

# VULCANIZATION OF RUBBER COMPOUNDS WITH PEROXIDE CURING SYSTEMS

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## ABSTRACT

Vulcanization or curing is one of the most important processes in rubber technologies. During this process, plastic rubber compounds by parallel and subsequent physical and mainly chemical reactions change into highly elastic products—vulcanizates. The fundamental goal of curing is forming chemical cross-links between rubber macromolecules, which leads to the formation of a three-dimensional network or rubber matrix. A number of curing systems have been introduced in cross-linking of elastomers; each system has its own characteristics and composition; therefore, vulcanizates with different properties also can be prepared. We characterize organic peroxides as curing agents and their decomposition mechanisms and characteristics and bring a detailed view to understanding mechanisms between peroxides and different types of rubber matrices. Then, we focus on the classification and characterization of co-agents used in peroxide cross-linking and explain the mutual interactions and reaction mechanisms between peroxide, co-agents, and rubber matrices in relation to the properties of prepared materials. Finally, the drawbacks and the main features of final cross-linked materials are outlined. [doi:10.5254/rct.16.83758]

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## I. INTRODUCTION

Rubbers—vulcanizable elastomers—are unique and versatile materials characterized by their ability to be reversibly deformed under the influence of external deformation forces. The degree of deformation depends on the structure and molecular weight of the rubber and external conditions of deformation; at low deformation strains it can reach from percentages in the hundreds to the thousands. This property is called elastic or highly elastic deformation. It relies on the ability of rubber macromolecules to get into more ordered states under the influence of deformation forces, from the most thermodynamically favorable clew shape into stretched form, without breaking chemical bonds between rubber chains or deforming bond angles. In the ideal case, when deformation forces are removed, the rubber chains can return back to their initial positions. Elastomers thus exhibit elastic or viscoelastic behavior.<sup>1</sup>

In the amorphous, un-cross-linked elastomers over their glass transition temperature, the ability to resist deformation is directly proportional to the entanglements of the constituting macromolecular chains. However, these chain entanglements and bindings are not permanent, and elastomers are not able to maintain their resistance to deformation. For this reason, the rubber materials are not suitable for use in applications requiring dimensional stability under prolonged periods of strain.<sup>2</sup> The dimensional stability of elastomers can be achieved during the process of vulcanization, often called curing or cross-linking among engineers. The foundation of vulcanization is the formation of chemical cross-links between rubber macromolecules, which leads to the formation of a three-dimensional network within the rubber matrix, by reactions between the functional groups of elastomer chains and suitable curing agents. This network can keep the chains in position after being submitted to the prolonged deformation forces, thus providing the required stability. Moreover this network improves elasticity, strength, and modulus and reduces hysteresis and plasticity.<sup>3</sup>

A number of curing systems have also been developed in order to vulcanize rubber compounds, such as sulfur, peroxides, metal oxides, phenolic resins, quinones, and so on. The type of applied curing system determines the structure and the quality of the cross-links. Also, the type of rubber matrix must be considered when cross-linking elastomers, especially their chemical nature and the presence of suitable functional groups. Recently, sulfur and peroxide curing systems are the most frequently used for cross-linking of rubber materials.

The sulfur vulcanization of rubber compounds was first introduced in 1839 by American Charles Goodyear (patent from 1844) and Englishmen Thomas Hancock in 1842 (patent from 1843), and it is still the most widely used method for cross-linking of unsaturated rubbers.<sup>4-6</sup> Despite the fact that sulfur vulcanization has been known for over 150 years, the chemistry of sulfur vulcanization is very complex and still not clearly understood. Both free radical and ionic mechanisms relating to the chemical pathways running during sulfur vulcanization have been suggested and considered.<sup>7,8</sup> Application of sulfur curing systems leads to the formation of different types of sulfidic cross-links between rubber macromolecules. Generally, sulfur cured vulcanizates exhibit good elastic and dynamic behavior and possess high values of tensile and tear strength. However, due to the low dissociation energy of sulfidic cross-links, sulfur cured vulcanizates exhibit poor high temperature properties like aging, for instance.<sup>1,9</sup>

Cross-linking of rubbers with organic peroxides was first examined by Ostromislensky in 1915.<sup>10</sup> Peroxides can be used to vulcanize both unsaturated and saturated elastomers. The latter cannot be cross-linked with sulfur curing systems. Industrial interest in application of peroxides as cross-linking agents became more obvious with the introduction of many saturated rubbers, mainly ethylene-propylene type rubbers (EPM, EPDM), or fluoro elastomers (FKM), and so on.<sup>11-13</sup> At the present time, peroxides are used as cross-linking agents for elastomers to prepare vulcanizates

with good high temperature aging resistance or to vulcanize blends, which consist of a combination of saturated and unsaturated elastomers.<sup>1</sup>

## II. PEROXIDE VULCANIZATION

### A. ORGANIC PEROXIDES AS CURING AGENTS

Organic peroxides are molecules containing of at least two oxygen atoms connected by a single bond to organic chemical groups. The general structure of organic peroxide can be described as  $R-O-O-R'$ , where  $R$  and  $R'$  represent other chemical groups, which are bonded to peroxy  $O-O$  group. The relatively weak oxygen–oxygen bond (bonding energy  $\sim 150$  kJ/mol) undergoes homolytic cleavage to form oxygen centered alkoxy radicals ( $R-O\cdot$ ) as their primary decomposition products.<sup>14–16</sup> The breakage of the labile  $O-O$  bond is usually triggered by heat.

According to the chemical composition, organic peroxides introduced in cross-linking of elastomers belong to the aliphatic, aromatic, and mixed peroxides, and some of them can have more than one peroxy group. In addition to symmetrical peroxides, those with asymmetrical or polymeric structure are applied, too.<sup>17</sup> Depending on the chemical nature, peroxides used in cross-linking of rubber compounds can be classified into six groups:<sup>18,19</sup>

- dialkylperoxides,  $R-O-O-R$ ;  $R$ , alkyl group
- alkyl–aralkyl peroxides,  $R-O-O-R'$ ;  $R$ , alkyl group,  $R'$ , aryl group
- diaralkyl peroxides,  $R'-O-O-R'$ ;  $R'$ , aryl group
- diacylperoxides,  $R-C(O)-O-O-(O)C-R'$ ;  $R$ ,  $R'$ , alkyl and/or aryl groups
- peroxyketals,  $R-O-O-(R)C(R')-O-O-R'$ ;  $R$ ,  $R'$ , alkyl and/or aryl groups
- peroxyesters,  $R-C(O)-O-O-R'$ ;  $R$ ,  $R'$ , alkyl and/or aryl groups

In addition to the ability of peroxides to perform efficient cross-linking of the rubber matrix, there are also some other requirements for the selection of a suitable peroxide: it must be stable during preparation, processing, and storage of rubber compounds; it should decompose fast at vulcanization temperature; and the concentration of active radical fragments must be sufficiently high to generate an adequate cross-link network structure within the rubber matrix.<sup>20–22</sup> These requirements are fulfilled mainly by peroxides with peroxy group fixed to the tertiary carbon. Peroxides with peroxy group bonded to the primary or secondary carbon are less stable.<sup>17</sup> Generally dialkyl, alkyl–aralkyl, and diaralkyl peroxides belong to the most thermally stable class of peroxides. Their thermal decomposition leads to the formation of  $R-O\cdot$  and/or  $\cdot O-R'$  free radicals. Diacylperoxides exhibit limited thermal stability, decomposing at relatively low temperatures into  $R-C(O)-O\cdot$  and  $\cdot O-(O)C-R'$  radicals. Similarly peroxyketals (also known as perketals) and peroxyesters (peresters) are thermally less stable compounds, forming  $R-O-O-(R)C(R')-O\cdot$  and  $\cdot OR'$  radicals in the case of peroxyketals, and  $R-C(O)-O\cdot$  and  $\cdot O-R'$  free radical fragments in the case of peroxyesters when heating. Owing to the low thermal stability, the use of these peroxides in cross-linking of rubber compounds is fairly restricted.<sup>23</sup> For example, diacylperoxides are primarily used as cross-linking agents for some types of silicone rubbers.<sup>1</sup> Peroxides applied as cross-linking agents for rubber compounds should also be nonvolatile, nontoxic, nonirritating, and safe to handle.

The most important characteristics of the peroxide used for cross-linking is its decomposition rate generally expressed by half-life time or half-life temperature.<sup>23–25</sup> The half-life time ( $t_{1/2}$ ) is defined as the time required to decompose one half of the initial amount of the peroxide at a certain temperature. Correspondingly, the half-life temperature is the temperature at which one half of the initial amount of the peroxide is decomposed in a given time. The correlation between the number of half-lives and the percentage of peroxide decomposition is shown in Table I.<sup>26</sup> This means that after

TABLE I  
HALF-LIVES VS PERCENTAGE OF PEROXIDE DECOMPOSITION<sup>26</sup>

Number of half-lives	Peroxide decomposition (%)
0	0
1	50
2	75
3	87.5
4	93.75
5	96.9
6	98.4
7	99.2
8	99.6
9	99.8
10	99.9

one half-time, 50% of the peroxide is decomposed, 75% after two half-times, 87.5% after three half-times, while almost total decomposition of the peroxide occurs after 10 half-times.

The rate of cross-linking initiated by the peroxide is determined by its rate of thermal decomposition. Half-life data are important in the selection of the optimal peroxide for specific time/temperature applications. The peroxide stability is often expressed in terms of 1 minute, 1 hour, and 10 hour half-life temperatures, which are the temperatures at which one half of the peroxide is decomposed in 1 minute, 1 hour, and 10 hours, respectively.

The cross-linking is directly proportional to the amount of the peroxide decomposed; therefore at least 6 to 10 half-lives of the peroxide decomposition are suggested for cross-linking reactions. For a typical peroxide, the half-life time falls by one-third of its value for each 10 °C rise in temperature.<sup>14,27</sup>

The half-life is usually evaluated by using differential scanning calorimetry–thermal activity monitoring (DSC-TAM) of a dilute solution of the peroxide in monochlorobenzene.<sup>28–30</sup> Theoretically, the dependence of the half-life on temperature can be described by an Arrhenius equation;<sup>25</sup>

$$k_d = A e^{-\frac{E_a}{RT}} \quad (1)$$

$$t_{1/2} = \frac{\ln 2}{k_d} \quad (2)$$

where  $k_d$  = rate constant for the peroxide decomposition ( $s^{-1}$ )

$A$  = Arrhenius frequency factor ( $s^{-1}$ )

$E_a$  = activation energy for the peroxide decomposition (J/mol)

$R$  = 8.314 J/mol K, gas constant

$T$  = temperature (K)

$t_{1/2}$  = half-life time (s)

Some of the peroxides used as cross-linking agents for rubber compounds are mentioned in Table II, while Table III reveals their half-life temperatures at certain times and their typical cross-linking temperatures.

TABLE II  
PEROXIDES APPLIED IN CROSS-LINKING OF ELASTOMERS

Types of peroxides	Examples
Dialkyl peroxides	2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (DTBPH) 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3 (DTBPHY) Di-tert-butyl peroxide (DTBP)
Alkyl-aralkyl peroxides	Tert-butyl cumyl peroxide (TBCP) Di(tert-butylperoxyisopropyl)benzene (DTBPIB)
Diaralkyl peroxides	Dicumyl peroxide (DCP)
Diacyl peroxides	Dibenzoyl peroxide (BPO)
Peroxyketals	1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane (DTBPTC) Butyl 4,4-di(tert-butylperoxy)valerate (BDTBPV)
Peroxyesters	Tert-butyl peroxybenzoate (TBPB)

#### B. MECHANISM OF PEROXIDE VULCANIZATION

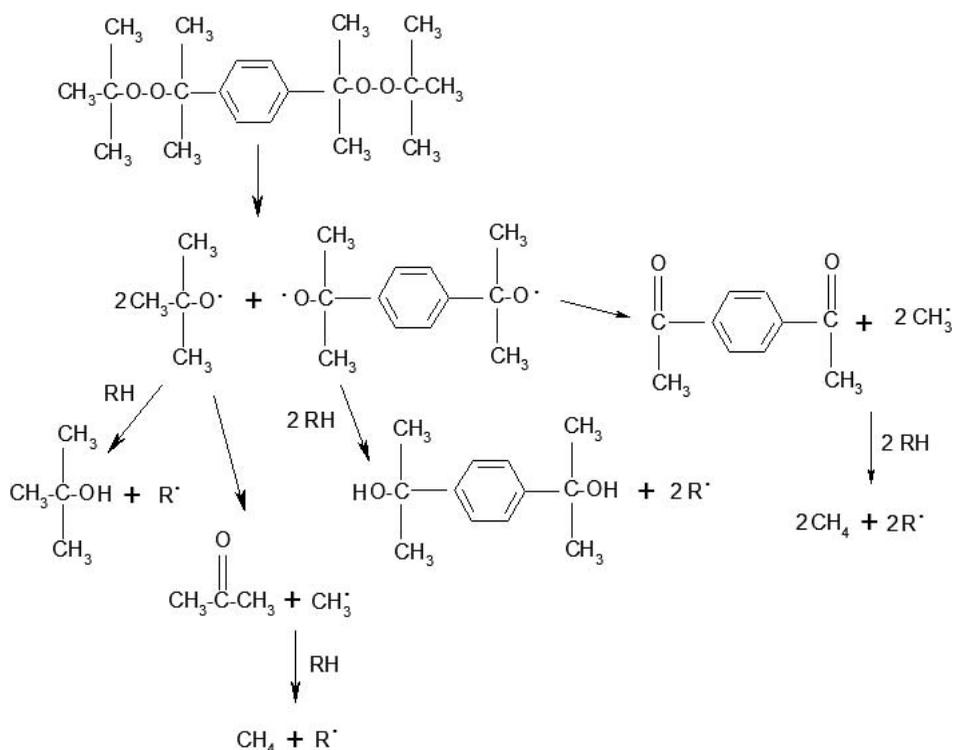
Generally, it is supposed that cross-linking of rubbers with peroxides has radical character in substance. In the first step, peroxide molecules undergo homolytic cleavage to form primary alkoxy radicals by breaking the labile oxygen–oxygen bond, which is usually triggered by heat. The O–O bond strength depends on the chemical nature of the hydrocarbon group attached and the polarity of the substrate in which peroxide is dispersed. The influence of the chemical nature of the hydrocarbon group depends on structural effects such as resonance stabilization of the free radicals generated upon decomposition of the peroxide, respectively steric and inductive effects.<sup>23</sup> The primary radicals can be a source for secondary alkyl or aryl radicals, which are formed by  $\beta$ -scission of primary radicals.<sup>2,31–35</sup>  $\beta$ -scission reaction of alkoxy radicals is strongly temperature dependent. Higher temperatures promote tert-alkoxy radicals to undergo  $\beta$ -scission over either abstraction or addition and abstraction over addition.  $\beta$ -scission is usually related to cleavage of the weakest C–C bond. Bonds to tertiary carbon are broken rather than bonds to primary (acetylenic) or secondary (aromatic, olefinic) carbons. Bonds to higher alkyl chains are scissioned in preference to those to

TABLE III  
HALF-LIFE TEMPERATURES OF PEROXIDES AT GIVEN TIMES

	$T$ (°C) for $t_{1/2}$ <sup>a</sup>			Cross-linking temperature (°C)
	0.1 h	1 h	10 h	
DTBPH	156	134	115	180
DTBPHY	164	141	120	180
DTBP	164	141	121	180–190
TBCP	159	136	115	180
DTBPIB	156	134	114	180
DCP	154	132	112	170
BPO	113	91	71	100–110
DTBPTC	128	105	85	150
BDTBPV	143	121	102	160
TBPB	142	122	103	140

<sup>a</sup> Data of half-life provided by AkzoNobel Polymer Chemistry; solution—chlorobenzene.

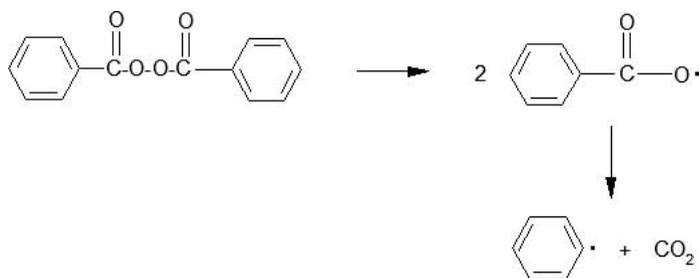




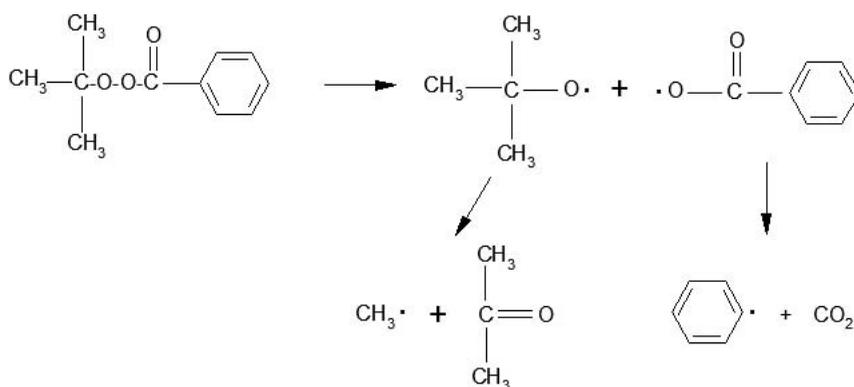
SCHEME 2. — Decomposition mechanism of di(tert-butylperoxyisopropyl)benzene.<sup>38</sup>

rubbers.<sup>23,44</sup> The relative reactivity or stability of the free radicals generated is related to the hydrogen bond dissociation energy of the parent compound.<sup>23</sup> Based upon the values of bond dissociation energy, it can be concluded that methyl, phenyl, tert-butoxy, and other alkoxy radicals are highly reactive and are good hydrogen abstractors. By contrast, ethyl, tert-butyl, and isopropyl radicals have lower energy and are poor hydrogen abstractors or prefer addition to the double bonds of elastomers.<sup>22,23,36,45</sup>

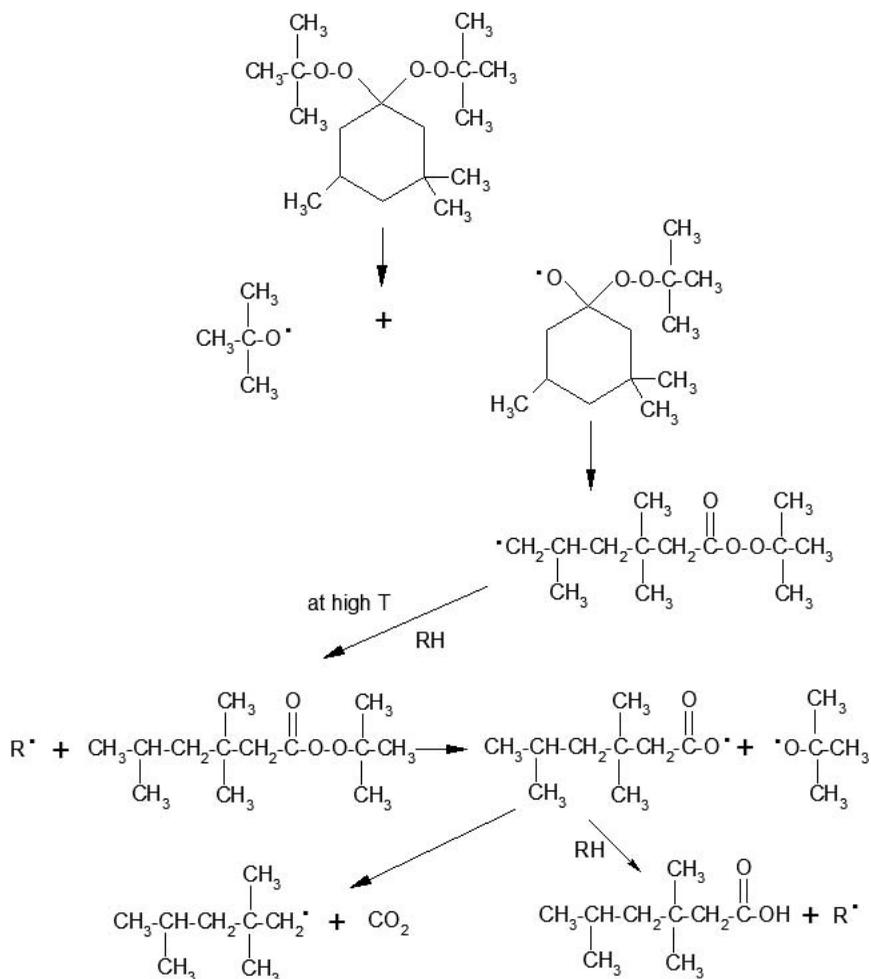
The reactivity of peroxide radicals depends not only on their structure but also on their size. Secondary methyl radicals are smaller, and therefore they are less sterically hindered than the initial alkoxy radicals.<sup>3,22,44</sup> At the same time they are more accessible to reactive centers of elastomers, and thus they provide good cross-linking activity. Most of the peroxides used in cross-linking of elastomers generate tert-butoxy radicals, which can be subsequently scissioned into methyl radicals



SCHEME 3. — Decomposition mechanism of dibenzoyl peroxide.<sup>2</sup>



SCHEME 4. — Decomposition mechanism of tert-butyl peroxybenzoate.<sup>36</sup>



SCHEME 5. — Decomposition mechanism of 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane.<sup>32</sup>

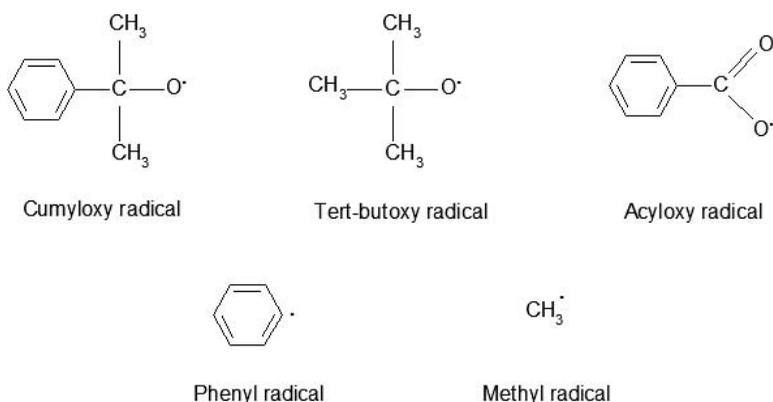


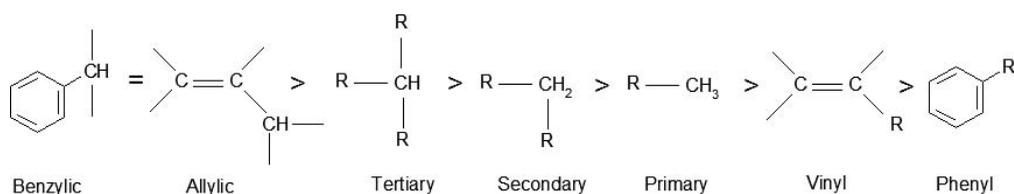
FIG. 1. — The most common radicals derived from homolytic cleavage of peroxides.

and other products. The sum of the relative amounts of methane and tert-butanol per peroxide shows a good indication of the peroxide to perform cross-linking reactions by hydrogen abstraction.<sup>23</sup>

The peroxide decomposition step follows first order rate reaction kinetics; therefore, the dissociation of the peroxide molecule is adequate to the peroxide concentration at any time. This step is also the rate determining step of the overall reaction.<sup>14,20,44</sup> Subsequent reactions between peroxide radicals and functional groups of elastomers lead to the formation of cross-linked network

TABLE IV  
RELATIVE AMOUNTS OF DECOMPOSITION PRODUCTS FROM VARIOUS PEROXIDES IN PENTADECANE<sup>38</sup>

Peroxide	Experimental temperature (°C)	Decomposition products	Relative amount (mol/mol peroxide)
DCP	160	methane	0.91
		acetophenone	0.91
		2-phenylpropanol-2	1.06
		$\alpha$ -methylstyrene	0.01
		water	0.01
		DTBPIB	155
acetone	0.13		
methane	1.10		
di-(hydroxyl-i-propyl) benzene	0.30		
acetyl hydroxy-i-propyl benzene	0.54		
diacetyl benzene	0.14		
DTBPH	145	methane	0.31
		ethane	0.40
		acetone	1.62
		tert-butanol	1.65
		tert-amylalcohol	0.23
		DTBPHY	180
carbon dioxide	0.02		
acetone	0.57		
tert-butanol	1.39		
2,5-dimethyl-2,5-dihydroxyhexyne-3	0.79		

FIG. 2. — Order of hydrogen stability.<sup>44</sup>

structure. As already outlined, peroxide free radical species could potentially react with elastomers by two mechanisms:

1. by abstraction of hydrogen atoms from elastomer chains or
2. by addition to the double bonds of unsaturated rubbers

Both mechanisms lead to the formation of radical centers on elastomer chains (macroradicals), which usually mutually recombine to form carbon-carbon cross-links.<sup>46-51</sup>

The ability of hydrogen atom transfer is dependent not only on the type and properties of abstracting radical, but also on the structure of hydrogen donor. The sequence displayed in Figure 2<sup>44,52</sup> shows the facility that radicals can be formed via abstraction of a hydrogen atom from different chemical groups, while C-H bond strength of the presented groups is listed in Table V.<sup>2</sup> It must be noted that peroxide derived radicals can abstract hydrogen not only from elastomer chains, but also from other accessible sources. Resonance stabilization of allylic and benzylic structures makes these positions better hydrogen donors than corresponding alkyl groups.<sup>2</sup> Owing to high abstractibility of benzylic and allylic hydrogen atoms, the use of aromatic oils and some types of antidegradants in rubber compounding should be restricted in order to avoid the consumption of peroxide radicals, which could negatively influence the cross-linking efficiency.<sup>53</sup>

The second mechanism by which elastomer radicals can be formed is addition of peroxide radical species to the double bonds of unsaturated rubbers. The double bonds situated at the end of elastomer chains (terminal) or in the side-chain groups (vinyl) are less sterically hindered when compared with in-chain double bonds (cis/trans). Therefore they are more amenable and more likely take part in addition reactions.<sup>7,54</sup>

Both reaction types, hydrogen abstraction and addition reactions, may proceed simultaneously to form elastomer radicals.<sup>54</sup> The balance of both mechanisms is influenced by the elastomer structure, peroxide type, and concentration and reaction temperature. Higher peroxide concentrations and higher temperatures shift toward addition reactions.<sup>3,55</sup>

TABLE V  
BOND STRENGTH OF VARIOUS TYPES OF C-H BONDS<sup>2</sup>

Type of C-H bond	C-H bond strength (kJ/mol)
benzylic	368
allylic	368
tertiary	380
secondary	405
primary	435
vinyl	464
phenyl	468

TABLE VI  
RELATIVE CROSS-LINKING EFFICIENCIES OF SOME ELASTOMERS CURED  
WITH DCP

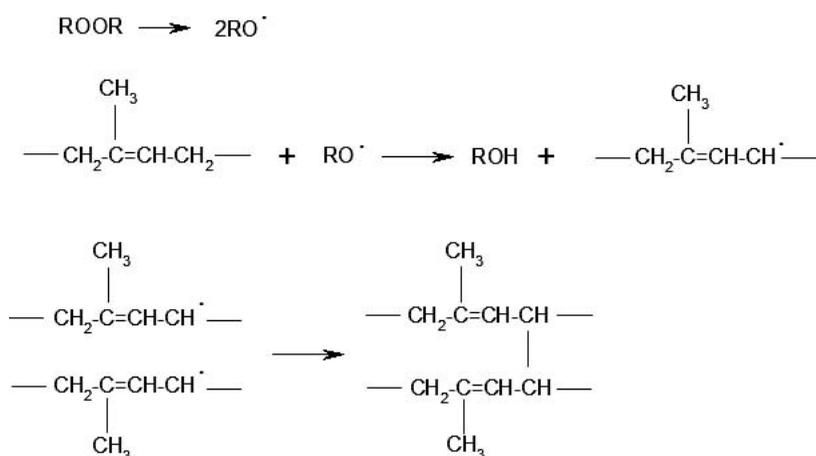
Elastomer	Cross-linking efficiency
BR	$\geq 10$
SBR	$\geq 10$
NBR	$\geq 1$
NR	1
EPM	0.1–0.8
CR	0.5
IIR	0

The number of moles of chemical cross-links that are formed from a mole of reacted peroxide is called peroxide efficiency or cross-linking efficiency. In the abstraction mechanism, the peroxide efficiency equals 1, since 1 mole of peroxide is able to form only 1 mole of cross-link. In addition reactions, the peroxide efficiency is thought to be much higher, because one radical can initiate the formation of several chemical bonds.<sup>46,56</sup> The relative cross-linking efficiencies of some elastomers cured with dicumylperoxide are mentioned in Table VI.<sup>7,23,46</sup>

*1. Peroxide Cross-Linking of Unsaturated Rubbers.* — The general scheme for peroxide cross-linking mechanism of natural rubber (NR) is illustrated in Scheme 6. The primary mechanism is abstraction of allylic hydrogen from the elastomer backbone by peroxide radical species.<sup>3,57</sup> The abstraction reaction is supported by the presence of high amounts of easily abstractable allylic hydrogens in the chemical structure of NR. The addition reactions are much less pronounced, probably due to the sterically hindered in-chain double bonds and of course due to the quantum of allylic H-atoms. Two elastomer radicals subsequently recombine to form a cross-link. From an analysis of the stoichiometry for peroxide cross-linking of natural rubber using DTBP and DCP, it was concluded that these peroxides form one mole of cross-links per mole of peroxide, that is, they are quantitative cross-linking agents.<sup>7</sup> But some other experimental works<sup>58,59</sup> showed that addition reactions should also be under consideration. The peroxide cross-linking efficiency then would be higher than one. It is supposed that addition reactions occur mainly at higher peroxide concentrations and higher temperatures.<sup>3</sup>

The amount of addition reactions becomes more significant when cross-linking butadiene type rubbers such as butadiene rubber (BR) and styrene-butadiene rubber (SBR), mainly those with higher amounts of 1,2-butadiene structural units.<sup>49,60–62</sup> When peroxide cross-linking of BR and SBR, it is expected that peroxide radicals can react by hydrogen abstraction, at which more reactive macroradicals than in the case of NR are formed, and also by addition reactions to the double bonds. The formed macroradicals, in addition to mutual recombination reactions, can also participate in addition reactions to the double bonds in elastomer chains (Scheme 7). The chain character of addition reactions results in high cross-linking efficiency, that is, 10–50 depending on the microstructure of polybutadiene. High cross-linking efficiency can be observed mainly by peroxide cross-linking of butadiene type rubbers with high amounts of 1,2-butadiene units, suggesting that the side-chain vinyl units participate in addition reactions more easily than in-chain double bonds.<sup>1,7</sup>

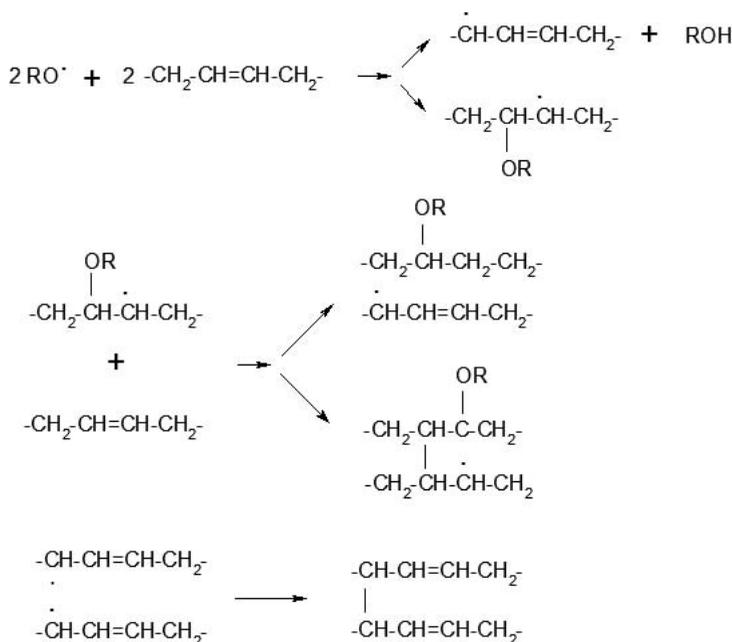
The cross-linking efficiency of acrylonitrile butadiene rubber (NBR) was reported to be 1, which indicates that the abstraction mechanism is prevailing. The addition mechanism is of minor importance, arguably due to the electron withdrawing nitrile groups, which make double bonds in the structure of NBR less reactive.<sup>56</sup> Although this statement is generally accepted, factors such as



SCHEME 6. — Peroxide cross-linking of NR.

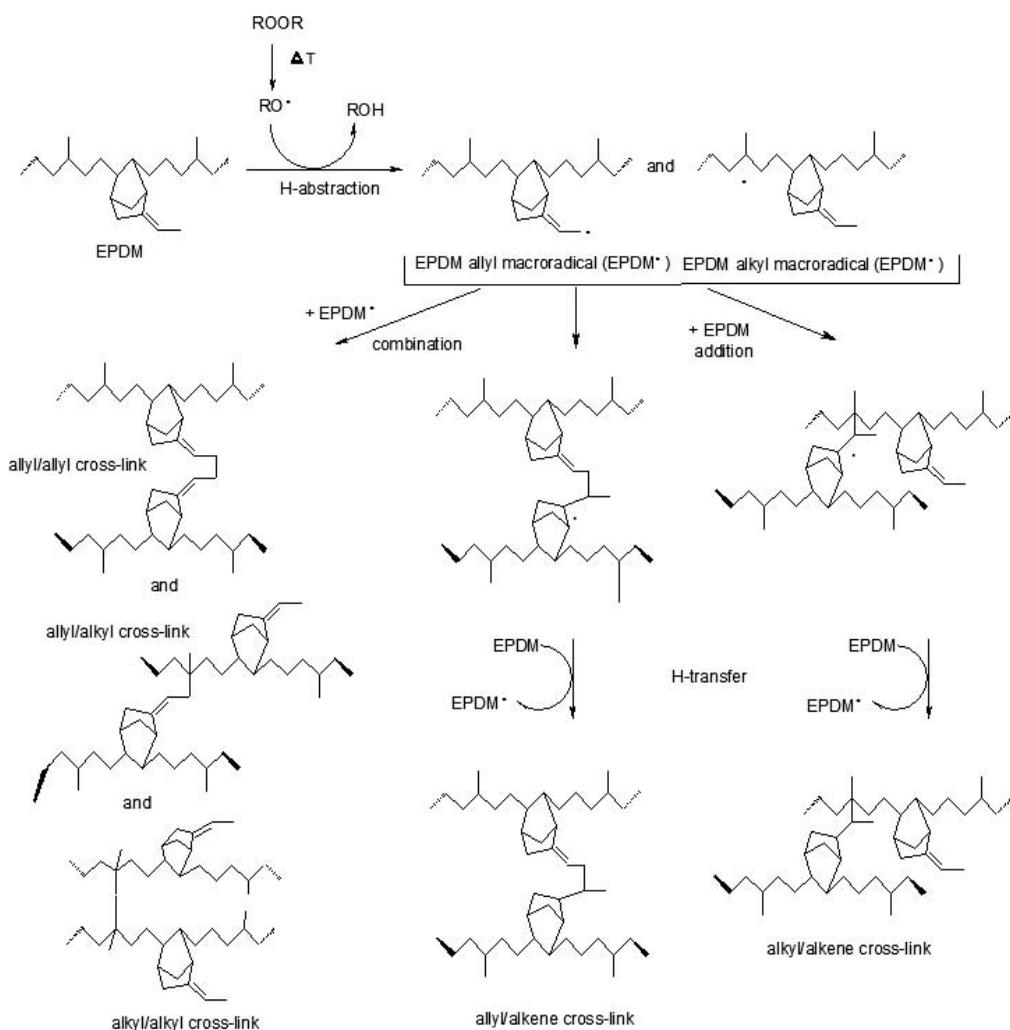
the amount of acrylonitrile structural units (ACN) in the structure of NBR, peroxide concentration, and cross-linking temperature must be considered. The higher the amount of ACN, the lower the cross-link density, suggesting that the abstraction reaction is predominant. By contrast, decreasing the amount of acrylonitrile and increasing the amount of butadiene results in an increase in the cross-link density. The increase in cross-linking degree of NBR is also promoted with the increase in peroxide concentrations, while both higher peroxide concentrations and higher cross-linking temperatures favor an increase in cross-linking degree of NBR with lower ACN content (higher butadiene content).<sup>46</sup> Based upon that, it is suggested that peroxide radicals can, in addition to abstraction of hydrogen atoms from elastomer chains, initiate the additional reaction to the double bonds, which makes the cross-linking process more efficient. The addition mechanism needs suitable orientation of double bonds to be attacked by radicals, and this can be supported by increasing the temperature to improve the mobility of elastomer chains.<sup>46,56</sup>

Ethylene-propylene-diene terpolymer (EPDM) is an elastomer with a saturated polymer backbone with pendant unsaturation of randomly distributed non-conjugated diene monomers. 5-Ethylidene-2-norbornene (ENB), 5-vinyl-2-norbornene (VNB), or dicyklopentadiene (DCPD) are the most common monomers introduced in commercially manufactured EPDM.<sup>63</sup> Peroxide cross-linking efficiency of EPDM is relatively high, involving both hydrogen abstraction and addition mechanisms (Scheme 8).<sup>64-68</sup> The second pathway is more promoted when the double bond is terminal, while the internal double bond is converted more via hydrogen abstraction.<sup>69</sup> Peroxide free radical species abstract hydrogen atoms from EPDM elastomer, both at the CH<sub>2</sub> and CH units in the EPM main chain and at the allylic positions of the diene unit, yielding EPDM alkyl and allyl macroradicals, in an approximately 1:1 ratio.<sup>70</sup> The allylic H-atoms of the diene monomer have a higher intrinsic reactivity for hydrogen abstraction than the aliphatic H-atoms of the EPM chain. However, hydrogen abstraction also occurs from the elastomer backbone as a result of the large molar excess of aliphatic H-atoms in comparison with allylic hydrogens in EPDM. Cross-linking can proceed via two pathways. First, termination of two EPDM macroradicals via combination yields ~25% alkyl/alkyl, ~25% allyl/allyl, and ~50% alkyl/allyl combination cross-links with 0, 1, and 2 diene units and with 0, 1, and 2 unsaturations in the actual cross-link between the two elastomer chains. Second, an EPDM macroradical adds to an EPDM unsaturation. For steric reasons the macroradical thus formed will probably not propagate with a second diene unsaturation. It

SCHEME 7. — Peroxide cross-linking of BR.<sup>1</sup>

likely terminates via H-transfer, forming allyl/alkene and alkyl/alkene cross-links with 2 and 1 diene units and with 1 and 0 unsaturation in the actual cross-link. The total amount of cross-links formed via combination is constant and independent of the EPDM structure. The total number of cross-links formed via addition reactions increases with increasing diene content and in the sequence ENB ~ DCPD < VNB. Typical diene conversions are ~25% for ENB and DCPD and ~50% for VNB.<sup>69,71,72</sup> High reactivity of EPDM with VNB in its structure can be explained by low steric hindrance of the terminal VNB unsaturation.<sup>73</sup>

*2. Peroxide Cross-Linking of Saturated Rubbers.* — In the case of fully saturated rubbers, the abstraction of hydrogen from their chains by peroxide reactive species is the only mechanism for elastomer radical formation. Cross-link formation between elastomer chains is performed only by recombination of macroradicals.<sup>1,2,44,74,75</sup> When cross-linking saturated elastomers, the cross-linking efficiency is usually low. In the case of ethylene-propylene rubber (EPM), the abstraction of hydrogen occurs on both ethylene and propylene structural units. But while cross-linking of an ethylene phase leads to the cross-linking and increase in molecular weight, the abstraction of hydrogen from propylene structural units leads to the formation of tertiary radicals, which are more prone to scission reactions, causing usually the opposite effect connected with a decrease in molecular weight (Scheme 9).<sup>14,21,76,77</sup> Abstraction of hydrogen from chlorinated polyethylene (CM) and chlorosulfonated polyethylene (CSM) occurs at the carbon adjacent to the halogenated site. For ethylenevinylacetate elastomers (EVM), methyl hydrogen is the most likely site for abstraction. Fluoroelastomers are also peroxide curable, but C–F bonds are very strong, and fluorine is therefore much more difficult to abstract than hydrogen, resulting in reduced cross-linking efficiency. For that reason copolymerization or terpolymerization of some types of fluoroelastomers are performed in the presence of small amounts of other monomers with reactive groups able to participate in cross-linking reactions.<sup>25</sup> Peroxide curing systems can also be used for some types of silicone rubbers (Q), where peroxide radicals can abstract hydrogen from methyl substituents or add to vinyl substituents (Scheme 10).<sup>78</sup>

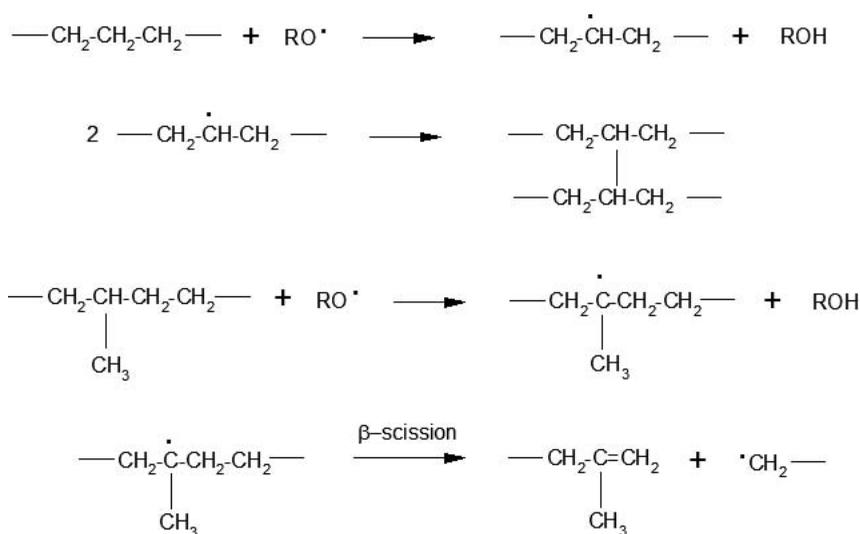


SCHEME 8. — Peroxide cross-linking of EPDM with ENB as third monomer.<sup>69</sup>

### C. SIDE REACTIONS

Peroxide cross-linking of elastomers is usually accompanied by a number of side reactions, which compete with the main cross-linking process and very often reduce vulcanization yield. The most common undesirable side reactions include main chain scission, disproportionation, oxygenation, dehydrohalogenation, radical transfer, acid-catalyzed decomposition of the peroxide, or branching of elastomers.<sup>25,79–81</sup> The proportion of each reaction depends mainly on the nature of elastomers, but also on the type and concentration of the peroxide applied and on the cross-linking conditions.

*1. Main Chain Scission.* — Main chain scission is one of the most frequent undesirable side reactions leading to the lowering of cross-linking efficiency.<sup>38,82</sup> The elastomer chain breaks to form a double bond and a radical. The scission of the elastomer backbone is usually promoted by tertiary radicals. The primary and secondary radicals are much less prone to scission reactions and more readily undergo coupling reactions than tertiary ones.<sup>60</sup> Therefore elastomers with the

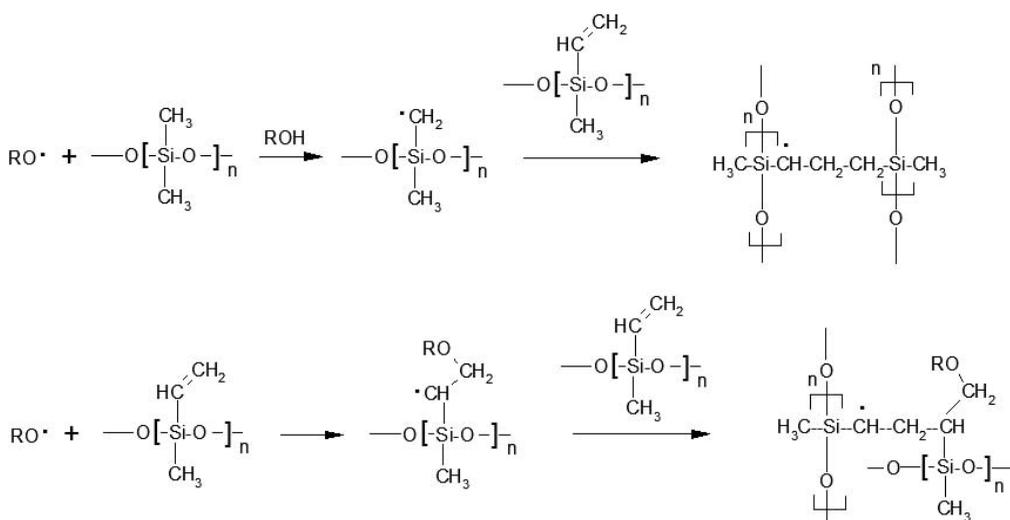


SCHEME 9. — Cross-linking and scission in peroxide curing of EPM.

presence of tertiary carbon atoms, like EPM, are more prone to scission reactions. As already mentioned in the section above, the peroxide cross-linking of EPM can be understood as a mixture of cross-linking of an ethylene phase and scission of a propylene phase, the so called  $\beta$ -scission (Scheme 9).<sup>75,83</sup> EPDM is also sensitive to  $\beta$ -scission, which also most likely occurs at the propylene units.<sup>14,84,85</sup> The ethylene/propylene ratio, type, and amount of diene monomer; randomness of monomer distribution; elastomer molecular weight; and molecular weight distribution have been proposed to be the main factors influencing the peroxide cross-linking efficiency of EPM and EPDM.<sup>21,23,86</sup> The higher the ethylene/propylene ratio, the higher the cross-linking efficiency. Increasing randomness of diene monomer distribution helps to minimize scission reactions.<sup>14,27</sup> Van Duin and Dikland<sup>73</sup> studied the effect of the type and content of diene monomer on the cross-linking efficiency of EPDM cured with peroxide by identification of the products formed from peroxide decomposition in low molecular weight model substrates (alkanes, alkenes) by employing gas chromatography with mass spectroscopy detection (GC-MS). The research revealed that EPDMs having diene monomers with terminal unsaturations are more reactive than those with internal unsaturations (for instance VNB).

The tertiary carbon atoms are also present in the structure of NR and markedly contribute to the poor peroxide cross-linking performance of natural rubber.<sup>60</sup> The competition between cross-linking and scission is also influenced by the temperature and peroxide concentration. Scission predominates at higher temperatures and lower peroxide concentrations.<sup>75,82,87</sup> The excessive main chain scissions prevail also by peroxide curing of isobutylene isoprene rubber (IIR) and lead to the degradation of elastomer backbone (Scheme 11).<sup>1,88</sup> Therefore this type of rubber can not be cured with peroxides.

2. *Disproportionation*. — Disproportionation is another very common side reaction also promoted by the presence of tertiary radicals.<sup>14,44,89</sup> The ratio of the rates of disproportionation  $k_{td}$  to combination  $k_{tc}$  for some radical species is listed in Table VII.<sup>2</sup> It becomes evident that allylic radicals prefer to terminate purely via combination, probably due to the presence of unsaturation. Benzylic and primary alkyl radicals also prefer to terminate via combination but not exclusively, while tertiary alkyl radicals prefer disproportionation. Although this type of reaction does not cause

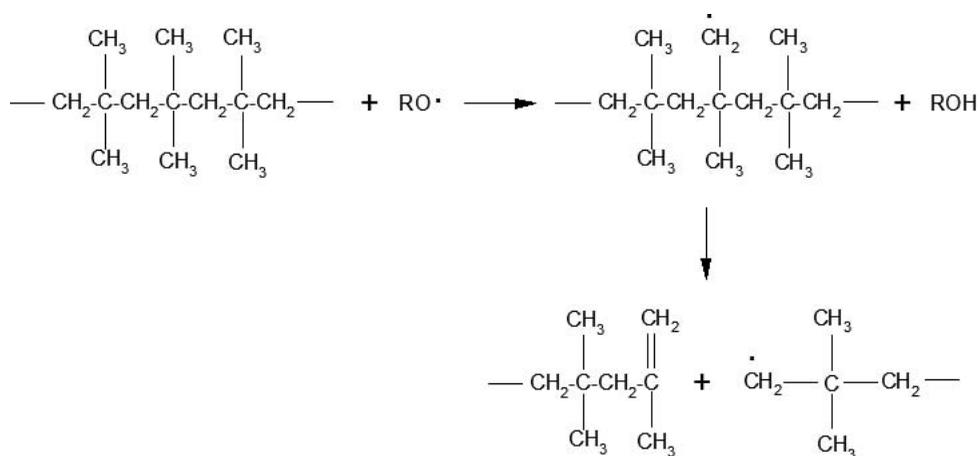


SCHEME 10. — Peroxide cross-linking of silicon rubbers.<sup>78</sup>

a decrease in molecular weight of the elastomer, it reduces the efficiency of the peroxide used because reactive radical centers on elastomer backbone are unfavorably terminated (Scheme 12).

3. *Oxygenation.* — The presence of oxygen in the cured mixture might cause coupling of oxygen molecules to the radical in the elastomer chain to form hydroperoxide radicals, which leads to rubber degradation instead of cross-linking (Scheme 13). Typical accompanying manifestation of this negative phenomenon is surface tackiness.<sup>44,90</sup>

4. *Dehydrohalogenation.* — Dehydrohalogenation typically reduces the cross-linking efficiency of halogenated elastomers. During this reaction the radical centers on elastomer backbones are terminated by forming a double bond while releasing a halogen radical (Scheme 14).<sup>3,91</sup>



SCHEME 11. — Degradation of IIR in the presence of peroxides.<sup>1</sup>

TABLE VII  
RATIO OF DISPROPORTIONATION TO COMBINATION OF RADICALS IN  
SOLUTION<sup>2</sup>

Radicals	$k_{td}/k_{tc}$
$2\text{CH}_3\text{CH}_2\cdot$	0.15 <sup>a</sup>
$2(\text{CH}_3)_2\text{CH}\cdot$	1.2 <sup>a</sup>
$2(\text{CH}_3)_3\text{C}\cdot$	7.2 <sup>a</sup>
$2\text{CH}_2=\text{CHC}\cdot(\text{CH}_3)_2$	$\sim 0$ <sup>b</sup>
$2\text{C}_6\text{H}_5\text{CH}\cdot\text{CH}_3$	0.14 <sup>c</sup>

<sup>a</sup> 30°C in n-pentane.

<sup>b</sup> 49°C in o-dichlorobenzene.

<sup>c</sup> 105°C in benzene.

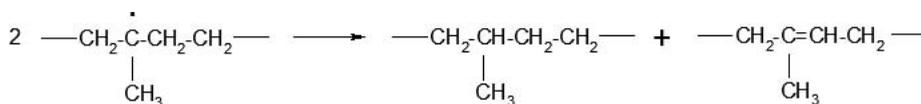
5. *Radical Transfer*. — Radical transfer often occurs between macroradicals or peroxide radicals and chemicals that contain easily abstractable H-atoms, such as some antidegradants (mainly amine and phenolic types) or aromatic and naphthenic oils (Scheme 15).<sup>14,91</sup> As a result, the concentration of reactive radical sites is reduced because the radicals formed from antidegradants and oils are stable with little reactivity.<sup>1,3,77</sup> Therefore the use of such chemicals should be avoided in rubber formulations cured with peroxides.

6. *Branching of Elastomers*. — Reactions of radicals in the elastomer backbone with radicals formed at the end of macromolecular chains often lead to the branching of elastomers instead of forming cross-links (Scheme 16).<sup>81</sup>

7. *Acid-Catalyzed Decomposition of Peroxides*. — If acidic substances are present during vulcanization, they can cause ionic or heterolytic decomposition of peroxides (Scheme 17). As a result no radicals are formed, so cross-linking does not take place.<sup>3,44,52,92</sup> In order to prevent this problem, acidic substances, for example acidic carbon black, should be excluded from rubber compounding.

#### D. CO-AGENTS

Cross-linking of elastomers with peroxides can be effectively improved by using co-agents<sup>93–103</sup> Co-agents are multifunctional organic molecules that are highly reactive toward free radicals<sup>9,22,88,104</sup> The efficiency of peroxide curing in the absence of co-agents is sometimes rather low due to the occurrence of side reactions, which consume radicals. Co-agents are able to boost peroxide efficiency by suppressing side reactions to a large extent, like chain scission and disproportionation.<sup>14,23,105</sup> But it is believed that the main reason that co-agents increase cross-linking efficiency is mainly because of the formation of co-agent bridges between rubber chains as extra cross-links.<sup>44,69,104,106</sup> They are used both to increase the cross-linking efficiency of the vulcanization process and to increase the cross-link density of final vulcanizates<sup>47,107,108</sup> Several advantages have been reported for the rubber compounds cured with peroxides and co-agents in comparison with those cured in the absence of co-agents:<sup>1,23,44,104,109,110</sup>



SCHEME 12. — Disproportionation of elastomer radicals.<sup>44</sup>





SCHEME 15. — Radical transfer.

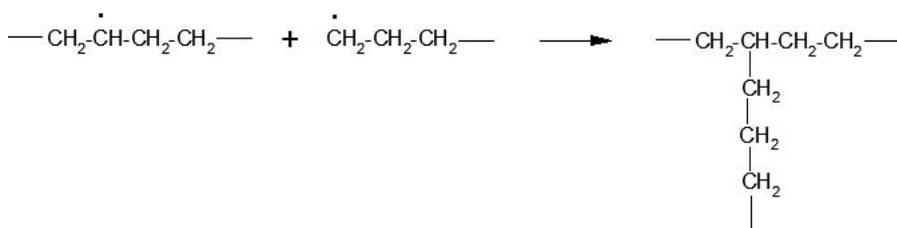
able to increase the cure rate. Owing to their low polarity, these co-agents have good compatibility with most elastomers. Phthalates, cyanurates and isocyanurates, homopolymers of dienes and copolymers of dienes, and vinyl aromatics belong to this class. Some of the commonly used co-agents are presented in Table VIII.

The ideal representation of the multifunctional co-agent is shown in Figure 3. The number or the functionality of chemical groups through which reaction with rubber chains can occur can alter. This structure mainly represents type I co-agents, but also most type II co-agents (non-polymeric) can be illustrated by this model. The reactive groups can differ in form from simple allylic and pendant vinyl structures to maleimides, methacrylates, and acrylates. The functionality can range from one (monofunctional) to five (pentafunctional) or greater. The properties of final vulcanizates can also be affected by the structure of the bridging group. This group can have the form of a straight chain (difunctional) or a branch structure (multifunctional), or it can consist of a cyclic alkyl or aromatic ring. Linear structures can be either nonpolar (alkyl) or polar (polyether) and of varying length, providing proximal or widely separated reactive groups. The bridge may also include highly ionic bonds (metal salts, such as zinc acrylate and zinc methacrylate) or other bonds with weaker dissociation energies.<sup>96</sup>

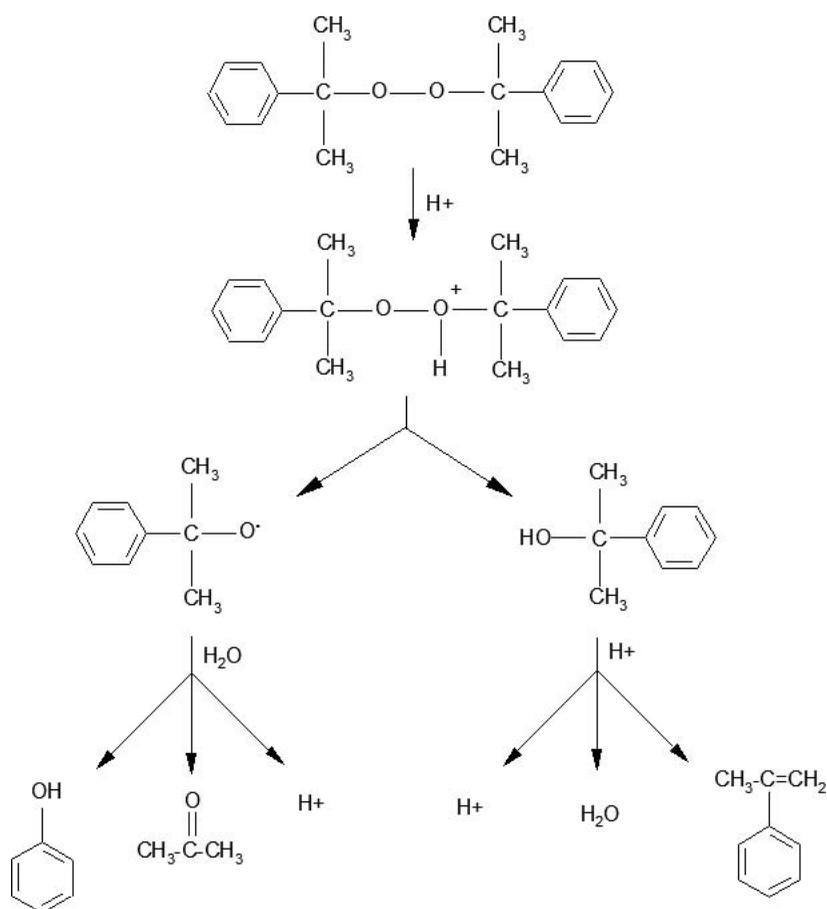
Since many of the commercially available co-agents are liquid in their form, they can reduce the viscosity of rubber mixtures. Co-agents with low molecular weight act, more or less, as plasticizers and can make processing of rubber compounds easier.<sup>69</sup> Additionally, by introducing co-agents, the amount of peroxide can be reduced while maintaining or even increasing the cross-link density of cured elastomers.

#### E. CO-AGENT ASSISTED PEROXIDE VULCANIZATION

The reaction mechanisms of co-agents in peroxide vulcanization of elastomers have been a subject of ongoing research, and several reaction pathways have been suggested for particular types of co-agents. As outlined, type I and II co-agents differ in their chemical nature and reactivity, and subsequently various reaction mechanisms also have been under consideration. Most type I co-agents can homopolymerize and/or graft to macroradicals forming effective cross-links through radical addition reactions (Scheme 18).<sup>101,114–119</sup> Some type II co-agents with easily extractable allylic hydrogens have been demonstrated to take part in intermolecular propagation reactions as well as intramolecular cyclization reactions.<sup>93,120</sup> Trifunctional allylic co-agents, such as triallyl cyanurate (TAC) and triallyl isocyanurate (TAIC), can form cross-



SCHEME 16. — Branching of elastomers.

SCHEME 17. — Acid-catalyzed decomposition of dicumylperoxide.<sup>3</sup>

links through the cyclopolymerization products as well as grafting through pendant allyl groups (Scheme 19). The polymeric co-agents, mainly high-vinyl polybutadienes (HVPBD), just increase the concentration of side-chain unsaturated units, which are very reactive toward addition reactions and thus propagate cross-linking.<sup>54,96,121</sup> Co-agents like zinc acrylate (ZDA) and zinc methacrylate (ZDMA) have been shown to form ionic cross-links when applied in cross-

TABLE VIII  
TYPE I AND II CO-AGENTS APPLIED IN PEROXIDE VULCANIZATION OF ELASTOMERS

Type I	Type II
Ethylene glycol dimethacrylate (EGDMA)	Diallyl phthalate (DAP)
Zinc acrylate (ZDA)	Triallyl isocyanurate (TAIC)
Zinc methacrylate (ZDMA)	Triallyl cyanurate (TAC)
N,N'-m-phenylenedimaleimide (PDM)	Divinylbenzene (DVB)
Trimethylolpropane trimethacrylate (TMPTMA)	Triallylphosphate (TAP)
Pentaerythritol triacrylate (PETRA)	High-vinyl 1,2-polybutadiene (HVPBD)

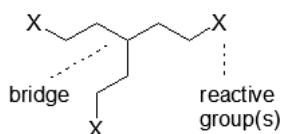
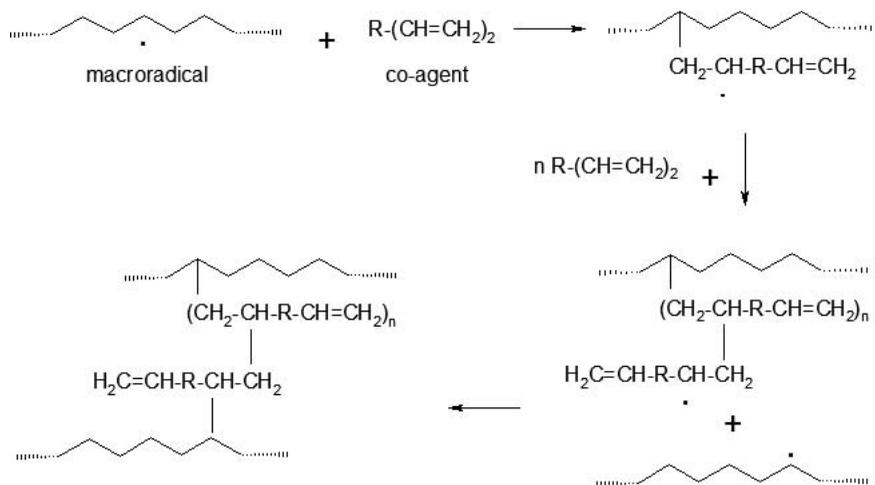


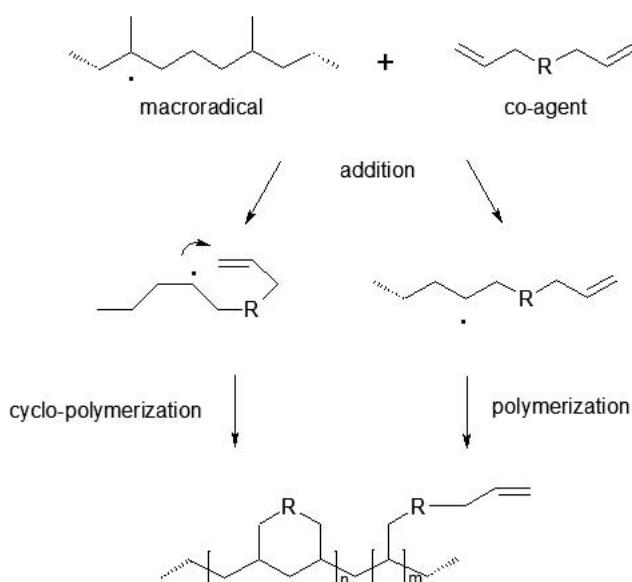
FIG. 3. — Idealized representation of multifunctional co-agent.<sup>96</sup>

linking of elastomers, which leads to the enhancement in the mechanical properties of cured rubber materials and improves the adhesion between elastomer and metal substrates.<sup>94,99,104</sup> Lu et al.<sup>109</sup> proposed a model of rubber/ZDMA interactions. They reported that the in situ radical polymerization of ZDMA takes place during the curing process of the rubber matrix with peroxide. Poly-ZDMA generated by this reaction aggregates to form the granular nanoparticles, which can be physically adsorbed or chemically grafted onto rubber chains. These structures can be considered the chemical or physical cross-linking points of the composites. Additionally, the formation of ionic clusters through static electronic attractions with the contribution of zinc ions from co-agent molecules was also observed. Covalent cross-links were also formed between elastomer chain segments as a result of peroxide cross-linking. Rubber composites with this type of morphology reveal the ability for stress relaxation, due to rubber chain slippage on the ionic cluster surface and reformation of ionic bonds upon external deformation of the sample.

Network enhancement through the grafting of co-agents between elastomer chains,<sup>44,96,121</sup> the formation of an interpenetrating network of homopolymerized co-agents,<sup>114,122,123</sup> and the formation of higher modulus filler-like domains of thermoset co-agent<sup>54,115,124,125</sup> have been suggested. In general, co-agents are rather polar materials, mainly those of type I; therefore, they are not very miscible with nonpolar elastomers and may tend to phase separate and homopolymerize.<sup>51,69,95</sup> The homopolymerized co-agent domains can be co-vulcanized with the rubber matrix and behave as filler particles.<sup>14,44,69,109</sup> Even if polymerized co-agent molecules are not grafted to elastomer chains, they can improve mechanical properties of vulcanizates since they act as reinforcing fillers formed in



SCHEME 18. — Reaction mechanism of certain type I co-agents with elastomers.<sup>118</sup>



SCHEME 19. — Reaction mechanism of certain type II co-agents with elastomers.<sup>120</sup>

situ during vulcanization. Moreover, polymerized co-agent domains can act as centers of stress redistribution in vulcanizates upon external strain.<sup>104</sup> The polymeric type II co-agents are typically much more soluble in the rubber matrix, since the difference in solubility parameters is much less pronounced. Therefore domain formation is usually not expected.<sup>54,96</sup>

The effect of co-agent domains on mechanical properties of vulcanizates depends on the rigidity of co-agent molecules. The domains with high rigidity (for instance domains formed from co-agents containing rigid aromatic structures) partially contribute to the transfer of stresses in the rubber network. The stress concentration near the hard co-agent domains upon deformation may deteriorate the mechanical properties of the cured elastomers.<sup>126</sup> Improvement in the mechanical properties can be achieved using co-agents with more flexible structures to form soft domains of lower stiffness during the curing process. These domains can deform more readily under the influence of an external stress similar to the network formed by reinforcing filler particles.<sup>44,127</sup>

A lot of factors determine the reaction pathways and distribution of co-agents in the rubber matrix, such as co-agent loading, the difference in polarity between the co-agent and the rubber matrix (solubility), adequacy of mixing, and the relative reactivity of the co-agent compared with the rubber.<sup>22,93,121</sup> Figure 4 illustrates an idealized network structure of elastomer formed from peroxide curing in the presence of co-agents.

#### F. GENERAL FEATURES OF PEROXIDE CROSS-LINKING

The peroxide vulcanization process is usually performed at temperatures 140–180 °C, and not only unsaturated but also saturated elastomers and their blends can be cured with peroxides (Table IX). The application of peroxide curing systems in cross-linking of elastomers leads to the formation of covalent carbon–carbon cross-links between elastomer chain segments. C–C bonds have higher dissociation energy in comparison with sulfidic cross-links, which are formed between

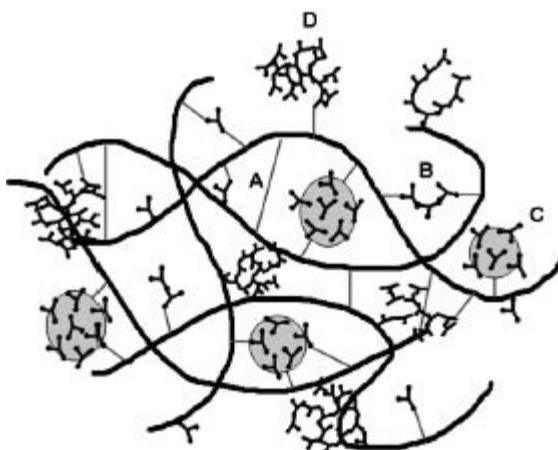


FIG. 4. — Cross-linked network structure of rubber matrix cured with peroxide in the presence of co-agent.<sup>54</sup>

elastomer chains by applying sulfur curing systems. Therefore the main features of peroxide cured elastomers are high thermal stability and good resistance to thermo-oxidative aging. The general advantages of peroxide cross-linking systems can be summarized as follows:<sup>1,22,25,38,44,113,128</sup>

- good heat-aging stability of vulcanizates
- good electrical properties of vulcanizates
- low compression set of vulcanizates at elevated temperatures
- ability to cross-link unsaturated as well as saturated rubbers and their blends
- simple formulation of rubber compounds
- rapid vulcanization without reversion
- no staining or discoloration of the finished parts
- possible to prepare transparent products

TABLE IX  
ELASTOMERS AND BLENDS THAT CAN BE CURED WITH PEROXIDE CURING SYSTEMS

Elastomers	Blends
Natural rubber (NR)	NBR/EPDM
Isoprene rubber (IR)	SBR/EPDM
Butadiene rubber (BR)	PE/EPDM
Styrene-butadiene rubber (SBR)	PP/EPDM
Acrylonitrile-butadiene rubber (NBR)	PP/NR
Hydrogenated acrylonitrile-butadiene rubber (HNBR)	
Ethylene-propylene rubber (EPM)	
Ethylene-propylene-diene rubber (EPDM)	
Chlorinated polyethylene rubber (CM)	
Chlorsulfonated polyethylene rubber (CSM)	
Silicone rubbers (Q)	
Fluoroelastomers (FKM)	
Polysulfide rubbers (TM)	
Urethane rubbers (U)	

However, the main disadvantages of peroxide cross-linking in comparison with sulfur curing systems are as follows:<sup>1,23,44,113,128</sup>

- worse tensile, elastic, and dynamic properties of vulcanizates
- lower abrasion resistance of vulcanizates
- low scorch safety
- sensitivity to elemental oxygen during curing, which can lead to surface tackiness
- certain components of rubber compounds, such as antidegradants or oils, may consume free radicals
- decomposition products from peroxides are more or less volatile, provide typical smell, show blooming effect, or can be extracted from vulcanizates by solvents
- generally higher cost

One of the biggest problems of peroxide curing systems is the complicated regulation of scorch safety. It is determined mainly by type of peroxide and its ability to dissociate into free radicals at the vulcanization temperature. Peroxide free radicals then rapidly react with macromolecules of rubber to form cross-links. The regulation of scorch time, but also the whole vulcanization process, can hardly be influenced by concentration of peroxides or by using inhibitors of radical reactions, because their presence in rubber compounds usually leads to the lowering of cross-linking efficiency. The problem can be partially overcome by using scorch retardants or scorch protectants. A number of scorch retardants have been developed and applied commercially, each working on different principles. Some scorch retardant systems have been reported in the literature in more detail, like multifunctional acrylic monomers, phenolic antioxidants, or functional nitroxyls.<sup>44,110,129-134</sup> The most studied include 2,6-di-tert-butyl-4-methylphenol (BHT) or 2,4-diphenyl-4-methyl-1-pentene (methyl styrene dimer, MSD).<sup>44,131,135</sup> Others include 1,1-diphenylethylene (DPE),<sup>129,136</sup> (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO),<sup>137,138</sup> bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate (bis-TEMPO),<sup>133</sup> or acrylate-functionalized TEMPO, 4-acryloyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (AOTEMPO).<sup>139</sup>

### III. CONCLUSION

Since the discovery of cross-linking in elastomers with organic peroxides by Russian chemist Ostromislensky in 1915, this process has been a subject of continual increasing interest by a lot of engineers and scientists. Attributes such as high temperature aging stability and high resistance to thermo-oxidative degradation make peroxide cured articles suitable for special applications required mainly for good environmental stability. Although in general, the mechanical properties of peroxide cured elastomers are worse when compared with sulfur vulcanizates, these disadvantages can be to a certain extent eliminated by the proper selection of peroxide, but mainly by the suitable choice of co-agent type and content. Therefore it is believed that the research relating to the peroxide vulcanization and cross-linking of rubber compounds will be oriented mainly toward the examination and testing of new types of co-agents and their reaction mechanisms with different types of organic peroxides.

### IV. ACKNOWLEDGEMENT

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