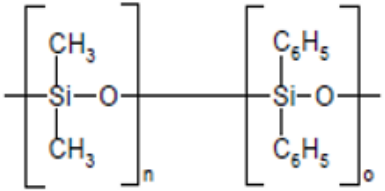
MQ	polydimethylsiloxane (PDMS), 2 methyl groups bound to the siloxane backbone
VMQ	vinyl methyl polysiloxane vinyl improves crosslink density
PVMQ	phenyl vinyl methyl polysiloxane phenyl group acts as scorch retarder
FMQ	trifluoropropyl vinyl polysiloxane polarity boosts cure speed



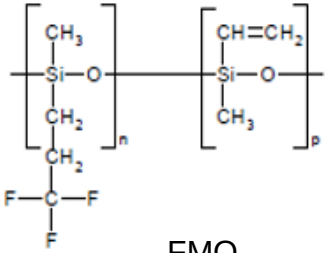
MQ



VMQ



PVMQ



FMQ

Fast curing peroxides

Product	Composition	Physical form	Recommended minimum cure temperature (°C)	Dosing (phr)
Perkadox PD-50S-PS*	50% active di(2,4-dichlorobenzoyl) peroxide	Paste	90	1.1 – 2.3
Perkadox L-50S-PS	50% active Dibenzoyl peroxide	Paste	105	0.7 – 1.4
Perkadox PM-50S-PS*	50% active Di(4-methylbenzoyl)peroxide	Paste	105	0.8 – 1.6
Trigonox C	Tert-butyl peroxybenzoate	Liquid	140	0.3 – 0.6
Trigonox C-40B-PD	40% active Tert-butyl peroxybenzoate	Powder		0.8 – 1.5

***Can be used in pressureless cure (infra-red, hot air)**

Paste formulations are recommended in silicone rubbers, they are easy to handle, easy to mix in and safe in use. Also, paste formulations yield transparent final articles.

For applications where transparency is not of importance, a powder formulation can be applied as well.

High temperature peroxides

Product	Chemical name	Physical form	Recommended minimum cure temperature (°C)	Dosing (phr)
Perkadox BC-FF	40% active Dicumyl peroxide	Crystalline	150	0.4 – 0.8
Perkadox BC-40S-PS		Paste		1.0 – 2.0
Perkadox BC-40B-PD		Powder		1.0 – 2.0
Perkadox 14S-FL	40% active Di(tert-butylperoxyisopropyl) benzene	Flakes	160	0.15 – 0.3
Perkadox 14-40B-PD		Powder		0.4 – 0.8
Trigonox 101	45% active 2,5-di(tert-butylperoxy)-2,5-dimethylhexane	Liquid	160	0.4 – 0.8
Trigonox 101-45B-PD		Powder		1.0 – 1.9
Trigonox 101-45S-PS		Paste		1.0 – 1.9

High temperature peroxides are preferred peroxides when compression set is an important parameter.

Perkadox BC and Trigonox 101 are positive listed in various food- and drinking water guidelines.

Summary

Perkadox PD
Halogen containing peroxide, quick onset, no external pressure needed, sensitive to carbon black, potential bloom formation

Perkadox PM
Halogen free peroxide, higher crosslinking temp. than Perkadox PD, sensitive to carbon black, less blooming than Perkadox PD.

Perkadox BC
Pure product is crystalline material with a melting point close to 40°C, formation of typical smell (acetophenone) after cure

Perkadox 14
Very efficient peroxide

Trigonox 101
Positive listed in various food- and drinking water guidelines

Concluding remarks

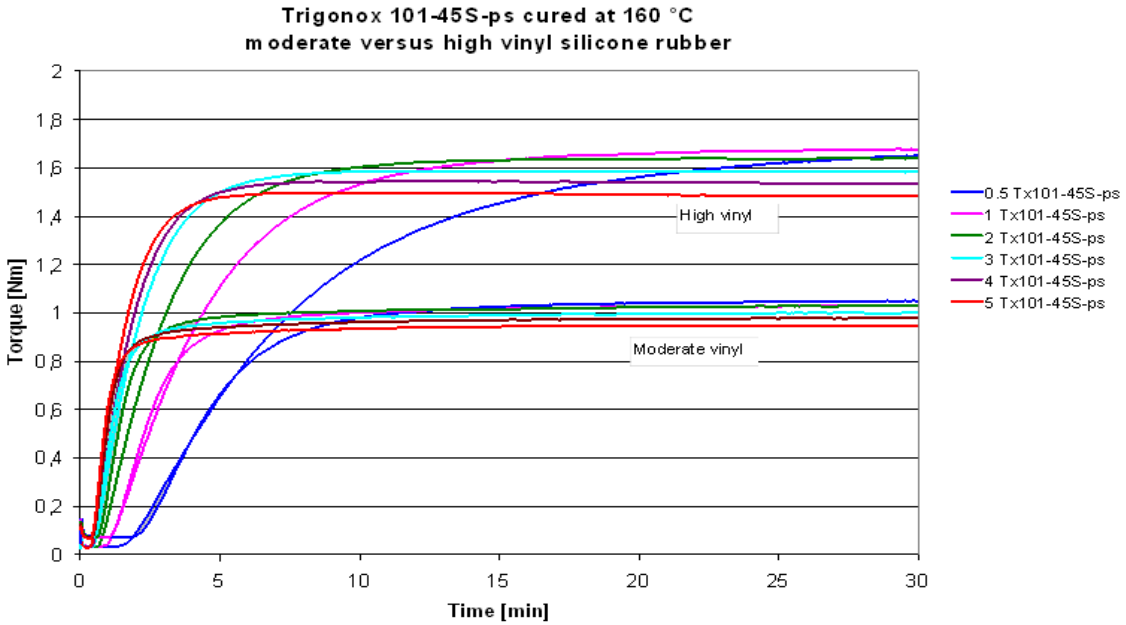
- A broad range of organic peroxides is available for the crosslinking of silicone rubber.
- Paste based formulations are recommended for safety, and to facilitate handling, mixing, and processing.
- Care should be taken in selecting specific compounding ingredients, e.g. conductive black does have a dramatic impact on the crosslink efficiency of diacyl peroxides (Perkadox PD and Perkadox PM).
- Physical properties of peroxide cured silicone rubber, strongly depend on polymer composition, silicone rubber with a high vinyl content does lead to higher crosslink densities.
- Silicone formulations containing thermal stable peroxides can be stored at ambient temperature over a long period of time without starting to react.

Tips & Tricks

Impact vinyl content on crosslink density

Silicone rubbers are available with different vinyl content. High vinyl content results in higher crosslink density.

Increasing the amount of peroxide has limited effect on the final crosslink density, but a large influence on the crosslink speed!

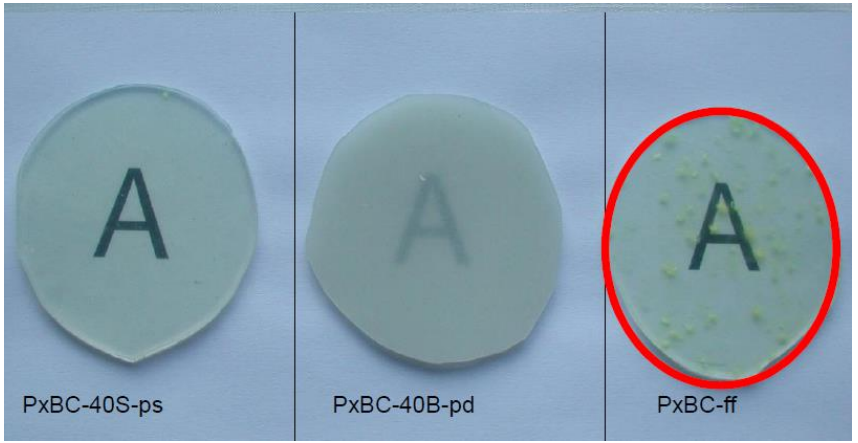


Perkadox BC: impact formulation type

Due to the low temperature and friction during silicone rubber compounding, the Perkadox BC crystals are not dispersed optimal into the compound (the crystals remain). After cure, they appear as yellow spots in the compound, which is seen in the right sample in the picture.

Perkadox BC-40B-pd can be used to crosslink silicone rubber, but the $CaCO_3$ causes a hazy end product (middle example).

For a clear product, Perkadox BC-40S-ps is recommended.



Perkadox PD vs Perkadox PM

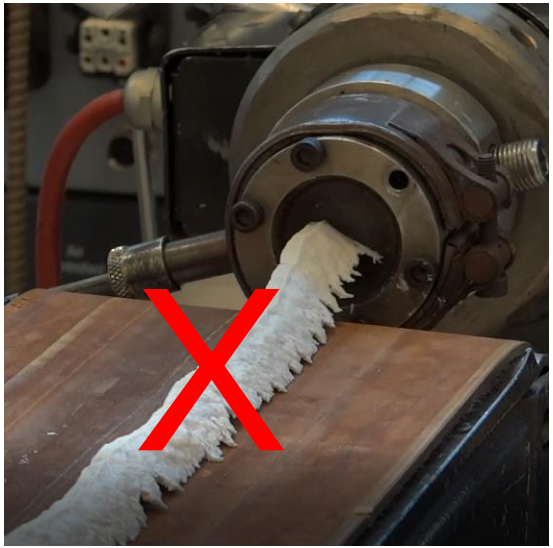
Influence of storage temperature

Impact storage time and temperature on processing performance.

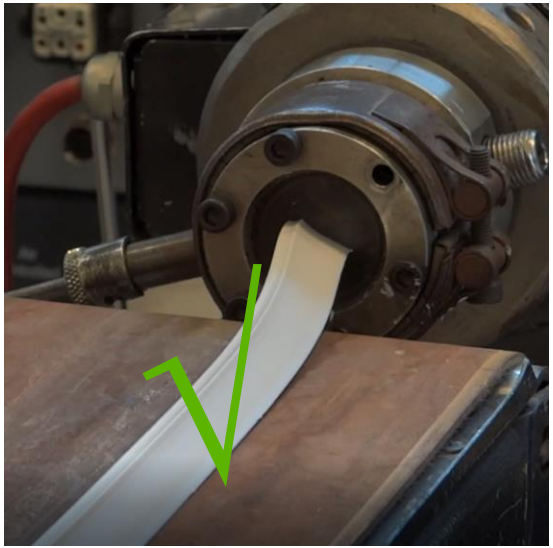
Extruder equipped with a Garvey die - test at room temperature.

Perkadox PD is more reactive than Perkadox PM and shows scorch behavior in the left figure. This is unwanted behavior during processing, as crosslinking should only occur in the final crosslinking step.

1 phr Perkadox PD-50S-ps 1 week storage (45°C)



0.8 phr Px PM-50S-ps 1 week storage (45°C)



Post-cure

The aim of post-cure is to outgas volatile components. These components are either originating from the SI rubber compound or related to decomposition products of the peroxide. Furthermore, the post-cure process is helpful in completing the cure (optimizing properties).

Typical post-cure settings are 4 hours at 200°C. For very critical parts like medical applications, 8 hours at 200°C could be used. Products should be placed in an oven with sufficient ventilation and products should have open air surrounding it.

For large sized articles, longer post-cure settings are recommended.

Source: https://www.simtec-silicone.com/secondary-operations/post-cure