Rubber Production Methods-2. Vulcanization Types

Vulcanization is the process by which plastic rubber is converted into the elastic rubber or hard rubber state. The process, which is brought about by the linking of macromolecules at their reactive sites, is also known as crosslinking. Vulcanizing agents are substances that bring about the actual crosslinking process. The properties of the vulcanised rubber are influenced by the course of vulcanization.

In particular the modulus, hardness, elastic properties and resistance to swelling are considerably modified during the course of vulcanization. The extent of the changes is governed by the choice of the vulcanization ingredients added to the rubber to bring about the vulcanization process and also by the

Other properties, such as tensile strength, gas permeability, low temperature flexibility and electrical resistance, change less with the degree of vulcanization.

To obtain rubber products with the best possible properties, it is therefore always necessary to use the most suitable combination of vulcanization ingredients and the most suitable vulcanization conditions subjected to the application concerned.

Various chemical - vulcanizing - agents are used to create the chemical transverse bonds between rubber macromolecules (such as sulphur, peroxides, metal oxides, resins, quinones and others), which can react with appropriate functional rubber groups in the process of vulcanization to create transverse bonds between them.

Anyway, the optimum vulcanizate (rubber) properties cannot be achieved only by cross-linking rubber molecules, but other additives must be added. Besides crosslinking agents and antidegradants, they include fillers that have a positive influence on some of the utilisation properties and make them cheaper, as well as additives allowing admixture of all the powdery or liquid

Peroxide Vulcanization

In peroxide vulcanization, direct carbon cross-links are formed between elastomer molecules as shown in Figure (i.e., no molecular bridges as there are in sulfur cures.)

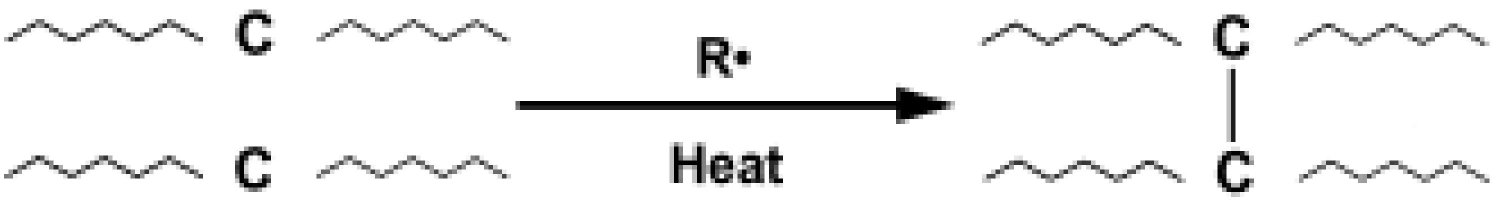
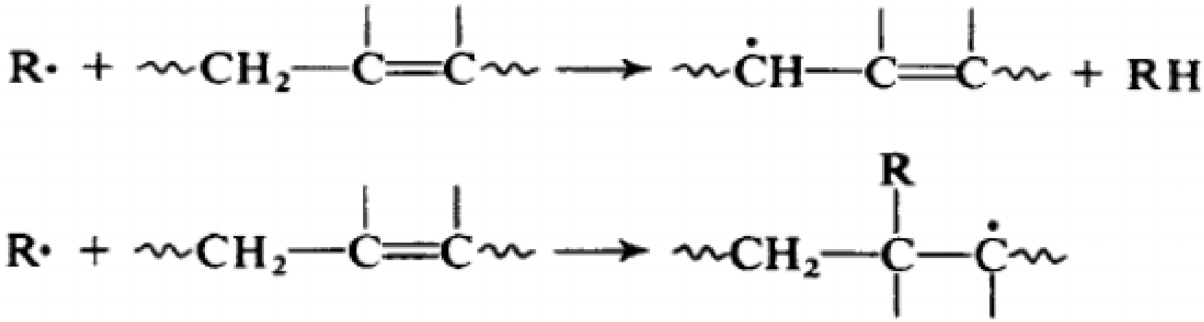
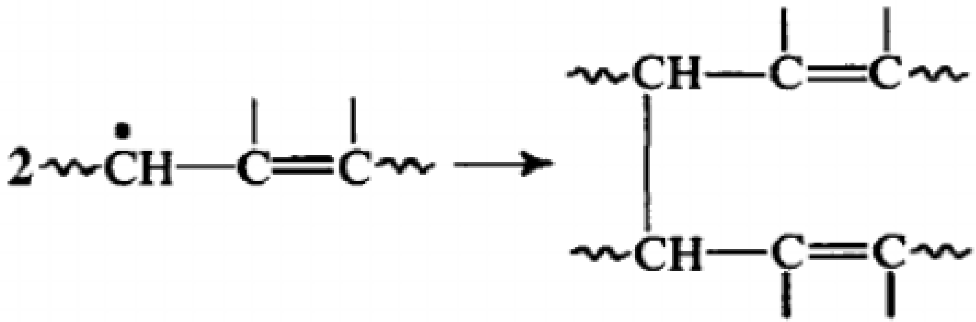


Figure 5 Peroxide-initiated vulcanization.

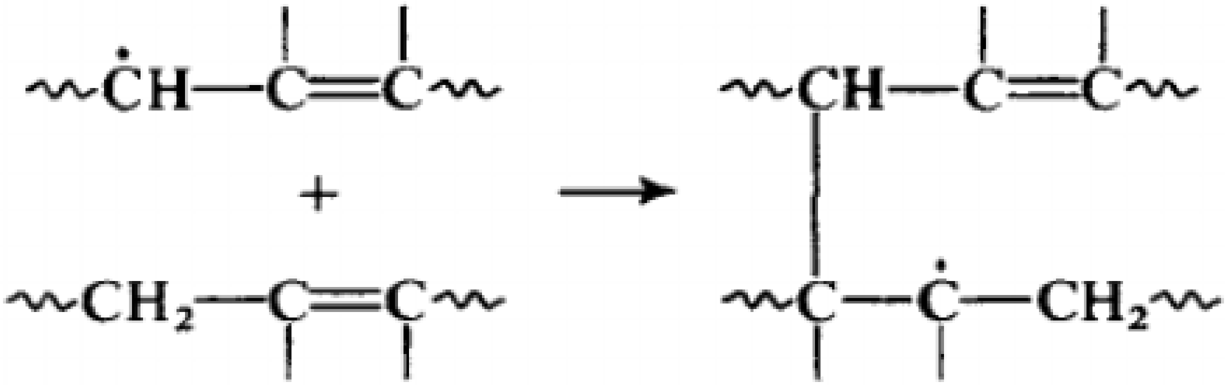
The peroxides decompose under vulcanization conditions, forming free radicals on the polymer chains, which leads to the direct formation of crosslinks.

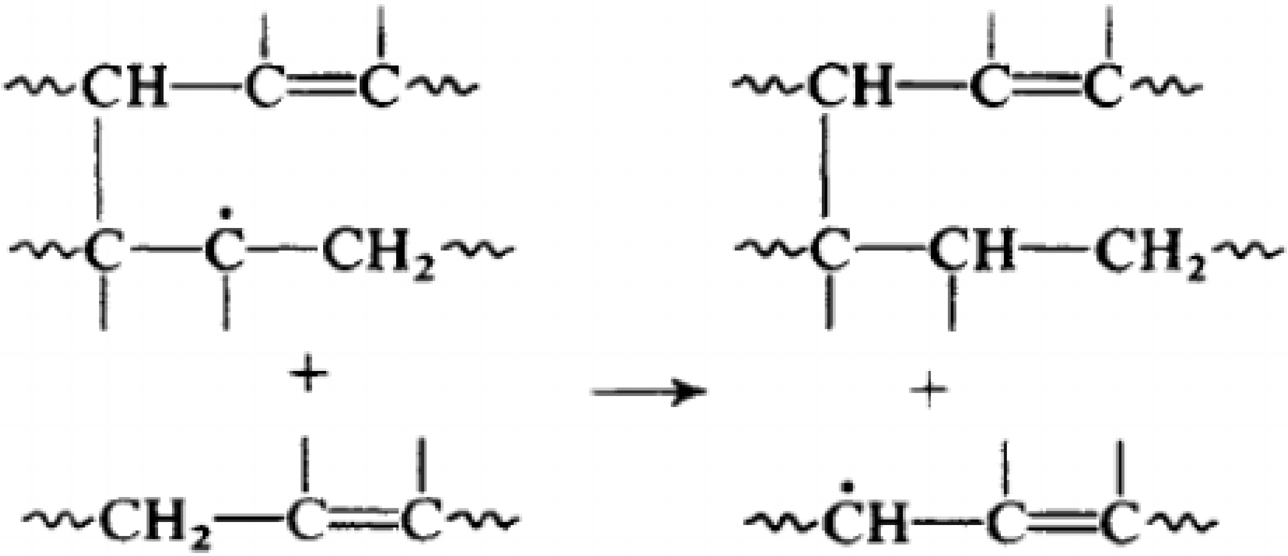


For isoprene rubber, the abstraction route predominates over radical addition. Two polymeric free radicals then unite to give a crosslink.



In this case crosslinking occurs without the loss of a free radical so that the process can be repeated until termination by radical coupling. Coupling can be between two polymeric radicals to form a crosslink or by an unproductive processes





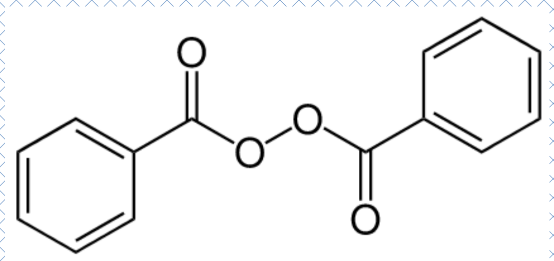
Peroxides can be used to cross-link a wide variety of both saturated and unsaturated elastomers, whereas sulfur vulcanization will occur only in unsaturated species.

In general, carbon–carbon bonds from peroxide-initiated cross-links are more stable than the carbon–sulfur–carbon bonds from sulfur vulcanization.

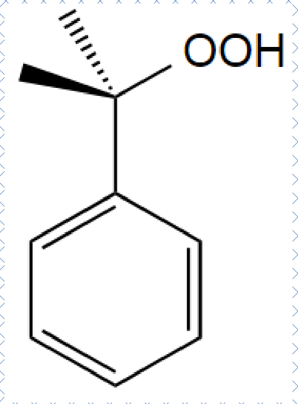
In theory, peroxide vulcanization, giving simple carbon-carbon crosslinks, (Greensmith, Mullins and Thomas [1]) should provide a close to ideal crosslinking system with good heat resistance. However, in practice the system have a number of disadvantages such as scorch times are short and cure times are long. Furthermore, many antioxidants, particularly p-phenylenediamines, interfere with peroxide vulcanization such as reducing efficiency.

REF: [1]: Jurnal Teknologi, bil. 25, Disember 1996 him. 19-25 -1. Ref

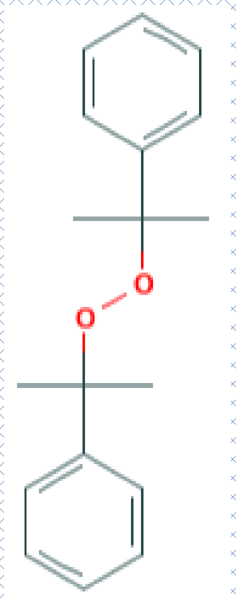
A wide variety of organic peroxides are available, including products such as benzoyl peroxide and dicumyl peroxide. Proper choice of peroxide class must take into account its stability, activity, intended cure temperature, and effect on processing properties.



Benzoil peroksit

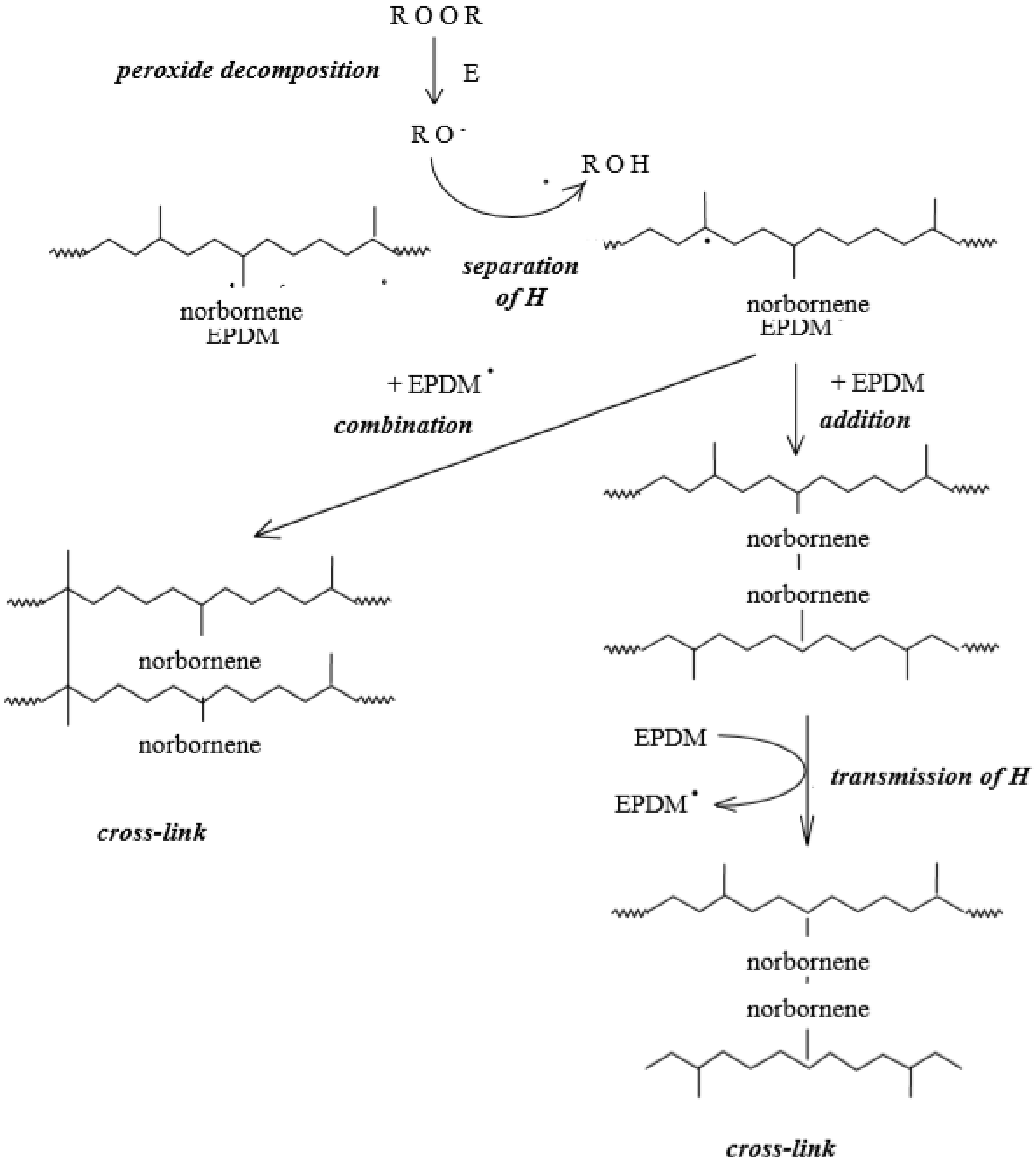


Kümen hidroperoksit



Dikümil peroksit

Carbon–carbon cross-links can also be initiated by gamma or X-radiation; these presently find limited commercial application.



Simplified reaction scheme of peroxide cross-linking of EPDM

A study shows that the better antioxidant cause the greatest reduction in crosslinking density, Baker [2]. Another disadvantage is in w1 aged vulcanizates properties, both tensile and tear strength are inferior to conventionally cured NR vulcanizates and tension fatigue lifetimes are slow. Abrasion resistance is also inferior to conventional sulphur cure and the used of dicumyl peroxide imparts unpleasant odour to the vulcanizates. The advantages of peroxide systems lie in excellent reversion resistance, good oxidative ageing resistance and improved high temperature set properties . The problem of the slow vulcanization characteristic of peroxide can be overcome by increasing their concentration in the mix. Since the system is non-reverting, vulcanizates of the same modulus can be obtained by the used of increased concentration of dicumyl peroxide with shorter cure times. However, traces of peroxide that are still

REF: [2]: Jurnal Teknologi, bil. 25, Disember 1996 hlm. 19-