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REVIEW

Sulphur and peroxide vulcanisation of rubber compounds[‡] – overview

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Vulcanisation is a process of transforming a plastic rubber compound into a highly elastic product by forming a three-dimensional cross-linked network structure in the rubber matrix. Many systems have been developed to vulcanise rubber compounds, among which sulphur and peroxide curing systems remain the most desirable. The application of sulphur systems leads to the forming of sulphidic cross-links between elastomer chains, while carbon-carbon bonds are formed in peroxide-curing. Both vulcanisation systems provide certain benefits to the cross-linked rubber articles, but also some disadvantages. The present work seeks to provide an overview on both vulcanisation systems; their composition, possibilities of their application, reaction mechanisms, structure of the cross-links formed and the main feature of the final cross-linked materials – vulcanisates.
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Keywords: sulphur vulcanisation, peroxide vulcanisation, vulcanisate, cross-linked density, cross-linked structure

Introduction

Elastomers or rubbers are polymer materials which are characterised by their ability to be reversibly deformed under the influence of external forces; this property is known as elasticity. In conformity with the theory of rubber elasticity, the retractive forces which resist deformation are proportional to the forces carrying network chains per unit volume of rubber. An increase in the number of junctions or cross-links causes an increase in the number of network chains. In the non-cross-linked linear high molecular mass elastomer, only chain entanglements induce viscoelasticity (Orza, 2008).

The first reference in writing to natural rubber (NR) dates from the beginning of the sixteenth century, when Columbus discovered America. The first samples of natural rubber arrived in Europe in 1736. At this time, rubber was used in its natural form – latex. Its potential applications were restricted due to its

spontaneous coagulation, in consequence of which it became unworkable. Accordingly, at the early stages, an effort was made to process natural rubber in the form of an emulsion. Rubber emulsion was first used commercially in 1791 to make waterproof boat-sheets, post-carrying bags; later it was used to produce waterproof raincoats (Mark, 1988). However, the products were soft and sticky in the summer months, but hard and brittle in the winter period.

A major development in natural rubber use occurred in 1820 when Englishman Thomas Hancock found that the properties of rubber could be changed by applying mechanical stress – hard unworkable rubber was changed into a soft viscous material. The revolutionary discovery was that when rubber was heated with sulphur the product obtained possessed properties rendering it pliable at ambient temperature and not sticky at elevated temperature. This experiment was first performed by an American, Charles Goodyear (1839, patent from 1844) and an English-

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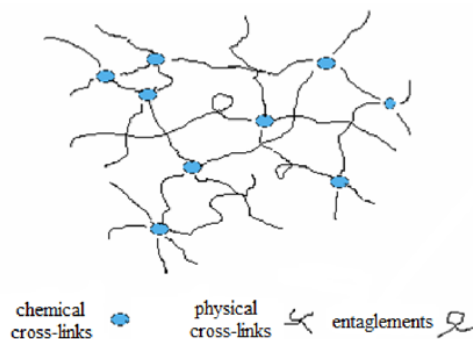


Fig. 1. General scheme of cross-linked network structure of vulcanisate.

man, Thomas Hancock (patent from 1843) independently of each other (Blow & Hepburn, 1981; Coran, 1994; Cowie, 1998). Hence, they found the basis of the process for the vulcanisation of rubbers and all rubber products. The term vulcanisation was introduced by William Brockedon (1842), because the smell arising when rubber was heated with sulphur was very similar to that which accompanies a volcanic eruption.

Currently, vulcanisation, or what engineers often refer to as cross-linking or curing, is one of the most important processes in rubber technologies. Almost every rubber product undergoes a vulcanisation process, by which in parallel and sequential physical and mainly chemical reactions the plastic rubber compound changes into a highly elastic final product – vulcanisate (Baranwal & Stephens, 2001). The fundamental principle of vulcanisation is the forming of chemical cross-links between rubber macromolecules which lead to the formation of a three-dimensional network of rubber matrix by the reactions between functional groups of elastomer chains and suitable curing agents. In the cross-linked vulcanisate network, physical couplings are also present as hydrogen bonds, polar, dispersion forces between elastomer chains and various intramolecular and intermolecular entanglements (Fig. 1) (Kyselá et al., 2010).

Nowadays there are many commercially available elastomers, distinguished by their structure and chemical nature. Accordingly, a number of curing systems have also been developed in order to vulcanise rubber compounds such as sulphur, peroxides, metal oxides, phenolic resins, quinones etc. The type of curing system applied determines the structure and the quality of the cross-links. In addition, the type of rubber matrix must be considered in the cross-linking of elastomers, especially their structure and the presence of suitable functional groups. However, most of the vulcanisation systems are rarely used and some of them are of minor importance. At the present time, the sulphur and peroxide curing systems are those most widely used for the cross-linking of rubber materials.

Sulphur vulcanisation

Sulphur vulcanisation agents

Sulphur vulcanisation is the oldest and remains the most widely used method for the cross-linking of unsaturated elastomers. The effective and rapid cross-linking of rubber materials with sulphur proceeds only in the presence of accelerators and activators (Coran, 1978, 2003; Abi et al., 2003; Heideman et al., 2005, 2006). In their absence, sulphur reacts very slowly with elastomer chains and it couples onto them in the form of side cyclic structures and not in the form of sulphur cross-links. Accelerators and activators influence the kinetic parameters of vulcanisation – time and temperature; they affect the processing safety of the vulcanised rubber compounds and the amount of sulphur needed for the optimal cross-linked structure of vulcanisate (Heideman, 2004). The type and amount of accelerator and the ratio of the accelerator to sulphur in the rubber mixture also influence the final properties of vulcanisates, especially their thermo-oxidative stability and some mechanical and dynamic properties (Kresja & Koenig, 1993a; Mark et al., 2005).

The vulcanisation agent in common use is elementary crystalline sulphur in milled form with a specific oil content. Elementary sulphur consists of cyclic molecules with eight sulphur atoms. The average S—S bonding energy is approximately 252 kJ mol^{-1} . During the vulcanisation process in the presence of accelerators and activators, sulphur decomposes into sulphur fragments which react with the functional groups of elastomers to form cross-links (Morrison & Porter, 1984). In addition to sulphur, sulphur donors can be used as sulphur vulcanisation agents. In the presence of very low levels of sulphur, ultimately without sulphur, these substances are able to generate cross-links between rubber chains.

Accelerators are essential ingredients in all sulphur vulcanisation systems. They increase the reaction speed and cross-linking density they improve the yield of the sulphur forming cross-links and can be used to adjust the ratio between the induction period, reaction speed and types of cross-links. From a technological perspective, the presence of accelerators in the vulcanisation process leads to a reduction in vulcanisation time, they reduce the vulcanisation temperature and the amount of sulphur in the rubber mixture. Accelerators are exclusively organic compounds containing, in almost all cases, nitrogen and sulphur in the molecules (Hofmann, 1994). Organic compounds based on nitrogen, mainly aniline and its derivatives were first used as accelerators by Oenslager in 1906 (Oenslager, 1933). Subsequently, many organic accelerators with various structures and different effects in the vulcanisation process have been developed (Quirk, 1988; White & De, 2001). Accord-

Table 1. Accelerators for sulphur vulcanisation

Type of accelerators	Examples
Guanidines	<i>N,N'</i> -diphenylguanidine (DPG) Di- <i>o</i> -tolylguanidine (DOTG)
Aldehydamines	Butyraldehyde aniline (BAA) Hexamethylene tetramine (HEXA)
Thiazoles	2-mercaptobenzothiazole (MBT) Dibenzothiazyl disulphide (MBTS)
Sulphenamides	<i>N</i> -cyclohexyl-2-benzothiazole sulphenamide (CBS) <i>N,N</i> -dicyclohexyl-2-benzothiazole sulfenamide (DCBS)
Thiurams	Tetramethylthiuram disulphide (TMTD) Tetraethylthiuram disulphide (TETD)
Dithiocarbamates	Zinc dimethyldithiocarbamate (ZDMC) Zinc diethyldithiocarbamate (ZDEC)
Xanthates	Zinc isopropylxanthate (ZIX) Sodium isopropylxanthate (NaIX)
Other sulphur donors	Dithiodimorfoline (DTDM) Caprolactam disulphide (CLD)

ing to the activity in the vulcanisation process, accelerators can be divided into four groups (Gupta et al., 2014): i) slow (guanidines, some aldehydamines); ii) fast (thiazoles, sulphenamides); iii) very fast (thiurams); iv) ultra-accelerators (dithiocarbamates, xanthates).

Table 1 shows a list of the fundamental accelerators from each group. The activity of accelerators also depends on the type of vulcanised rubber, the composition of the rubber mixture and the vulcanisation conditions. The more effective the accelerator, the smaller the amount added to the mixture, and the lower the amount of sulphur needed to achieve the optimal properties of the vulcanisate. With regard to the processing properties and toxicity of the reaction products, the class of benzthiazolsulphenamides is favoured. Those accelerators are characterised by a long induction period (delayed action) and rapid main cross-linking reaction. The first delayed action accelerators, 2-mercaptobenzothiazole (MBT) and dibenzothiazyl disulphide (MBTS), were introduced in 1921. The introduction of sulphenamides such as *N*-cyclohexyl-2-benzothiazole sulphenamide (CBS) and *N*-tert-butyl-2-benzothiazole sulphenamide (TBBS) in 1937 led to vulcanisation with a faster main cross-linking phase and improved induction period (Harman, 1937). Among them, CBS is probably one of the most widely used.

The optimal effect of sulphur vulcanisation systems is achieved in the presence of activators. The most common activator for sulphur vulcanisation is zinc oxide, which is almost always used in combination with appropriate fatty acids, mainly stearic, lauric acid or their zinc salts (González et al., 2005). It is presumed that zinc oxide with fatty acids forms a salt which, together with accelerators, gives intermediate complexes (Ohm, 1997; Nieuwenhuizen et al., 1999). The complex is more effective in activating the sulphur present in

the rubber compound, hence leading to the increase in reaction rate.

Retarders and prevulcanisation inhibitors can also take part in sulphur vulcanisation systems. Retarders slightly prolong the induction period, but they reduce the speed of the main cross-linking phase. Their presence in the rubber mixture can also lead to the decreasing the cross-linking density of vulcanisates. These materials are usually weak organic acids such as phthalic acid, salicylic or benzoic acid.

From a practical perspective, prevulcanisation inhibitors are of greater importance. During the vulcanisation, they also prolong the induction period, but have no influence on the main cross-linking reaction and the cross-linking density of the final articles. The most frequently used prevulcanisation inhibitor is *N*-cyclohexylthiophthalimide (CTP) (White & De, 2001).

Mechanism of sulphur vulcanisation

Despite the fact that vulcanisation process has been known for more than 150 years, the chemistry of accelerated sulphur vulcanisation is complex and is still not fully understood. The entire course of sulphur vulcanisation may be represented by the simplified reaction sequence shown in Fig. 2, originally proposed for natural rubber by Bateman et al. (1963) and Chapman and Porter (1988), Chapman and Johnson (2005). The course of sulphur vulcanisation outlined in Fig. 2 is generally accepted, but there is still no comprehensive agreement relating to the substance of the active sulphurating agent and the mechanism of its reaction with the rubber molecules, in particular as to whether or not zinc is involved. Accordingly, instead of the zinc complex (1) shown in Fig. 2, Coleman et al. (1974) and Coran (1989, 1994) proposed the active sulphurating agent to be

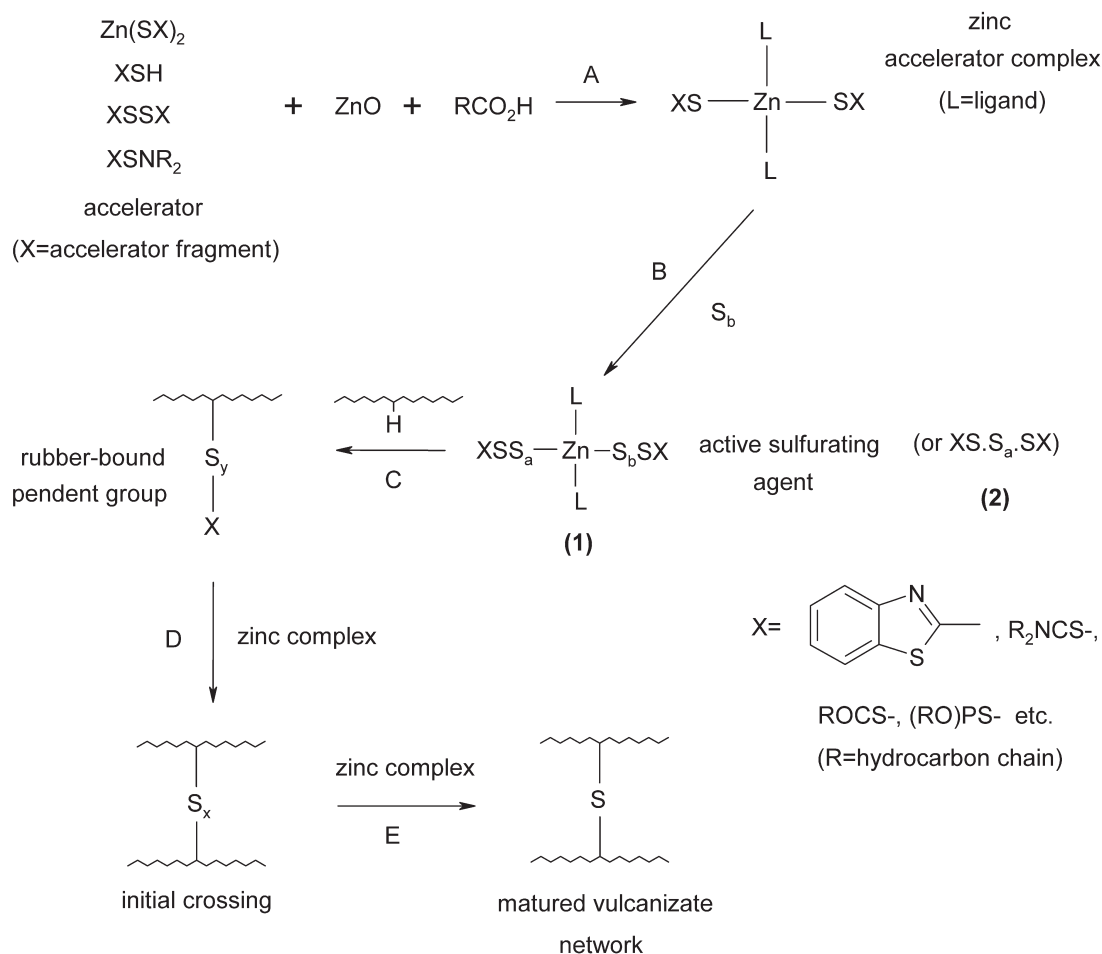
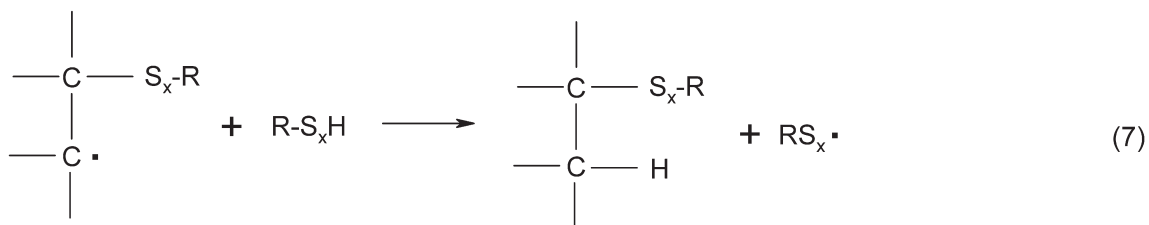
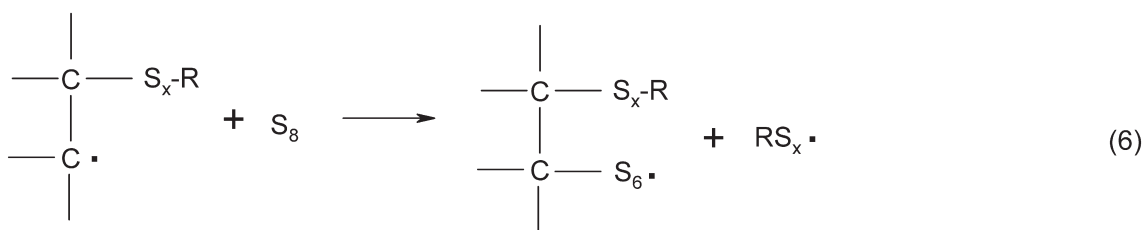
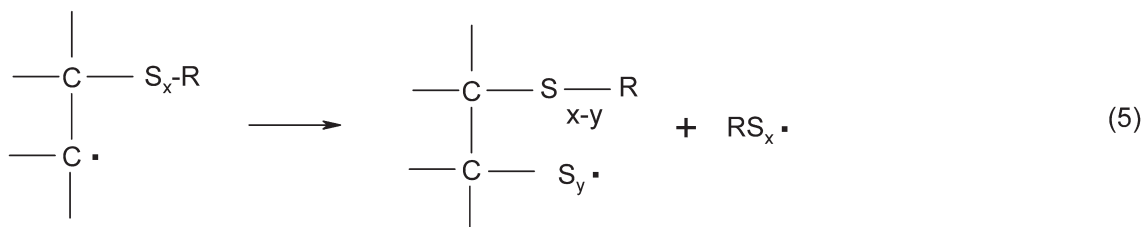
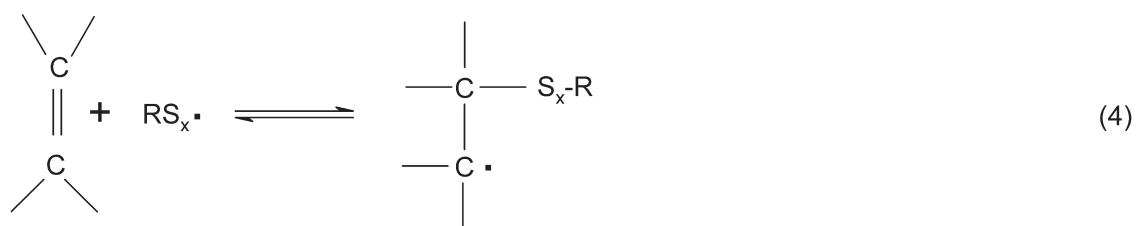


Fig. 2. Simplified reaction sequences in sulphur vulcanisation (Chapman & Johnson, 2005).

an accelerator polysulphide (2), even when zinc is present, while Chapman and Porter (1988) proposed that both the zinc complex (1) and polysulphide (2) could act as the active sulphurating agent, depending on the conditions and the extent of vulcanisation. However, there is good evidence (at least for natural rubber) that zinc, when present, plays an active role in stages D and E in Fig. 2 (Chapman & Porter, 1988). Hence, the inclusion of a zinc activator in accelerated vulcanisation of NR has little effect on the rate but leads to an increase in the cross-linking efficiency. It has a marked effect on the chemical pathways: the sulphuration is almost entirely led by the substitution of allylic hydrogen atoms, rather than by the combination of the substitution and addition to the C=C double bonds that occur when zinc is absent. Cross-linked shortening is catalysed; this leads to a network with a greater proportion of mono- and disulphidic cross-links and to reduced reversion, arguably to the most important benefit in NR. The presence of zinc oxide also results in a small

increase in the induction period and vulcanisation time.

Ideas on the chemism of elastomer cross-linking with sulphur systems were published in many older scientific works and have been processed in a number of monographs and summary works. Among these, the most significant are the works of Bateman et al. (1963), Coran (1994), Morrison and Porter (1984), Saville and Watson (1967), Chapman and Porter (1988) or Russian authors, e.g. Dogadkin, Šeršnev, Feldštejn, whose works were also presented in Bloch's monograph about the action of organic accelerators in the sulphur vulcanisation of elastomers (Bloch, 1972). The issue of sulphur vulcanisation, from both the theoretical and practical perspectives, has attracted interest in many contemporary scientific studies (Ghosh et al., 2003; Pierre & Datta, 2004; González et al., 2005; Choi, 2006; Zhang et al., 2010; Leroy et al., 2013; Milani et al., 2013; Milani & Milani, 2014; Polacco & Filippi, 2014; Ikeda, 2014; Mansilla et al., 2015; Dondi et al., 2015, etc.). Regarding the extended possibilities



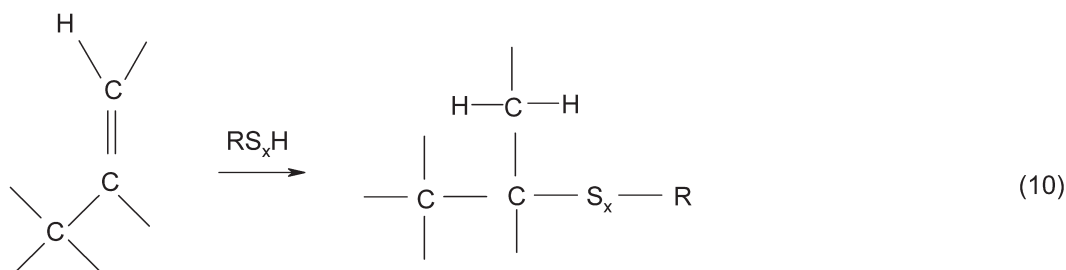
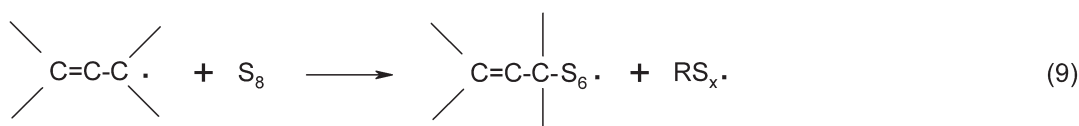
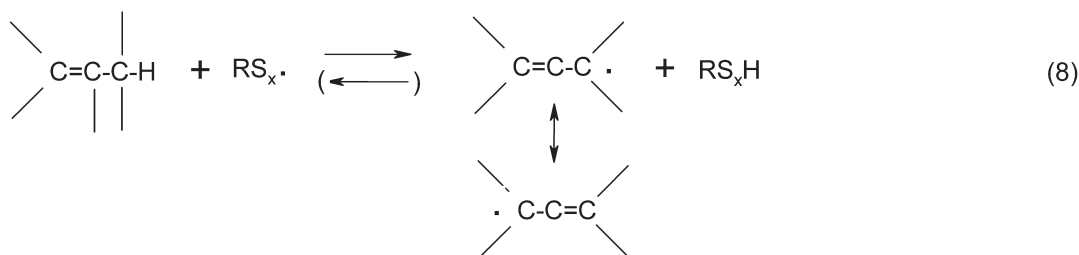


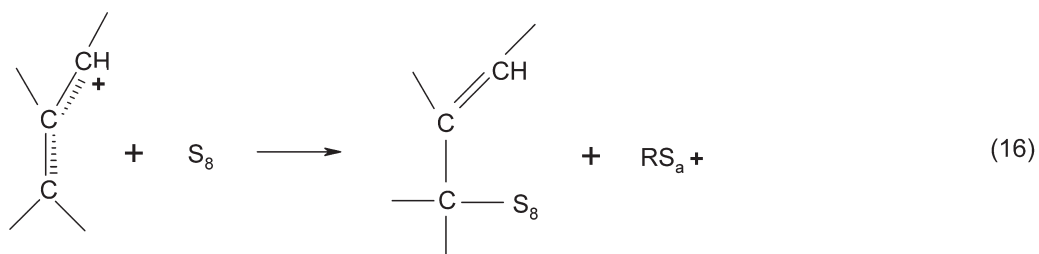
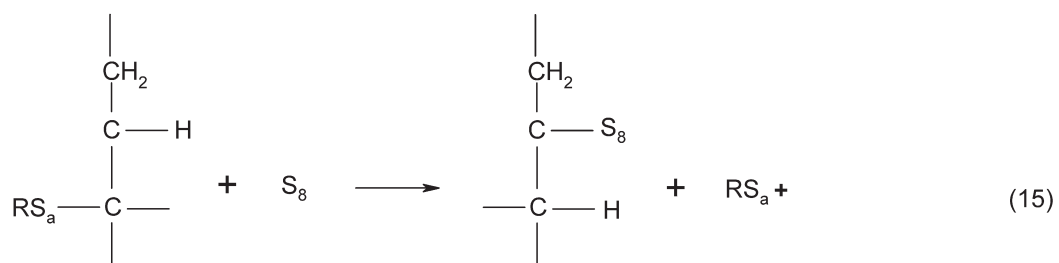
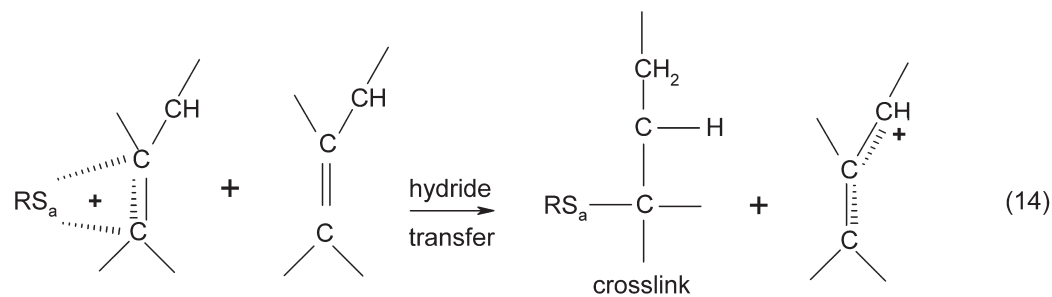
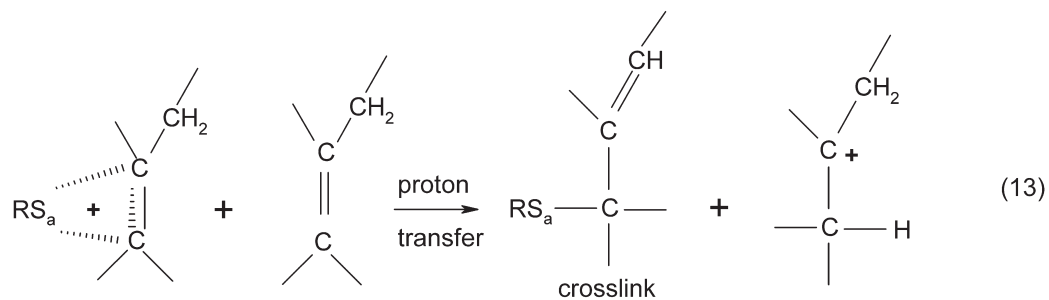
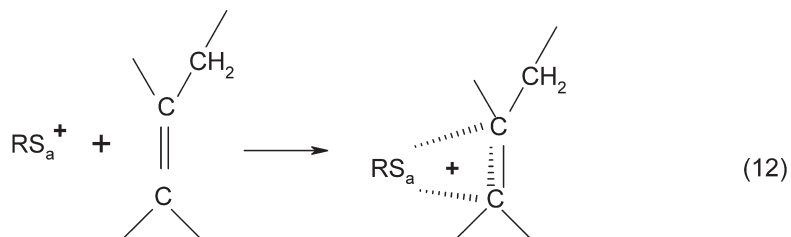
Fig. 3. Free-radical mechanism for sulphur vulcanisation (Akiba & Hashim, 1997).

of the analysis of the resulting products, or intermediate products and the final cross-linked articles – vulcanisates, in which various models of low molecular or oligomer rubber equivalents or intermediate products of their cross-linking reactions are used, most of the studies have focused on the quantitative character. The results thereby achieved make it possible, in some cases, to describe the chemical changes of the components in sulphur vulcanisation systems, as well as the structure in the cross-linked network of vulcanisates and modification changes of elastomer chains, but the degree of generalisation about the whole vulcanisation process is limited to particular compositions of rubber mixtures and specific components of vulcanisation systems.

In general, it is presumed that the sulphur vulcanisation of unsaturated diene elastomers proceeds in three stages. In the first stage, the interaction of the components of the curing system leads to the formation of transition complexes which, together with rubber, form the active cross-linking agent. The second stage is characterised by formation of a primary vulcanisate network with the dominance of polysulphidic cross-links. During the third stage, this network is restructured as a consequence of the modification of

cross-links (polysulphidic cross-links are transferred into di- and monosulphidic cross-links) and macromolecules of rubber (isomerisation, dehydrogenation, cyclisation) and the final spatial network of vulcanisate is formed (Kyselá et al., 2010).

In terms of chemism, two reaction pathways, proceeding via ionic or free-radical intermediates, have been considered. Eventually, both mechanisms may run simultaneously. The reaction sequence of sulphur vulcanisation, as illustrated in Fig. 2, is highly intricate and the mechanisms of particular reactions remain unclear and somewhat controversial. The radical and ionic chemical pathways suggested by Akiba and Hashim (1997) and Quirk (1988) are represented in Figs. 3 and 4, respectively. The sulphur curing kinetics is integrated and compliant with the autocatalytic reaction of the kinetic rate > 1 for sulphur (Waddell et al., 1991). At high temperatures, the cyclic molecular ring of sulphur can be broken by heterolytic or homolytic scission Eq. (1). The Arrhenius activation energy for the vulcanisation reaction of elastomers with sulphur is similar to the homolytic dissociation energy of S—S bonds in the molecules of sulphur and in polysulphides (Kresja & Koenig, 1993b). With regard to the proposed radical mech-

InitiationPropagation

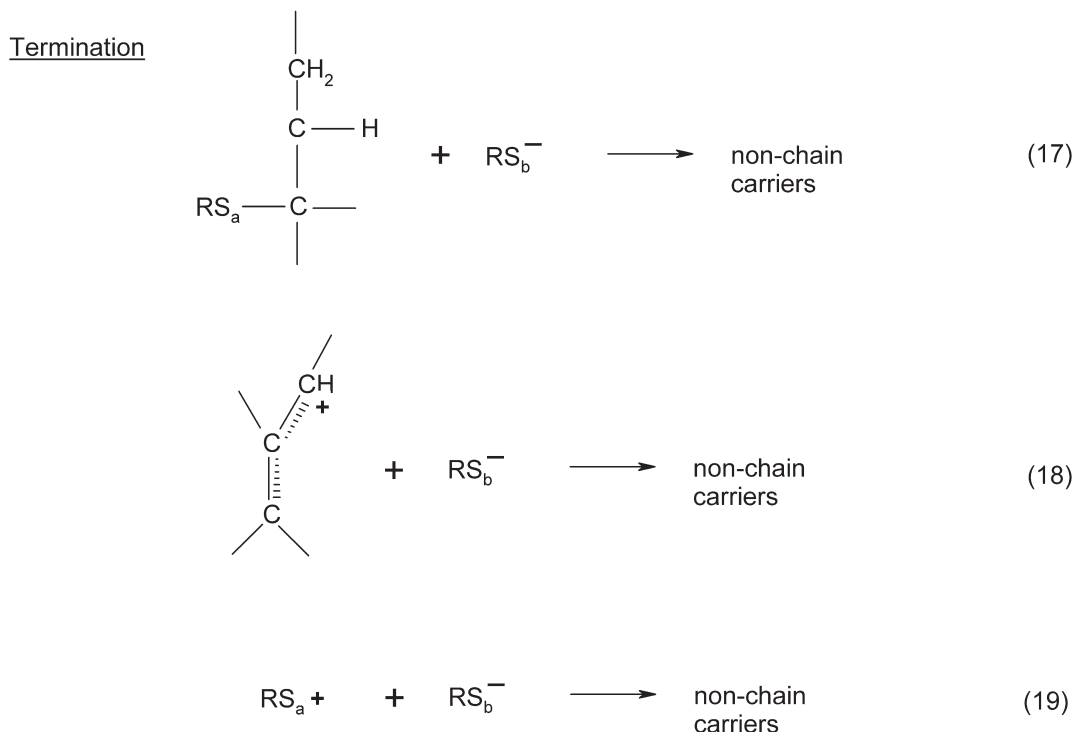


Fig. 4. Ionic mechanism for sulphur vulcanisation (Quirk, 1988).

anism, the consistent formation of polysulphide organic molecules in the first stages of the process may proceed as a homolytic reaction (Eq. (2) in Fig. 3). Polysulphide molecules could subsequently undergo homolytic cleavage to form polysulphenyl radicals, Eq. (3), which take part in free-radical chain reactions Eqs. (4)–(9) and accelerate the reaction speed. In addition, polar mechanisms have been suggested to accompany the free-radical sequences of chain reactions with respect to the prevalent Markovnikov regiospecificity in the articles Eq. (10).

The equivalent ionic mechanism can be represented by the sequences of chain reactions shown in Fig. 4, in which R is the alkyl or alkenyl group, and a or b can alter from 2 to 8. The nature of the ionic reaction mechanism is based on its ability to elucidate the composition of the products from all types of olefins and 1,5-dienes (Akiba & Hashim, 1997). It is probable that both mechanisms can play the role in the vulcanisation process, although this assumption has not yet been confirmed.

During the vulcanisation process, a complicated sequence of parallel and subsequent reactions occurs, which may have a substitutive, addition, perhaps even elimination character. It is not only the initial components of vulcanisation systems, but also the products of their conversion that can take part in these reactions. In addition, unsaturated rubbers have several

types of functional groups in their structures (mainly reactive allylic hydrogens and double bonds), which can react with sulphur cross-linking systems with different speeds and different mechanisms to form various intermediate products or final products. Side-reactions, such as isomerisation, dehydrogenation, cyclisation, the formation of diene and triene structures in elastomer chains also play a significant part in this process. The course of the reactions can be influenced by the composition of the vulcanisation systems, especially by the type and content of accelerator and activator, by the presence of retarders or prevulcanisation inhibitors and usually also other additives in rubber compounds. The study of the detailed mechanism of cross-linking is also impeded by the fact that the resultant product – vulcanisate – is a complicated system and the analytical methods which are generally used for operations in solution, or a homogeneous medium, cannot be applied to analyse it.

Structure of sulphur-cured vulcanisates

The general scheme of sulphur-cured vulcanisates can be represented by the illustration shown in Fig. 5. The structures of sulphur-cured vulcanisates have been investigated by spectroscopic analyses such as UV, IR, NMR, ESR and Raman (Yu & Guo, 1990; Dikland & Van Duin, 2002; Orza et al., 2009; Che

Table 2. Level of sulphur and accelerator in sulphur vulcanisation systems

Type	Sulphur (S)/phr	Accelerator (A)/phr	A/S ratio
Conventional	2.0–3.5	1.2–0.4	0.1–0.6
Semi-EV	1.0–1.7	2.4–1.2	0.7–2.5
EV	0.4–0.8	5.0–2.0	2.5–12.0

phr – Parts per hundred rubber.

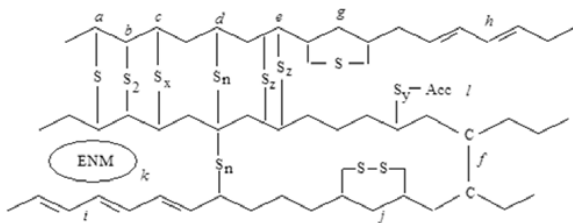


Fig. 5. General scheme of sulphur-cured vulcanisates: *a* – monosulphidic cross-links; *b* – disulphidic cross-links; *c* – polysulphidic cross-links ($x = 3–6$); *d* – polysulphidic cross-links connected several elastomer chains; *e* – vicinal cross-links; *f* – carbon-carbon cross-links; *g*, *j* – cyclic sulfides; *h*, *i* – conjugated segments of elastomer chains; *l* – pendant side-group (Acc – accelerator residue); *k* – chemically non-bonded additives.

et al., 2012) and by chemical methods (Gupta et al., 2014). Several structural groups have been determined as present in the networks of vulcanised elastomers (Akiba & Hashim, 1997; Koenig, 2000). These include isomerised double bonds (*cis/trans*), conjugated unsaturated bonds, cyclic sulphide units, pendant side-groups (for instance accelerator residue) and, in addition to a variety of sulphur cross-linking units (mainly monosulphidic $C-S-C$, disulphidic $C-S_2-C$ and polysulphidic $C-S_x-C$, $x = 3–6$).

The structure of the cross-links formed can be influenced by various technological parameters of the vulcanisation process, but it depends in particular on the type and amount of accelerator in the rubber mixture. The presence of slow accelerators mainly leads to the formation of polysulphidic cross-links while, by the application of fast accelerators, the number of sulphur atoms in the sulphidic bridges is lower.

The structure of the cross-links formed in vulcanisates has a significant influence on their properties (González et al., 2005). The longer the sulphidic cross-links are (the more sulphur atoms they contain), the more readily they decompose and the lower the resistance to elevated temperature they have. Accordingly, vulcanisates with high levels of polysulphidic cross-links are not very heat-proof and exhibit a high compression set (mostly at higher temperatures). This is largely due to the low bonding energy of sulphidic cross-links with a higher number of sulphur atoms: $C-S_x-C < 252 \text{ kJ mol}^{-1}$; $C-S_2-C < 268 \text{ kJ mol}^{-1}$; $C-S-C < 285 \text{ kJ mol}^{-1}$; $C-C < 352 \text{ kJ mol}^{-1}$.

On the other hand, they generally show good physical-mechanical and dynamic properties and good resistance to dynamic fatigue. This is largely due to the capacity of polysulphidic cross-links to be rearranged under the influence of external stress and to dissipate it without reducing the number of cross-links. In vulcanisates with a dominance of polysulphidic cross-links, elastomer chains are connected with longer sulphur bridges which render the micro-Brown motion of rubber chain segments between the cross-links easier, which subsequently results in an improvement in the elastic and dynamic properties of vulcanisates (Kyselá et al., 2010).

The crucial factor determining the number of sulphur atoms in sulphidic cross-links is the amount of sulphur and the ratio between the accelerator and sulphur. Based upon this, sulphur vulcanisation systems are specified as conventional, semi-efficient (semi-EV) and efficient (EV) as shown in Table 2 (Dijkhuis et al., 2009; Gupta et al., 2014; Hernández et al., 2015). Conventional vulcanisation systems are characterised by the amounts of sulphur being higher than the amount of accelerator. When introduced in the cross-linking of elastomers, polysulphidic cross-links are mainly formed (up to 70–80 %). Semi-EV vulcanisation systems with approximately the same level of sulphur and accelerator provide the vulcanisates with a high ratio of polysulphidic cross-links (up to 50 %); however, those vulcanisates also contain a substantial proportion of monosulphidic cross-links and lower amounts of unfavourable elastomer chain modifications, which contribute to their improved resistance to ageing and elevated temperatures. In EV vulcanisation systems, a low level of sulphur is combined with a relatively high amount of accelerator. As illustrated in Table 3, the final vulcanisates make use of sulphur efficiently to form networks in which the cross-links are mainly monosulphidic and which exhibit a low degree of main-chain modifications. Hence, they exhibit the highest resistance to increased temperatures and thermo-oxidative ageing and the best resistance to compression set and reversion. Vulcanisates with a dominance of mono- and disulphidic cross-links show worse initial physical-mechanical properties, lower elongation and dynamic characteristics, but over time their properties deteriorate more slowly than with conventional vulcanisates.

In general, sulphur-cured vulcanisates exhibit good tensile properties, high tear strength, good dynamic characteristics, but weak high temperature stability

Table 3. Structure of vulcanisates and properties of sulphur-curing systems (Akiba & Hashim, 1997)

Parameter	Conventional	Semi-EV	EV
Poly- and disulphidic cross-links/%	95	50	20
Monosulphidic cross-links/%	5	50	80
Cyclic sulphide concentration	high	medium	low
Heat-ageing resistance	low	medium	high
Reversion resistance	low	medium	high
Fatigue resistance	high	medium	low
Tear resistance	high	medium	low
Compression set	high	medium	low

Table 4. Peroxides for cross-linking of elastomers

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

and poor resistance to ageing (Kyselá et al., 2010; Manaila et al., 2014).

Peroxide vulcanisation

General features of peroxide cross-linking

The cross-linking of rubbers with organic peroxides was first examined by Ostromislensky in 1915 (Ostromislensky, 1915). Not just unsaturated, but also saturated elastomers can be efficiently cured with peroxides. The latter do not have the capacity to be cross-linked with sulphur-curing systems. Industrial interest in the application of peroxides as cross-linking agents increased with the introduction of a number of saturated rubbers, mainly ethylene–propylene type rubbers (EPM, EPDM), or fluoro elastomers (FKM), etc. (Dikland et al., 1993a, 2002; Tao et al., 2005). Peroxides are currently used as cross-linking agents for elastomers to prepare vulcanisates with good high-temperature ageing resistance or to vulcanise blends which consist of a combination of saturated and unsaturated elastomers (Kyselá et al., 2010).

The application of organic peroxides in cross-linking elastomers leads to the formation of covalent carbon–carbon cross-links between the elastomer chain segments. C–C bonds have a higher dissociation energy than sulphidic cross-links, so peroxide-vulcanised elastomers also exhibit higher thermal stability and good resistance to thermo-oxidative ageing. Good electrical properties, low compression set and

no discoloration of the final products are the next distinctive features of peroxide-cured vulcanisates (Dluzneski, 2001; Alvarez Grima, 2007; Visakh et al., 2013).

Aliphatic, aromatic and mixed peroxides can be introduced in the cross-linking of elastomers and some of them have more than one peroxidic group (White & De, 2001). Table 4 reveals the types and designations of peroxides in commercial use.

The basic assumption in selecting a suitable peroxide, in addition to its ability to perform efficient cross-linking of rubber compounds, is that it is stable in the preparation and processing of rubber compounds and it decomposes rapidly at vulcanisation temperature. These requirements are largely fulfilled by peroxides where the peroxidic group is fixed to the tertiary carbon. Peroxides with the peroxidic group fixed to the primary or secondary carbon are less stable. In the first stage of peroxide decomposition, the peroxides undergo homolytic cleavage to form primary radicals. The primary radicals can be a source for the secondary radicals which are formed by the fragmentation of primary radicals (Thitithammawong et al., 2007). These new radicals can be more or less reactive than the initial radicals, which is usually reflected in the cross-linking efficiency. Accordingly, the choice of the peroxides introduced in the vulcanisation of elastomers needs to be given due consideration. For example, when using dicumyl peroxide (DCP), one of the cross-linking peroxides in most frequent use (Thitithammawong et al., 2009), the decomposition yields methyl radicals (Fig. 6). These radical species are less

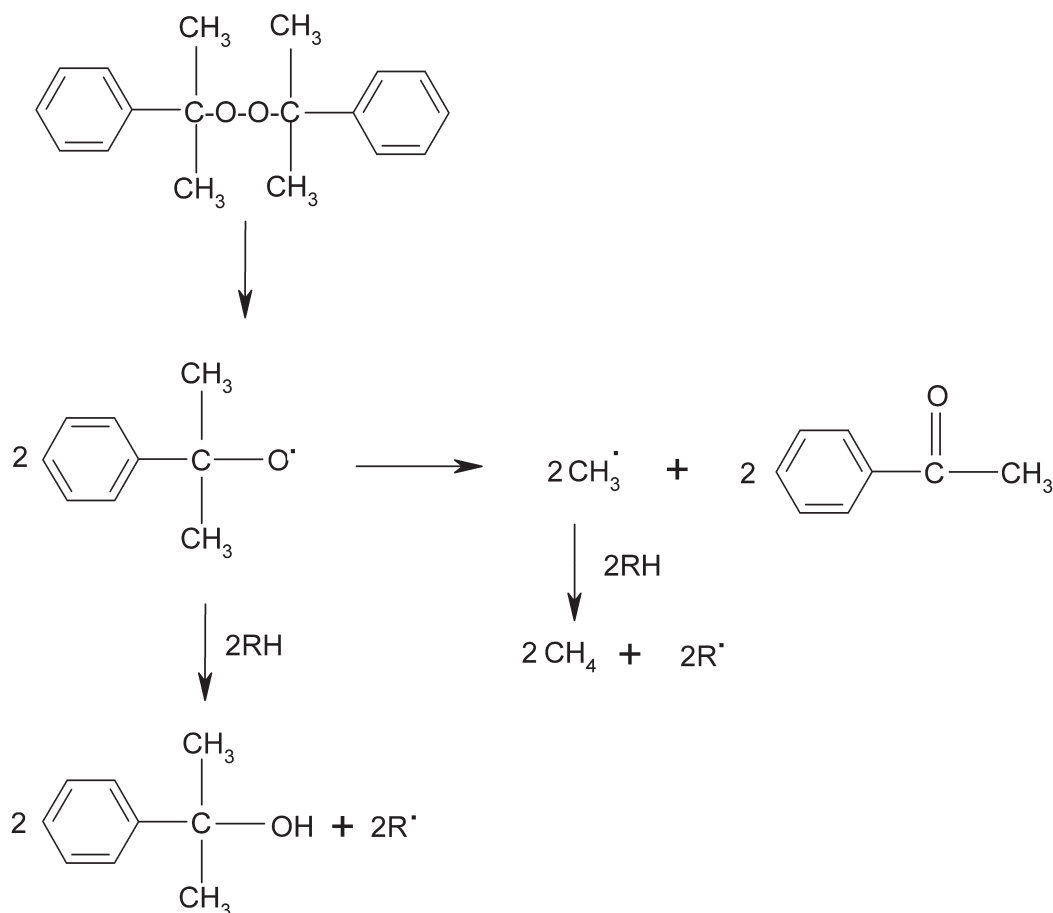


Fig. 6. Decomposition mechanism of dicumylperoxide (Thitithammawong et al., 2007).

sterically hindered than the initial cumyloxy radicals, hence more accessible to the reactive centres of elastomers. As a result of this, good cross-linking efficiency is obtained. In general, peroxide radicals which act predominantly as hydrogen abstractors are more convenient for peroxide cross-linking than those radicals whose primary mechanism is an addition to double bonds of unsaturated rubbers (Alvarez Grima, 2007).

Mechanism of peroxide vulcanisation

It is generally presumed that the cross-linking of rubbers with peroxides has a radical character in its substance. In the first step, peroxides are homolytically dissociated into free radicals which are eventually fragmented into secondary reactive species at high temperatures. Subsequent reactions between the peroxide radicals and functional groups of elastomers lead to the formation of a cross-linked network structure (Dluzneski, 2001; González et al., 2007). The peroxide decomposition step follows first-order reaction kinetics (Alvarez Grima, 2007), hence the dissociation

of the peroxide molecule is dependent on to the peroxide concentration at any time. Peroxide free-radical species could potentially react with elastomers by the abstraction of hydrogen from the elastomer chains or by the addition to a double bond of unsaturated rubbers (Valentín et al., 2005; Kyselá et al., 2010; El-Nemr, 2011; Shanmugam, 2012; Li, 2013). The elastomer radicals that are formed during these reactions subsequently mutually recombine to form cross-links.

The facility of hydrogen abstraction depends on the structure of rubber. The following sequence shows the facility by which elastomer radicals can be formed via the abstraction of hydrogen from different chemical groups: benzylic = allylic > tertiary carbon > secondary carbon > primary carbon > vinyl > phenyl.

The second mechanism by which elastomer radicals can be formed is the 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 to in-chain double bonds (*cis/trans*), hence they are more

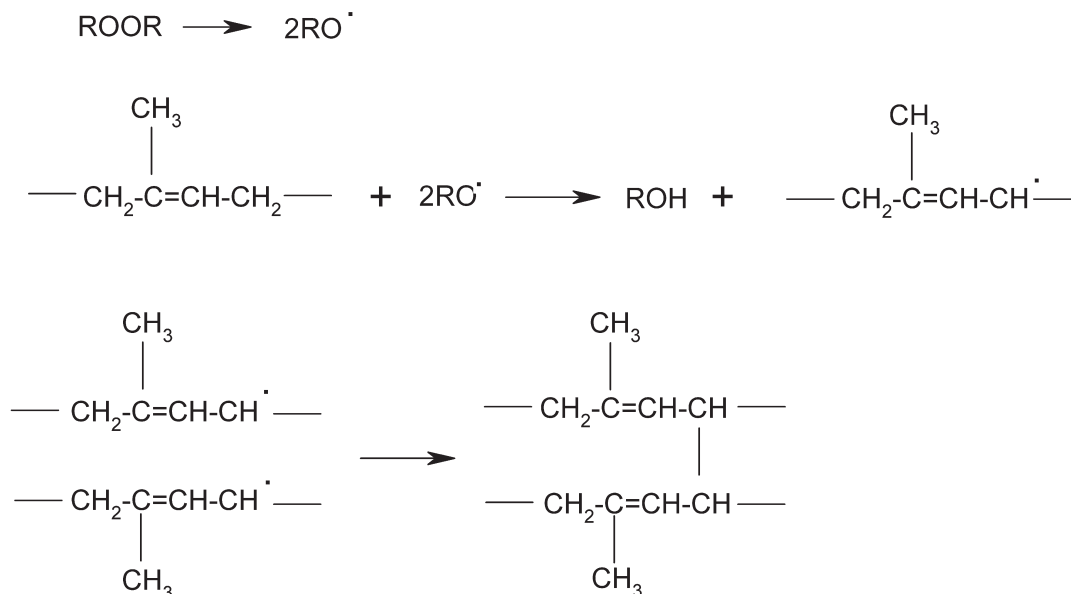


Fig. 7. Peroxide cross-linking of natural rubber.

amenable and more likely to take part in addition reactions. Both mechanisms, hydrogen abstraction and addition reactions may proceed simultaneously to form elastomer radicals (macroradicals) (Henning, 2007). To determine which mechanism is prevalent largely depends on the microstructural elements of elastomers.

The general scheme for the peroxide cross-linking mechanism of NR is illustrated in Fig. 7. The primary mechanism is the abstraction of allylic hydrogen from the elastomer backbone by peroxide radical species (Valentín et al., 2007). The addition reactions are much less pronounced, probably due to sterically hindered in-chain double bonds. Two elastomer radicals subsequently recombine to form the cross-link. On the basis of an analysis of the stoichiometry of peroxide cross-linking for natural rubber with DTBP and DCP, it was demonstrated that these peroxides formed one mole of cross-links per mole of peroxide; this means that they are quantitative cross-linking agents (Akiba & Hashim, 1997; Valentín et al., 2005).

It was also proposed that the elastomer radicals formed by hydrogen abstraction, besides mutual recombination reactions, can also undergo addition reactions. In the case of ethylene-propylene diene terpolymer (EPDM), the forming of chemical intermolecular bonds by the addition of EPDM macroradicals to the double bonds in its unsaturated structural units is practically equivalent to the recombination of macroradicals (Fig. 8) (Van Duin, 2002; Van Duin et al., 2009, 2010; Orza et al., 2009).

The amount of addition reactions is more significant when the cross-linking of butadiene rubber BR and/or its copolymers occurs, mainly with a higher quantity of 1,2-butadiene structural units. In the per-

oxide cross-linking of BR, it is expected that peroxide radicals can react by hydrogen abstraction, at which a more reactive macroradical than in the case of NR is formed, and also by the addition reaction with the double bond. The macroradicals so formed can undergo addition reactions with the double bonds in elastomer chains in addition to the mutual coupling reactions (Fig. 9). The chain character of addition reactions results in a high cross-linking efficiency, i.e. 10–50 for BR depending on the microstructure of polybutadiene. The high cross-linking efficiency can mainly be observed by the peroxide cross-linking of butadiene rubber and its copolymers with a high number of 1,2-butadiene units, suggesting that the pendant vinyl units participate in addition reactions more readily than the internal double bonds (Akiba & Hashim, 1997; Kyselá et al., 2010).

In the case of fully saturated rubbers, the abstraction of hydrogen from their chains by peroxide reactive species is the sole mechanism for elastomer radical formation. The formation of cross-links between elastomer chains is performed only by a recombination of macroradicals (Henning, 2007).

Simultaneously with the main cross-linking process, side-reactions which reduce the vulcanisation yield can occur. Side-reactions are usually promoted by tertiary radicals. The main chain scission (Fig. 10) and disproportionation (Fig. 11) are two of the most frequent undesirable reactions leading to a reduction in cross-linking efficiency (Lazár et al., 2000; Alvarez Grima, 2007). Then, the reactions of radicals in the elastomer backbone with radicals formed at the end of the macromolecular chains often lead to the branching of elastomers instead of forming cross-links. The

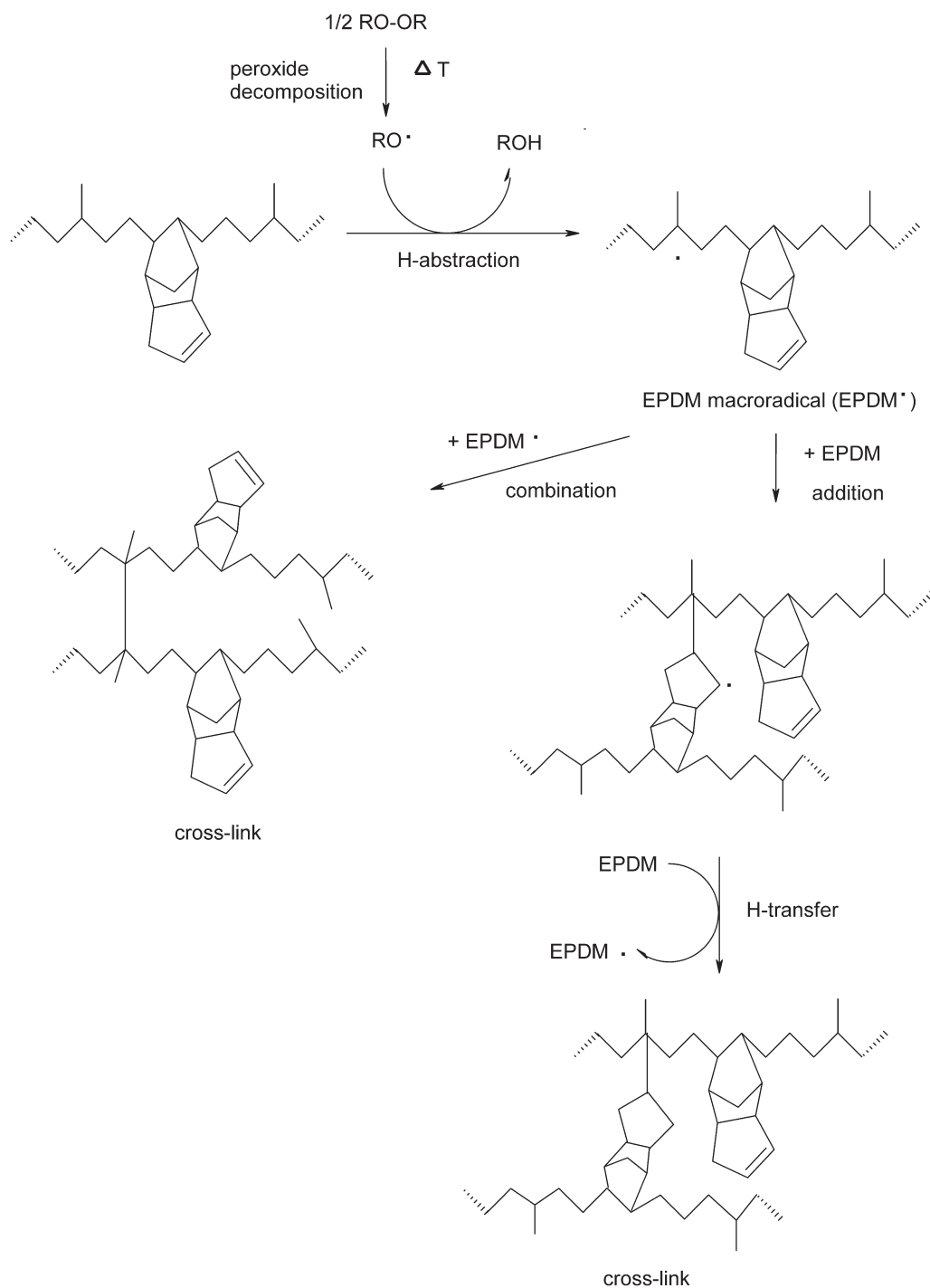


Fig. 8. Peroxide cross-linking of EPDM with dicyclopentadiene as third monomer (Van Duin, 2002).

presence of oxygen in the cured mixture might cause the coupling of oxygen molecules with the radical in the elastomer chain to form hydroperoxide radicals, which lead to rubber degradation instead of cross-linking. In addition to that, there are other side-

reactions which can negatively influence the vulcanisation process, such as metal-catalysed decomposition of the peroxide molecules, radical transfer, oxygenation, dehydrohalogenation, etc. (Braun et al., 1998; González et al., 2007; Li, 2013). If acidic substances

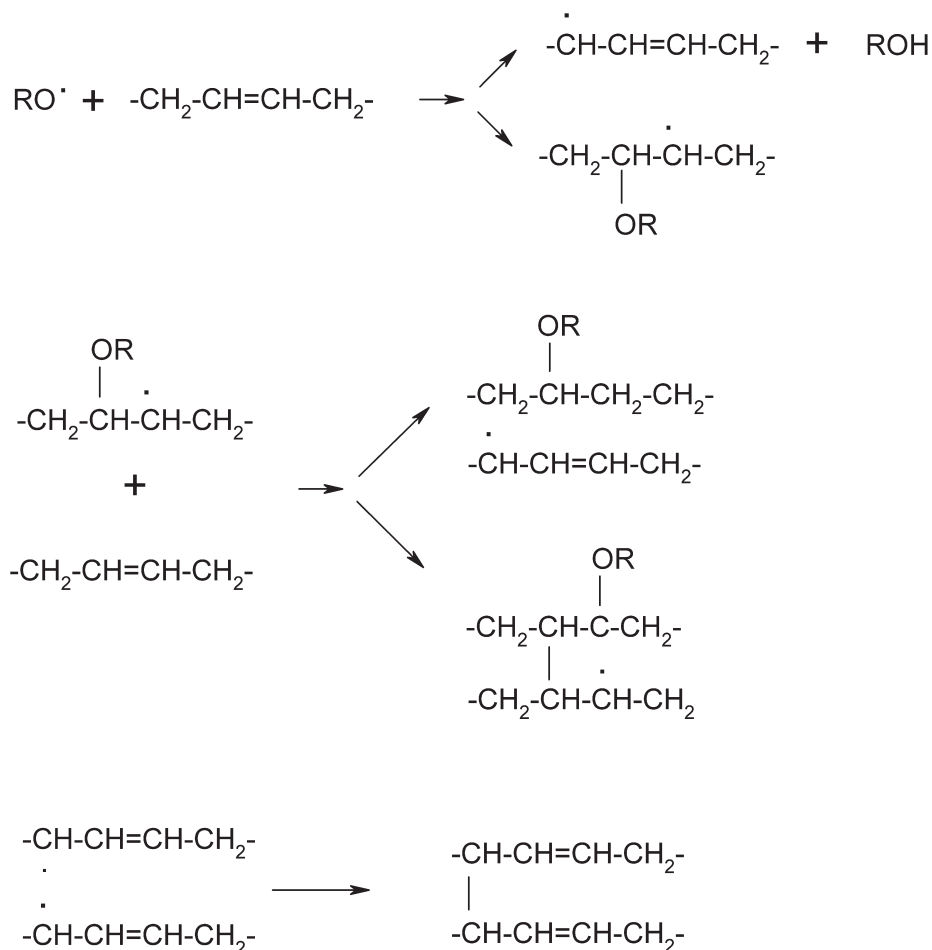


Fig. 9. Peroxide cross-linking of butadiene rubber (Kyselá et al., 2010).

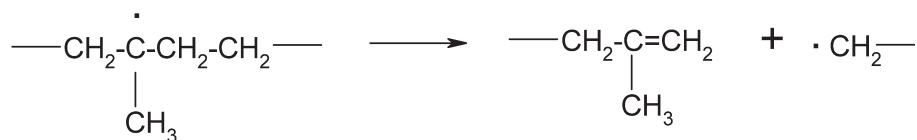


Fig. 10. Chain scission in elastomer chains.

are present during vulcanisation, they can cause the ionic or heterolytic decomposition of peroxides. As a result, no radicals are formed, so cross-linking does not take place (Alvarez Grima, 2007).

Co-agents

The cross-linking of rubbers with organic peroxides can be effectively enhanced by the application of co-agents (Dikland et al., 1993b; Murgic et al., 1998; Peng et al., 2002; Henning & Costin, 2006; De Risi & Noordermeer, 2007; Przybyszewska & Zaborski, 2009; Nie et al., 2010; Rajan et al., 2013; Vieira et al., 2015). Co-

agents are multi-functional organic compounds which exhibit high reactivity towards free radicals (Dluzneski, 2001; Manaila et al., 2014). The performance of peroxide-curing in the absence of co-agents is sometimes fairly low due to the occurrence of side-reactions which can deplete free radicals. Co-agents are able to boost peroxide effectivity by suppressing unfavourable side-reactions to a large extent, such as disproportionation and chain scission (Búcsi & Szöcs, 2000). However, it is believed that the main reason why co-agents increase the cross-linking efficiency and yield is the formation of co-agents' bridges between rubber chains as extra cross-links. They are introduced

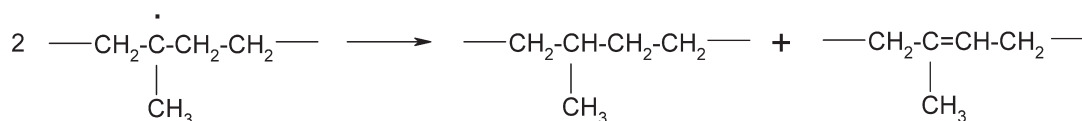


Fig. 11. Disproportionation of elastomer radicals.

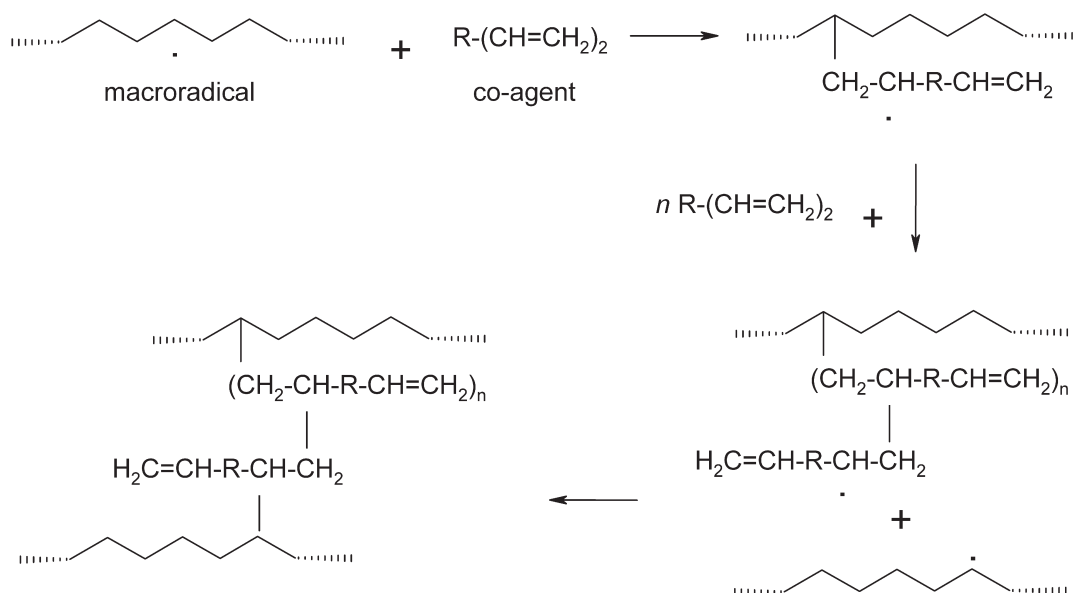


Fig. 12. Reaction mechanism of certain Type I co-agents with elastomers (Kyselá et al., 2010; Kruželák et al., 2015).

to increase the cross-linking performance of the vulcanisation process but also to increase the cross-link density of final vulcanisates (El-Nemr, 2011; Likožar & Krajnc, 2008). Accordingly, physical-mechanical properties, such as tensile strength, modulus, abrasion resistance, dynamic properties, adhesion to polar substrates and the process ability of peroxide-vulcanised elastomers are also improved (Lu et al., 2005; Alvarez Grima et al., 2006; Alvarez Grima, 2007; Kyselá et al., 2010). Independent of their chemical structure, co-agents can react in the peroxide vulcanisation of unsaturated elastomers via addition and hydrogen abstraction or via addition reactions only. In the case of fully saturated elastomers, addition reactions are largely preferred. According to their contribution to the vulcanisation process, co-agents are divided into two basic groups: Type I and Type II (Alvarez Grima, 2007; Visakh et al., 2013; Manaila et al., 2014).

Type I co-agents are polar multi-functional organic substances with low molecular mass which proliferate highly reactive radicals largely through addition reactions. They are highly reactive towards free radicals, hence the induction period of vulcanisation is usually very short. The application of this type of co-agents in the vulcanisation of elastomers leads not only to an increase in the cure rate but also to an increase

in the cross-link density or state of cure. As they are rather polar materials, their miscibility and compatibility with non-polar rubber matrices can be limited. Type I co-agents include multi-functional methacrylates, acrylates, bismaleimides or zinc salts of acrylic and methacrylic acid.

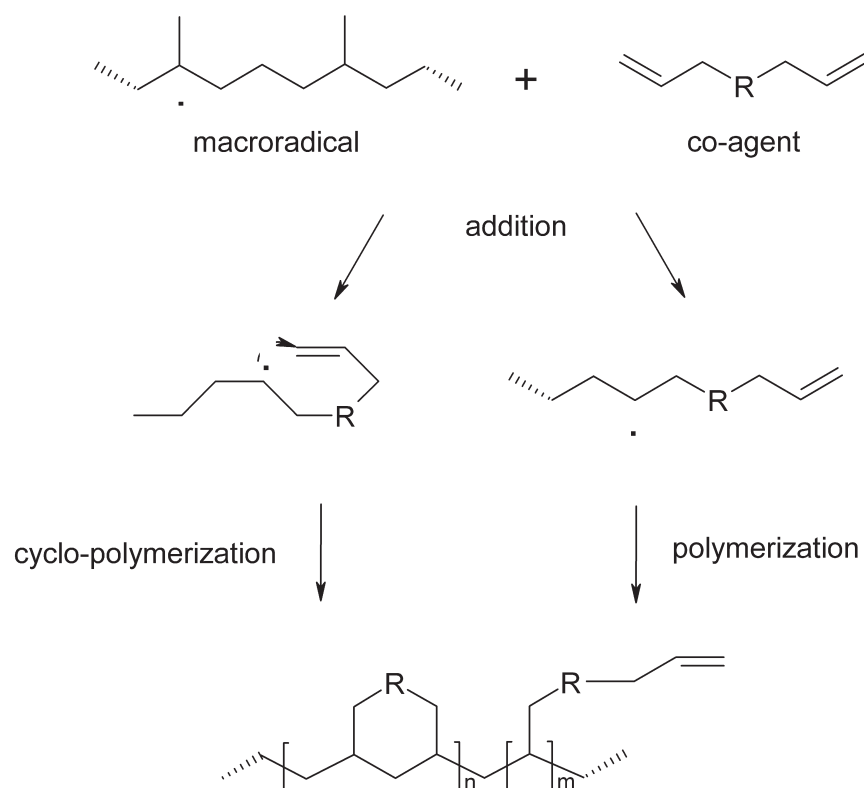
In general, Type II co-agents are less polar materials, which form more stable free radicals, so the induction period is not as short as in the previous case. They form radicals primarily through hydrogen abstraction. The presence of these co-agents in the vulcanisation of rubber matrices results in an increase in the cross-link density of vulcanisates but, in contrast with Type I co-agents, they are not able to increase the rate of cure. They usually show good compatibility with most rubbers because of their low polarity. Phthalates, cyanurates and isocyanurates, homopolymers of dienes and co-polymers of dienes and vinyl aromatics belong to this class. Some of the commonly used co-agents are listed in Table 5.

Co-agent-assisted peroxide cross-linking

As outlined, both type co-agents vary in their reactivity and reaction mechanism in the vulcanisation process. Most Type I co-agents can be homopoly-

Table 5. Type I and II co-agents applied to peroxide vulcanisation 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)
<i>N,N'</i> - <i>m</i> -phenylenedimaleimide (PDM)	Divinylbenzene (DVB)
Trimethylolpropane trimethacrylate (TMPTMA)	Triallylphosphate (TAP)
Pentaerythritol triacrylate (PETRA)	High-vinyl 1,2-polybutadiene (HVPBD)

**Fig. 13.** Reaction mechanism of certain Type II co-agents with elastomers (Van Duin, 2002).

merised and/or grafted onto macroradicals forming effective cross-links through radical addition reactions (Fig. 12) (Oh & Koenig, 2000; Kyselá et al., 2010; Rajan et al., 2013; Kruželák et al., 2015). Some Type II co-agents with readily extractable allylic hydrogens have been shown to take part in intermolecular propagation reactions as well as in intramolecular cyclisation reactions (Murgić et al., 1998; Van Duin, 2002). As proposed by Van Duin (2002), trifunctional allylic co-agents such as TAC and TAIC can form cross-links through the cyclopolymerisation products as well as grafting through pendant allyl groups (Fig. 13). The polymeric co-agents, mainly high vinyl polybutadienes (HVPBD), just increase the concentration of side-chain unsaturated units which are highly reactive

towards addition reactions and thus propagate cross-linking (Henning, 2007; Babu et al., 2010).

Network enhancement through the grafting of co-agents between elastomer chains (Henning & Costin, 2006; Alvarez Grima, 2007), the formation of an interpenetrating network of homopolymerised co-agents (Maciejewska et al., 2011; Yu et al., 2011) and the formation of higher modulus filler-like domains of thermoset co-agent (Liu et al., 2004; Costin, 2004; Henning, 2007; Thitithammawong et al., 2012) have been suggested. A variety 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

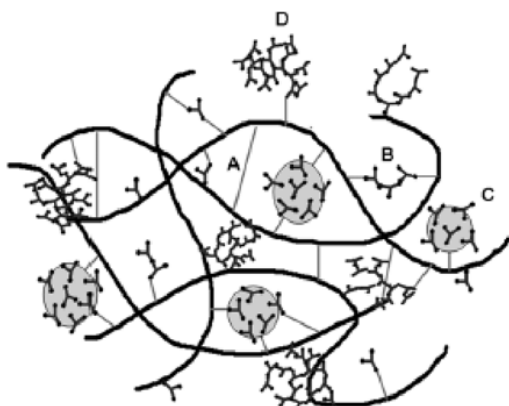


Fig. 14. Cross-linked network structure of rubber matrix cured with peroxide in the presence of co-agent (Henning, 2007); cross-links can be formed from: A – polymer radicals; B – co-agent forming cross-links; C – thermoset domains of co-agent grafted to elastomer chains and D – interpenetrating network of homopolymerised co-agents.

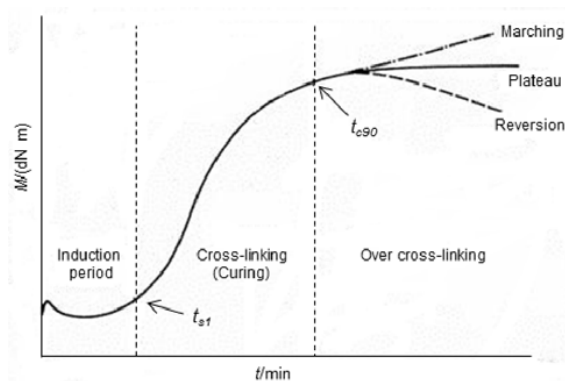


Fig. 15. Rheometer curve for vulcanisation.

reactivity of the co-agent in comparison with the rubber (Murgić et al., 1998; Dłuzneski, 2001). Henning (2007) provided an outline of the network structure of the elastomer cured with peroxide in the presence of the co-agent (Fig. 14).

Characterisation of vulcanisation reactions by means of rheometry

The time-course of a rubber compound cross-linking reaction is determined using a rotorless torsional shear rheometer, whereby the mixing specimen is pressed between two circular metal plates (one is fixed, the other is oscillating) and charged with a defined torsional vibration at vulcanisation temperature. Typical parameters are the vulcanisation temperature (150–190 °C), the oscillation frequency of 1 Hz and the deformation (angle) $\pm 1.5^\circ$. The vulcanisa-

tion isotherm registered in the rheometer characterises the time-course of the cross-linking reaction. The force generated by the deformation resistance of the specimen is measured as torque M . This parameter is proportional to the number of cross-links formed between the elastomer chains, hence it characterises the transformation degree of the virgin rubber compound into vulcanisate. The typical vulcanisation isotherm as shown in Fig. 15 can be divided into three stages that correspond to the three stages of vulcanisation process. In the first stage, known as the induction period or scorch time, the mutual interaction of the components of the vulcanisation systems occurs. The cross-links are not yet formed, or only in a small amount. The second stage is associated with the main vulcanisation process – the rapid cross-linking of elastomer chains and formation of the vulcanisate network. The restructuring of the cross-links so formed and modifications of the elastomer chains are the main features of the third stage. In the ideal case, the torque M at its maximum attains a plateau. This means that the cross-link density and the structure of the cross-links formed are not subject to further change. This stage can also be associated with decreasing the number of previously formed cross-links (reversion). When curing some synthetic rubbers, the vulcanisation isotherm can sometimes neither reach a maximum nor a plateau, but monotonously increases with time (marching modulus). The shape of the vulcanisation curves depends on the type of the vulcanised rubber, the vulcanisation temperature and also on the type and composition of the vulcanisation system applied.

Based upon the vulcanisation isotherms, the basic characteristics of the entire cross-linking process can be determined: M_L – minimum torque value (N m); M_H – maximum torque value (N m); ΔM – difference between the maximum and the minimum torque (N m); t_{s1} , t_{s2} – scorch time (min) – time at which the value torque M is by 0.1 (0.2) N m higher than M_L ; t_{c90} – optimum vulcanisation time (min) – time which can be attributed to the torque; $M_{c90} = M_L + 0.9\Delta M$.

These characteristics are important not only from a theoretical perspective (e.g. determination of kinetic parameters of cross-linking), but also in terms of practice. Scorch time (induction period) represents the time in which the cross-links are not yet formed. This time is important when, for instance, cross-linking thick-walled or strati-form materials, because vulcanisation must proceed throughout the volume at the same time, so the material must first be heated uniformly. Also, when processing rubber compounds at elevated temperatures, if cross-linking starts during their compounding, the viscosity of the mixture increases rapidly and the processing is no longer possible. The optimal vulcanisation time corresponds to the time of cross-linking needed to achieve the optimal properties of the final vulcanisates. The torque difference ΔM is roughly proportional to the cross-

link density of vulcanisates.

One of the most important structural parameters characterising cross-linked elastomers is cross-link density ν (concentration of elastically-effective network chains) and the average molecular mass of the elastomer chain segments between the two cross-links M_c :

$$\nu = \frac{\rho}{M_c} \quad (1)$$

where ν is cross-link density (mol cm^{-3}); ρ is the density of the elastomer (g cm^{-3}) and M_c is the average molecular mass of elastomer chain segment between the two cross-links (g mol^{-1}).

The network of vulcanisate can also be characterised by the number of cross-links formed in the volume unit of vulcanisate. It can be calculated from the cross-link density assuming that the cross-link is formed between the two elastomer segments.

$$n = \frac{\nu}{2} \quad (2)$$

where n is the number of cross-links in the volume unit of the vulcanisate.

Information on the network structure formed during the vulcanisation of elastomers can be obtained by different experimental approaches such as dynamic mechanical analysis (Liau & Cheng, 1998), deformation measurements (Kruželák et al., 2012a), equilibrium swelling experiments (Valentín et al., 2008; Kruželák et al., 2012b; Choi & Kim, 2015), dielectric measurements (Hernández et al., 2010, 2012), high resolution solid-state NMR (Che et al., 2012) or scattering techniques (Ikeda et al., 2008; Hernández et al., 2011).

Influence of cross-link density and cross-link structure on vulcanisate properties

The final vulcanisate is a complex system. The basis is a three-dimensional spatial network formed from elastomer chains which are connected with chemical cross-links (depending on the type of vulcanisation system applied). Also present are various types of physical bonds; not only the couplings formed between elastomer chains or their segments as a consequence of the chemical structure (hydrogen bridges, polar forces), but also various intramolecular and intermolecular entanglements form a part of the vulcanisate networks. Other additives present in rubber compounds in the original or chemically modified form are dispersed in the matrix, and dissolved or chemically, eventually physically bonded to the elastomer chains. Due to the complexity of the cross-linking process, the possibilities of cross-links restructuring and the non-homogeneity of the mixture, the spatial vulcanisate network is not ideal. In addition to the various types of cross-links and the free ineffective end-chains, there

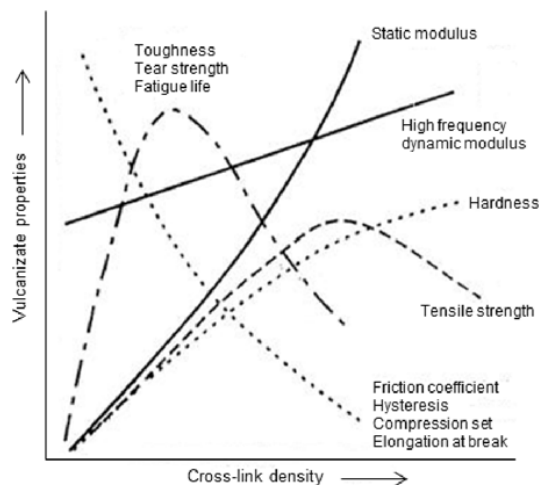


Fig. 16. Dependence of vulcanisate properties on cross-link density.

are also spaces with higher or lower local cross-link densities.

By the formation of the cross-linked network structure during vulcanisation, the free mobility of the elastomer chains is inhibited and the typical properties of the original rubber or rubber mixture are changed. Taking changes in cross-link density (quantity) into consideration, the physical-mechanical properties of the vulcanisates are influenced in different ways.

The solubility of the vulcanisates is eliminated. The vulcanisates can only swell in the solvents up to the equilibrium swelling degree. Based on the volume of solvent in the vulcanisate in the equilibrium swelling, the cross-link density can be calculated by the Flory–Rehner equation (Flory, 1953). The higher the cross-link density, the lower the volume of the solvent that can diffuse into the structure of vulcanisates.

The tensile strength of vulcanisates increases significantly, but only up to the optimal degree of cross-linking, then it decreases. The modulus and hardness are directly proportional to the cross-link density. The elongation first increases at a low cross-link density, then it decreases with the increase in cross-link density. The permeability of gases is inhibited with the increase in cross-link density. Fig. 16 gives an overview of the change in vulcanisate properties dependent on cross-link density (Coran, 1994, 2003; Li, 2013).

The second parameter influencing the properties of vulcanisates is the structure of the cross-links (quality) (González et al., 2005). The longer sulphur bridges formed between the elastomer chains by applying the sulphur curing systems lead to the formation of a more elastic and flexible cross-linked network structure in elastomers. Sulphidic cross-links also have a lower dissociation energy than the C—C bonds, which are formed between the macromolecular chains by ap-

Table 6. Main features of sulphur and peroxide-cured vulcanisates

Sulphur-cured vulcanisates	Peroxide-cured vulcanisates
Advantages	
good tensile and tear strength good dynamical properties good abrasion resistance good regulation of scorch safety and optimal cure time good resistance to dynamic fatigue	good heat-ageing stability good electrical properties low compression set simple formulation of rubber compounds rapid vulcanisation without reversion no discoloration of finished parts
Disadvantages	
low resistance to thermo-oxidative ageing high compression set possibility of reversion during vulcanisation	possibility of preparing transparent products worse tensile, elastic and dynamic properties low scorch safety sensitivity to elemental oxygen during curing certain components of rubber compounds, such as anti-degradants, may consume peroxide radicals generally higher cost

Table 7. Overview of vulcanisation systems applied to different rubbers

Type of rubber	Sulphur systems	Peroxide systems
Natural rubber (NR)	+	+
Isoprene rubber (IR)	+	+
Butadiene rubber (BR)	+	+
Styrene-butadiene rubber (SBR)	+	+
Acrylonitrile-butadiene rubber (NBR)	+	+
Hydrogenated acrylonitrile-butadiene rubber (HNBR)	–	+
Isobutylene isoprene rubber (IIR)	+	–
Ethylene-propylene rubber (EPM)	–	+
Ethylene-propylene diene monomer rubber (EPDM)	+	+
Chlorinated polyethylene rubber (CM)	–	+
Silicone rubbers (Q)	–	+
Fluoroelastomers (FKM)	–	+
Acrylic rubbers (ACM)	+	–
Polysulphide rubbers (TM)	–	+

plying peroxide-curing systems and which are also situated in the main elastomer chains. When sulphur-cured vulcanisates are stretched and deformed, the sulphidic cross-links are disrupted earlier than the carbon–carbon bonds; this leads to the formation of macroradicals which may have sufficient time to form new cross-links in the microregions with a lower stress. This cross-link distribution results in a less stressed, stronger network, in which the stress is uniformly distributed to a higher number of elastomer chains. Such network stress relaxation results in higher tensile characteristics for the cross-linked materials (Kyselá et al., 2010). By contrast, the less mobile C—C bonds restrict the mobility and orientation of the rubber chain segments in the cross-linked elastomers when they are subjected to deformation forces. In addition, the cross-links thus formed cause increased deformation stiffness, because of the reduced mobility of the elastomer chains, which subsequently leads to a re-

duction in mechanical properties (Basfar et al., 2002). On the other hand, due to the higher stability of the C—C cross-links, peroxide-cured vulcanisates exhibit a higher resistance to elevated temperatures and thermo-oxidative ageing (Dluzneski, 2001; Valentín et al., 2005; Visakh et al., 2013). Table 6 summarises the main features of sulphur- and peroxide-cured vulcanisates.

Concerning the different microstructure and functionality of rubbers, different vulcanisation systems need to be used. Table 7 shows a list of elastomers cured with either sulphur or peroxide vulcanisation systems, revealing that many elastomers can be cross-linked using both vulcanisation systems.

Conclusions

Historically, sulphur vulcanisation represents the oldest and the most extensively used method for the

cross-linking of rubber materials. It is a complex process leading to the formation of different types of sulphidic cross-links in the rubber matrix. Peroxide vulcanisation combines the pattern of C—C cross-links with multi-functional cross-links by the application of different types of co-agents. Both systems exhibit certain advantages but also disadvantages. Deciding on the system to be applied largely depends on the properties required of the rubber materials, but also on the microstructure of the elastomers in order to adequately use the cross-linking potential of vulcanisation agents. Not only the cross-linking degree (quantity) but, to a large extent, the structure of the cross-links (quality) and, of course, the micro- and macrostructure of the rubber matrix, influence the property spectrum of the final cross-linked elastomers.

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