Rubber Science, **27**(1): 98-126, 2014 *REVIEW ARTICLE*

PEROXIDE VULCANIZATION OF POLYMERS

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Received: 22 March 2014 Accepted: 05 May 2014

R. Rajan, S. Varghese and K.E. George (2014) Peroxide vulcanization of polymers. *Rubber Science*, **27**(1): 98-126.

The present article reviews the use of different organic peroxides used for the crosslinking of various types of rubbers. The rubbers include both unsaturated and saturated elastomers as well as elastomer blends. The use of co-curing agents (coagents) to improve the vulcanizate properties is also discussed. Peroxide cure depends upon a number of factors like type and concentration of peroxides, type of elastomers, compounding ingredients like fillers, antioxidants, processing aids *etc.* However, by the proper selection of elastomers and coagents, peroxide cure systems can be effectively used as an alternative to sulphur cure system.

Keywords: Coagent, Natural rubber, Organic peroxide, Vulcanization

INTRODUCTION

When rubber is exposed to atmosphere, oxygen present in air easily oxidizes rubber and gradually transforms it into a solid substance at room temperature. This fact laid the foundation stone of rubber vulcanization by means of organic peroxides. In 1915, Ostromislensky (Ostromislensky, 1930) used benzoyl peroxide to vulcanize natural rubber. However, vulcanization of rubber with benzoyl peroxide never found wide applications because of the large proportion of benzoyl peroxide necessary for a good level of cure and blooming of the decomposition products, benzoic acid, on to the vulcanizate.

Although peroxides and sulphur can cure most types of rubbers, the chemistry behind peroxide crosslinking and the properties it provide, are much different. Due to these chemical differences, many additives that are essential in sulphur cured formulations might interfere with peroxide curing. There are many types of vulcanizing systems and hence deciding which system is ideal for a given application depends on the required curing conditions, the elastomer or elastomers blend employed and the desired physical properties of the vulcanizates. The process has acquired very little importance in unsaturated rubbers since the mechanical properties are inferior to those obtained with accelerated sulphur cure. However, peroxide vulcanization has got good ageing and low set properties. Interest in the industrial use of peroxides as curing agents increased with the introduction of a number of fully saturated elastomers (Hofman, 1999) for which the usual accelerated sulphur systems are unsuitable and also with the commercial introduction of dicumyl peroxide (DCP) in

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the late1950s (Class, 1999). DCP produces vulcanizates with better heat resistance and lower set than sulphur-accelerator cure systems. Saturated rubbers are, in general, resistant to ageing, thermally stable and mostly used under severe conditions. The study of cure systems available for crosslinking of rubbers is therefore of considerable importance and organic peroxides, being one such category are worthy of detailed examination.

Peroxide type

Factors governing the selection of an ideal peroxide (Braden *et al.*, 1955) are given in Table 1.

The primary criteria for selecting a peroxide is the activation temperature, or the temperature at which crosslinking will proceed at a satisfactory rate. Peroxides with lower activation temperatures will provide fast cure, but will have poor scorch resistance and *vice versa.* Peroxide efficiency is another important factor to be considered while selection. Usually peroxy group (-O-O-) attached to tertiary carbon atoms are more stable than those attached to primary and secondary carbon atoms. A relative measure of peroxide stability is the ten-hour half life temperature (10h HLT). It is the temperature required to decompose 50 per cent of a peroxide sample in ten hours. The measure of stability is important to rubber formulations since relatively stable peroxides will provide greater scorch resistance, but generally provide slower cure rates. Most of the peroxides that are commonly used in rubber formulations are highly stable and require high temperature for decomposition.

Organic peroxides that can be used for crosslinking polymers mainly include diacyl peroxides, dialkyl or diaralkyl peroxides and peresters (Ogunniyi, 1999). Brinkman *et al.* (1966) presented data on both physical properties of vulcanizates and cure time of a number of more technologically useful peroxides in a variety of rubbers. At present it is the only vulcanisation method that can compete with accelerated sulphur vulcanisation, with respect to vulcanization rates. Organic peroxides that are suitable for crosslinking of elastomers are given in Table 2. All these peroxides are capable of reacting with rubber, but their efficiency may vary considerably. Dialkyl peroxides are less prone to oxidation when compared to diacyl peroxides and peroxy esters (Ogunniyi, 1999).

Table 1. **Factors governing selection of peroxide (Braden *et al.*, 1955)**

Reactivity	It must react to give crosslinks as the only modification of the polymer.
Decomposition characteristics	Must give a rapid cure at temperatures approximately 150 °C, with no tendency to scorch at processing temperatures.
Volatility	Must be non-volatile to prevent loss during mixing
Solubility	Must be soluble in rubber and plastics
Ageing characteristics	Neither the peroxide nor its decomposition products must accelerate the ageing of the rubber or plastic
Effectiveness	It must be effective in the presence of reinforcing fillers.
Safety	It must be safe to handle, non-irritating and non-toxic at processing temperatures.

Table 2. **Examples of typical peroxides**

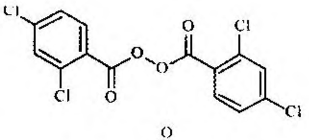
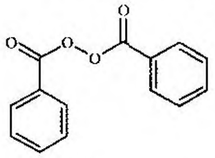
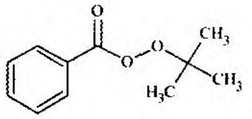
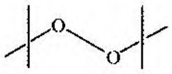
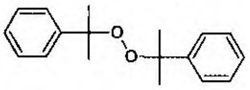
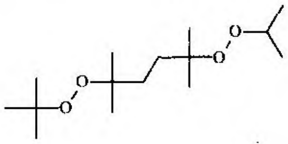
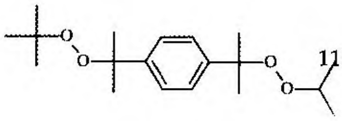
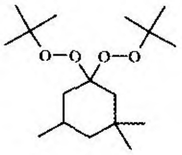
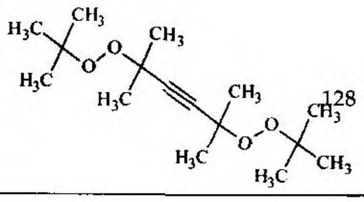
Name	structure	Ten hour half-life temperature, °C
di (2,4- dichloro benzoyl) peroxide		54
dibenzoyl peroxide		73
t- butyl perbenzoate		105
di- tertiary- butyl peroxide		126
dicumyl peroxide		114
2,5 dimethyl-2,5,-di (t- butyl peroxy) hexane		119
1,4- *bis* (t- butyl peroxy isopropyl) benzene		117
1,1′- di (t- butyl peroxy)- 3, 3,5- tri methyl cyclohexane		92
2,5-dimethyl- 2,5-di (t-butyl peroxy) hexane		128

Table 3. **Polymers and polymer blends which are curable with peroxide (Hoffman, 1999)**

Curable	Not curable	
Natural rubber (NR)	Polyethylene (PE)	Polyacrylate rubber (ACM)
Polyisoprene rubber (IR)	Chlorinated polyethylene(CM)	Butyl rubber (IIR)
Polybutadiene rubber (BR)	Chlorosuphonated polyethylene (CSM)	Chlorobutyl rubber (CIIR)
Polychloroprene rubber (CR)	Ethylene vinylacetate copolymer (EVA)	Epichlorohydrin rubber (CO)
Styrene butadiene rubber (SBR)	Acrylonitrile styrene *vinyl copolymer (ABS)*	*Polypropylene (PP)*
Acrylonitrile butadiene rubber (NBR)	Ethylene butylacrylate copolymer (EBA)	Polybutene-1 (PB)
Hydrogenated acrylonitrile butadiene rubber (HNBR)	Fluoro elastomers (FKM)	Epichlorohydrin copolymer (ECO)
Silicone rubber (Q)	NR/EPDM	Polyisobutene (PIB)
Polyurethane rubber (AU/EU)	SBR/EPDM	Polyvinylchloride (PVC)
Ethylene propylene rubber (EPM)	PE/EPDM	
Ehylene propylene diene rubber (EPDM)	NBR/EVA	
Polysulphide rubber (T)	PP/EPDM	

Choice of polymer

Peroxide cure can be used to vulcanize both saturated and unsaturated elastomers. Nevertheless, there are some polymers which cannot be crosslinked by peroxide vulcanization. The polymers which can be crosslinked with peroxides are shown in Table 3.

Mechanism of peroxide vulcanization

The generalized mechanism of peroxide vulcanization is a three step process *viz* initiation, propagation and termination. The process is initiated by the thermal (Keller, 1988) homolytic cleavage of a peroxide molecule to form two high energy free radicals as shown in Fig. 1. The initiation step follows first order kinetics and therefore the rate depends only upon the concentration of the peroxide at any time.

$$R{-}O{-}O{-}R \longrightarrow 2\,R{-}O^{\bullet}/\ R^{\bullet}$$

Fig. 1. Initiation by homolytic cleavage of peroxide

During the propagation step, the *radicals produced by homolytic cleavage* react with the polymer chain removing the more labile allylic hydrogen atoms from the polymer (H- abstraction) (Fig. 2) or radical addition (Fig. 3) across the unsaturation of the polymer chain resulting in the formation of a polymer radical.

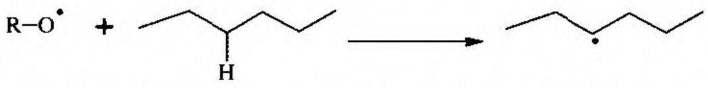


Fig. 2. Propagation by hydrogen abstraction from the polymer chain

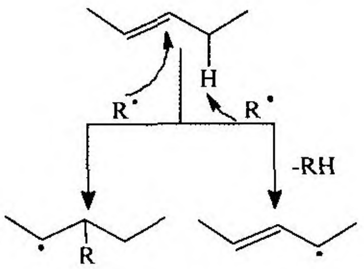


Fig. 3. Propagation by radical addition/ hydrogen abstraction from the polymer chain

An alkoxy /alkyl radical can abstract hydrogen atom not only from the polymer chain but also from any other available source. The order of lability of hydrogen atoms are shown in Fig. 4 [Class, 1999; Dluzneski, 2001(a)].

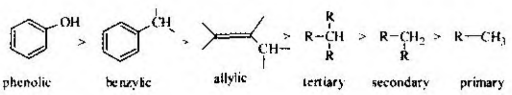


Fig. 4. Order of hydrogen lability

Finally, in the termination step two radicals couple to from a carbon-carbon covalent crosslink between two adjacent polymer chains (Fig. 5).

Fig. 5. Termination by coupling of two polymer radicals

Even though this three step reaction appears to be simple, the actual mechanism is quite complex due to numerous side reactions like acid catalyzed decomposition of peroxide, beta cleavage of oxy radical, radical transfer (abstraction of hydrogen from non polymeric sources), polymer scission, dehydrohalogenation and oxygenation [Dluzneski, 2001(b)].

Coagents

Co-curing agents or coagents are multifunctional organic molecules. They are highly reactive towards free radicals generated by homolytic cleavage of peroxides [Dluzneski, 2001(b)]. Examples of coagents are given in Fig. 6. Coagents improve the efficiency of peroxide cure by suppressing the side reactions like chain scission and disproportionation. Synergistic use of coagents along with peroxides can improve the good heat ageing stability and low compression set of vulcanizates by increasing the crosslink density and altering the crosslink composition. The commonly used coagents are molecules with maleimide groups (Kovacic and Hein, 1962), acrylates [Costin *et al.*,1991(a)], methacrylates (Peng *et al.*, 2002), high vinyl 1,2- polybutadiene, allyl esters of cyanurates (Dikland, 1993; Zlata *et al.*, 1998), isocyanurates, *etc.* The action of sulphur or sulphur donors as coagents has been investigated (Ghosh *et al.*, 1977). Some of the advantages provided by coagents in peroxide cure are shown in Table 4 [Class, 1999; Dluzneski 2001(a)].

Table 4. **Advantages of coagents**

Improved heat ageing	Higher hardness
Higher modulus	Increased abrasion resistance
High tensile strength	Improved resilience
High tear strength	Lower Mooney viscosity
Improved rubber/ metal adhesion	Improved dynamic flexibility
Improved resistance to oils and fuels	Improved crosslink density

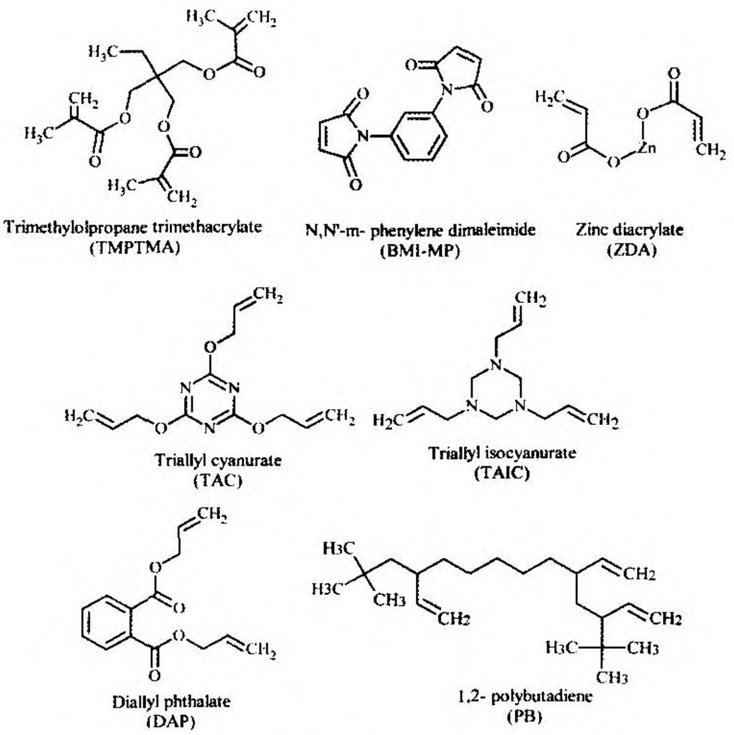


Fig. 6. Chemical structures of coagents

Classification of coagents

Coagents are classified into two types: type I and type II, based on their contribution to cure. Type I coagents increases both the rate and state of cure. They are typically polar, multifunctional low molecular weight compounds which form very reactive radicals through addition reactions. They include multifunctional acrylate, methacrylate esters, zinc salts of acrylic, methacrylic acid and dimaleimides. Since they are highly reactive towards radicals, scorch takes place very fast. Another disadvantage arises due to polarity, the compatibility of these coagents with the polymer matrix is limited. Type II coagents form less reactive radicals (primarily through hydrogen abstraction) and contribute only to the state of cure. These include allyl cyanurates, isocyanurates, phthalates, homopolymers of dienes and copolymers of dienes and vinyl aromatics. They contain extractable allylic hydrogen, participate in intramolecular cyclisation reaction and intermolecular propagation reaction.

Coagent reactivity

Coagents, due to their high reactivity, sometimes suppress non- network forming side reactions (Garcia- Quesada *et al.*, 2000) or generate additional crosslinks. As type I and type II coagents differ in their reactivity, the reaction mechanism that they follow may differ (Dikland *et al.*,(a) 1993; Dikland *et al.*,(b) 1993). Metallic coagents like zinc acrylates and diacrylates are used to introduce ionic crosslinks into the polymer matrix; Oh *et al.*, 1999). It provides increased modulus, improved tear strength, increased dynamic flex fatigue properties, and improved adhesion to metals and polar fabrics. The possible mechanism of incorporation of metallic coagent was illustrated (Peng *et al.*, 2002).

Peroxide vulcanization of unsaturated rubbers

Unsaturated rubbers like NR, IR, BR and copolymers of polybutadiene (SBR, NBR) contains many easily abstractable allylic hydrogen atoms as well as many double bonds that can undergo addition reaction. In most cases H- abstraction at allylic position is dominant (Brinkman *et al.*, 1966) although a significant amount of addition reactions also occur. The balance

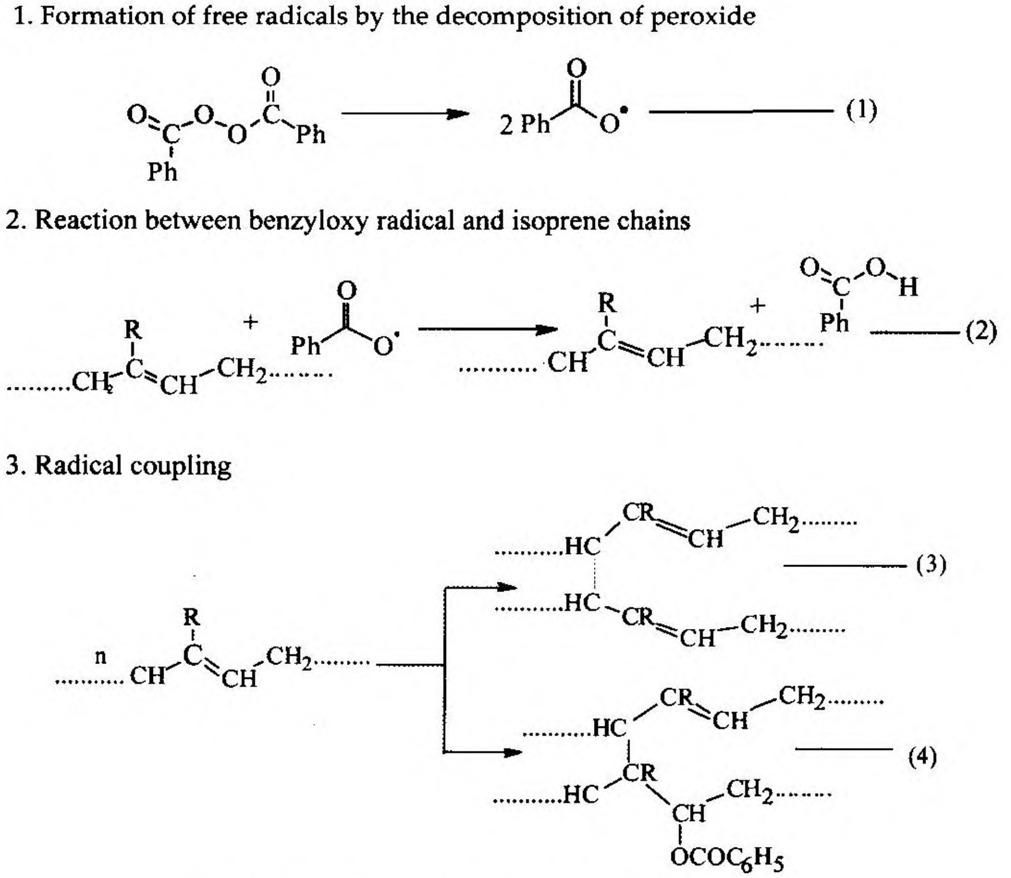


Fig. 7. Mechanism of peroxide vulcanization with benzoyl peroxide

between H abstraction and addition depends on a number of factors like peroxide type, peroxide concentration, temperature *etc.* [Loan, 1963; González *et al.*, 1998(a); González *et al.*, 1998(b)].

Although the reaction mechanism for peroxide cure is similar for all polymers, each has its unique aspects. Therefore, a discussion of the peroxide vulcanization of a wide range of both unsaturated elastomers are included.

Natural rubber

When Ostromislensky (1915) first discovered vulcanization of natural rubber with benzoyl peroxide, it was assumed that the process was due to an oxidation reaction. But the saturation level of rubber was not found to be altered and hence it was assumed that the vulcanization of rubber does not lead to saturation of double bond of rubber by oxygen. Later, van Rossem *et al.* (1932) and his collaborators carried out a series of reactions and concluded that since benzoic acid is formed as a by-product, C-C crosslink is formed in between the polymer chains by dehydrogenation. The mechanism suggested by Farmer and Michael (1943) is given in Fig. 7.

They suggested that for diene elastomers, at high curing temperature and high DCP loading, both allylic H abstraction and addition to the double bond results in crosslinking and at relatively low temperature (140 °C) and low DCP concentration allylic H abstraction is the predominant mechanism (González *et al.*, 1992(c); González *et al.*, 1992(d); González *et al.*, 1996). The changes in crosslinking mechanism at high curing agent concentration and at high temperature were confirmed by ^{1}H NMR spectroscopy (González *et al.*, 1998(a)). Addition reaction requires a favourable orientation of the double bond in order to be attacked by the peroxide radical and this can be boosted by raising the temperature. Further, addition mechanism causes adjacent polymeric chains with double bonds to polymerize, to form non homogeneous clusters or highly crosslinked zone which confer greater stiffness to the cured vulcanizates, having negative impact on physical properties of the vulcanizates. The over crosslinked portion when subjected to stress, generate stress accumulation and hence lower physical properties. At high temperatures (140 °C), peroxide decomposes rapidly and cure time should be appropriately selected to ensure complete decomposition of peroxide.

Synthetic polyisoprene

The vulcanization of synthetic *cis*-polyisoprene is very similar to that of the naturally occurring polymer as expected. The crosslinking efficiency has been found to be slightly but significantly greater than unity (van der Hoff, 1963). Polyisoprenes of higher 3, 4 content show higher crosslinking efficiencies. The microstructure of the polymer has little effect on the course of peroxide crosslinking reaction. *Cis - trans* isomerization occurred in polyisoprenes crosslinked with benzoyl peroxide, whereas no isomerization was found in samples initiated by dicumyl peroxide. The thermal stability of crosslinked polyisoprene has been investigated and there was found to be some enhancement in the thermal and thermal oxidative stability due to crosslinking with peroxides (Jiang *et al.*, 2000).

Polybutadiene

Polybutadiens or copolymers of butadiene usually contain various amounts of vinyl unsaturation. Using the relationship observed in natural rubber networks a physical versus chemical "calibration" has been developed by Kraus (Kraus, 1963) for polybutadiene. Peroxide decomposition followed a first order kinetics in polybutadiene rubber (Scheele *et al.*, 1966). A reaction scheme was proposed to explain the high crosslinking efficiency (Fig. 8). For *cis* 1, 4- polybutadiene containing 2 phr dicumyl peroxide, the polymer lost 30 per cent of its main chain unsaturation and this loss is attributed to a process of "polymerization" between the double bonds of the adjacent polymer molecule (Loan, 1967). In a variety of polybutadiene, the microstructure has got greater importance for the crosslinking efficiency (Gonzalez *et al.*, 1998 (b); Loan, 1967).

Further, the crosslinking of polybutadienes with varying vinyl content displays strange temperature behaviour (Gonzalez *et al.*, 1996). The vinyl content plays a very important role in peroxide vulcanization of BR, and there is no doubt that the addition reaction has a key role.

Copolymers of butadiene (SBR, NBR and HNBR)

The crosslinking behaviour of styrene butadiene rubber with peroxides is similar to that of *cis*-polybutadiene (Loan, 1963). Gonzalez (1996) studied the effect of peroxide loading and cure temperature on the crosslinking reaction mechanism. At lower peroxide loading, crosslink density was found to be independent of cure temperature and crosslinking mechanism is assumed to be through allylic hydrogen abstraction. In

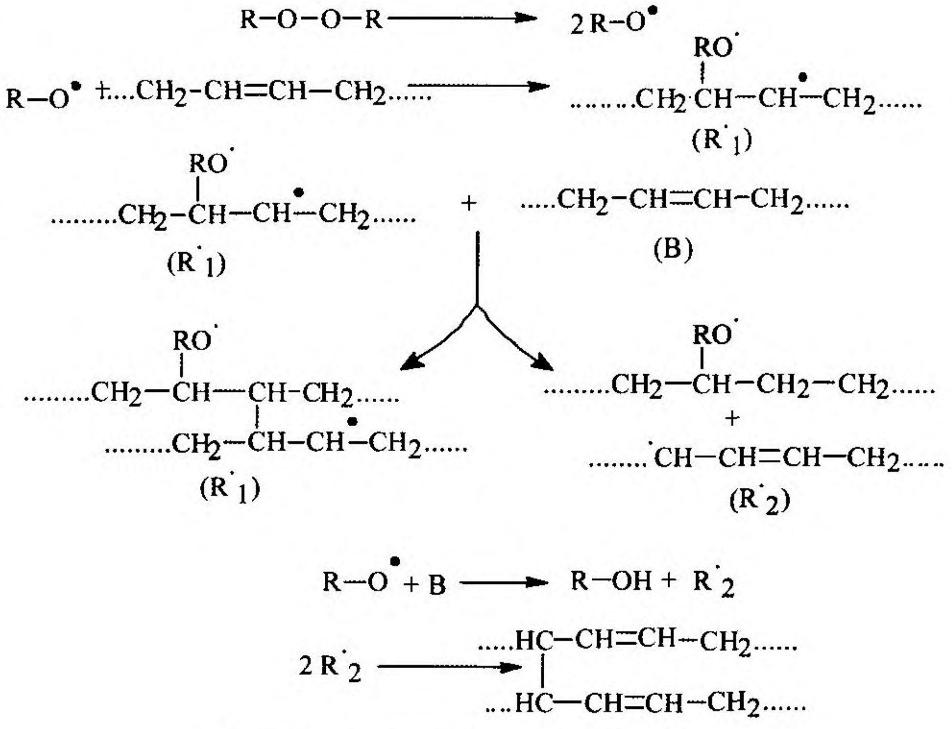


Fig.8. Crosslinking mechanism of polybutadiene

contrast, at high peroxide loading maximum torque is cure temperature dependant and the increase in crosslink density was accounted for the addition mechanism.

The crosslinking efficiency of peroxide in nitrile rubber has been reported to be predominantly through the abstraction mechanism (Loan, 1963; 1967), presumably because of the electron withdrawing nitrile group. Valentin *et al.* (2005) studied the efficiency of dicumyl peroxide in the crosslinking of NBR rubbers with low and high nitrile content. The curing of high butadiene NBR depends not only on peroxide content but also on cure temperature, and the maximum torque is far superior to that reached by the low butadiene NBR. The differences in peroxide curing of nitrile rubbers are explained by an addition mechanism or "polymerization" between the double bonds of the adjacent rubber chains at high butadiene rubber. In saturated rubber (HNBR), the crosslinking is possible only through hydrogen abstraction mechanism, without the formation of non-uniform distribution of network. The crosslinks are uniformly distributed in the network and physical properties are found to increase with peroxide content (Gonzalez *et al.*, 2004). The main difference between HNBR and NBR compounding is that HNBR uses a significantly higher quantity of peroxide. Normally it uses 7-12phr of peroxide while an NBR compound uses 2.5-3.5 phr of the same peroxide.

Butyl rubber and polyisobutylene

Butyl rubber is a copolymer of isobutene with a small amount of isoprene. It is one of the very few examples of a rubber which may not be cured with peroxides. A detailed investigation of peroxide curable butyl rubber derivatives were done by Shanmugam (2012). During reaction with peroxides, the presence of isoprene leads to the possibility of crosslinking reactions. The reaction mechanism of butyl rubber with different peroxides has been extensively investigated (Loan, 1964; Kawachi *et al.*, 1999). It was found that scission efficiency of peroxide depend quite markedly upon the unsaturation. However, these isoprene levels are insufficient to support the crosslink densities required for most engineering applications. The cumyloxy radicals react with isoprene units in the chain about 300 times as fast as with isobutylene units. The mechanism of degradation of butyl rubber with peroxide radical is shown in Fig. 9 (Loan, 1964).

One interesting feature of this reaction is its apparent dependence on the peroxide used. Polyisobutylene may be vulcanized with t-butyl peroxide in the presence of sulphur whereas cumyl peroxide is unable to produce such a reaction. The increased content of isoprene in butyl rubber along with dicumyl peroxide and coagent in the formulation provided superior cure yields (Resendes *et al.*, 2005; Knight *et al.*, 2010). The residual C=C bond in elastomers may pose a problem on the long term ageing characteristics due to its susceptibility to oxidation and ozonolysis (Webb *et al.*, 2002).

Polychloroprene

Loan, 1965 has studied the crosslinking efficiency of cumyl peroxide in chloroprene rubber and it has been shown to be 0.48 crosslinks per molecule of peroxide. This rather low figure shows that the double bonds in the polymer are unreactive. This interference may result from more strongly bound hydrogen or from some heterolytic or induced decomposition of peroxide in the rather more acidic environment (Archer and Hinshelwood, 1961).

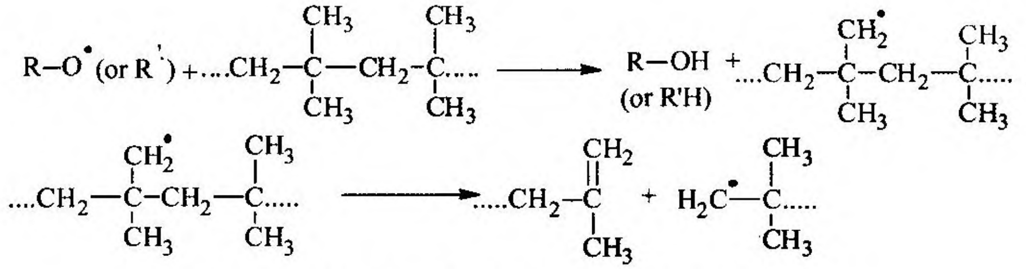


Fig. 9. Butyl rubber degradation in the presence of peroxide radical

Comparison of properties of peroxide cured unsaturated rubbers

Dicumyl peroxide (DCP) is an effective vulcanizing agent for NR, IR, BR, SBR and NBR. The formulation is given in Table 5 and their corresponding properties in Table 6 (Arkema Technical Information, 2000).

Peroxide vulcanization of saturated polymers

Organic peroxides are widely used for the vulcanization of a number of saturated rubbers like, ethylene propylene rubber (EPR), polyolefins, poly (alkyl vinyl ethers), ethylene vinyl acetate copolymers, silicone rubbers *etc.*

Ethylene propylene rubber and ethylene propylene diene rubber (EPR and EPDM)

The growing popularity of peroxide cure of both EPR and EPDM is due to the excellent properties like oxidation, heat, UV and ozone resistance (Noordermeer, 1993). For simple peroxide cure of a commercial ethylene propylene rubber a peroxide concentration of about 4 phr is found necessary, suggesting that the crosslinking efficiency is quite low, significantly less than unity, together with a drop in efficiency as the propylene content of the rubber is increased. In ethylene propylene rubber both crosslinking and scission reactions will occur. Tertiary hydrogen of the propylene unit is the most labile hydrogen towards radical attack (Lal *et al.*, 1968). Abstraction of tertiary hydrogen gives rise to tertiary radical which, unlike the similar radical from polypropylene, cannot easily lead to scission. The crosslinking efficiency of ethylene propylene rubber can be enhanced by the introduction of unsaturation. Saturated copolymers have crosslinking efficiencies in the range 0.4 to 0.7 whereas typical unsaturated terpolymers may show efficiencies greater than unity (Aahikari *et al.*, 1969).

Table 5. **Formulation**

Elastomers, phr	NR	IR	BR	SBR	NBR
Rubber	100	100	100	100	100
HAF black	50	50	50	50	50
Zinc oxide	5	5	5	5	5
Antioxidant	1	1	1	1	1
DCP	4	3.2	1.2	2.4	2.5

The peroxide curing is most efficient when the olefinic moiety presents a vinyl or vinylidene group. The reactivity of the terpolymers is dependent on the type and amount of diene utilized in the polymer synthesis (Keller, 1988). The termonomer content of EPDM is important for peroxide curing since it is the source of easily

Table 6. **Comparison of peroxide cured unsaturated elastomers**

Parameter	NR[a]	IR[b]	BR[c]	SBR[d]	NBR[e]*
Unaged properties					
100% Modulus, MPa	2.1	1.3	2.1	1.9	3.2
200% Modulus, MPa	9.1	4.0	5.1	6.6	9.9
Tensile strength, MPa	19.7	17.5	7.7	20.5	21.2
Elongation,%	300	450	270	360	345
Hardness, Shore A	58	52	57	63	65
After ageing properties for 70 h at 100 °C					
100% Modulus, MPa	1.6	1.1	2.3	2.7	8.4
200% Modulus, MPa	5.2	3.2	5.4	8.3	-
Tensile strength, MPa	11.2	14.9	7.6	19.2	20.7
Elongation,%	500	270	320	320	195
Hardness, Shore A	45	45	55	61	75
Set, %, 70 h at 100 °C	12.0	18.5	30.0	31.0	20

a- smoked sheet, b- cariflex polyisoprene 309, c- CB 220, BF Goodrich, d- SBR 1500, e- Nipol®1032, *NBR air aged, 70 h at 125 °C

abstractable hydrogen atoms which are useful in crosslinking. Other factors which influence the peroxide cure efficiency of EPR and EPDM are ethylene content, randomness of monomer distribution, polymer molecular weight and molecular weight distribution, peroxide, coagent, fillers and antidegradants [Dluzneski, 2001(b)]. A simplified mechanism of peroxide cure of EPDM is shown in Fig.10 (Peters *et al.*, 2008; Van Duin and Dikland, 2003).

Extensive low-molar-mass model (Peters *et al.*, 2008), Fourier transform infrared spectroscopy (Fujimoto and Wataya, 1969), solid state ^{1}H NMR relaxometry (Orza *et al.*, 2007), magic angle spinning ^{13}C NMR spectroscopy (Orza *et al.*, 2009), and electron spin studies (Zachary *et al.*, 2008), had provided detailed insight on the mechanism of peroxide cure and the corresponding structures formed. Studies on cure kinetics have been carried out using rheometry (Rosca *et al.*, 2001), differential scanning calorimetry (DSC) (Markovic *et al.*, 1999), and high throughput experimentation (HTE) (Kranendurg *et al.*, 2011) approach. The residual peroxide has an influence on the degradation of EPDM (Nakayama *et al.*, 2008). The reactions accelerating oxidative degradation and softening of the polymer has been extensively investigated (Delprat *et al.*, 1995). Due to polarity most of the coagents are incompatible with non-polar EPDM (Dikland *et al.*, 1993(b)). Upon peroxide decomposition these coagent domains are rapidly crosslinked via free radical addition and cyclo-polymerization reactions, resulting in small vitrified thermoset particles (Dikland *et al.*, 1993(a); Zlata *et al.*, 1998). These particles act as multifunctional crosslink nodes, linking a large number of EPDM chains. Classical explanations that coagents enhance the peroxide crosslinking efficiency by suppressing chain scission or termination via disproportionation of EPM macro radicals have been investigated (Dikland, 1992).

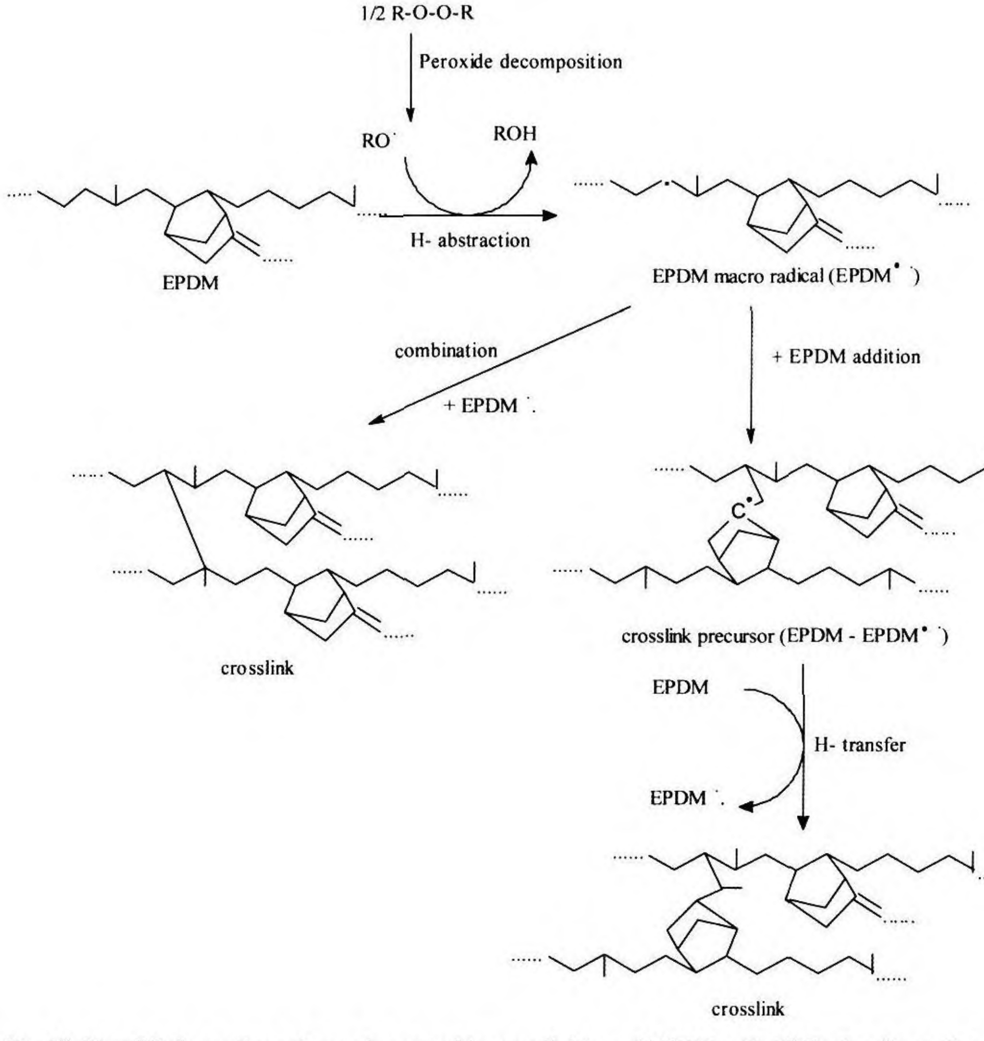


Fig. 10. Simplified reaction scheme for peroxide crosslinking of EPDM with ENB athe diene (Peters *et al.*, 2008)

Ethylene vinyl acetate (EVA)

Several researchers studied the peroxide induced crosslinking of EVA (Fargere *et al.*, 1995). The crosslinking mechanism (Loan, 1967) of EVA is somewhat complicated due to the presence of two active sites, tertiary hydrogen and the methyl hydrogen of the acetic acid residue, in addition to the methylene groups in the polymer chain. NMR analysis provided evidence that the methyl hydrogens of the acetate group were the most reactive sites for abstraction (Parent *et al.*, 2002). In the past, crosslinking of EVA had only been initiated by DCP. Recently modified organic peroxides have been applied to improve the crosslinking efficiency of EVA (Khonakdar *et al.*, 2007; Thaworn *et al.*, 2012).

Poly vinyl chloride (PVC)

Earlier attempts on peroxide crosslinking of PVC have been found to be unsatisfactory because thermal decomposition of organic peroxide in PVC leads to crosslinking, rapid degradation and darkening (Grossman, 1993). Later, dicumyl peroxide was found to be able to crosslink PVC to some extent. Very little further research has been reported due to the fact that the dehydrochlorination accelerated by the peroxide and the consequent side reactions, complicates the crosslinking process, in addition to PVC's poor thermal stability. Several mechanisms proposed for thermal degradation of PVC suggested that the recombination of radicals, derived from thermal degradation, would stop continuous dehydrochlorination and give rise to the formation of crosslinked network (Gupta and Pierre, 1973). If a suitable peroxide has well dissolved in the plastisol, and in the presence of a crosslinking monomer, uniformly crosslinked forms could be produced. Due to their good compatibility with PVC, the most effective monomer has shown to be poly functional acrylates and methacrylates. The gel formation and changes in mechanical properties of peroxide crosslinked plasticized PVC, blended with TMPTMA has been studied by Saethre (1996). The careful choice of peroxide type and reaction conditions are necessary for the preparation of plasticized PVC sheets which could be thermally crosslinked.

Polyethylene (PE)

For polyethylenes, peroxide crosslinking is the most common curing method. The mixing of polyethylene and peroxide should be carried out at low temperature, below the decomposition temperature of peroxide. The crosslinking reaction occurs until all peroxide is consumed or the temperature falls below the decomposition point (Narkis and Tobolsky, 1970). Crosslinking reaction takes place in melt condition and network develops along the production line (Krupa *et al.*, 2001). The rheological properties change with network formation and it is often vital to know the trend of these variations and the time for reaching the gel point (Ghasemi *et al.*, 2005). The main polymer radical species is at the secondary carbon sites due to their prevalence in the polymer (Yamazaki *et al.*, 2000), although it has been reported that the concentration of branch points (tertiary carbons) and presence of unsaturated structures like vinyl groups also has an impact on crosslink efficiency.

Coagents can increase unsaturation and hence crosslinking efficiency of polyethylene (Novits *et al.*, 2001). During the crosslinking reaction, coagents are grafted to PE chains, which increase the number of vinyl groups, thus creating more active sites for crosslinking. The kinetic approach to crosslinking of polyethylene by DCP and the effects of various coagents on crosslinking has been investigated by Ghasemi (2003). The role of various peroxides on crosslinking polyethylene has been investigated (Khonakdar *et al.*, 2003) and crosslinking efficiency was found to be more for DCP. For most applications involving low density polyethylene, dicumyl peroxide is commonly used. However, for applications involving high density polyethylene usually require more stable peroxides such as di-*tert*-butyl peroxide or 2, 5- dimethyl-2, 5-di-(*tert*- butylperoxy) hexane *etc.* (Tae-Kyu Kang Kangand Ha 2000). These are used to avoid scorch caused by high processing temperatures.

Polypropylene (PP)

In contrast to other saturated polymers, the addition of organic peroxide degrades the polypropylene backbone by beta scission, instead of crosslinking (Fig.11). This phenomenon is usually called '*vis* breaking' or 'PP controlled rheology'. The most commonly used peroxide for *vis* breaking are 2, 5- dimethyl 2, 5- di (t-butylperoxy) hexane, di tertiary butyl peroxide and dicumyl peroxide. The reaction of polypropylene with peroxides has been reported by Rado (1963). The polymeric radicals are formed by scission and branching reactions, hence there is a competition between reactions which either decrease or increase the molecular weight of the polymer. Crosslinking efficiency of isotactic polypropylene was found to be influenced by both the type of primary radicals formed and temperature. *p*- benzoquinone was found to be an effective coagent and use of sulphur prevent scission during the crosslinking reaction (Capla *et al.*, 1985)

With *t*- butyl perbenzoate as crosslinking agent, a predominance of build-up reactions was observed at higher peroxide concentration (Lazar *et al.*, 2000). Isotactic and syndiotactic polypropylene differ in cure behaviour and isotactic polypropylene crosslinked more tightly than syndiotactic polypropylene presumably due to the greater steric hindrance in the syndiotactic form.

Silicone rubbers

Silicone elastomers are vulcanized commercially with organic peroxides. Peroxides that are used for curing silicones fall into two groups the "general purpose" (2, 4-dichlorobenzoyl peroxide) and "vinyl specific" (dialkyl (di- *tert*- butyl peroxide, 2, 5- dimethyl-2, 5-di-(*tert*- butylperoxy) hexane) and diaralkyl peroxides (dicumyl peroxide)) peroxides. A post cure in a circulating oven is necessary to remove the acidic materials in the rubber produced during polymerization and cure, which can acts as degradents during use. In addition to the effect on crosslinking efficiency, the use of different types of peroxides also affects the dynamic modulus of silicone rubber (Warley *et al.*, 2005). The crosslinking reaction of silicone rubber is shown in Fig.12 (Bueche, 1955).

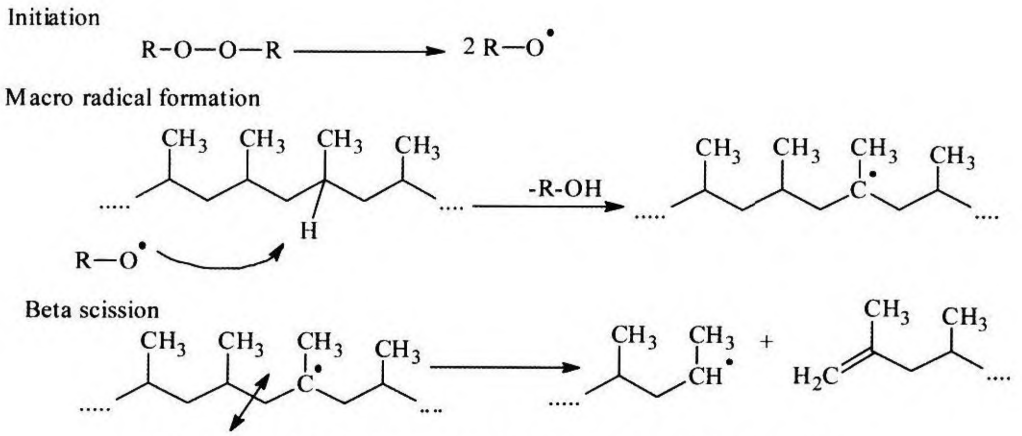


Fig. 11. Degradation of PP by beta scission in the presence of peroxide

For pharmaceutical applications and articles which come in direct contact with food materials peroxide curing is not suitable since there is a chance for post curing if the articles are sterilized (Heiner *et al.*, 2003).

Elastomer blends

Elastomeric blends are usually phase separated but mechanical compatibilization can be achieved by crosslinking between the phases resulting in unique and useful blends with a compromise in properties, offering useful commercial products (Robeson, 2007). Blends of natural rubber and ethylene vinyl acetate (NR/EVA) had gained a lot of interest and the mechanical properties, vulcanization kinetics (Koshy *et al.*, 1990), rheological behaviour [Koshy *et al.*, 1993(a)], ageing properties (Koshy *et al.*, 1992), effect of blend ratio and crosslinking system (sulphur, peroxide, mixed) has been extensively studied (Koshy *et al.*, 1993(b)). It was found that when DCP is added as the curing agent, it crosslinks both the phases and in mixed system, crosslinking efficiencies of the system in the NR phase varied in the order mixed > sulphur > peroxide. For 50/50 blends of NR and HNR (hydrogenated natural rubber) (Hinchiranan *et al.*, 2009), efficient vulcanization system with peroxide exhibited best mechanical properties. Utara and Boochathum (2011) studied the effect of curing system (sulphur and peroxide) and blend ratio of low density polyethylene (LDPE) and ozonolyzed natural rubber blends.

The curing behaviour, morphology, mechanical properties, swelling and ageing behaviour (Radhakrishnan *et al.*, 2006) of SBR/EVA blends vulcanized by different curing systems (sulphur, peroxide, mixed) showed that mechanical properties were found to increase with increasing EVA content up to 60-80 per cent and the best retention of ageing properties was exhibited by peroxide of cure system. The low acrylonitrile NBR can be blended with SBR without significantly deteriorating the mechanical properties of the vulcanizate (Rahiman *et al.*, 2005) and the homogeneity of blends can be improved by using polyglycidylmethacrylate-g-butadiene rubber (Botros *et al.*, 2006). SBR/NBR blends are used to compensate for the volume decrease in oil seal applications.

Thermoplastic elastomer blends

Though several crosslinking agents have been employed to crosslink elastomer

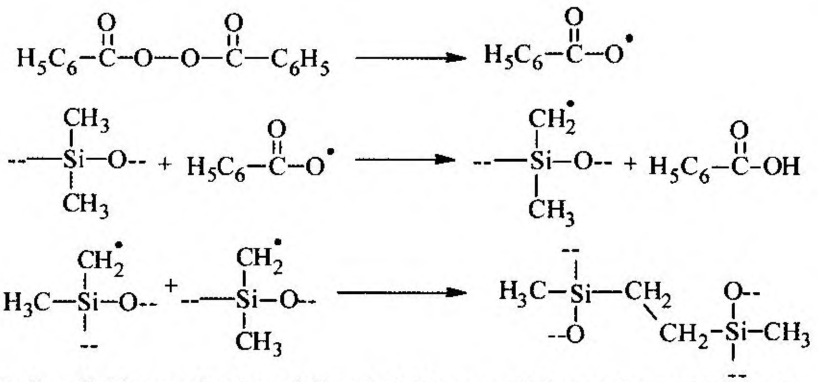


Fig. 12. Crosslinking mechanism of dimethyl silicones with benzoyl peroxide (Bueche, 1955)

phases in TPVs, peroxide, phenolic resin and silane crosslinking systems have gained commercial importance. Nasakar and Noordermeer (2006) investigated the possible use of peroxides in the production of PP/EPDM TPVs. The physical properties of TPVs change significantly with the PP/EPDM blend ratio, chemical nature of peroxides, extent of crosslinking in EPDM phase and in the extent of degradation of the PP phase. Dicumyl peroxide was found to give the best overall balance of properties (Brostow *et al.*, 2010). Multifunctional peroxides, having peroxide and coagent functionality in a single molecule was also explored to overcome the unpleasant smell and blooming characteristics produced by decomposed products of some peroxides (de Rishi and Noordermeer, 2007; Nasakar and Noordermeer, 2004). In ENR/PP and NR/PP TPVs, two peroxides DCP and DTBPIB [di (*tert* - butylperoxyisopropyl) benzene] were found to be effective in both the blends at low temperature but they form more smelly byproducts having surface bloom [Thitithammawong *et al.*, 2007(a)]. Physical properties of m-EPM (maleated ethylene propylene rubber)/PP TPVs were to found change significantly with DCP concentrations and rubber/plastic blend ratio (Chatterjee and Nasakar, 2007). Properties of TPVs depend on their morphology and crosslink density in the elastomer phase.

Thermoplastic elastomer blends of natural rubber and polypropylene (NR/PP) has been an area of research for many years (Kuriakose and De, 1985; Kuriakose, *et. al.*, 1986). The typical crosslinking temperature, crosslinking efficiency and relative amount of decomposition products of each peroxide used [Thitithammawong *et al.*, 2007(b)] and also the effect of DCP, which not only initiated crosslink reaction in NR phase, but also degraded the polypropylene molecules, played an important role in the morphology and properties of TPVs (Sang *et al.*, 2011; Thitithammawong *et al.*, 2012).

Scorch safety and scorch retarders

One of the most important issues in peroxide vulcanization is scorch safety. This is caused by the fact that decomposition of crosslinking peroxides into radical fragments does not show an induction period. The usual solution to the scorch problem consists of the addition of a scorch retarder/cure suppressor (Kovacic *et al.*, 1962) to the formulation. A scorch retarder is a chemical which consumes peroxide radicals in the first stages of the vulcanization. The amount of scorch retarder is of crucial importance and it is normally adjusted according to the extent of delay that is desired. Because of the consumption of radicals, the efficiency of the crosslinking reaction is usually reduced and is reflected in the final properties of the material. To overcome this problem, either extra amount of peroxide is added to the system to compensate for the loss of radicals or coagents are introduced in the formulation. Both of this obviously results in a more expensive final product.

Most of the antioxidants used in the rubber industry readily react with radical species, in order to avoid polymer degradation. Because of this, antioxidants often also work as scorch retarders. These chemicals contain readily abstractable hydrogen atoms. Normally, they release a hydrogen atom to the radical species and the radical is in this way transferred to the antioxidant molecule. When antioxidants act as scorch retarders, they scavenge the first radicals formed by peroxide decomposition, until the antioxidant is consumed. At that point the normal vulcanization mechanism takes over and crosslinking takes place.

Since some radicals are consumed, by reacting with the antioxidant, the crosslink efficiency is lowered. This means that larger amounts of peroxide or co-agent need to be added to the formulation in order to maintain a proper cure state. On the other hand, when antioxidants act as scorch retarders they also loose their long term antioxidant activity, since they are consumed during the first stages of vulcanization. Several chemicals are commercially available as scorch retarders (Schober *et al.*, 1977;Groepper *et al.*, 1989). Some examples are: derivatives from 4-*tert*-butylcatechol (TBC) (Demassa, 2003), methyl substituted amino alkyl phenols (Reiter *et al.*, 1989) and hydroperoxides (Schober *et al.*, 1977) and 2, 6- *bis* (t- butyl)-p- cresol (BHT) (Yamazaki and Seguchi, 2000). Some scorch retarding systems have been reported in literature (Costin *et al.*, 1991) and phenolic antioxidants (Akzo Nobel, 2004). Now-a-days a combination of suitable radical scavenger along with a coagent is used to impart scorch retardation. Ready-made mixtures containing a crosslinking peroxide, a coagent and a radical scavenger, has been introduced in order to facilitate compounding of 'scorch-retarded' or 'scorch- safe' recipes. Grima *et al.* 2(006; 2009) introduced a combination of bismaleimide type coagents in the peroxide cure of EPM. Similarly, stable free radical assisted and delayed action peroxide vulcanization has been extensively investigated (George *et al.*, 2010; 2012).

Effect of compounding ingredients on peroxide vulcanization

As the radicals formed during decomposition of the crosslinking peroxide are a very reactive species, it is essential to ensure that mainly those reactions that lead to crosslinks do occur. Other unwanted side reaction should be prevented as much as possible. Certain types of fillers and some special additives are known to interact with peroxide or peroxide radicals and inhibit the formation of crosslinks (Nijhof and Cubera, 2001). Besides the elastomer and cure system, other compounding ingredients like fillers, antidegradants, processing oils and plasticizers also influence the cure and scorch behaviour of vulcanizates. Usually, the effect of a material on vulcanization depends upon the pH of the material. Basic ingredients tend to accelerate the rate of both cure and scorch, whereas acidic materials exhibit the opposite effect.

Fillers

Unlike natural rubber most of the synthetic rubbers are hardly used as such because physical properties such as stiffness, hardness, stress-strain, *etc.* are very poor. Therefore the addition of reinforcement materials is a common practice. Fillers usually used in rubber industry are carbon black, fumed and precipitated silica, silicates and clays. Additionally, semi- or non-reinforcing fillers such as talc and whiting are practically used (Endstra and Wreesmann, 1993). A number of these fillers can show strong interference reactions with a peroxide cure system. These reactions can be based either on the high surface area of the filler, or on the acidity of the material (Class, 1999; Ogunniyi, 1999; Keller, 1988). In the former case it is expected that the crosslinking peroxide will be adsorbed on the filler during compounding and storage of the uncured stock. As a consequence the formation of radicals during the curing step is less homogeneous throughout the compound, and the crosslinking efficiency will be reduced. In the latter case, the peroxide can be partly decomposed by heterolytic reaction, whereby no peroxide radicals are formed. As an example the heterolytic decomposition of dicumyl peroxide is shown in Fig. 13. Thus depending upon the type and amount of filler, the peroxide cure may be inhibited completely.

Although all peroxides are decomposed by acids, the degree of vulnerability varies with different peroxides. Hydroperoxides and peroxyesters are more vulnerable than peroxyketals and dialkyl peroxides (Endstra *et al.*, 1993). However, the unwanted interference reactions of fillers and crosslinking peroxides can be prevented by the addition of pH-neutral or basic ingredients that will be preferentially adsorbed to the fillers surface. Examples of such additives in this respect are guanidines such as DPG and DOTG, ethylene glycols such as DEG and PEG, triethanol amine and quinolines such as TMQ. These additives must also be added to the rubber mix prior to the peroxide. There are several treatments for clay fillers that can minimize the effect by altering the surface chemistry. Heat treatment (calcination), treatment with resins, silanes or cationic species can also lead to a beneficial modification of the surface. This favourable effect in peroxide cured compounds is illustrated in Table 7.

Table 7. **Effect of surface treatment of a mineral filler on physical properties of a peroxide cured EPDM compound (Endstra *et al.*, 1993)**

Type of clay	Calcined clay	Silane treated calcined clay
pH(10% suspension)	5.0	7.0
Compound properties		
Hardness, Shore A	62	62
Tensile strength, MPa	6.7	9.2
Modulus (100%), MPa	1.8	3.3
Elongation at break, %	670	240
Compression set (24h/100 °C), %	22	11

Compound composition: Keltan 520: 100; ZnO: 5; PbO: 4; clay: 120; Sunpar 150:25; Permanax TQ: 1; Perkadox 14-40: 4.2, Mold cure conditions: 15 minutes at 180 °C

The interference of different types of carbon black on the peroxide cure of EPDM

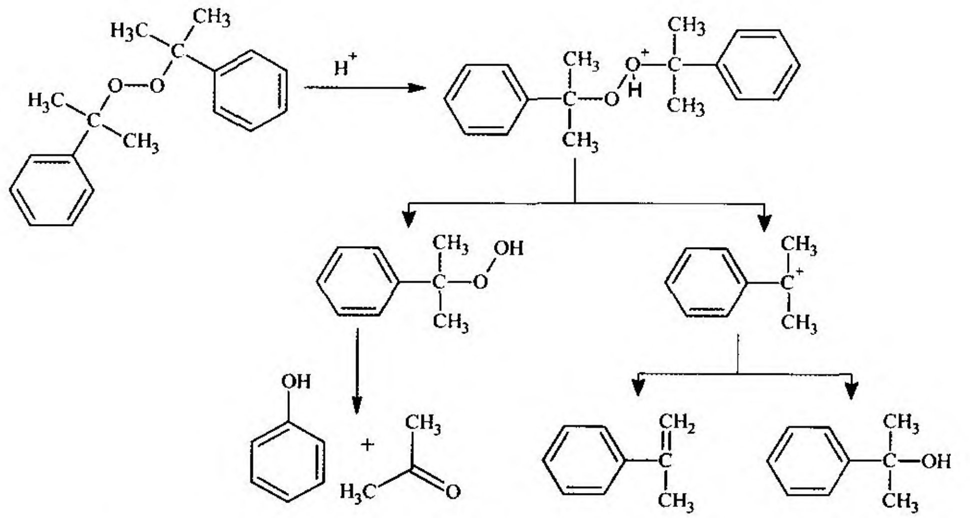


Fig.13 Heterolytic decomposition of dicumyl peroxide (Endstra *et al.*, 1993)

has extensively been investigated (Litvinov *et al.*, 1999; Li *et al.*, 2008). The effect of different types of carbon black with different class of peroxides is shown in Table 8.

The peroxy ketal illustrate the differences in the reinforcing effect that could be expected between the different types of carbon black: the small particle size material such as N326 and N330 shows grater reinforcement than the coarser material N774. The peroxy ester type peroxide shows a substantial influence of carbon black type on physical properties after cure. Smaller particle size material shows a detrimental effect on final crosslink density. A certain state of cure can be achieved only by the use of coarse type of carbon black. This effect on cure is caused by an adsorption of peroxide to the carbon black surface, where a heterolytic decomposition can be expected. The peroxy ester compounds are more prone to acid catalyzed decompositions than peroxy ketals or alkyl- or aralkyl peroxides.

Oils and plasticizers

Usually rubber processing oils interfere with free radical vulcanization. The extent of interference is dependent on the molecular structures of oils. Rubber oils contain three types of molecular structures, saturates, aromatics and polar. One or more carbon side chains are usually attached to the cyclic structures present in any of the three fractions (Chasey, 1992). The free radicals generated by the homolytic cleavage of peroxides can abstract hydrogen from oils rather than the polymer or the radical can undergo addition reaction with an aromatic nucleus in the oil. Both these reactions decrease the peroxide vulcanization efficiency. EPDM compounds are generally formulated with substantial amounts of mineral processing oils, to reduce compound cost and improve processing characteristics. The comparative effect of aromatic, naphthenic and paraffinic oils on the cure of an EPDM: clay: oil formulation is shown in Fig. 14 [Class, 1999; Dluzneski, 2001(b)].

Table 8. **Influence of different types of carbon black on physical properties of an EPDM compound (Endstra *et al.*, 1993)**

Properties	Carbonblack type	Peroxy ketal (7.6phr)	Peroxy ester (5.8 phr) Perkalink 350 (1.0 phr)
Hardness, Shore A	N326	60	54
	N330	62	55
	N774	59	56
Tensile strength, MPa	N326	18.1	1.6
	N330	19.1	1.6
	N774	15.1	10.3
Elongation at break, %	N326	370	305
	N330	315	300
	N774	320	350
Compression set (24h/100 °C), %	N326	24	69
	N330	17	62
	N774	18	35

Compound composition: Keltan 520: 100; carbon black: 50; Sunpar 150: 10; crosslinking peroxide (as indicated); Mold cure conditions: peroxy ketal: 15 min at 150 °C, peroxy ester: 15 min at 140 °C

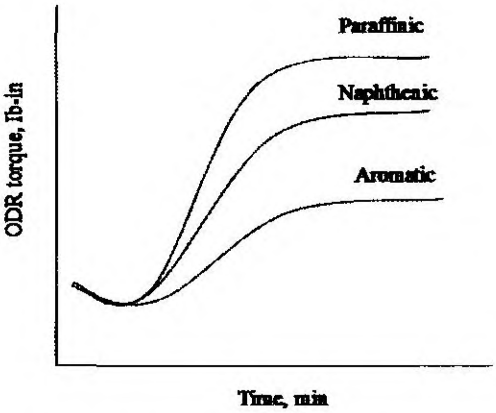


Fig. 14. The effect of oils on peroxide vulcanization of EPDM compound [Class, 1999:;Dluzneski 2001(b)]

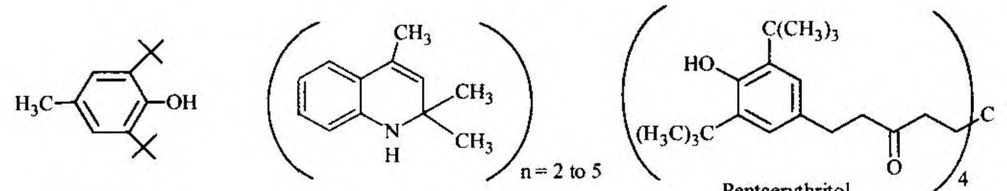
It was observed that paraffinic oil has the least and aromatic oil has worse effect on peroxide cure efficiency. The aromatic oil contains a substantial amount of labile benzylic hydrogens which can promote the abstraction of hydrogen in the oil phase. Due to the effect on peroxide cure mechanism, the use of paraffinic oil is preferred in peroxide vulcanization. The standard paraffinic processing oils can be replaced with more expensive technical white oil without the compound cost being affected because peroxide dosages can be lowered substantially (Dikland and Maag, 1999).

Antioxidants and antiozonants

Since the driving force behind peroxide vulcanization is free radicals, the use of antioxidants is a critical issue. It has been reported that the most effective antioxidants are also the most potent inhibitors of peroxide curing (Ogunniyi, 1999). Ferradino (2003) presented a detailed review of the best antioxidant systems for peroxide cured elastomers. The use of antioxidant for peroxide cures is virtually unavoidable. Antioxidant selection needs to be made by considering the balance between antioxidant activity and interference with peroxide crosslinking. Some of the best recognized antioxidants for peroxide cured elastomers are shown in Fig. 15.

The effect of both amine and phenolic antioxidants on peroxide vulcanization process has been extensively investigated (Yamazaki and Seguchi, 2000). The inhibition of unhindered phenolic antioxidants is more pronounced in PE than in EPR and even less in EPDM since there is progressively more active competition for radicals in the latter polymers (Harpell and Walrod, 1973). It has also been recommended to avoid antiozonants entirely since they are potent radical inhibiters. TMQ (1, 2 – dihydro – 2, 2, 4 - trimethylquinoline) is one of the most effective, peroxide compatible primary antioxidant with a high molecular weight and economical price. It also has a mild antiozonant effect. The use of antioxidant TMQ is limited to black filled compounds since it is somewhat discolouring and staining. Antioxidant - 445 is a more powerful hindered aromatic type antioxidant having minimum staining and discolouring qualities. Hence it can be used in some non-black rubber articles. Antioxidant – 1010 shows excellent compatibility with peroxides, imparting minimum reduction in crosslink density. It is most persistent at higher temperatures since it exhibit one of the lowest diffusion rates of phenolic antioxidants (Pushpa *et al.*, 1995). Further, it is non-staining, non – discolouring and effective in non- black, colourable rubber compounds.

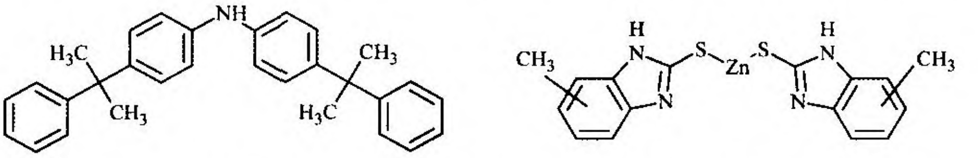
A combination of antioxidant-1010 with ZMTI is more effective in retaining the physical properties (Walters *et al.*, 1981). While hundreds or more of antioxidants are available to protect elastomers against oxidation and heat, only a handful can



Butyrated hydroxytoluene (BHT)

1,2 - dihydro- 2,2,4-trimethylquinoline (TMQ)

Pentaerythritol *tetrakis*(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) (AO - 1010)



4.4'-*bis* (alpha, alpha-dimethylbenzyl) diphenylamine (AO- 445)

Zinc 2- mercaptotoluimidazole (AO - ZMTI)

Fig. 15. Antioxidants for peroxide cured elastomers

successfully function under the constraints imposed by peroxide crosslinking (Ferradino, 2003).

Comparison of peroxide and sulphur vulcanization

Peroxide cure system gains importance not only with the development of saturated rubbers but, in the meantime, it starts to be widely used in NR and the diene type of rubbers. Peroxide cured diene elastomers, especially, NBR and EPDM give very outstanding heat stability of the vulcanizate. The properties of the cured vulcanizate depend on the type and nature of crosslinks formed during vulcanization. Peroxide cure results in the formation of strong and rigid carbon - carbon (C - C) crosslinks between polymer chains. Fig. 16 compares the dissociation energies of C-C as well as different sulphidic crosslinks. The higher thermal stability of C-C crosslinks is responsible for the improved compression set and heat ageing resistance of peroxide cured vulcanizates. Compared to sulphur vulcanization, organic peroxide cured elastomers exhibit superior properties such as low compression set, improved heat resistance, and rapid vulcanization without reversion. But due to lack of flexibility, it produces vulcanizates with poor mechanical and dynamic properties.

Applications of peroxide vulcanization

Organic peroxides play a vital role in the manufacture of elastomeric products. Automotive parts, golf ball cores, footwear soles, adhesive tapes, wire & cable and foamed products (rubber or thermoplastic) are examples of everyday products that use organic peroxides. Excellent heat resistance has been reported for peroxide cured EPDM rubber compounds for the manufacture of automotive radiator hoses (Beal, 1999). By applying fast reacting, crosslinking peroxide types, short production cycle times can be achieved in injection moulding technique by increasing mould temperature. The scorch

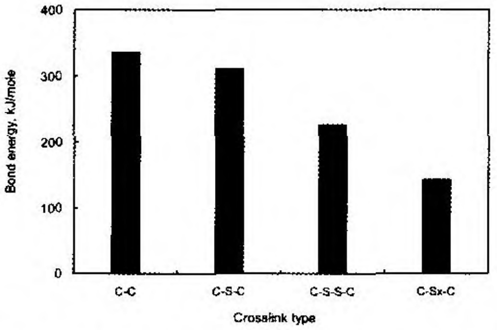


Fig. 16 Comparison of crosslink type and bond dissociation energies

problem at higher cure temperature can be avoided by the addition of suitable radical scavenger (Endstra *et al.*, 1993). It has been reported that golf balls with excellent rebound resilience can be prepared from diene rubber with a suitable peroxide-peoxy ester combination (Shindo *et al.*, 2007). Usually, ethylene vinyl acetate (EVA) is used for the manufacture of sandals, slippers and shoe soles. When crosslinked by DCP, the foamed EVA possess special properties better than that of other foamed materials in light-weight coloured articles (Fujita and Nishida, 1983). Several polymers and elastomers used by wire and cable industry like EPDM, EOM (poly ethylene co-octene), EVA, AEM (poly ethylene-co-methacrylate), LDPE (low density polyethylene), HNBR and CPE (chlorinated polyethylene) utilizes organic peroxides as curing agent. When using organic peroxides for crosslinking wire and cable, balancing cable compound processability with reactivity, is the key objective that must be met to achieve the goal of increased productivity with consistent quality (Palys *et al.*, 2007).

CONCLUSION

A review of the peroxide vulcanization of natural rubber, synthetic rubbers and elastomeric blends has been presented. The generalized crosslinking mechanism and different types of available peroxides and coagents for crosslinking elastomers were discussed. Dicumyl peroxide is the commonly used peroxide in polymer industry and is found to give the best overall balance in properties. Now-a-days different multifunctional peroxides, having peroxide and coagent functionality in a single molecule have also been explored to overcome the unpleasant smell and blooming characteristics caused by decomposed products of some peroxides. The influence of compounding ingredients like fillers, oils, plasticizers, antioxidants and antiozonants are also discussed. With the discovery of peroxide-coagent cure system, the inherent drawbacks of peroxide cure system can be avoided. By the proper control of polymer, peroxide and other compounding ingredients in the formulation the peroxide cure system can be usedmore effectively.

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