Crosslinking of EP(D)M with peroxides

Application guide

Nouryon

Properties of EP(D)M rubber

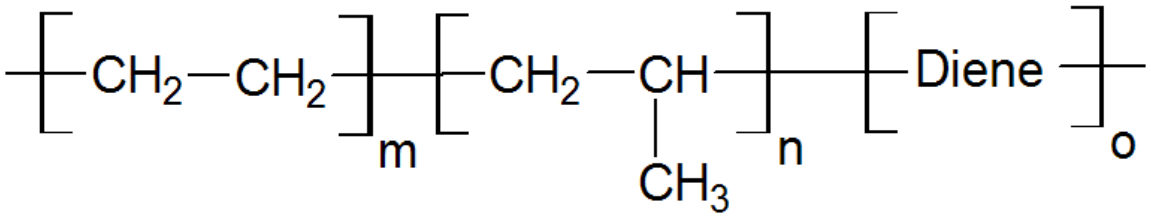
EP(D)M is a rubber with an excellent:

- Resistance to heat
- Resistance to oxidation
- Resistance to ozone
- Resistance to weather aging due to saturated polymer backbone
- Good electrical resistivity
- Chemical resistance to polar solvents
- Low crystalline grades have good temperature flexibility

With usage in:

- Transport
- Building & Construction
- Wire & Cable
- General rubber goods

What is EP(D)M rubber?



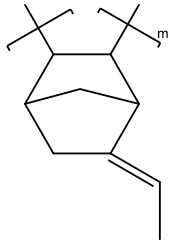
EP(D)M (ethylene propylene diene monomer rubber) has a saturated backbone and is therefore classified as a M-type rubber. There are mainly three parameters that influence the rubber properties:

- Diene type (not applicable for EPM rubber!)
- Ethylene-Propylene ratio
- Mol. weight distribution

Note: EPDM rubbers in general are low reactive rubbers, hence needing relative high amounts of curatives.

Influence of EP(D)M parameters

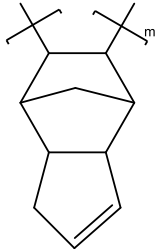
Diene type (not applicable for EPM rubber!)
The number of types of third monomer used for commercial EPDM grades is limited: usually DCPD or ENB. Although in case of sulfur-based systems, the influence of the diene type on the curing characteristics is pronounced, only minor differences between the diene types are usually observed when crosslinking peroxides are used.



Ethylidene norbonene (ENB)

Molecular weight distribution
This parameter in combination with molecular weight distribution (MWD), mainly affects rubber processing behavior. Nevertheless, an influence on the efficiency of peroxide crosslinking can be expected too. Crosslinking of high molecular weight material will be more efficient with the identical amount of peroxide than a low molecular weight material.

The same holds for a narrow MWD in comparison with a broad MWD polymer. The former type can be crosslinked more efficiently, due to the absence of low molecular weight polymer.



Dicyclopentadiene (DCPD)

Influence of EP(D)M parameters

Ethylene-propylene ratio

The ethylene-propylene ratio and especially the alternating character are important factors influencing the results of peroxide crosslinking, as in particular consecutive propylene units are prone to give rise to unwanted scission reactions in presence of reactive peroxides. The scission reaction can be counteracted by the use of effective coagents, see page 9.

Although scission reactions can be expected in all polymers where adjacent propylene units are present, the effect is more pronounced for ethylene-propylene copolymers (e.g. EPM) than for the terpolymer types.

Higher ethylene content is typically better (less chain scission).

Peroxides used for EP(D)M rubber

Product	Chemical name	Physical form	Recommended minimum cure temperature (°C)	Dosing (phr)
Perkadox BC-40	40% active dicumyl peroxide	Powder, granule or polymer bound	170	6.1 – 10.1
Perkadox 14-40	40% active di(tert-butylperoxyisopropyl)benzene	Powder, granule or polymer bound	175	3.8 – 6.3
Trigonox 101-45	45% active di(4-methylbenzoyl)peroxide	Powder, granule or polymer bound	175	3.7 – 6.1
Alternatively, below peroxides can be used as kicker for a fast onset of cure, in combination with the peroxide types above.				
Trigonox 17-40	40% active butyl 4,4-di(tert-butylperoxyl)valerate	Powder, granule or EPR bound	160	7.5 – 12.5
Trigonox 29-40	40% active 1,1-di(tert-butylperoxyl)-3,3,5-trimethylcyclohexane	Powder, granule or EPR bound	145	6.8 – 11.3

The carrier system can be based on calcium carbonate, silica, and/or clay.

For fast dispersion, polymer bound formulations are recommended!

Remarks per peroxide

All below peroxides have a good efficiency.

Perkadox BC
Excellent price-performance ratio! Acetophenone is formed after decomposition, which has a typical smell.

Perkadox 14
Preferred peroxide for EP(D)M. Can form decomposition products showing potential to migrate to the surface (bloom). This depends on concentration and polymer polarity.

Trigonox 101
Aromatic free crosslinking peroxide! Low molecular weight decomposition products, which are relatively easy to remove by post-cure. Frequently applied for rubber articles coming into contact with food- and/or drinking water.

Advantages of peroxide crosslinking in comparison to sulfur cure

- Simple formulation
- Storage of the peroxide-containing compound without bin scorch
- High processing temperature
- Rapid vulcanization without reversion
- Good compression set, particularly at elevated temperatures
- High temperature resistance
- Limited extractable constituents from final product
- No staining of the finished parts
- No discoloration of crosslinked product by contact with metals and PVC
- Most peroxides do not cause blooming
- Co-vulcanization of saturated and unsaturated elastomers
- Co-vulcanization of elastomers and thermoplastics
- Copolymerization with polymerizable plasticizers or coagents to give controlled hardness and stiffness, coupled with easy processing.

Points of attention for peroxide crosslinking

- Sensivity to oxygen under curing conditions
- Certain components of the rubber compound such as
  - Fillers
  - Extender oils
  - Antioxidants
  - Resins

  must be selected with care because they may, under certain conditions, consume free radicals
- Usually, tensile and tear strength properties are reduced by about 15%, when compared to a conventional sulfur based crosslinking system.
- Scorch and cure time are less flexible, since they are determined mainly by the temperature
- During cure, some peroxides may lead to distinct odors
- Post cure may be necessary

Coagents

By using a coagent, several properties can be improved. Typical coagents for peroxide cure are:

Allyl-containing	TAC, TAIC
Methacrylate	TRIM, E(G)DMA
Various	Sulfur, 1,2-BR, bimaleïmide

Dosing range: 0.5 – 2% (for sulfur 0.1 – 0.3%)

Property	Allyl	Metacrylate	Sulfur
Rheology			
Min. viscosity	Reduced	Reduced	No effect
Scorch time	Small / no effect	Reduced	No effect
Cure time	Small / no effect	Reduced	No effect
Degree of XL	Increased	Increased	Increased
Physical properties			
Hardness	Increased	Increased	Small / no effect
Tensile strength	Small effect	Small effect	Increased
Modulus	Increased	Increased	Increased
Elongation at break	Reduced	Reduced	Increased
Tear strength	Small effect	Small effect	Increased
Deformation resistance	Improved	Improved	Reduced
Heat resistance	Improved	Improved	Reduced

Concluding remarks

- A broad range of organic peroxides is available for the crosslinking of EP(D)M rubber.
- Peroxide formulations are recommended for safety, and to facilitate handling, mixing, and processing.
- For fast dispersion, polymer bound formulations are highly recommended!
- The application of coagents can improve several properties