STUDIES ON PEROXIDE VULCANIZATION OF NATURAL RUBBER

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STUDIES ON PEROXIDE VULCANIZATION OF NATURAL RUBBER

Ph.D. Thesis

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Certificate

This is to certify that the thesis entitled **"Studies on peroxide vulcanization of natural rubber"**which is being submitted by Mrs. Rejitha Rajan, in partial fulfillment of the requirements of the degree of Doctor of Philosophy, to Cochin University of Science and Technology (CUSAT), Kochi, Kerala, India is a record of the bonafide research work carried out by her under our joint guidance and supervision. All the relevant corrections and modifications suggested by the audience during the pre-synopsis seminar and recommended by the Doctoral committee of the candidate have been incorporated in the thesis. The thesis fulfills all the requirements of the University. The results embodied in this thesis have not been submitted for any other degree or diploma.

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Declaration

I hereby declare that the thesis entitled**, "Studies on peroxide vulcanization of natural rubber"** is the original research work carried out by me under the joint guidance and supervision of Dr. Siby Varghese, Joint Director, Technical Consultancy Division, Rubber Research Institute of India, Kottayam-6860009and Dr. K.E. George, Professor, Department of polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi-682 022 has never been included in any other thesis submitted previously for the award of any degree.

Rejitha Rajan

Kottayam
11-08-2015.

"Difficulties in your life do not come to destroy you, but to help you realise your hidden potential and power. Let difficulties know you too are difficult"

Dr. A.P.J. Abdul Kalam

TO MY BELOVED PARENTS, DEAR HUSBAND, DAUGHTER AMRITA, AND FAMILY MEMBERS

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PREFACE

Even though peroxide curing was discovered in the early twentieth century, it gained wide industrial importance after the discovery of dicumyl peroxide in 1961. Peroxide generates thermally stable C-C crosslinks between the polymer chains. As a result the vulcanizates exhibit high temperature ageing resistance and low compression set properties compared to other vulcanizing systems. Moreover, vulcanization using organic peroxides can be successfully applied to a wide variety of saturated, unsaturated rubbers and their blends.

Organic peroxides are compounds containing O-O (peroxide) bond. It is one of the weakest bonds in organic molecule and its homolytic cleavage produces highly reactive odd electron fragments called free radicals. These free radicals can abstract allylic hydrogen (saturated polymers) or undergo addition reaction (unsaturated polymers) resulting in the formation of crosslinks between polymer chains. Relatively simple formulation, rapid vulcanization without reversion, high resilience etc. are other inherent advantages of peroxide cure. Though peroxide vulcanization can be performed very easily, its use is limited due to poor mechanical properties of resulting vulcanizates, long cure time, offensive odour of vulcanizates and poor scorch safety. Introduction of co-curing agents (coagents) in the formulation overcomes most of the problems associated with peroxide cure. These coagents improve the crosslinking efficiency of vulcanizates. Moreover, a wide range of coagents are available and proper selection of coagents is critical in achieving the optimum performance.

In this work peroxide vulcanization of natural rubber is carried out mainly with dicumyl peroxide. The present study is divided in to 9 chapters under different headings as follows.

Chapter 1 gives a general introduction to peroxide vulcanization. A review of the peroxide vulcanization of natural rubber, synthetic rubbers and elastomeric blends has been presented. The different types of peroxides and coagents for crosslinking elastomers were discussed. The influence of compounding ingredients viz. fillers, oils, plasticizers, antioxidants and antiozonants are also discussed.

Chapter 2 describes the details of materials used in the present work, experimental techniques and instruments used for the preparation and characterization of the vulcanizates.

Chapter 3 deals with kinetics of peroxide vulcanization. The kinetics has been studied at various temperatures using dicumyl peroxide (DCP) was used as the crosslinking agent. The effect of residual peroxide on mechanical properties was studied at various peroxide levels and also by extending the cure time. Mechanical properties like tensile strength, elongation at break, modulus and compression set (70^o and 100^oC) were measured.

The role of various coagent such as zinc diacrylate (ZDA), trimethylolpropane trimethacrylate (TMPTMA) and triallyl cyanurate (TAC) in the peroxide vulcanization of natural rubber (NR) were studied by Fourier Transform infrared spectroscopy (Chapter 4). Crosslinking mechanism of peroxide in natural rubber was interpreted. A crosslink mechanism was proposed to coagent ZDA in natural rubber.

Chapter 5 includes the effect of various coagents on the mechanical properties of peroxide cured natural rubber vulcanizates. Comparison of mechanical properties of peroxide cured vulcanizates with those of coagents showed that all coagent enhanced the crosslink density of the vulcanizates.

The effect of various compounding ingredients, zinc oxide, antioxidant, coagent, oil and filler in peroxide vulcanization of natural rubber is given in Chapter 6. A Face Centred Central Composite Design (FCCD) with four factors and three levels was used to obtain the relationship between vulcanizate properties and levels of ingredients. Regression equations were generated to model the properties of interest and generated response surface and contour plots.

Chapter 7 is divided into part A and part B. Part A reports the preparation, cure behaviour, characterization, mechanical, dynamic mechanical and barrier properties of natural rubber/layered silicate nanocomposites. The four different types of nanoclays selected were, cloisite Na^+, cloisite 10A, cloisite 15A and cloisite 93A. Commercial clay (English Indian clay) was included in the study for comparison. The thermal stability and kinetics of thermal degradation of natural rubber/layered silicate nanocomposites were presented in part B.

In chapter 8, peroxide vulcanization of natural rubber was carried out with four different peroxides. The aged and unaged mechanical properties were studied and thermal oxidative behaviour of vulcanizates was characterized by Fourier Transform infrared spectroscopy (FTIR) and Thermogravimetric analysis (TGA).

Chapter 9 is the summary and conclusion of the studies presented in the thesis.

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CHAPTER 1

GENERAL INTRODUCTION

This chapter gives an overview of the different organic peroxides used for the crosslinking of various types of rubbers. This includes unsaturated and saturated elastomers as well as elastomer blends. The uses of co-curing agents (coagents) to improve the vulcanizate properties are also discussed. The recent developments in peroxide vulcanization and its potential applications are included. The crosslinking efficiency of peroxide cure system depends upon a number of factors viz. type and concentration of peroxides, types of elastomers and blends, coagents, other compounding ingredients like fillers, antioxidants, processing aids etc.The scope and objectives of the present work are also discussed.

The contents of this chapter has been published in Rubber Science, 27(1), 98-126, 2014

1.1 INTRODUCTION

When rubber is exposed to atmosphere, the 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 [1] used benzoyl peroxide to vulcanize natural rubber. However, the vulcanization of rubber with benzoyl peroxide never found very wide application because of the large proportion of benzoyl peroxide necessary for a good level of cure and blooming of decomposition product, benzoic acid, on to the vulcanizates surface.

Although peroxides and sulphur can cure most types of rubbers, the chemistry behind the peroxide crosslinking and the properties it provide are very much different. Due to these chemical differences, many additives that are essential in sulphur vulcanization might interfere with the peroxide curing. There are many types of vulcanizing systems and 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 compression set properties. Interest in the industrial use of peroxides as curing agents increased with the introduction of a number of fully saturated elastomers [2] for which the usual accelerated sulphur systems are unsuitable and also with the commercial introduction of dicumyl peroxide (DCP) in the late1950s [3]. DCP produces vulcanizates with better heat resistance and lower compression set than sulphur accelerator cure systems. Saturated rubbers are, in general, resistant to ageing, thermally stable and mainly used in severe conditions. The study of cure systems available for crosslinking rubbers is therefore of considerable importance and organic peroxides, being one such category are worthy of detailed examination.

1.2 Selection of peroxides

Factors governing the selection of ideal peroxide [4] are given in Table 1.1. The primary criteria for selecting a peroxide is the activation temperature, or the temperature at which crosslinking will proceed at a satisfactory rate.

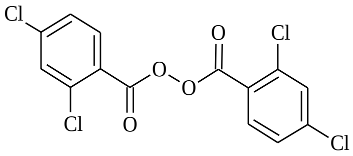
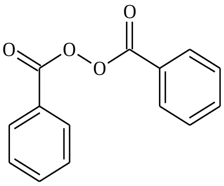
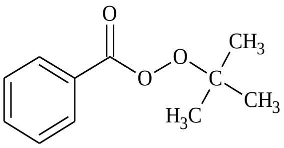
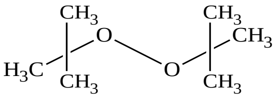
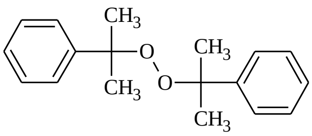
Table 1.1 Factors governing the selection of ideal peroxide

Reactivity	It must react to give crosslinks as the only modification of the polymer.
Decomposition characteristics	Must give a rapid cure at temperatures of 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.
Odour	It must have mimimum residual odour

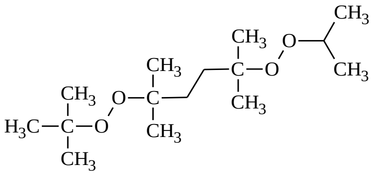
Peroxides with lower activation temperatures will provide rapid cure, but will have poor scorch resistance and *vice versa*. Peroxide efficiency is another important factor to be considered while selection. Usually peroxy group (-O-O-) attached to tertiary carbon atoms are more stable than those attached 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 slower processing 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, peresters and peroxyketals [5]. Brinkman [6] 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 vulcanization method that can compete with accelerated sulphur vulcanization, with respect to vulcanization rates. Organic peroxides that are suitable for crosslinking elastomers are given in Table 1.2. 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 [5].

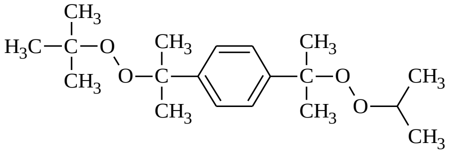
Table 1.2 Examples of typical peroxides

Name of peroxide	Structure
di(2,4-dichlorobenzoyl) peroxide	
dibenzoyl peroxide	
t- butyl perbenzoate	
di- tertiary- butyl peroxide	
dicumyl peroxide	

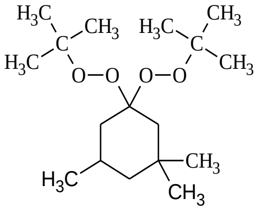
2,5 dimethyl-2,5,-di (t- butyl peroxy) hexane



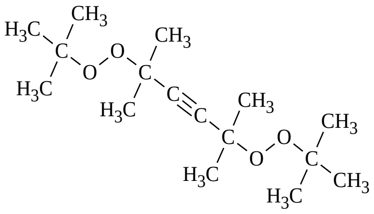
1,4-*bis* (t- butyl peroxy isopropyl) benzene



1,1'- di (t- butyl peroxy)- 3, 3,5-tri methyl cyclohexane



2,5-dimethyl- 2,5-di (t-butyl peroxy) hexyne



1.3 Choice of polymer

Organic peroxides can be used to crosslink both saturated and unsaturated elastomers. Nevertheless, there are some polymers which cannot be crosslinked by peroxide vulcanization. The polymers and polymer blends which were curable and not curable with peroxides are shown in Table 1.3 [2].

Table 1.3 Polymers and polymer blends which are curable and not curable with peroxides

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

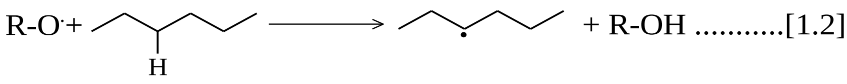
1.4 Mechanism of peroxide vulcanization

The generalized mechanism of peroxide vulcanization is a three step process *viz* initiation, propagation and termination. The process is initiated by the thermal [7] homolytic cleavage of a peroxide molecule to form two high energy free radicals as shown in Equation. 1.1. The initiation step follows first order kinetics and therefore the rate depends only upon the concentration of peroxide at any time.

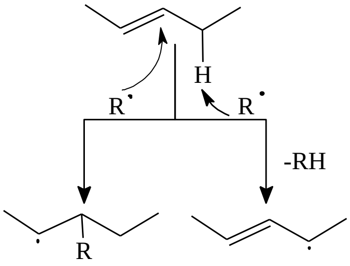
$$\text{R-O-O-R} \longrightarrow 2\text{R-O}^{\bullet} / 2\text{R}^{\bullet} + 2\text{O}^{\bullet} \quad \text{.................[1.1]}$$

Equation 1.1 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) (Equation 1. 2) or radical addition (Equation 1. 3) across the unsaturation of the polymer chain resulting in the formation of a polymer radical.



Equation 1.2 Propagation by hydrogen abstraction from the polymer chain



.... [1.3]

Equation 1.3 Propagation by radical addition/hydrogen abstraction from unsaturated 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 Figure 1.1 [3, 8].

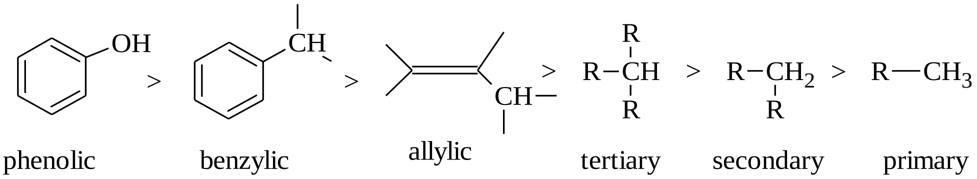
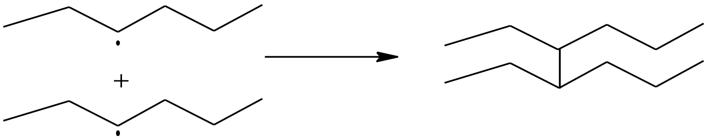


Figure 1.1 Order of hydrogen lability

Finally, in the termination step two radicals couple to from a carbon-carbon covalent crosslink between two adjacent polymer chains (Equation 1.4)



..................[1.4]

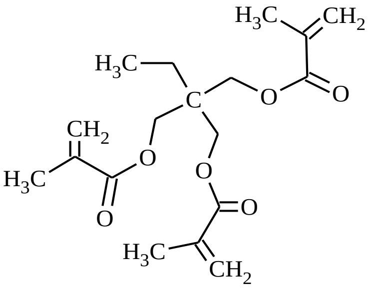
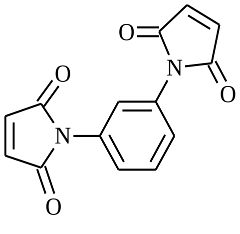
Equation 1.4 Termination by coupling of two polymer radicals

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 [9].

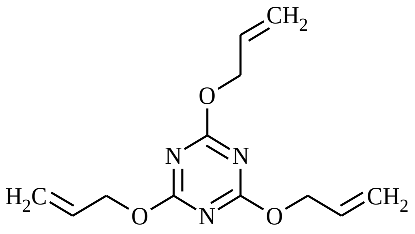
1.5 Coagents

Co-curing agents or coagents are multifunctional organic molecules. They are highly reactive towards free radicals generated by homolytic cleavage of peroxides [9]. Examples of coagents are given in Table 1.4.

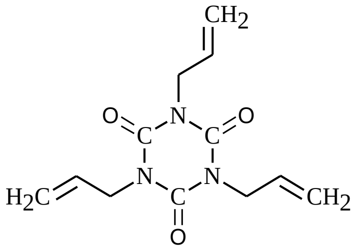
Table 1.4 Examples of coagents

Name of coagent	Structure
Trimethylolpropane trimethacrylate (TMPTMA)	
N,N'-m- phenylene dimaleimide(BMI-MP)	

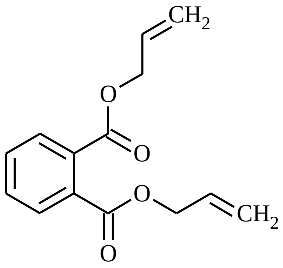
Triallyl cyanurate(TAC)



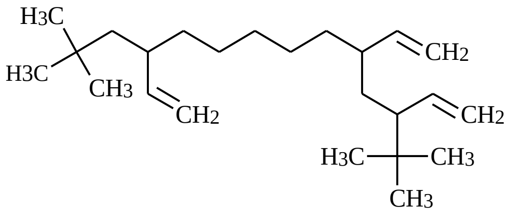
Triallyl isocyanurate(TAIC)



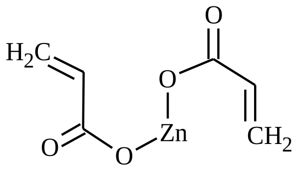
Diallyl phthalate(DAP)



1,2- polybutadiene(PB)



Zinc diacrylate (ZDA)



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 heat ageing stability and low temperature compression set of vulcanizates by increasing the crosslink density and altering the crosslink composition. The commonly used coagents are molecules with maleimide groups [10] acrylates [11], methacrylates [12], high vinyl 1, 2- polybutadiene, allyl esters of cyanurates [13, 14], isocyanurates, etc. The action of sulphur or sulphur donors as coagents has been investigated [15]. Some of the advantages provided by coagents in peroxide cure are shown in Table 1.5 [3, 8].

Table 1.5 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

1.5.1 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 acrylates, 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 both intramolecular cyclisation reaction and intermolecular propagation reaction.

1.5.2 Coagent reactivity

Coagents, due to their high reactivity, sometimes suppress non-network forming side reactions [16] or generate additional crosslinks. As type I and type II coagents differ in their reactivity, the reaction mechanism that they follow may differ [13, 17]. Metallic coagents like zinc acrylates and diacrylates are used to introduce ionic crosslinks into the polymer matrix [18]. 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 [12, 19].

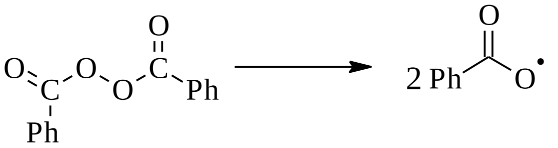
1.6 Peroxide vulcanization of unsaturated rubbers

Unsaturated rubbers like natural rubber (NR), synthetic isoprene rubber (IR), polybutadiene (PB) and copolymers of butadiene (SBR, NBR) contains many easily abstractable allylic hydrogen atoms as well as several double bonds that can undergo addition reaction. In most cases H-abstraction at allylic position is dominant [6] even though a significant amount of addition reactions also occurs. The balance between abstraction and addition depends on a number of factors like peroxide type, peroxide concentration, temperature etc [20-22]. 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 and saturated elastomers are included.

1.6.1 Natural rubber

When Ostromislensky [1] first discovered vulcanization of natural rubber with benzoyl peroxide, it was assumed that the process was due to oxidation. But the saturation of rubber was not found to be altered and hence it was assumed that the vulcanization of rubber does not depend upon saturation of double bond of rubber by oxygen. Later, van Rossem [23] 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 [24] is given in Figure 1.2.

1. Formation of free radicals by the decomposition of peroxide



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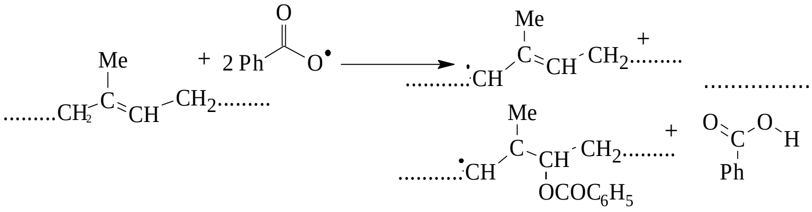
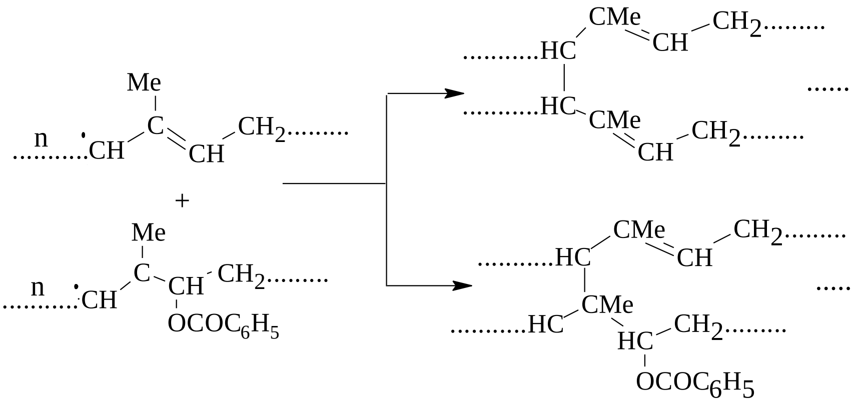
2. Reaction between benzyloxy radical and isoprene chains



................[1.6]

3. Radical couple



...........[1.7]

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Figure 1.2 Mechanism of peroxide vulcanization with benzoyl peroxide

Later, when DCP was discovered, Gonzalez *et al.*, investigated the mechanism of peroxide vulcanization of unsaturated rubbers in detail. They concluded 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 while at low temperature and low DCP concentration allylic H- abstraction is the predominant mechanism [25-27]. The changes in crosslinking mechanism at high peroxide concentration and high temperature were confirmed by ^{1}H NMR spectroscopy [21]. 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. These are having negative impact on the physical properties of the vulcanizates. The over-crosslinked portion when subjected to stress, generate stress accumulation and hence lower physical properties.

1.6.2 Synthetic polyisoprene

As expected the vulcanization of synthetic *cis*- polyisoprene is very similar to that of naturally occurring polymer. The crosslinking efficiency has been found to be slightly but significantly greater than unity [28]. Polyisoprenes of higher 3, 4 content show higher crosslinking efficiencies, although below 30 per cent 3, 4 addition no significant change occur. With a 60 per cent 3, 4 polyisoprene the crosslinking efficiency drops from about three at 130^{o}C to one at 160^{o}C. Sol-gel analysis showed that during the crosslinking of synthetic cis-1, 4-polyisoprene by cumyl peroxide, there are only 2-3 sites of scission per 100 crosslinked isoprene units [29, 30]. The crosslinking efficiency of 95 per cent trans-1, 4-polyisoprene (balata) has also been shown to have very close to unity. Thus, the microstructure of the polymer has little effect on the course of peroxide crosslinking reaction. Only with high contents of 3, 4 additions, the crosslinking efficiency showed significant deviation from unity. *Cis-trans* isomerization occurred in polyisoprene crosslinked with benzoyl peroxide, whereas no isomerization was found in samples crosslinked with dicumyl peroxide. Upon heating, rearrangements occur which leads to the formation of terminal double bonds.The thermal and thermal oxidative stabilities of crosslinked polyisoprene were found to be enhanced due to crosslinking with peroxides [31].

1.6.3 Polybutadiene

Polybutadiene and copolymers of butadiene usually contains various amount of vinyl unsaturation.

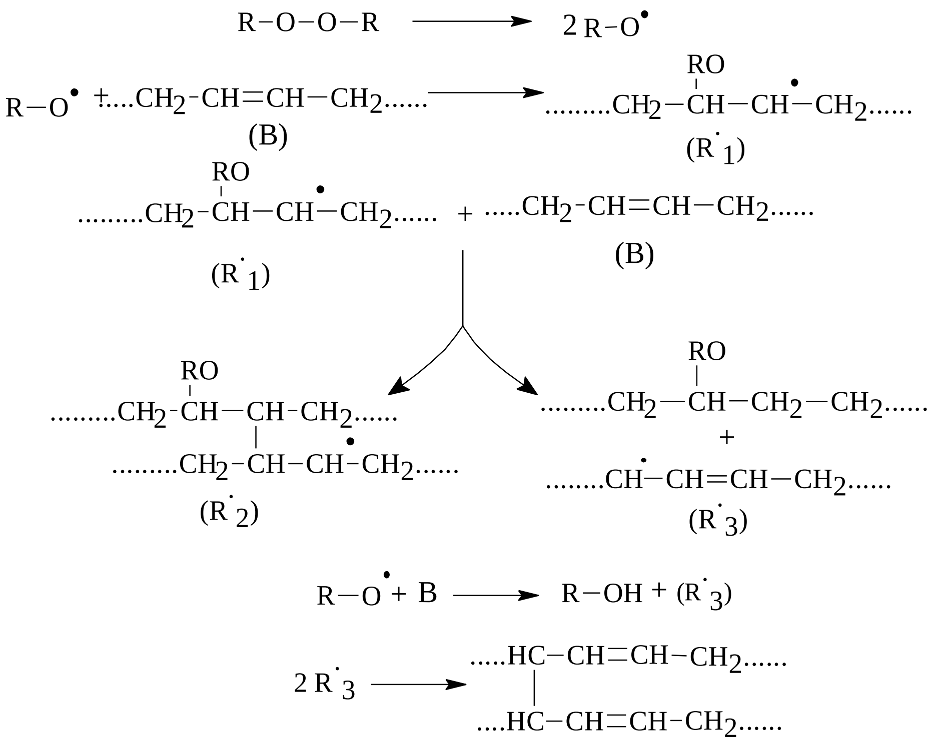


Figure 1.3 Crosslinking mechanism of polybutadiene

Using the relationship observed in natural rubber networks in establishing the contributions of chemical crosslinking, entanglements and network defects to physical crosslinking, a physical versus chemical “calibration” has been developed by Kraus [32] for polybutadiene. The crosslink yield has been found to be greater than unity due to a polymerization kind of reaction involving vinyl group resulting from 1, 2-addition reaction.

A reaction scheme was proposed to explain the high crosslinking efficiency (Figure 1.3) [33]. Addition reactions are more favoured with increasing vinyl content and when acyl peroxides are used [8]. Further, the crosslinking of polybutadienes with varying vinyl content displays strange temperature behaviour [27]. For *cis* 1, 4- polybutadiene containing 2phr dicumyl peroxide, the polymer lost 30 per cent of its main chain unsaturation and this loss is attributed to a process of “polymerization” of double bonds [34].

Scheele and Rohde [33] studied the kinetics of benzoyl peroxide decomposition in natural rubber and polybutadiens. In both cases, peroxide decomposition followed a first order kinetics with respect to concentration. The decomposition rate is independent of the constitution of the polymer chains of the polybutadiene (tacticity, vinyl side groups and the like). Somewhat higher activation energy of peroxide decomposition was observed for polybutadiene than for natural rubber and the yield of benzoic acid showed practically no temperature dependence.Benzoyloxy radicals are incorporated into the elastomer as benzoate groups [35].

The nature of free radical chain reaction leading to crosslinking involves aloss in double bond concentration roughly equal to the number of crosslinks formed and the propagation reaction appears to be polymerization of the double bonds. Infrared determinations of the vinyl group concentration in 93 per cent 1,4-polybutadiene have shown that, while vinyl unsaturation is removed, substantial amounts of main chain double bonds were also reacted

[36]. Thus, in a variety of polybutadiene, the microstructure is of greater importance for the crosslinking efficiency [22, 34]. The vinyl content plays a very important role in peroxide vulcanization of BR, and there is no doubt that the addition reaction also has a key role.

1.6.4 Copolymers of butadiene (SBR, NBR and HNBR)

The crosslinking behaviour of styrene butadiene rubber with peroxide is similar to that of *cis*-polybutadiene [20]. Gonzalez [27] studied the effect of peroxide loading and cure temperature on the crosslink reaction mechanism. At lower peroxide loading, crosslink density was found to be independent of cure temperature and crosslinking mechanism was assumed to be allylic hydrogen abstraction. In contrast, at high peroxide loading maximum torque is cure temperature dependent and the increase in crosslink density was accounted by the addition mechanism.

The crosslinking efficiency of peroxide in nitrile rubber has been reported to be one, indicating the predominance of abstraction mechanism [20, 34], presumably because of the electron withdrawing nitrile group. Valentin *et al.*, [37] 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.

Polymerization of double bond produces areas of high crosslink density or clusters that induce early failure and are visible as dramatic drop in physical properties for the high butadiene nitrile rubber.The significantly lower tensile strength of NBR compounds with higher unsaturation can be explained [38]by the fact that, the network chains will bear different forces when the material is continuously deformed, magnifying chain forces locally. This will initiate a fracture in the molecule, crack formation starts, the chain breaks quickly and transfers the load to surrounding chain, which in turn become overloaded and break. When the molecular fracture is initiated, surrounding chains break quickly. The over crosslinked region (cluster) will experience the highest forces and network strand will reach a critical force and break. Some chains in this cluster surpass the critical stress levels and their rupture is focalized in such a way that an anticipated material rupture is induced.

In saturated rubber (HNBR), the crosslinking is possible only through hydrogen abstraction mechanism, with the formation of homogeneous network. The crosslinks are uniformly distributed in the network and physical properties are found to increase with peroxide content [39]. Although a selected group of HNBR elastomers are sulphur curable, most are peroxide cured because of the enhanced heat and oil resistance attained via peroxide crosslinking. The most common peroxides used in HNBR compounds areα, α’-*bis* (t-butyl peroxy) diisopropyl benzene, dicumyl peroxide and 2, 5- dimethyl-2, 5- di- (t-butyl peroxy) hexane.The main difference between HNBR and NBR compounding is HNBR uses a significantly higher quantity of peroxide. Normally it uses 7-12phr of peroxide while an NBR compound uses only 2.5-3.5 phr of the same peroxide.

1.6.5 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. During reaction with peroxides, the presence of isoprene leads to the possibility of crosslinking reactions. The reaction mechanism of butyl rubber with different peroxide has been extensively investigated [40-42]. It was found that for butyl rubber, scission efficiency of peroxide depend quite markedly upon the unsaturation [42].As the amount of unsaturation increases, the effectiveness of peroxide in degrading the polymer decreases. When the level of isoprene in the polymer is about 3per cent, the crosslinking and scission reactions balance out. However, these isoprene levels are insufficient to support the crosslink densities required for most engineering applications [43].At higher levels of peroxide, all the available isoprene units become used up and an increase in the rate of degradation takes place. 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 Figure 1.4 [42]. Such a reaction is supported by the observed increase in unsaturation. One interesting feature of this reaction is its apparent dependence on the peroxide used. A detailed investigation of peroxide curable butyl rubber derivatives were done by Shanmugam [44].

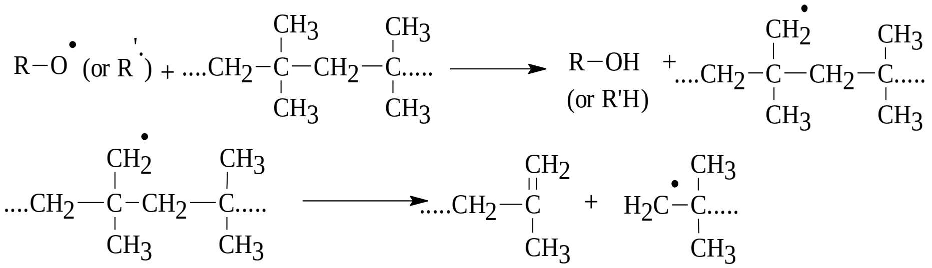


Figure 1.4 Butyl rubber degradation in presence of peroxide radical

For polyisobutylene with benzoyl peroxide, the amount of scission was found to be proportional to the square root of the peroxide concentration. Interpretation in this case is hampered by the induced decomposition of the peroxide [45].Dialkyl peroxides such as cumyl peroxide do not undergo this induced decomposition and the reactions of the polymer chain with radicals are thus more easily studied in a system employing such peroxide. Polyisobutylene may be vulcanized with t-butyl peroxide in presence of sulphur whereas cumyl peroxide is unable to produce such a reaction [46].Calculation of the ratio of ketone to alcohol formed during the reaction between peroxide and isobutylene suggested that t-butyl peroxide removes methyl hydrogen to a greater extent than cumyl peroxide, which attacks the methylene groups. Although there is no obvious reason for this difference it is consistent with scission efficiencies, which are 0.36 and 0.7 respectively.Since the highly shielded radicals formed by abstraction of methylene hydrogen would not be expected to combine with other macro radicals to give crosslinks, such combination might be possible for the radicals formed by attack on methyl groups. These observations are also consistent with the observed delayed scission [42] that could be resulted from the long life-time of the shielded radicals before the decomposition as shown in Figure 1.5.

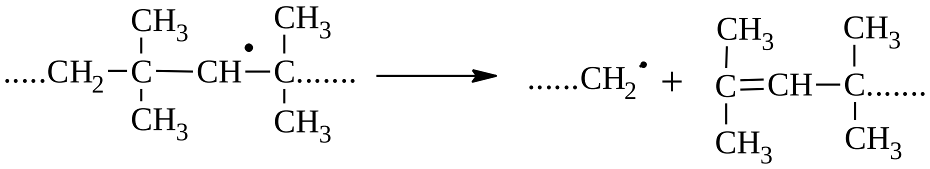


Figure 1.5 Scission of polymer radical

Eventhough, the compounds containing butyl rubber and polyisobutylene decomposes under the action of organic peroxides, these compounds can be cured in the presence of cure promoters or coagents. In 1999, Sudo *et al.*, cured butyl rubber with isoprene content in the range 0.5 to 2.5 mol% using 3.5 parts by weight organic peroxide and 0.3 to 4 per cent by weight of *bis* maleimide based compounds [47]. The rubber composition optionally contained an organosilicone compound and the articles are useful for pharmaceutical chemicals or medical treatments.

Resendes *et al.*, [48] increased the content of isoprene in butyl rubber to 7.5 mol%, using 0.1 mol% divinylbenzene to offset the molecular weight loss incurred when high isoprene levels are used in cationic polymerization. Their formulation contained four parts by weight dicumyl peroxide, 2.5 parts by weight N, N’-m- phenylene dimaleimide and provided superior cure yields than those generated by Sudo *et al.* [47]. Similar results were reported on butyl rubber containing 8 mol per cent isoprene, wherein 10 parts by weight peroxide and 4-6 parts by weight bismaleimide coagent [49]. Although these butyl rubber compositions have better peroxide cure performance, they require very high isoprene content to achieve such results. The increased content of isoprene in butyl rubber along with dicumyl peroxide and coagent in the formulation provided superior cure yields. 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 [50].

1.6.6 Polychloroprene

Loan [51] 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 [52].

1.7 Comparison of properties of peroxide cured unsaturated rubbers

Dicumyl peroxide is an effective vulcanizing agent for natural rubber (NR), synthetic polyisoprene rubber (IR), polybutadiene rubber (BR), styrene butadiene rubber (SBR) and acrylonitrile butadiene rubber (NBR).Formulations (Table 1.6) and their properties are shown in Table 1.7 [53].

Table 1.6 Formulations

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 (40%)	4	3.2	1.2	2.4	2.5

Table 1.7 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 70h 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, %, 70h 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,

1.8 Peroxide vulcanization of saturated rubbers

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

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

The growing popularity of peroxide cure of both EPM and EPDM is due to the excellent properties like oxidation, heat, ultraviolet and ozone resistance [54] which is helpful for outdoor and elevated temperature applications, such as automotive sealing systems, window gaskets and roof sheeting. The ethylene propylene rubber is fully saturated and since the commercial importance of this rubber is very high, a number of curing systems have been investigated [7, 55, 56]. Of these peroxide curing appears to be most suitable. For 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 [57].Tertiary hydrogen of the propylene unit is the most labile hydrogen towards radical attack [58]. Abstraction of tertiary hydrogen give rise to tertiary radical which, unlike the similar radical from polypropylene cannot easily lead to scission.

A simple reaction leading to scission producing a primary radical from the original tertiary one seems to be unfavourable. Abstraction of secondary hydrogen β to the methyl group also leads to an easy scission reaction (Figure 1.6).

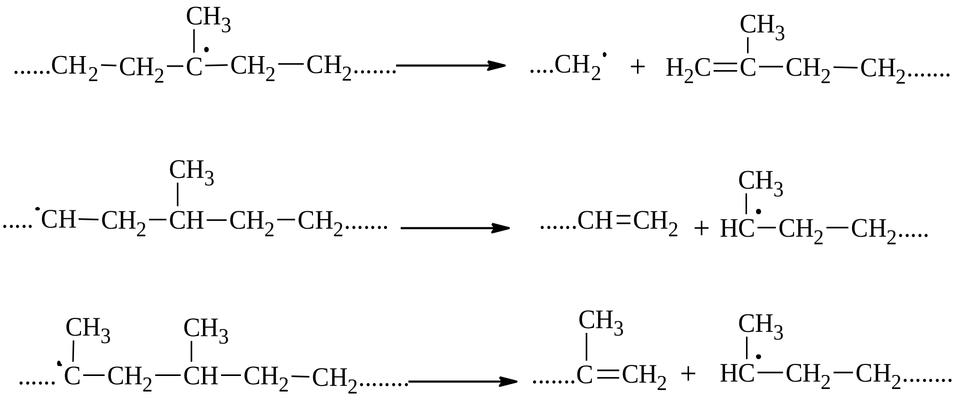


Figure 1.6 Possible scission reactions in ethylene- propylene rubbers

Thus, even though the propylene groups in ethylene propylene rubbers have been shown to be the really important groups in providing scission sites, their exact part in the reaction is not yet clear.

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 [57, 59]. The effect of unsaturated monomers on the crosslinking efficiency in an ethylene propylene copolymer is shown in Table 1.8 [60].Structural features of the pendent olefinic residues have been shown to influence both vulcanization activity and efficiency.

Table 1.8 Crosslinking efficiencies in EPDMs

Olefins	Crosslinking efficiency
5-methylene-2- norbornene	1.78
5-ethylidene-2- norbornene	0.61
5-vinyl-2- norbornene	1.55
5-propenyl-2- norbornene	0.61
5-isopropenyl-2- norbornene	1.06
5-crotyl-2- norbornene	0.51
5-(2-buten-2-yl)-norbornene	0.62
5-methallyl norbornene	0.79
5-methyl-5-vinyl norbornene	0.61
None*	0.28

*cumyl peroxide concentration 7.54 pphr

The monomers giving the highest efficiencies are those with unsubstituted terminal double bonds and since the efficiencies observed are greater than one. Somewhat lower efficiency was found where the residual unsaturation was terminal but substituted as in the case of the polymer made with the isopropenyl substituted norbornene. Lowest efficiencies were shown by monomers with internal double bonds, except 5-methyl-5-vinyl norbornene. All of the terminal unsaturated polymers showed a similar dependence of crosslink efficiency on peroxide concentration. The peroxide curing is most efficient when the olefinic moiety presents a vinyl or vinylidene group [57].The reactivity of the terpolymers is dependent on the type and amount of diene utilized in the polymer synthesis [7]. The termonomer content of EPDM is important for peroxide curing since it is the source of easily abstractable hydrogen atoms which are useful in crosslinking. A simplified mechanism of peroxide cure of EPDM is shown in Figure 1.7 [59, 61].

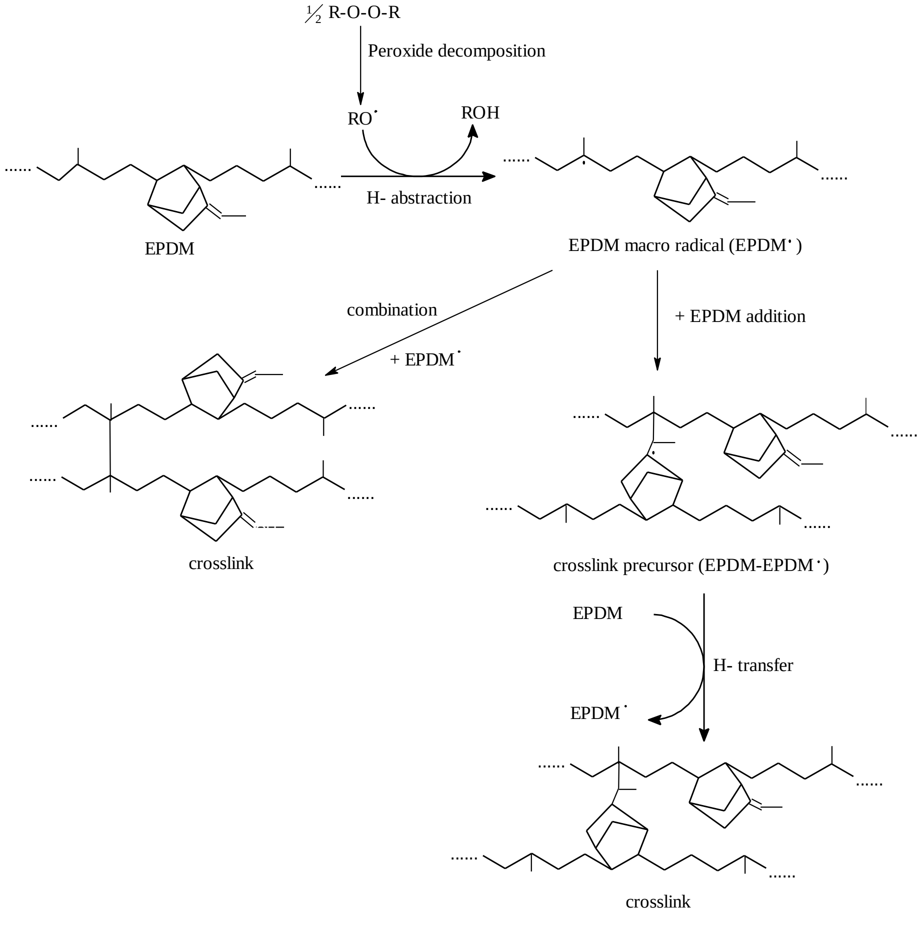
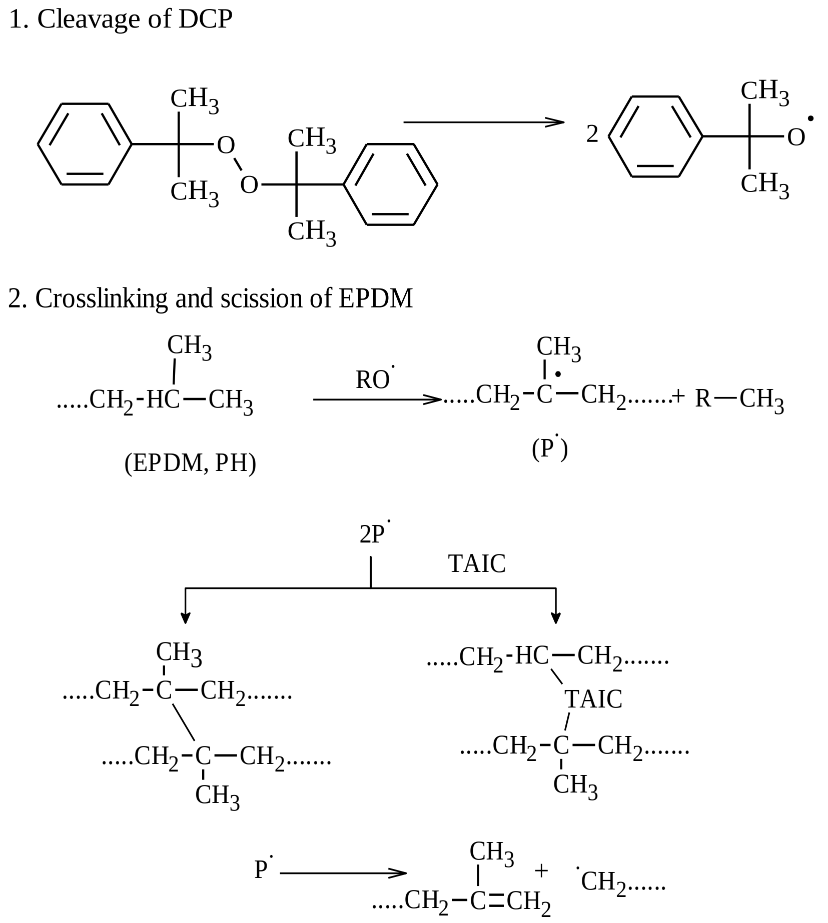


Figure 1 .7 Simplified reaction scheme for peroxide crosslinking of EPDM with ENB as the diene [59, 61]

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 [8]. Thermal decomposition of peroxide initiator results in free radicals, which abstract H atom from the allylic position of the polymer back bone yielding EPDM macro radicals. Crosslinks are formed via two routes: by combination of two macro radicals and by addition of an EPDM macro radical to the EPDM unsaturation [62]. The latter addition reaction results in the conversion of the diene unsaturation in to a saturated crosslink. The extent of crosslinking is governed by the peroxide content, whereas the addition crosslinking is governed by the structure and content of the diene monomer. Extensive low-molar-mass model [61],Fourier transform infrared spectroscopy [63], solid state ^{1}H NMR relaxometry [64], magic angle spinning ^{13}C NMR spectroscopy [65] and electron spin studies [66] had provided detailed insight in the mechanism of peroxide cure and the corresponding structures formed. Studies on cure kinetics has been carried out using rheometry [67], differential scanning calorimetry (DSC) [68] and high throughput experimentation (HTE) [69] approach.

Peroxide crosslinking has a tendency to often fall into a state of undercrosslinking. When it is generated, a part of peroxide remains in the under crosslinked rubber. This residual peroxide has an adverse effect on the final product especially for those of long- term use.The influence of residual peroxide on the degradation of EPDM has been investigated by Nakayama [70] and proposed a degradation mechanism of EPDM by DCP (Figure 1.8). The decomposition of the residual DCP can be considered to yield peroxy radicals which react with the polymer to generate polymer radicals, and it causes crosslinking reaction as well as scission reaction of the main chains.Softening arises as a result of such reactions, at the same time it accelerate oxidative degradation [71].



3. Oxidation of EPDM

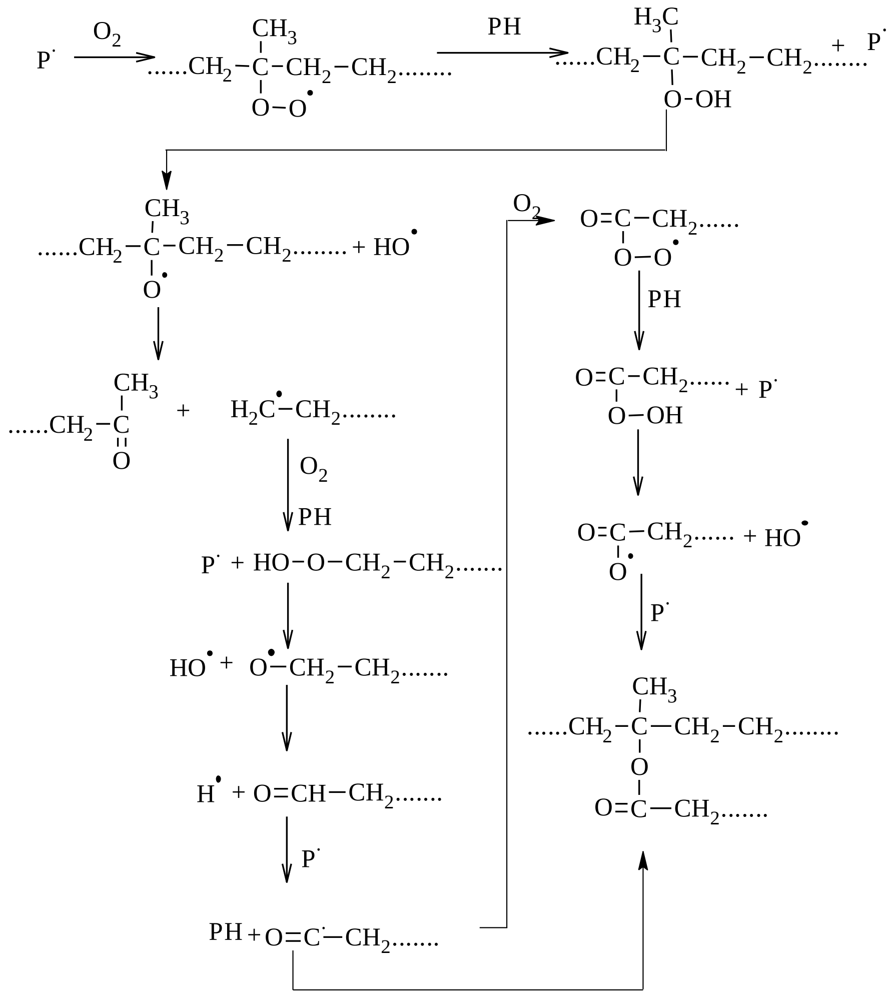


Figure 1.8 Estimated degradation mechanism of EPDM by DCP

Peroxide cure of EPM and EPDM leads to the irreversible formation of carbon-carbon crosslinks resulting in the formation of vulcanizates with poor mechanical and dynamical properties.Therefore, the mechanism of action and use of different types of coagents in peroxide cure of both EPM and EPDM has been extensively studied [13, 25, 72]. Coagents such as triallyl isocyanurate, trimethylolpropane trimethacrylate or m-phenylenebismaleimide etc. are used to enhance the crosslinking efficiency of EPDM [73]. Coagents are actually built in to the elastic EPDM network [13, 72] in contrast to the peroxide, which “only” initiate the crosslinking reaction. Due to the polarity most of the coagents are incompatible with non-polar EPDM [17]. Upon peroxide decomposition these coagent domains are rapidly crosslinked via free radical addition and cyclo-polymerization reactions, resulting in small vitrified thermoset particles [13, 14]. These particles act as multifunctional crosslink nodes, linking a large number of EPDM chains. Thus, the effect of coagent is very similar to the effect of third monomer.Classical explanations that coagents which enhance the peroxide crosslinking efficiency by suppressing chain scission or termination via disproportionation of EPR macro- radicals have been investigated [74].

1.8.2 Ethylene vinyl acetate (EVA)

Several researchers studied the peroxide crosslinking of EVA [75-78]. The crosslinking mechanism [34] ofEVA 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. A simplified mechanism of peroxide cure of EVA is shown in Figure 1.9 [79]. NMR analysis provided evidence that the methyl hydrogens of the acetate group were the most reactive sites for abstraction [80]. In past, crosslinking of EVA had initiated only by DCP now-a-days modified organic peroxides have been used to improve the crosslinking efficiency of EVA [81, 82].

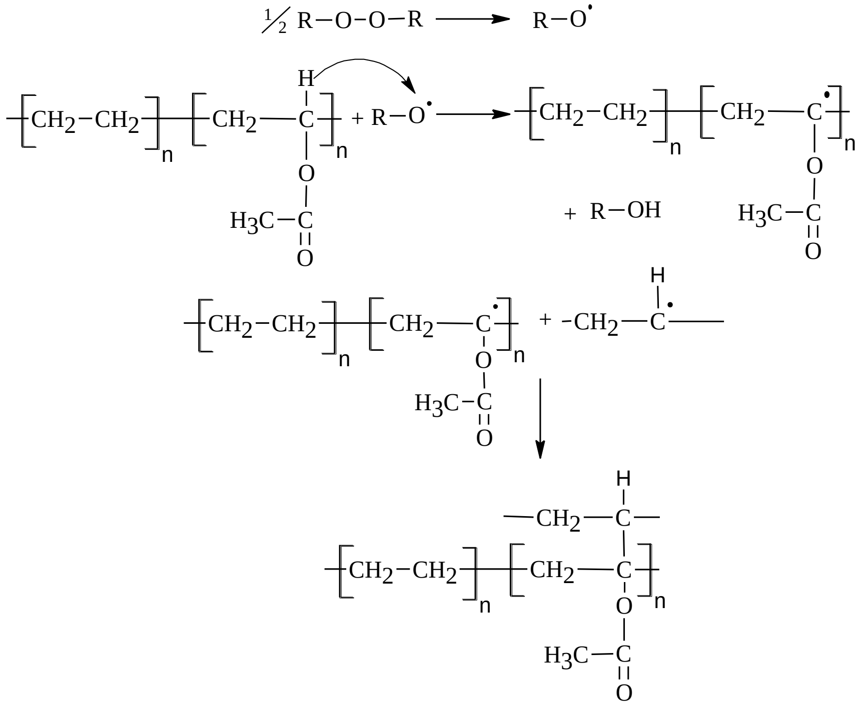


Figure 1 .9 Simplified reaction scheme for peroxide crosslinking of EVA

1.8.3 Poly vinyl chloride (PVC)

Earlier studies on peroxide crosslinking of PVC were found to be unsatisfactory because thermal decomposition of organic peroxide in PVC leads to crosslinking, rapid degradation and darkening [83]. Later, dicumyl peroxide was found to be capable of crosslinking PVC to some extent. Few studies has been reported in the literature due to the fact that the dehydrochlorination accelerated by the existence of peroxide and 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 [84-86].

Uniformly crosslinked vinyl foams could be produced by dissolving suitable peroxide in a plastisol in the presence of a crosslinking monomer [87, 88]. Due to their good compatibility with PVC, the most effective monomer has shown to be poly functional acrylates [89] and methacrylates [90-93]. Phthalate plasticizer considerably enhanced the crosslinking action and sufficient crosslinking is achieved for plasticized compound at lower TMPTMA levels [91]. Even though plasticizer type affects both the crosslinking efficiency and the network stability of TMPTMA crosslinked PVC, a phthalate plasticizer does not take part in actual gel formation [94].The gel formation and changes in mechanical properties of peroxide crosslinked plasticized PVC, blended with TMPTMA has been studied by Saethre [95]. Careful choice of peroxide type and favourable reaction conditions are necessary for the preparation of plasticized PVC sheets which could be crosslinked by heat.

1.8.4 Polyethylene (PE)

In polyethylenes, peroxide crosslinking is the most common vulcanization method. The compounding 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 [96]. Crosslinking reaction takes place in molten condition and network develops along the production line [97, 98]. The rheological properties change with network and it is often vital to know the trend of these variations and the time for reaching the gel point [99, 100]. The main polymer radical species is at the secondary carbon sites due to their prevalence in the polymer [101, 102], 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 crosslinking efficiency [76, 103].

Coagents can increase unsaturation and hence crosslinking efficiency of polyethylene. The use of 2, 4- diphenyl - 4 - methyl -1- pentene (MSD), ethylene glycol dimethacrylate, trimethylolpropane triacrylate (TMPTA), 1,2- polybutadiene, divinyl benzene (DVB) and triallyl cyanurate etc. as coagents in polyethylene have been reported [104-106]. During the crosslinking reaction, coagents are grafted to PE chains, which increase the number of vinyl groups, thus creating more active sites for crosslinking [107]. The kinetic approach to crosslinking of polyethylene by DCP and the effects of various coagents on crosslinking has been investigated by Ghasemi [108]. The role of various peroxides on crosslinking polyethylene has also been investigated [109].

When benzoyl peroxide was used crosslinking efficiencies approaching unity being observed only at low peroxide concentrations [110] and with cumyl peroxide, crosslinking efficiencies close to unity were obtained. Dialkyl peroxides are among the most efficient for crosslinking polyethylene. Peroxides that generate weaker (peroxyketals) or stronger (acyl peroxides) primary radicals are less efficient in abstracting hydrogens from the polymer or are susceptible to covalent bonding with polymer radicals [111].Crosslinking efficiency was found to be more for DCP.During the reaction of dicumyl peroxide with polyethylene, gas generated in reaction was found to contain 98% methane. For most applications involving low density polyethylene, dicumyl peroxide is commonly used. However, 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) hexyne *etc.* [112-114] to avoid scorch caused by high processing temperatures.

1.8.5 Polypropylene (PP)

In contrast to other saturated polymers, the addition of organic peroxide degrades the polypropylene backbone by beta scission, instead of crosslinking (Figure 1.10) [115]. This operation 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 [116]. 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 [117].

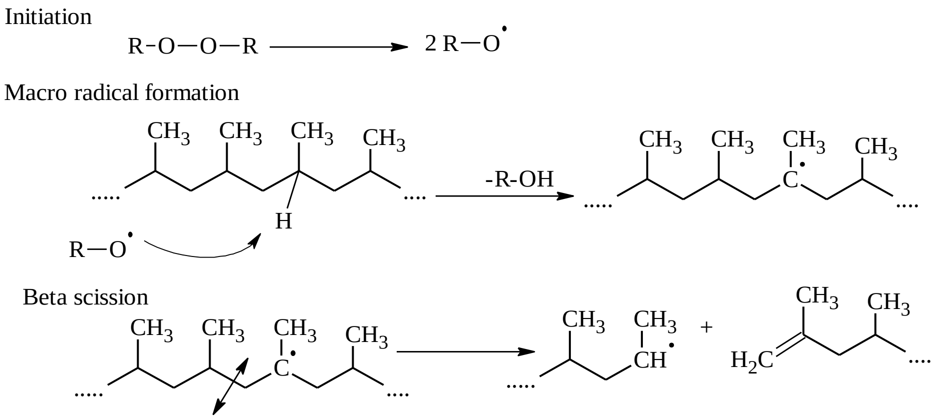


Figure 1.10 Degradation of PP by beta scission

Crosslinking efficiency of dicumyl peroxide in PP was found to increase with decrease in temperature [118]. *p*-benzoquinone was found to be an effective coagent and use of sulphur prevent scission during the crosslinking reaction [119].With *t*- butyl perbenzoate as the crosslinking agent, a predominance of build-up reactions was observed at higher peroxide concentration [120]. Isotactic and syndiotactic polypropylene differ in cure behaviour and isotactic polypropylene crosslinked more fully than syndiotactic polypropylene presumably due to the greater steric hindrance in the syndiotactic form [121].

1.8.6 Silicone rubbers

Silicone elastomers can be vulcanized by two groups of organic peroxides [122]. The first group contains “general purpose” peroxides. They have low decomposition temperatures and provide fast cures through either methyl or vinyl groups. 2, 4- dichlorobenzoyl peroxide [123] is the most widely used, due to its versatility, speed and low amount of gaseous hydrocarbon products. The second group of peroxides are commonly referred as “vinyl specific” because they activate the cure primarily through the vinyl groups. These peroxides have higher decomposition temperatures and can provide adequate scorch time for compression molding applications. The principal vinyl specific peroxides are dialkyl (di *tert*-butyl peroxide, 2,5-dimethyl-2,5-di-(*tert*- butylperoxy) hexane) and diaralkyl peroxides (dicumyl peroxide).

Peroxide cure of silicone rubber was first successfully done with benzoyl peroxide. The crosslinking efficiency of benzoyl peroxide in dimethyl polysiloxanes is quite small, with values in the range 0.05-0.35 [124], with a trend to lower peroxide efficiencies at higher peroxide concentrations. A post cure in an air circulating oven is necessary to remove the acidic materials in the rubber produced during polymerization and cure, which can acts as degradents during use. They may accelerate the hydrolytic break down of the polymer chain, and attempts have been made to remove these compounds by purification of the rubber [125]. Class *et al*., [126] studied the relationship between peroxide concentration and the physical properties of heat cured silicone rubbers as well as the difference in efficiency of two peroxides *α, α'* -di (tert- butylperoxy) -*m/p*-diisopropylbenzene and 2, 5-dimethyl-2, 5-di-(*tert*- butylperoxy) hexane. In addition to the effect on crosslinking efficiency, the use of different types of peroxides also affects the dynamic modulus of silicone rubber [127]. The crosslinking reaction of silicone rubber with benzoyl peroxide is shown in Figure 1.11 [128].

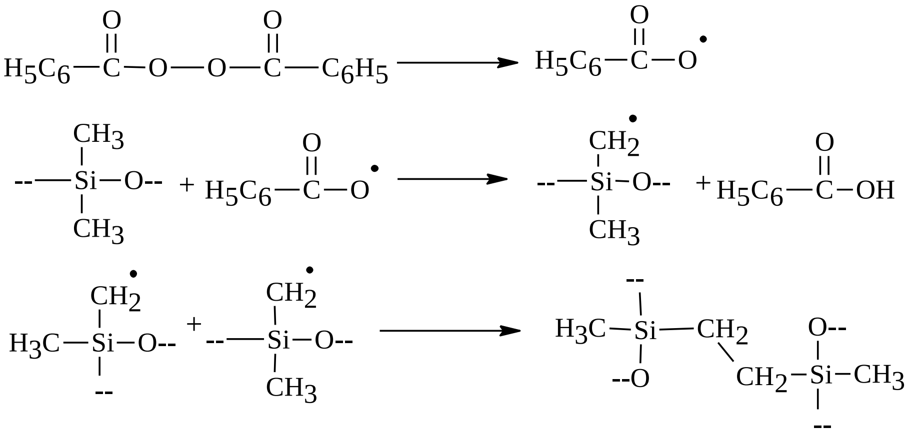


Figure 1.11 Crosslinking mechanism of dimethyl silicones

Although the mechanism of vinyl containing silicones has been discussed for many years [129-131], there is still no agreement on the crosslinking mechanism. A radical can form either at the methyl group or at the vinyl groups. The vinyl groups are more reactive but are present in a much lower concentration than the methyl groups. Reaction through a methyl group is pseudo first order since crosslinking has only small effect on the concentration of available methyl groups. 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 [132].

1.9 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 [133]. Blends of natural rubber and ethylene vinyl acetate (NR/EVA) had gained a lot of interestas they combine the excellent ageing and flex resistance of EVA and good mechanical properties of NR.The mechanical properties, vulcanization kinetics [134], rheological behaviour [135], ageing properties [136], effect of blend ratio and crosslinking system (sulphur, peroxide, mixed) has been extensively studied [137, 138]. 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 systems in NR phase varied in the order mixed > sulphur > peroxide. For 50/50 blends of NR and HNR (hydrogenated natural rubber) [139], efficient vulcanization system with peroxide exhibited best mechanical properties.

Utara *et al*., [140] 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 [141] and ageing behaviour[142] of SBR/EVA blends vulcanized by different curing systems (sulphur, peroxide, mixed) showed that mechanical properties was found to increase with increasing EVA content up to 60-80 per cent and the best retention of ageing properties was exhibited by peroxide only cure system. The low acrylonitrile NBR can be blended with SBR without significantly deteriorating the mechanical properties of the vulcanizate and the homogeneity of blends can be improved by usingpolyglycidylmethacrylate-g-butadiene rubber [143]. SBR/NBR blends are used to compensate the volume decrease in oil seal applications.

1.9.1 Thermoplastic elastomer blends

Though several crosslinking agents have been employed to crosslink elastomer phases in TPVs, peroxide, phenolic resin and silane crosslinking systems have gained commercial importance. Naskar and Noordermeer [144, 145] 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 [146]. Multifunctional peroxides, having peroxide and coagent functionality in a single molecule was also explored to overcome the unpleasant smell and blooming characteristics produced by decomposition products of some peroxides [147]. The role of different coagents, TAC and methacrylates on rheology and mechanical properties of PP/EPDM TPVs are also extensively investigated [144, 148]. In ENR/PP and NR/PP TPVs, two peroxides, DCP and DIPP (di (*tert*- butylperoxyisopropyl)benzene) were found to be effective in both the blends at low temperature but they form more smelly byproducts and cause blooming [149, 150]. Physical properties of m-EPM (maleated ethylene propylene rubber)/PP TPVs were found to change significantly with DCP concentrations and rubber/plastic blend ratio [151]. 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 [152, 153]. The typical crosslinking temperature, crosslinking efficiency and relative amount of decomposition products of each peroxide used [154] 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 [155, 156].

1.10 Drawbacks of peroxide vulcanization

Though vulcanization of rubbers with organic peroxides is an accepted procedure, there are some inherent problems associated with peroxide vulcanization which limits its applications in many areas. Peroxide cure results in the formation of strong and rigid carbon-carbon (C-C) crosslinks between polymer chains. Due to less flexibility of C-C crosslinks, the resulting vulcanizates have poor mechanical and dynamic properties. Residual odour of vulcaniztes, due to the decomposition products of organic peroxides is another area of concern. Tackiness of the vulcanizates to the mould surface, scorch safety, use of other compounding ingredients *viz*, fillers, oils, plastcizers, antioxidants etc. also have considerable effect on peroxide vulcanization.

1.11 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 [10] 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 work as scorch retarders [101,157]. 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 radicals initially 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 crosslinking 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 lose their long term antioxidant activity, since they are consumed during the first stages of vulcanization. Several chemicals are commercially available as scorch retarders [158, 159]. Some examples are: derivatives from 4-*tert*-butylcatechol (TBC) [160], methyl substituted amino alkyl phenols [161] and hydroperoxides [158] and 2, 6-di tert-butyl -p-cresol (BHT) [162]. Some scorch retarding systems have been reported in literature in more detail, such as multifunctional acrylic monomers [11] and phenolic antioxidants [163].

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 introduced [164,165] 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 and mechanism of scorch control is shown in Figure 1.12[166, 167].

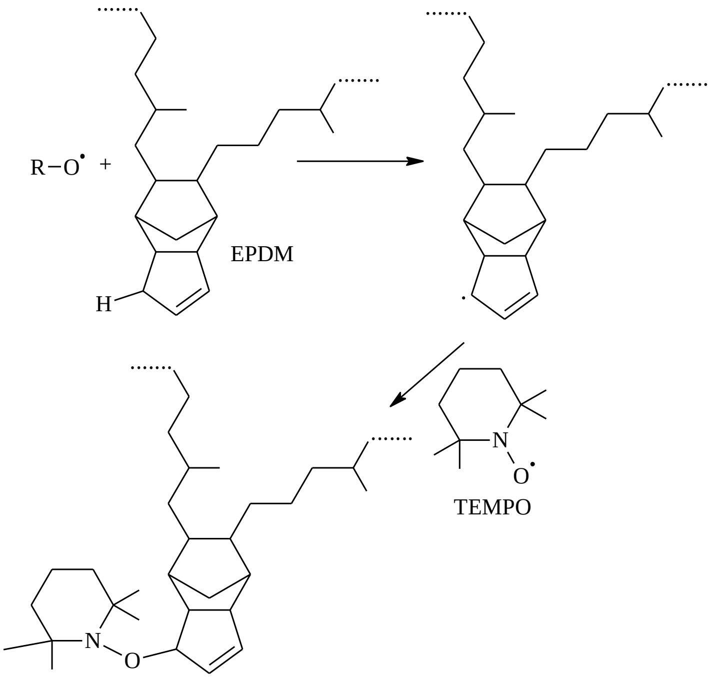


Figure 1.12 mechanism of Scorch control in EPDM

1.12 Effect of compounding ingredients on peroxide vulcanization

As the radicals formed during the decomposition of peroxide are very reactive species, it is essential to ensure that those reactions 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 [168].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 the compound 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.

1.12.1 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 applied [169]. A number of these fillers can show strong interference reactions with peroxide cure system. These reactions can be based either on the high surface area of the filler, or on the acidity of the material [3, 5, 7]. 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 Figure 1.13 [169]. Thus depending upon the type and amount of filler, the peroxide cure may be inhibited completely.

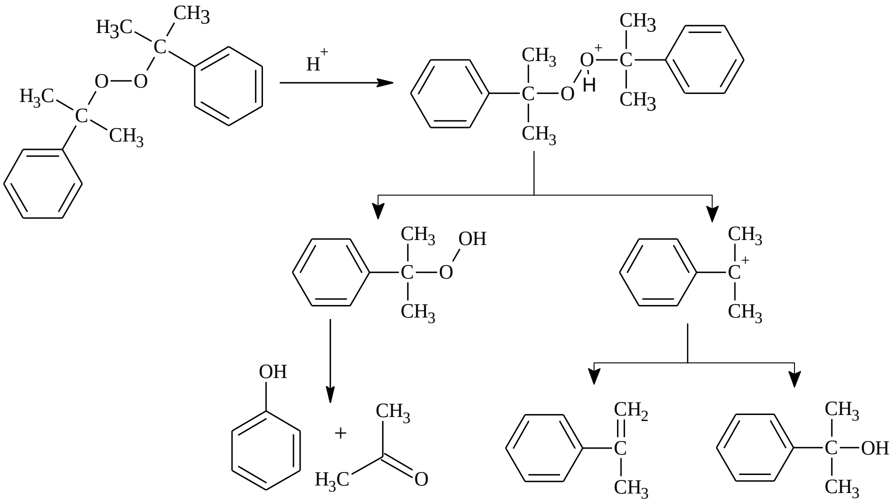


Figure 1.13 Heterolytic decomposition of dicumyl peroxide

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 [169]. 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 filler 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 crosslinking 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 1.9[169].

Table 1.9 Effect of surface treatment of a mineral filler on physicalproperties of a peroxide cured EPDM

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 has extensively been investigated [170, 171]. The effect of different types of carbon black with different class of peroxides is shown in Table 1.10 [169].

Table 1.10 Influence of different types of carbon black on physical properties of an EPDM compound

Properties	Carbon black 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

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 the 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.

1.12.2 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 processing oils contains 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 [172]. 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 decreases 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 Figure 1.14 [3, 9].

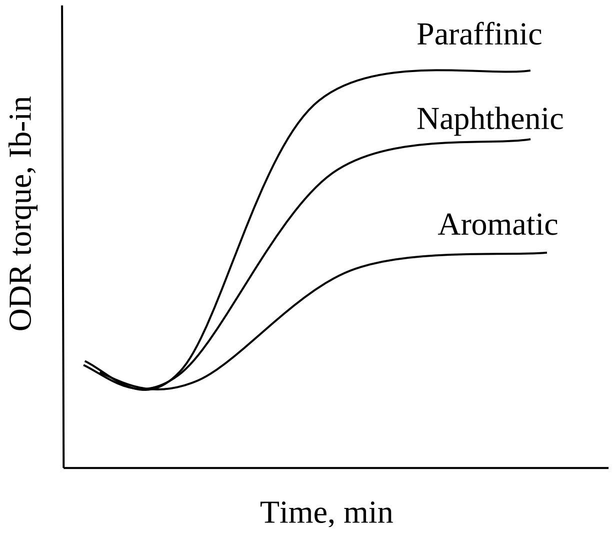


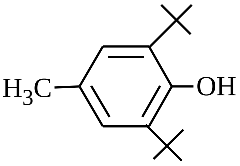
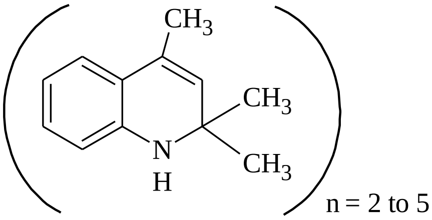
Figure 1.14The effect of oils on peroxide vulcanization of EPDM compound

It was observed that paraffinic oil has the least and aromatic oil has the worst 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 [173].

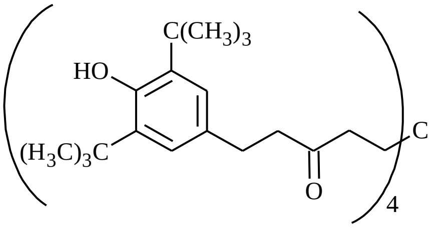
1.12.3 Antioxidants and antiozonants

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 [5]. Ferradino [174]has presented a detailed review of the best antioxidant systems for peroxide cured elastomers. The use of antioxidant for peroxide cure 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 Table 1.11.

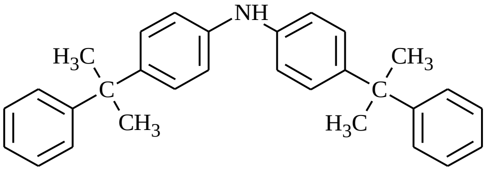
Table 1.11 Antioxidants for peroxide cured elastomers

Name of antioxidant	**Structure**
Butyrated hydroxytoluene (BHT)	
1,2 - dihydro- 2,2,4-trimethylquinoline (TMQ)	

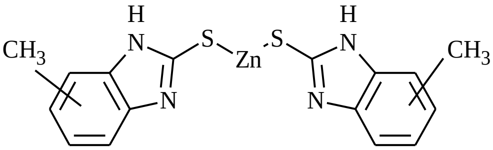
Pentaerythritol *tetrakis*(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) (AO - 1010)



4,4’-*bis*(α,α-dimethylbenzyl) diphenylamine (AO- 445)



Zinc-2-mercaptotoluimidazole (AO - ZMTI)



The effect of both amine and phenolic antioxidants on the peroxide vulcanization process has been extensively investigated [101, 157]. 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 [175]. 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 was somewhat discolouring and staining.Antioxidant-445 is a more powerful hindered aromatic type antioxidant having minimum staining and discolouring qualities, so, 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 [176]. Further, it is non-staining, non-discolouring and effective in non- black, colourable rubber compounds. A combination of antioxidant-1010 with zinc 2-mercapto-toluimidazole (ZMTI) is more effective in retaining the physical properties [177]. While there are hundreds or more antioxidants are available to protect elastomers against oxidation and heat, only a handful can successfully function with the constraints imposed by peroxide crosslinking [174].

1.13 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 outstanding heat stability of the vulcanizate. The properties of the cured vulcanizate depend on the type and nature of crosslinks formed during vulcanization. Figure 1.15 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.

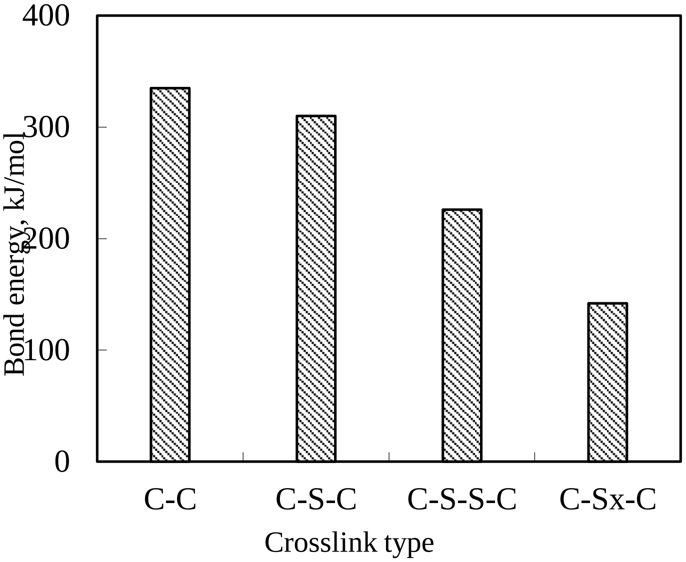


Figure 1.15 Comparison of crosslink type and bond dissociation energies

Compared to sulphur vulcanization, organic peroxide cured elastomers exhibit superior properties such as low compression set, improved heat resistance, and rapid vulcanization without reversion.

1.14 Applications of peroxide vulcanization

Organic peroxides play a vital component 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 [178]. By applying fast reacting, crosslinking peroxide types, short production cycle times can be achieved in injection molding technique by increasing mold temperature. The scorch problem at higher cure temperature can be avoided by the addition of suitable radical scavengers [167, 169]. It has been reported that golf balls with excellent rebound resilience can be prepared from diene rubber with a suitable peroxide-peoxy ester combination [179]. Usually, ethylene vinyl acetate (EVA) is used for the manufacture of sandals, slippers and shoe soles. The peroxide (DCP) crosslinked EVA foams possess special properties better than that of other foamed materials such as lightweight, colour and abrasion resistance [180]. 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 [181].

1.15 Motivation and objectives of the present work

From the ongoing discussion it can be concluded that curing of various saturated, unsaturated elastomers and their blends with organic peroxides is a highly promising area. Peroxide vulcanization is associated with relatively simple formulation compared to the widely used sulphur vulcanization. It finds wide applications in polymer industry. Their preparation, use of structurally different peroxides, characterization, properties and application will be beneficial to the mankind in a long way. In the present study, an attempt has been made to develop a suitable coagent - peroxide crosslinking system for NR so as to minimize the present problems associated with peroxide cured NR-vulcanizates. Mechanical properties like tensile strength, elongation at break, modulus *etc*. can be improved by including proper coagents in the formulation. DCP covers around 30 per cent of the total peroxide consumed by the polymer industry. One of the major disadvantages of DCP is the unpleasant odour of the vulcanizates due to its decomposition products. Therefore, in this work the utility of structurally different peroxides to overcome the present problems associated with DCP was also investigated.

The specific objectives of the present work are:

- Kinetics of peroxide vulcanization, optimization of peroxide loading and polymer crosslinking
- Evaluation of residual peroxide in the vulcanizates and to assess the effect of residual peroxide on mechanical properties
- Investigation of the role of various coagents in the peroxide vulcanization by FTIR spectroscopy and to propose a crosslinking mechanism
- The effect of various coagents on the mechanical properties of peroxide cured natural rubber vulcanizates
- Role of various compounding ingredients like ZnO, coagent, antioxidant, filler and oil on the mechanical properties of peroxide cured natural rubber vulcanizates using response surface methodology

- Preparation, characterization and mechanical properties of NR/layered silicate nanocomposites and its kinetic analysis by thermogravimetry
- Preparation of peroxide cured natural rubber vulcanizates with four chemically and structurally different peroxides and their thermal oxidative degradation behaviour by Fourier transform infrared spectroscopy (FTIR) and Thermogravimetric analysis (TGA).

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* * *

CHAPTER 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

This chapter deals with the specifications of materials and details of experimental techniques used for the preparation of peroxide cured natural rubber vulcanizates. The various characterization techniques such as Fourier transform infrared attenuated total reflectance (FT IR-ATR) spectroscopy, X-ray diffraction (XRD), dynamic mechanical analysis (DMA), Thermogravimetric analysis (TGA) and air permeability analysis are discussed.

2.1 Materials

2.1.1 Natural rubber

Natural rubber used in this study was ISNR 5 grade, obtained from Rubber Research Institute of India, Kottayam. Bureau of Indian Standards (BIS) specification for natural rubber is given in Table 2.1[1].

Table 2.1 BIS specifications of ISNR 5

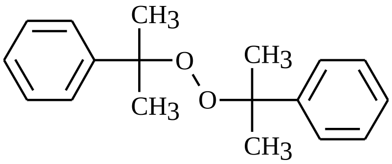
No.	Parameters	Limit
1.	Dirt content, % by mass, max	0.05
2.	Volatile matter, % by mass, max	0.80
3.	Nitrogen, % by mass, max	0.60
4.	Ash, % by mass, max	0.60
5.	Initial plasticity, P_o, Min	30
6.	Plasticity retention index, PRI, min	60
7.	Mooney viscosity(ML 1+4, 100^{o}C)	85

In a particular experiment, rubber from the same lot has been used. This is because the molecular weight distribution and non-rubber constituents of natural rubber are affected by clonal, seasonal variation and method of preparation etc. [2].

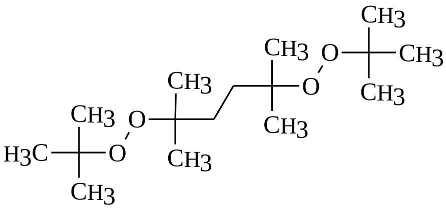
2.1.2 Crosslinking agent

Organic peroxides, used as the crosslinking agents, were supplied by Arkema Peroxides India Private Limited, Cuddalore, Chennai, India. Four different peroxides selected for the study were dicumyl peroxide (DCP), 2, 5-*bis* (*tert*-butylperoxy)-2, 5-dimethyl hexane (DHBP), 1,1’-di (*tert*-butyl peroxy)-3,3,5-trimethylcyclohexane (TMCH), and 1,3 1,4-bis (*tert*-butyl peroxy isopropyl) benzene (DIPP). The detailed specifications are given below [3].

2.1.2.1 Dicumyl peroxide (DCP)

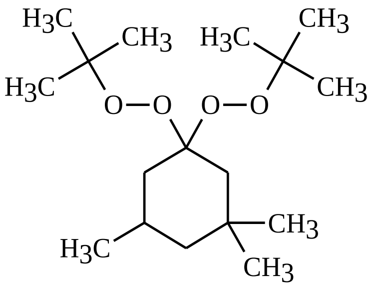
Structure	
Peroxide content (%)	40
Molecular weight	270.37
Filler/binder type	Calcium carbonate
Assay	39.0- 41.0 %
Active oxygen	2.31- 2.43 %
Recommended storage temperature	< 30^{o}C
Major decomposition products	methane, acetophenone, cumyl Alcohol

2.1.2.2 2, 5-*bis* (*tert*-butylperoxy)-2, 5-dimethylhexane(DHBP)

Structure	
Peroxide content (%)	45

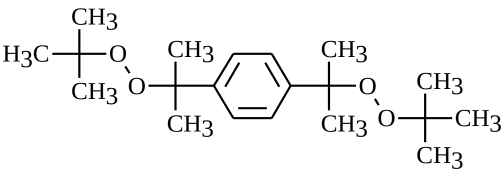
Molecular weight	290
Filler/binder type	Calcium carbonate
Assay	44.0- 46.0 %
Active oxygen	4.86- 5.08 %
Recommended storage temperature	< 30^{o}C
Major decomposition products	Ethane, methane, acetone, t-butyl alcohol, mixture of aromatic hydrocarbons

2.1.2.3 1, 1'-di (*tert*-butyl peroxy)-3, 3, 5-trimethylcyclohexane (TMCH)

Structure	
Peroxide content (%)	40
Molecular weight	302.44
Filler/binder type	Silica and Calcium carbonate
Assay	39.0- 41.0 %
Active oxygen	4.13- 4.34 %
Recommended storage temperature	< 25^{o}C

Major decomposition products	Methane, trimethyl-cyclopentane, 3,3,5, trimethyl-cyclohexanone, CO_2, acetone, t-butyl alcohol

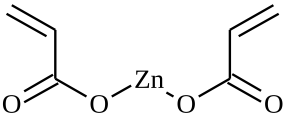
2.1.2.4 1, 3 1, 4-bis (*tert*-butyl peroxy isopropyl) benzene (DIPP)

Structure	
Peroxide content (%)	40
Molecular weight	338.47
Filler/binder type	Calcium carbonate
Assay	39- 41 %
Active oxygen	3.69 -3.88%
Recommended storage temperature	< 30°C
Major decomposition products	Methane, acetone , t-butyl alcohol, mixture of aromatic hydrocarbons

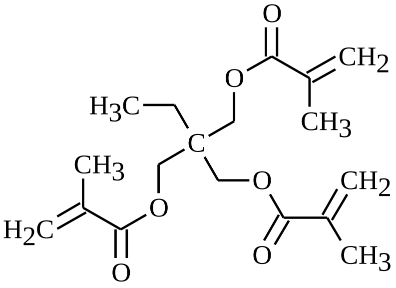
2.1.3 Coagents

The coagents used for the study were zinc diacrylate (ZDA), trimethylolpropane trimethacrylate (TMPTMA), triallyl cyanurate (TAC) and n- butyl acrylate (nBA). They were supplied by Meen Been Elastomers Private Limited, Gurgaon, Haryana, India. The specifications of coagents used were given below.

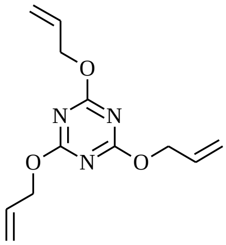
2.1.3.1 Zinc diacrylate (ZDA)

Structure	
Appearance	Yellow powder
purity	98%

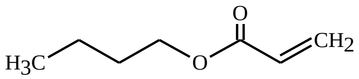
2.1.3.2 Trimethylolpropane trimethacrylate (TMPTMA)

Structure	
Appearance	Colourless liquid
purity	90 %

2.1.3.3 Triallyl cyanurate (TAC)

Structure	
Appearance	Colourless liquid
purity	90 %

2.1.3.4 n-butyl acrylate (nBA)

Structure	
Appearance	Colourless liquid
purity	99 %

2.1.4 Fillers used

The fillers used were carbon black and clays. Clays include four different types of nanoclays and commercial clay for comparison.

2.1.4.1 Carbon Black

High abrasion furnace black (N330) was supplied by Philips Carbon Black Limited, Kochi, India. Its specifications are given below

Appearance	Black granules
DBP absorption (cc/100gm)	102
Pour density (kg/m^3)	376
Iodine number (mg/g)	82
Loss on heating (%)	2.5

2.1.4.2 Organo clays

The organoclays were supplied by Southern Clay Products, USA and commercial clay was supplied by English Indian Clays, Trivandrum, India.The detailed specification is given in Table 2.2.

Table 2.2 Characteristics of the clays

Grade	Type	Inter layer distance, A^o
Cloisite Na$^+$ (MMT)	Natural montmorillonite	11.7
Cloisite 10A (MMT-2MBHT)	dimethyl, benzyl, hydrogenated tallow quaternary ammonium chloride modified montmorillonite	19.2
Cloisite 15A (MMT-2M2HT)	dimethyl, dihydrogenated tallow quaternary ammonium chloride modified montmorillonite,	31.5
Cloisite 93A (MMT- M2HT)	methyl, dihydrogenated tallow ternary ammonium modified montmorillonite	23.6
Commercial clay (CC)	Amorphous non layered clay	-

2.1.5 Other compounding ingredients used

2.1.5.1 Zinc oxide (ZnO)

Zinc oxide (White seal) was supplied by Meta Zinc Limited, Mumbai and had the following specifications.

Specific gravity (g/cm^3)	5.5
ZnO content (%)	98
Acidity (%)	0.4

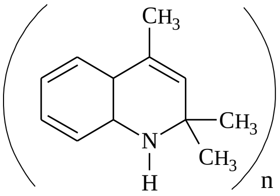
2.1.5.2 Stearic acid

Stearic acid was supplied by Goderej Soaps Private Limited, Mumbai and specifications are given below.

Specific gravity	0.85
Melting point (^{o}C)	65
Acid number	200

2.1.5.3 Antioxidant

Antioxidant TMQ was supplied by Suny Chem International Co. Ltd., Mainland, China. The detailed specifications are given below.

Chemical name	2,2,4-Trimethyl-1,2-Dihydroquinoline polymer
Structure	
Appearance	Light yellow powder
Softening point (^{o}C)	80-100

2.1.5.4 Paraffinic oil

Paraffinic oil was supplied by Hindustan Petroleum Limited. It had the following specifications.

Viscosity gravity constant (VGC)	0.85-0.9
Aniline point (^{o}C)	96

2.1.6 Solvents used

2.1.6.1 Toluene

Crosslink density measurements were carried out using Toluene. It was supplied by Fine Chemicals Limited, Mumbai and had the following specifications.

Molecular mass (g/mol)	92.14
Boiling point (^{o}C)	110.6
Specific gravity (25^{o}C)	0.859-0.863

2.1.6.2 Tetra hydro furan (THF)

Tetra hydro furan was supplied by A B Enterprises, Mumbai and had the following specifications.

Molecular mass (g/mol)	72.1
Boiling point (^{o}C)	66
Specific gravity (20^{o}C)	0.886-0.889

2.1.6.3 Ethanol (C_2H_5OH)

Triveni Chemiclas, Vapi, India suppliedethanol used for the study. The specifications are given below.

Molecular mass (g/mol)	47.07
Boiling point (^oC)	78.37
Specific gravity (15.5^oC)	0.8171

2.1.6.4 Chloroacetic acid

Chloroacetic acid for the study was supplied by Navin Chemicals, Vapi, India and had the following specifications.

Molecular mass (g/mol)	94.49
Boiling point (^oC)	189
Specific gravity (20^oC)	1.58

2.1.6.5 Sodium hydroxide (NaOH)

Sodium hydroxide (molecular mass, 37.7 g/mol and boiling point, 1388^oC) was of analytical grade and was supplied by Triveni Chemicals, Vapi, India.

2.2 Preparation of compounds

2.2.1 Two-roll mixing mill

The mixes were prepared on a laboratory size two-roll mixing mill (325 x 150 mm) at a friction ratio of 1:1.25 according to ASTM 3182-07[4] by careful control of temperature, nip gap, time of mixing and by uniform cutting operation. The temperature of the roll was maintained at 60^oC and the compound was homogenized by passing the rolled compound endwise six times through the tight nip and finally made into a sheet at a nip gap of 3mm.

2.2.2 Intermix

Masterbatch (Chapter 5) consisting of natural rubber, zinc oxide, carbon black (HAF) and paraffinic oil were prepared using intermix (Francis Shaw, KO intermix MK3) of capacity one litre. The mixing procedure was described in Table 2.3.The masterbatch was transferred into a two-roll mixing mill. Coagents and peroxides were added to the masterbatch on the two-roll mixing mill. The masterbatch was homogenized by passing the rolled compound end-wise six times through the tight nip and finally made into a sheet at a nip-gap of 3mm.

Table 2.3 Masterbatch preparation

Time, min	Step
1.00	Polymer
1.50	Adding ZnO
2.00-3.00	Adding filler and oil
3.00-5.00	Mixing
5.00	Dump batch

2.2.3 Haake Rheocord

Clays (chapter 7 (A)) were added to the natural rubber in an internal mixer, Haake Rheocord 90 at 60 rpm for 10 minutes. Peroxide was added to the compound in a two- roll mixing mill to ensure maximum dispersion.

2.3 Processing characteristics

2.3.1 Monsanto rheometer

The cure characteristics were determined using a Monsanto rheometer model R 100 (ASTM D 2084-11) [5]. The principle of rheometer is to apply a cyclic strain to a specimen and measure the associated force. Rheometer measures the torque developed as a function of time at predetermined temperature. The important parameters that can be obtained from a rheometer are given below

a) Minimum Torque (M_L): Measure of stiffness of the unvulcanized test specimen. It is the torque shown by the compound at the test temperature before the onset of cure.

b) Maximum Torque (M_H): Measure of the stiffness or shear modulus of the fully vulcanized specimen at the vulcanization temperature.

c) Optimum cure time (t_{90}): It is the time taken to attain 90% of the maximum torque. And it can be calculated using equation 2.1
Optimum cure time,

$$t_{90} = \text{minutes to } M_L + 0.9\,(M_H - M_L) \ldots\ldots\ldots (2.1)$$

d) Scorch time (t_2): It is the time taken to attain 2% of the maximum torque.

e) Cure rate index (CRI): It is a measure of the rate of cure and can be calculated from the cure graph using equation 2.2.

$$\text{Cure rate index} = 100/\,(t_{90} - t_2) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.2)$$

2.4 Moulding of test specimens

Vulcanization of various test samples was carried out in an electrically heated hydraulic press having 45cm x 45cm platen at 160°C at a pressure depending on the mould dimension (0.35 x mould area) up to optimum cure times. Moulded samples were conditioned for 24h before testing. For samples having thickness more than 6mm (eg. compression set) additional cure-time based on the sample thickness was given to ensure uniform curing.

2.5 Testing of vulcanizates

2.5.1 Tensile properties

Tensile properties of the vulcanizates were determined according to ASTM D412-06a (2013) [6]with dumbbell specimens using a universal testing machine (UTM) Zwick/Roell model Z 005 (Germany) with a crosshead speed of 500 mm/min at room temperature. The mean values of tensile properties taken from five specimens are reported. Samples were punched out from compression moulded sheets along the mill direction using a die. A thickness gauge was used to measure the thickness of the narrow portion. The modulus and tensile strength are reported in megapascal (MPa) and elongation at break in percentage (%).

2.5.2 Tear strength

The tear strength of the samples was tested as per ASTM D624-00(2012) [7], using unnicked 90^{o} angle test specimens punched out from the moulded sheets, along the mill grain direction. The measurements were carried out at a crosshead speed of 500mm/min on a universal testing machine (UTM) Zwick/Roell model Z005 (Germany). The tear strength was reported in N/mm.

2.5.3 Hardness

The hardness of the moulded samples was tested using a hardness tester in accordance with ASTM D2240 - 05(2010) [8]. The tests were performed on mechanically unstressed sample. A load of 12.5 Newton was applied and the readings were taken 10 seconds after the intender has made firm contact with the specimen. The mean value of three measurements is reported. The hardness values are reported in Shore A unit.

2.5.4 Compression set

The samples (6.5 mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25%) were kept 22h in an air oven at 70°C. After the heating period, the samples were cooled to room temperature for half an hour and the final thickness was measured. The compression set was calculated using equation 2.3.

$$C_B = \left[\frac{(t_0 - t_i)}{(t_0 - t_n)}\right] x100\% \ldots\ldots\ldots\ldots\ldots(2.3)$$

where, C_B - compression set expressed as percentage of original deflection, t_0 -original thickness of the specimen, t_i - final thickness of the specimen, t_n - thickness of the spacer bar used. The procedure used was (ASTM D395-03(2008)) [9]method B.

2.5.5 Crosslink density and swelling studies

The crosslink density of the vulcanized samples was determined by the equilibrium swelling method using Flory-Rehner equation [10].

Approximately 0.3g samples were accurately weighed and kept in toluene taken in an airtight container for 72h. The surface of the swollen samples was then gently wiped using a filter paper and weighed. The swollen samples were kept at 60°C for 24 h in an oven to remove the solvent. The deswollen weight was then determined.

Degree of crosslinking is given by equation 2.4 [11],

$$\upsilon = \frac{1}{2} Mc \text{ .... } (2.4)$$

Where, Mc is the molar mass between crosslinks, which can be calculated using the equation 2.5 [12],

$$Mc = \frac{-\rho_r V(\phi)^{1/3}}{\ln(1-\phi)+\phi+\chi\phi^2} \text{ ....} (2.5)$$

Where, ρ_r - density of rubber (ρ_r = 0.92 for NR), V - molar volume of the solvent (toluene), ϕ- volume fraction of rubber in the solvent swollen sample, χ - rubber solvent interaction parameter (χ = 0.3 for NR- toluene system).

Volume fraction of rubber in the swollen gel (equation 2.6),

$$\phi = \frac{Dw/\rho_r}{\left(Dw/\rho_r\right) + (Sw - Dw)/\rho_s} \text{ ....} (2.6)$$

Where, Sw-swollen weight, Dw-deswollen weight, ρ_s - density of solvent.

2.5.6 Ageing studies

The heat ageing resistance (Chapter 8) of the samples was measured by ageing the samples for 1, 3, 5, 7 and 14 days according to ASTM D573 - 04(2010) in a hot air oven. The aged specimens were left at room temperature for 16 hours and the mechanical properties were measured.

2.6 Characterization techniques

2.6.1 Fourier Transform infrared attenuated total reflectance spectroscopy(FT IR ATR)

The FT IR spectra of thin films were recorded in transmission mode using KBr pellet at room temperature using an IR spectrometer (Thermo Nicolet, Avatar 370). The spectra were recorded in the region 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} using attenuated total reflection (ASTM D2702 - 05(2011)) [13]. Different functional groups and structural features in the molecules absorb energy at characteristic frequencies. The frequency and intensity of absorption are the indication of the bond strength and structural geometry in the molecule. An attenuated total reflection accessory operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes in contact with the sample (Figure 2.1). ATR uses a property of total internal reflection resulting in an evanescent wave. A beam of infrared light is directed onto an optically dense crystal with a high refractive index at a certain angle. This internal reflection creates an evanescent wave that extends beyond the surface of the crystal in to the sample held in contact with the crystal.

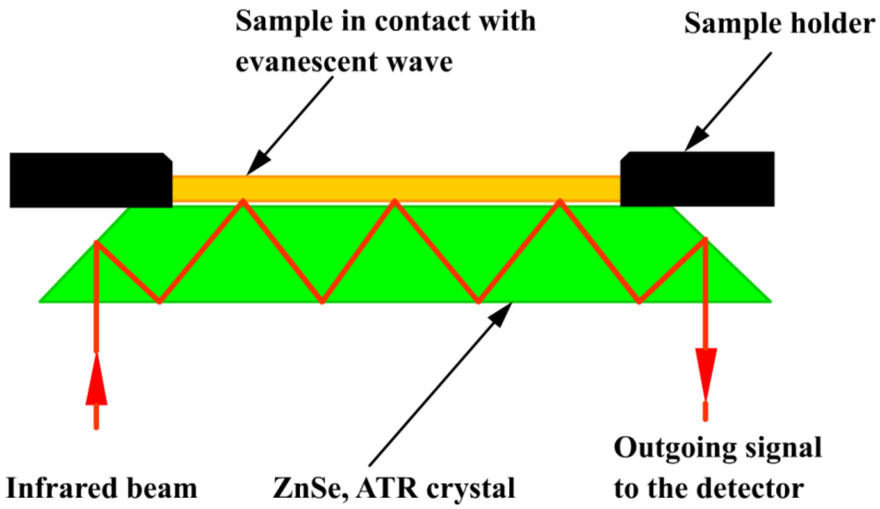


Figure 2.1 Multiple reflection ATR system

This evanescent wave protrudes only a few microns (0.5 -5 μ) beyond the crystal surface and on to the sample. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated or altered. The attenuated energy from each evanescent wave is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an infrared spectrum. In the present study FT IRATR technique has been utilized to study the role of various coagents (chapter 4) and thermal oxidative degradation behaviour (chapter 8) of peroxide cured natural rubber vulcanizates.

2.6.2 X-ray diffraction Analysis (XRD)

X-ray diffraction was used to study the nature and extent of dispersion of the clay in nanocomposites (Chapter 7 (A)). XRD patterns were obtained from Ni- filtered Cu Kα radiation (λ= 1.542 A°) by a D 500 diffractometer

(Siemens, Germany) at 40 kV and 35 mA. The samples were scanned in step mode at a scan rate of 1.5^o per min in the range 2θ< 12^o. Bragg's law was used to compute the crystallographic spacing (d) for nanoclay. The samples were scanned in step mode by 1^0/min, scan rate in the range of 2 to 12^0. The principle of X-ray diffraction is given in Figure 2.2. The diffraction from two consecutive silicate layers that are separated by a distance d, intercept X-rays of wavelength λ at an incident angle θ. The experimental 2θ values are the angle between the diffracted and incoming X-ray waves.

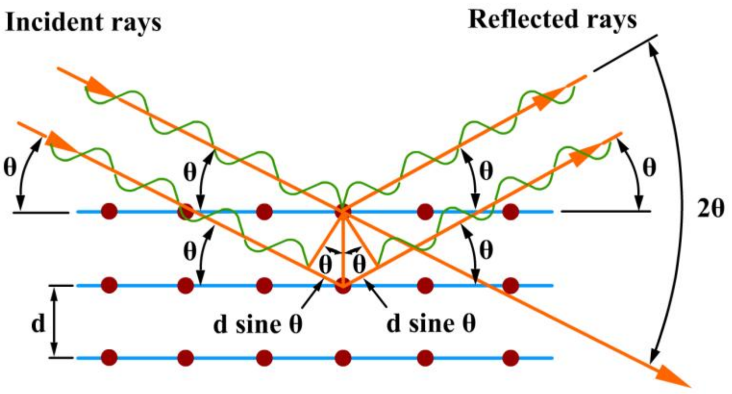


Figure 2.2 Principle of X-ray diffraction in crystals

The change in the'd' spacing of the rubber nanocomposites is observed from the peak position in the XRD graphs in accordance with the Bragg's equation 2.7

$$n\lambda = 2d \sin\theta \qquad \text{(2.7)}$$

Where, n is an integer, λ is the wavelength and θ is the incident angle.

2.7 Thermal analysis

2.7.1 Thermal ageing studies

Tests were carried out as per ASTM D573-04(2010) [15]. Specimens of vulcanized rubber were exposed to the deteriorating influence of air at 70°C in an air oven (Hot air oven, Memmert type BTI-20) for different intervals, say 1, 3, 5, 7 and 14 days, after which their physical properties were assessed. These were compared with the properties determined on the original specimens and the percentage change in each physical property (tensile strength, elongation, modulus at various elongations) were calculated using equation 2.8

$$P = [(A-O)/O] \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.8)$$

Where, P, is the percentage change in property, O, the original value and A, the value after ageing.

2.7.2 Dynamic mechanical analysis (DMA)

Dynamic mechanical measurements were carried out by applying a sinusoidal deformation to a sample of known geometry. The sample is subjected to a controlled stress or a controlled strain. For a known stress, the sample will deform a certain amount. In DMA this is done sinusoidally. The extent of deformation is related to its stiffness. A force motor is used to generate the sinusoidal wave and this is transmitted to the sample via a drive shaft. DMA measures stiffness and damping, these are reported as modulus and tan δ. The modulus is usually expressed as an in-phase component and the loss modulus as an out of phase component. The storage modulus, either E' or G', is the measure of the sample's elastic behaviour. The ratio of the loss to the storage is the tan δ and is often called damping. It is a measure of the energy dissipation of a material.

The dynamic mechanical analysis (DMA) spectra were recorded on rectangular specimens (30mm x 5mm x 2 mm) in tensile mode at a frequency of 10Hz using a dynamic mechanical analyzer (DMA 50N , 01dB-Metravib). Storage modulus and mechanical loss factor (tan δ) were measured in the temperature range -80 to 100°C at a heating rate of 2°C min^{-1}(ASTM E1640-13) [16].

2.7.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as the specimen is heated. The measurement is normally carried out in air or in an inert atmosphere and the weight is recorded as a function of increasing temperature. Thermogravimetric analysis was performed under nitrogen purge on a TGA 4000 Thermogravimetric analyzer (Perkin Elmer, Germany) with a temperature range of 30-800°C on 5-10 mg samples at a heating rate of 10°C/min. Figure 2.4 presents a schematic description of a thermo-balance used to carry out thermogravimetric measurements.It is constituted of a recording balance, a furnace and a temperature controller. The sample (1) (typically few mg) is placed in a crucible (2) inside the furnace. A change in sample mass causes a deflection of the beam (3), which interposes a light shutter between a lamp and one of two photodiodes

(4). The resulting imbalance in the photodiode is amplified (5) and fed into a coil (6) which is situated between the poles of a permanent magnet (7).

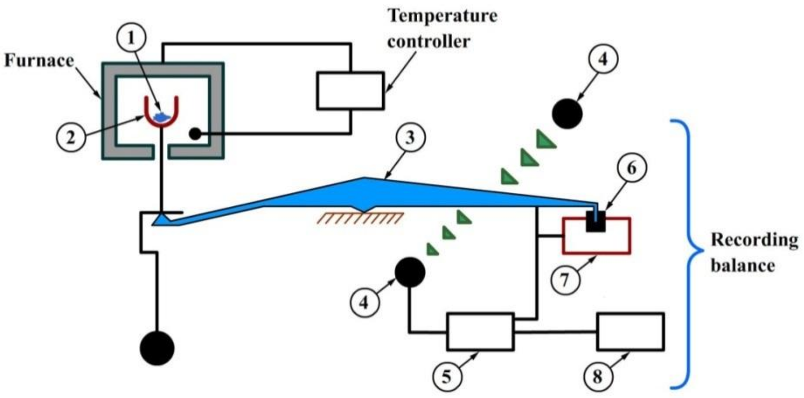


Figure 2.3 Schematic description of a thermo balance [17]

The magnetic field generated by the current in the coil restores the beam to its original position. The amplified photodiode current is monitored and transformed into mass or mass loss information by the data acquisition system (8). Analyses can be performed under different types of atmosphere and at temperature up to 2000 ^{0}C and at a heating rate up to 20^{0} C/min (ASTM D6370 - 99(2009))[18]. It should be noted that the sample size and shape have an influence on the thermo-gravimetric curve also called thermogram. In this study, TGA was used to study thermal stability and kinetics of NR/layered silicate nanocomposites.

2.8 Air permeability studies

The air permeability analyzer consists of a gas cell divided into two chambers by the membrane to be tested. The gas under test is admitted at known pressure from one side. The permeability can be studied either by measuring the pressure decrease at the high pressure side or the pressure increase at the low pressure side. A highly sensitive heat conductivity cell with temperature compensation of the signal to standard conditions, a chart recorder, a water cooling/heating thermostat for maintaining constant temperature in the measuring chamber and a rotatory two stage vacuum pump are the remaining portions of the measuring instrument. Permeability measurements were carried out according to ASTM D1434 - 82(2009) [19]. Test specimens of thickness 0.25mm were moulded and used for measurements. The equipment used was Lyssy Manometric Gas Permeability Tester L 100-2402 (Figure 2.5).

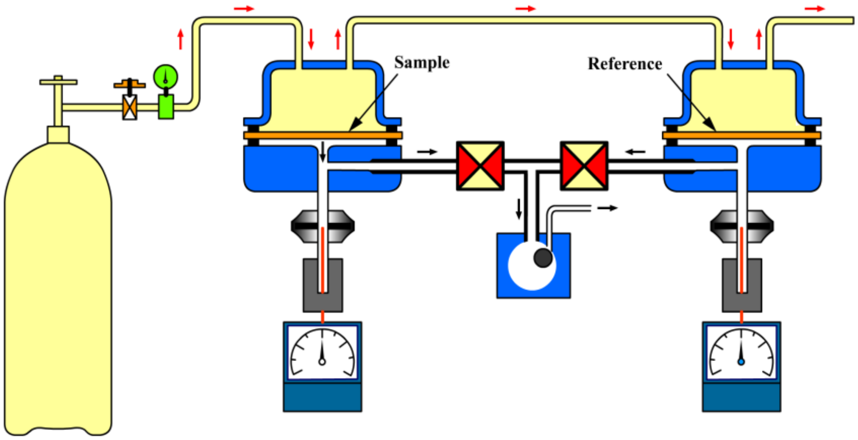


Figure 2.4 Schematic description of air permeability tester

The prepared film was used to divide the cell of the apparatus into chambers and air at a flow rate of 500ml/min was admitted from the upper compartment. The lower compartment was connected to a suction pump through a capillary U tube. The conditioning of the test specimen for a definite period is calculated from the equation 2.9.

$$T_m = \frac{b^2}{2D} \text{..................}(2.9)$$

Where, b is the thickness of the test piece in meter and D, the diffusion coefficient in meter square per second. The preconditioning times will vary from few minutes to several hours and even days depending on the type of the samples. In practice the preconditioning time is the time taken for attaining 10^{-4}torr pressure in the lowest compartment. Permeability of the sample is calculated by substituting the time taken by the standard PET sample (T_r) using equation 2.10.

Permeability of the sample,

$$P_m = \frac{T_r \times P_r}{T_m} \text{..............}(2.10)$$

where P_r is the permeability of the standard PET sample. If air is used the value of P_r is 30ml/m^2.day.

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* * *

CHAPTER 3

KINETICS OF PEROXIDE VULCANIZATION OF NATURAL RUBBER

This study was undertaken to optimize the vulcanization conditions and also to determine the effect of residual peroxide in the peroxide vulcanization of natural rubber. The study was followed through the kinetics of the vulcanization reaction. The kinetics has been studied at various temperatures viz 150,155,160 and 165°C. Dicumyl peroxide (DCP) was used as the crosslinking agent. Monsanto Rheometer was used to investigate the different crosslinking stages and vulcanization kinetics. Thermal decomposition of peroxide followed a first order free radical decomposition reaction. Half-lives at various temperatures were determined. The percentage of residual peroxide was calculated from the cure kinetic data. The effect of residual peroxide on mechanical properties was studied at various peroxide levels and also by extending the cure-time (from t_{90} *to* t_{95} *and then to* t_{100}*). Mechanical properties like tensile strength, elongation at break, modulus and compression set (70° and 100°C) were measured. Excess peroxide was found to cause high compression set at elevated temperature and the cure-time was selected in such a way to get minimum residual peroxide in the product. Results indicated that peroxide concentration is the dominant factor which controls the crosslink density and hence the properties of the vulcanizates.*

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3.1 INTRODUCTION

The crosslinking of elastomers with peroxide has been known for more than 90 years [1]. Peroxide curing was introduced to overcome the deficiencies of well-known sulphur vulcanization[2]. The peroxide crosslinked vulcanizates have very good heat resistance and hence the technique is important in automotive applications. Emerging trends for improved performance and longer service life, particularly in the transportation industry, have prompted a renewed interest and acceptance for peroxide vulcanization. Selection of a curing system for a particular application requires better understanding of crosslinking mechanism and also about the factors controlling rate of reaction (kinetics).

Peroxide vulcanization and the resulting crosslink structure of various rubbers have been studied by a number of researchers [3-10]. Hummel [11] studied the decomposition of dicumyl peroxide in natural rubber. The compression set (high temperature) and the vulcanization time of natural rubber-peroxide cure system were investigated by Bristow [12, 13]. Ogunniyi [14] studied the generalized mechanism of crosslinking reaction and the elastomers where only peroxide system is suitable. Dluzneski [15] reviewed the competing chemical reactions involved, selection of polymers, cure temperature and the effect of other compounding additives in the peroxide vulcanizates.

Though peroxide vulcanization of natural rubber has been widely explored, details of parameters like optimum peroxide required, effect of other ingredients, vulcanization time etc. till remain unanswered. Due to the marching cure behaviour of peroxide, the reported cure-time for a particular system is often inconsistent. This deviation of cure-time from actual values results in either over-cure or excess residual peroxide (under-cure) in the vulcanizates. Both cause reduction in mechanical properties. The physical properties of peroxide cured natural rubber were investigated [16], but the influence of residual peroxide on mechanical properties is not yet reported. Hence this study was proposed to optimize the vulcanization conditions and also to explore the effect of residual peroxide in the vulcanization of natural rubber. The study was followed through the kinetics of peroxide vulcanization at different temperatures. Assessment of mechanical properties was also performed to evaluate the cure level in the vulcanizates.

3.2 EXPERIMENTAL

3.2.1 Materials used

Detailed material description is given in section 2.1 (Chapter 2).

3.2.2 Methods

Formulation used for the study is given in Table 3.1. Preparation of the compounds and experimental procedures are gven in sections 2.2.1 and 2.5 respectively.The compounds were moulded to their respective t_{90}, t_{95} and t_{100} values as obtained from the Rheometer.

Table 3.1 Formulation of mixes

Ingredients	A	B	C	D	E	F
NR, phr	100	100	100	100	100	100
*DCP, phr	2.35	3.40	5.00	6.00	7.00	8.50

* dicumyl peroxide with 40% active ingredient

3.2.3 Cure characteristics

The cure kinetic data is collected in the temperature range 150 to 165°C.

3.2.4 Vulcanization kinetics

The kinetic order of the decomposition was determined by curing the compounds for various levels and then analyzing the unreacted or residual peroxide. The general equation for the kinetics of a first order chemical reaction is (equation 3.1)

$$\ln(a-x) = -kt + \ln a \quad\text{..............(3.1)}$$

Where, a- initial peroxide concentration, x- reacted quantity at time ‘t’, k- first order reaction rate constant. The half-life $t_{1/2}$ is obtained as

$$t_{1/2} = \frac{0.693}{k} \quad\text{.................(3.2)}$$

3.3 RESULTS AND DISCUSSION

Here an attempt was made to understand the effect of temperature in the crosslinking reaction of natural rubber with peroxide. Since the optimum amount of peroxide required for natural rubber based formulation is 5 phr (40 % DCP), mix C (Table 3.1) is the one selected for the kinetic study. Accordingly, different temperatures *viz* 150, 155, 160 and 165^0C were selected. The rheographs recorded at these temperatures are also given (Figure 3.1).

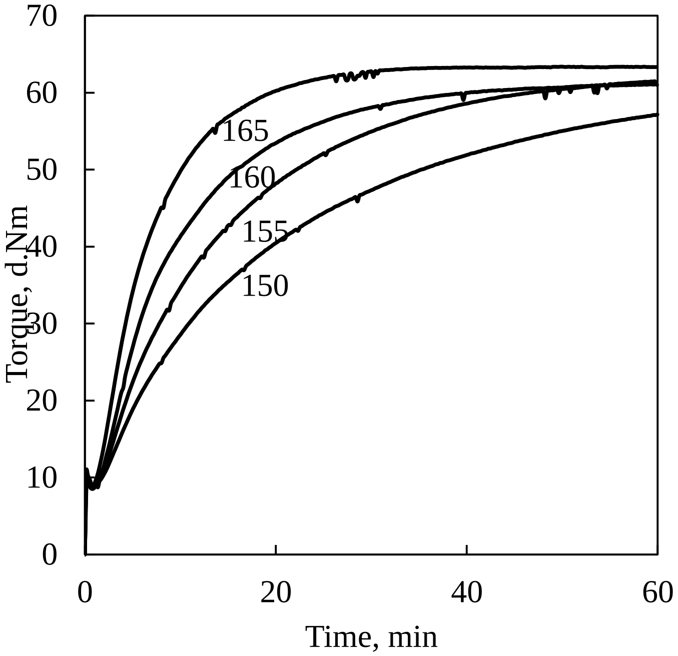

Figure 3.1 Rheometric curves of DCP cured NR at 150, 155, 160 and 165^{0}C of mix C

It can be seen that as temperature increases there is a marginal increase in torque due to the crosslinking of rubber with DCP and hence the maximum torque is temperature dependent. *ie,* as the temperature increases the rate of cure increases which leads to high torque [9]. The cure parameters that are drawn from the rheographs are given in Table 3.2. The scorch time, ts_2, is found to be longer at 150°C, due to the fact that, the rate of peroxide decomposition is very slow and hence, free radicals were generated and crosslinking occurs comparatively slowly.

Table 3.2 Rheometric properties of the vulcanizates (mix C, 5phr DCP loading)

Temperature, ^0C	M_H, d.Nm	M_H -M_L, d.Nm	t_{90}, min	t_{95}, min	t_{100}, min	ts_2, min
150	57.18	46.71	41.65	49.32	59.96	2.76
155	61.47	52.72	32.82	40.95	59.33	1.92
160	61.12	52.61	24.14	31.55	59.82	1.72
165	63.39	52.96	16.53	21.18	50	1.72

At 150°C, optimum cure is not reached, it will take a minimum of 2h for completely consuming the DCP in the vulcanizate. The curves (at 155 and 160°C) converge to a point and at 150, 155 and 160°C, t_{100} remains almost constant. At 165°C, rate of decomposition of peroxides is high and it is consumed in a limited time hence lower t_{100} value.

3.3.1 Optimum cure-time (t_{90})

The variation of t_{90} and t_{95} at different temperatures are given in Figure 3.2. It is observed that with increase of cure temperature there is a decrease in t_{90} and t_{95}. There exists an empirical relation between cure temperatures and cure-time. For every 5°C increase in temperature, optimum cure-time t_{90} decreases by 8unit and the t_{95} decreases by 10 units. The scorch time, ts_2, remains more or less constant except at 150°C.

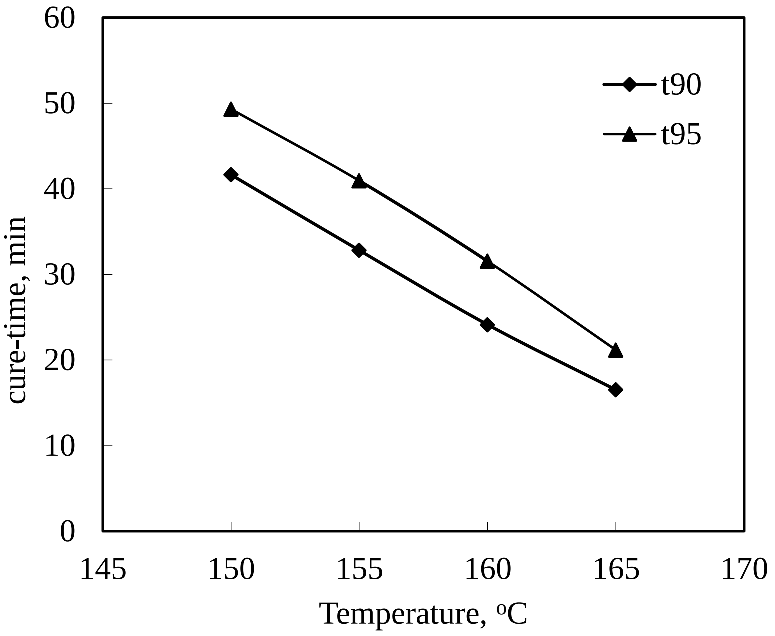

Figure 3.2 Variation of optimum cure-time t_{90} and t_{95} with temperature of mix C

3.3.2 Vulcanization kinetics

First order reactions are characterized by an exponential decay of reactant concentration with time. The larger the value of the first order rate constant k, the faster the reaction. A first order reaction is identified by linearity in the plot of log (a-x) against time. Figure 3.3 reveals that thermal decomposition of peroxide obeys first order kinetics at all temperatures. The advantage of first order kinetics is that the value of rate constant can be derived from a relative measure of the reactant concentration with time. The absolute concentration of reactant is not required.

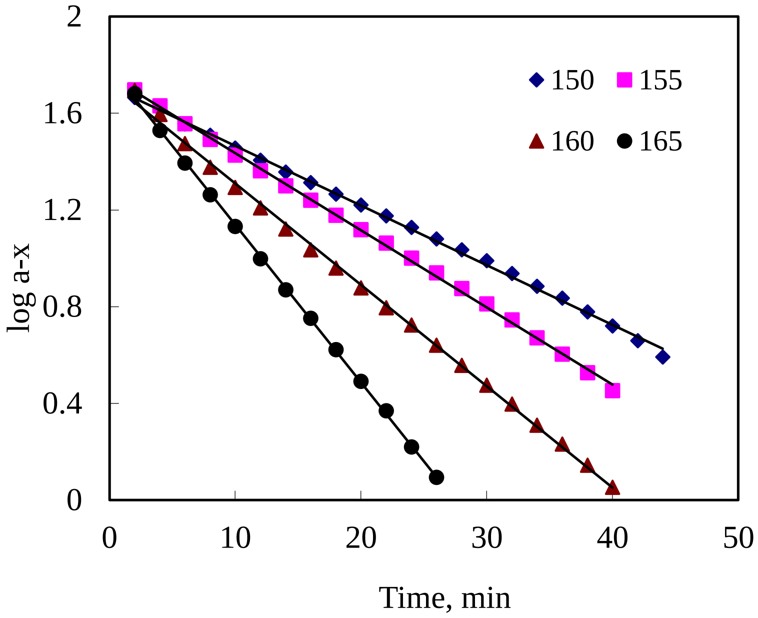

Figure 3.3 Variation of log (a-x) with time at 150, 155,160 and 165^{0}C

3.3.3 Temperature dependence of rate constant

The rate constant for a particular reaction has a constant value at a particular temperature. The temperature dependence of rate constant is described by Arrhenius equation,

$$\ln k = \ln A - \frac{E_a}{RT} \text{............}(3.3)$$

Where, A- pre- exponential factor or Arrhenius factor, E_a- activation energy. The two parameters A and E_a are together known as the Arrhenius parameters and are characteristic of each reaction. A plot of $\ln k$ against $1/T$ is a straight line with slope $-\frac{E_a}{R}$ and intercept $\ln A$.

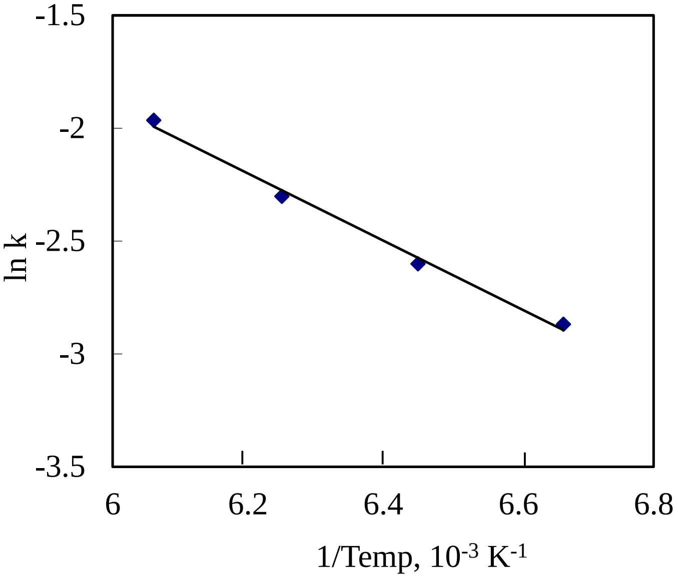

Figure 3.4 Variation of ln k with 1/T of mix C

Activation energy of the reaction is calculated (Figure 3.4) and it is found to be positive. When E_a is positive, reaction rate increases with increase in temperature. The larger the activation energy the greater is the sensitivity of the reaction to temperature changes. For every 10 K rise in temperature the rate constant doubles as shown in Table 3.3. The half-life, time required for half of the peroxide in the formulation to thermally decompose, decreases with increase in temperature. The half-life and the number of half-lives completed at t_{90}, t_{95} and t_{100} are also given in Table 3.3.

3.3.4 Decomposition of peroxide with cure-time

The characteristic of the peroxide crosslinking of rubber is its decomposition rate expressed as half-life (Table 3.3). In the first half-life, 50 per cent of the peroxide decomposes and it continues as given in Table 3.4. The process continues and theoretically never reaches 100 per cent decomposition/consumption. The following table shows the relationship between number of completed half-lives and the quantity of peroxide decomposed.

Table 3.3 Variation of rate constant and half-life with temperature

Temperature, ^{0}C	k, min^{-1}	t ½, min	t ½ completed at		
			t_{90}, min	t_{95}, min	t_{100}, min
150	0.056757	12.20	3.41	4.04	4.91
155	0.074249	9.33	3.51	4.38	6.35
160	0.096562	7.17	3.57	4.40	8.34
165	0.150188	4.61	3.59	4.59	10.00

Table 3.4 Variation of percentage of peroxide with half-lives

Half-lives	Amount of peroxide decomposed,%
1	50
2	75
3	87.5
4	93.75
5	**96.9**
6	98.4
7	99.2
8	99.6
9	99.8
10	99.9

For maximum decomposition of peroxide during vulcanization, requires the cure-time to be at least five half-lives at the cure temperature, giving 96.9 per cent decomposition, or preferably 10 half-lives, which accounts for 99.9 per cent decomposition. It is to be noted that t_{90}, accounts for an average of three half-lives (Table 3.3) leaving 12.5 per cent residual peroxide in the product. In t_{95} this is four half-lives and in t_{100} it varies between 6 to 10 half-lives according to the temperature. Since excess peroxide causes higher compression set, the cure temperature is to be selected so as to get minimum residual peroxide in the product.

3.3.5 Residual peroxide

The amount of residual peroxide at four different temperatures, 150, 155, 160 and165^{o}C, is calculated theoretically from the equation, ${(a-x)}/{a} \times 100$, where, 'a' is the initial concentration of peroxide (M_H-M_L) and 'x' is the reacted quantity of peroxide at time 't' (Mt-M_L). The results are given in Figure 3.5. It is to be noted that at 160^{0}C, the percentage of residual peroxide after the first half-life is approximately 50, but at all other temperatures it is slightly greater than the expected value.

Table 3.3 shows that at optimum cure-time t_{90}, peroxide decomposition accommodated three half-lives and the percentage of residual peroxide is approximately 12 per cent. At t_{95}, vulcanizates contain approximately 6 per cent residual peroxide since it includes more than four half-lives. At 150^{o}C, t_{100} accommodates 4.9 half-lives and about 97 per cent of the peroxide is expected to be reacted at this temperature. At 155^{o}C, the half-life is 9.33 minutes it completed 6.35 half-lives for t_{100} and consumed 98.4 per cent peroxide. At 160^{o}C for t_{100}, 99.6 per cent decomposition occurs as the cure-time is equal to 8.34 half-lives. At 165°C, the completed half-lives and peroxide consumption are 10 and 99.9 per cent respectively.

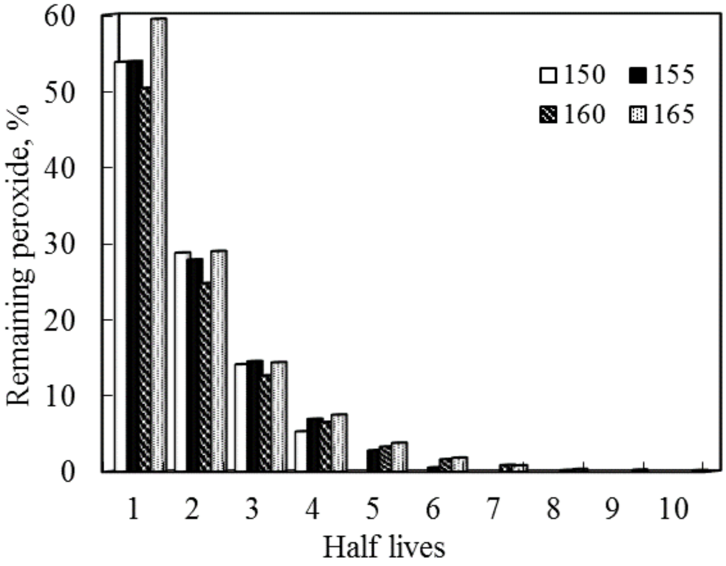

Figure 3.5 Variation of residual peroxide with half-lives at respective temperatures.

Hence the cure temperature (t_{90}, t_{95} or t_{100}) is to be calculated from a fully decomposed peroxide cure curve. For this the peroxide vulcanization reaction (rheographs) is to be run for a minimum time of 60 minutes.

3.4 Effect of varying concentration of peroxide on cure-time

Since the cure-time and residual peroxide influences mechanical properties, the studies have extended to vulcanizates with different loading of DCP. Figure 3.6 shows the variation of rheometric torque with different concentration of peroxide at 160^0C.

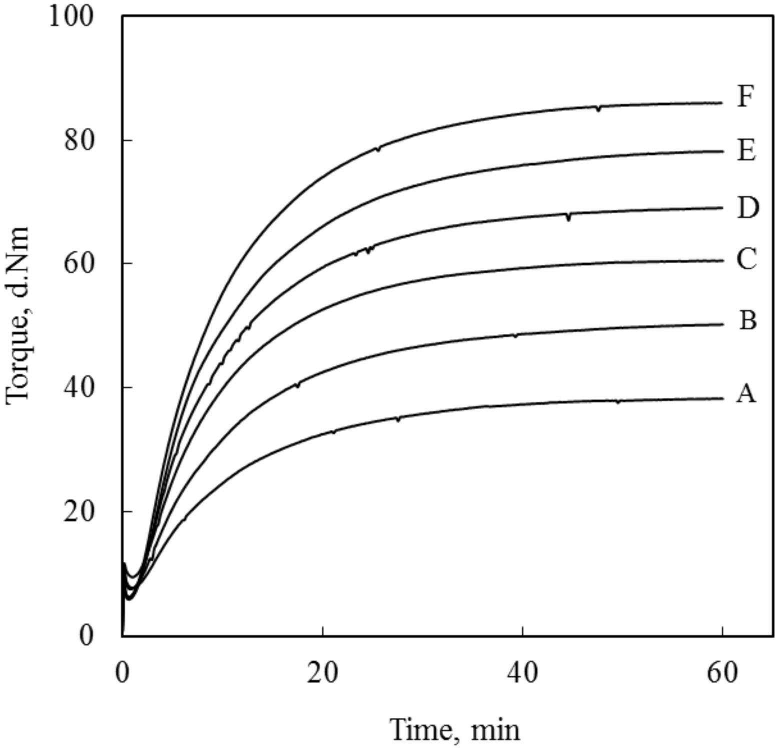

Figure 3.6 Variation of Rheometric torque with concentration of peroxide vulcanized

Rheometric properties of the vulcanizates are given in Table 3.5. As the concentration of peroxide increases the torque increases regularly. This is due to the fact that as the concentration of peroxide increases, more radicals are formed and thus crosslinking efficiency will be higher. It is also evident from the crosslink density measurement which will be discussed later (Table 3.6). It is seen that as the concentration of peroxide increases, M_H value increases, minimum torque M_L remains almost the same.

Table 3.5 Rheometric properties of the vulcanizates at 160^{o}C

Sample	M_H, d.Nm	M_H-M_L, d.Nm	t_{90}, min	t_{95}, min	t_{100}, min	ts_2, min
A	38.33	30.58	27.73	34.8	59.77	2.38
B	51.08	43.51	28.95	36.79	59.37	2.24
C	61.12	52.61	24.14	31.55	59.82	1.72
D	69.06	60.92	25.16	32.58	59.69	1.67
E	78.18	70.56	26.28	34.67	59.76	1.59
F	86	77.86	24.72	32.23	59.82	1.47

3.5 Mechanical properties

The mechanical properties of the vulcanizates were measured at different cure-times say t_{90}, t_{95} and t_{100}, to study the influence of cure-time and residual peroxide content on the mechanical properties like tensile strength, elongation, modulus etc. and after ageing properties. At higher peroxide level there is an increase in the amount of residual peroxide as well as the possibility of the formation of clusters due to non-homogeneous distribution of crosslinks [8, 10, 17]. Variation of tensile strength with concentration of peroxide and cure-time is shown in Figure 3.7. At t_{90} and t_{95}, tensile strength increased with increase in concentration of peroxide up to optimum level (5phr) and then decreased. This order is slightly different at t_{100} as there is an increase in tensile strength with concentration of peroxide up to 3.4 phr and thereafter it decreased. At low peroxide level (2.35 and 3.4), increasing cure-time (t_{90} to t_{100}) has a very small effect in tensile strength. When the cure temperature is high, the peroxide decomposes at faster rate and hence the crosslink density also increased and as a result an increase in tensile strength is expected. Increasing cure-time (decrease in residual peroxide content) has no significant effect on the tensile strength at very high (8.5 phr) peroxide loading. At or above 5phr, as the cure-time increases from t_{90} to t_{100}, amount of residual peroxide decreased and there is significant decrease in tensile strength at a particular loading of peroxide (C, D, and E) as shown in Figure 3.7.

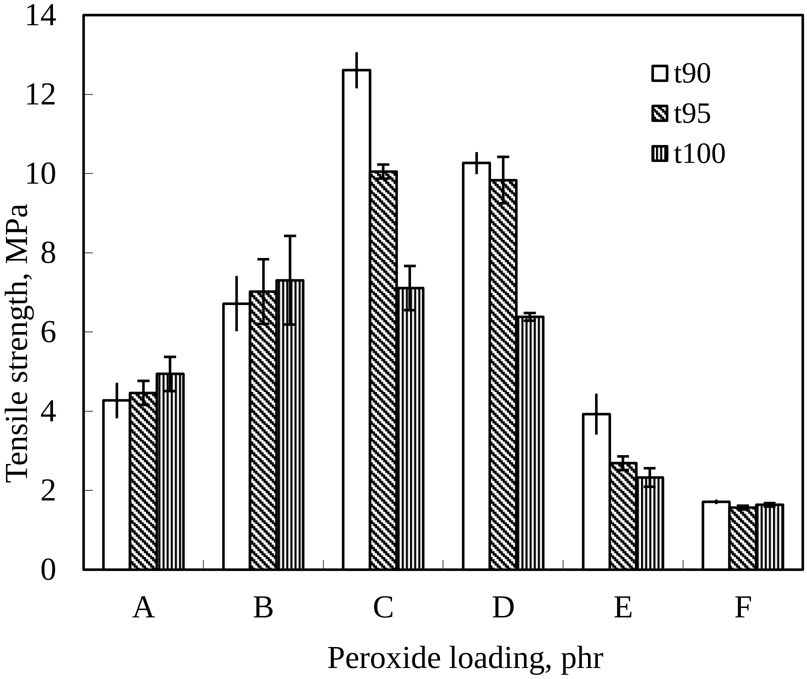

Figure 3.7 Variation of tensile strength as a function of peroxide concentration

Further as the number of crosslinks increases the shorter C-C crosslinks restrict the orientation of the macromolecular chains of the NR (strain crystallization) and producing stiffer vulcanizates with lower mechanical properties. This has been further confirmed from the stress-strain curves of mixes C, E and F in Figure 3.8. When the peroxide level was 5phr (optimum) the tensile strength was maximum as the strain induced crystallization comes to effect (strain induced crystallization usually occurs in NR above 400 per cent elongation). At high peroxide concentration (mixes E and F) the tensile strength was low as there is no strain induced crystallization due to the over crosslinking and hence the lower elongation.

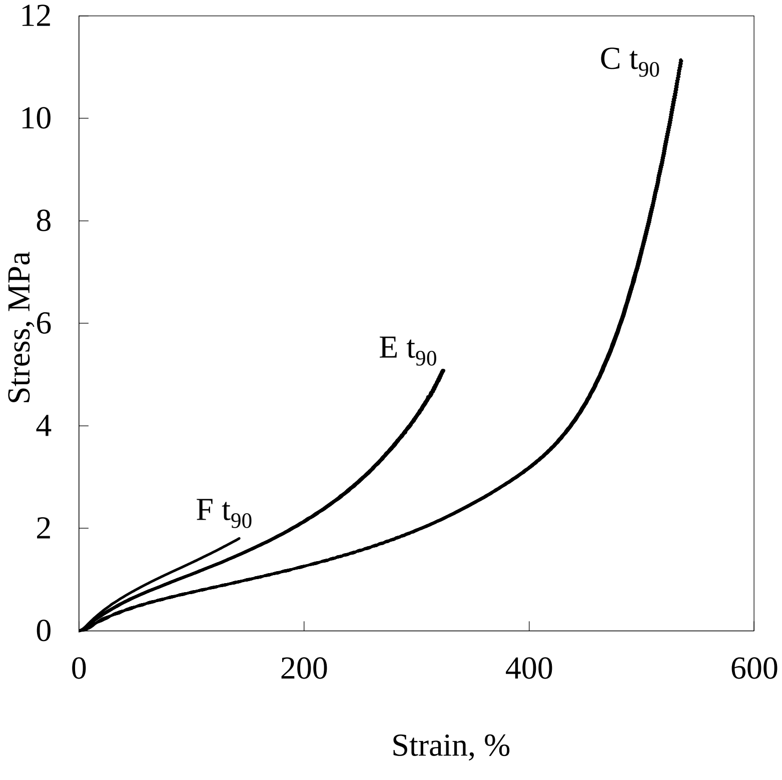

Figure 3.8 Stress- strain curves of mixes C, E and F vulcanized at 160^{o}C

Figure 3.9 shows the elongation at break as a function of concentration of DCP. It is clear that elongation is high for sample A and it decreased with increasing concentration of peroxide. Higher the level of peroxide greater will be the crosslink density and hence lower elongation at break (Table 3.6). Increasing cure-time from t_{90} to t_{100} (decreasing residual peroxide content) has no significant effect on elongation as shown in the figure.

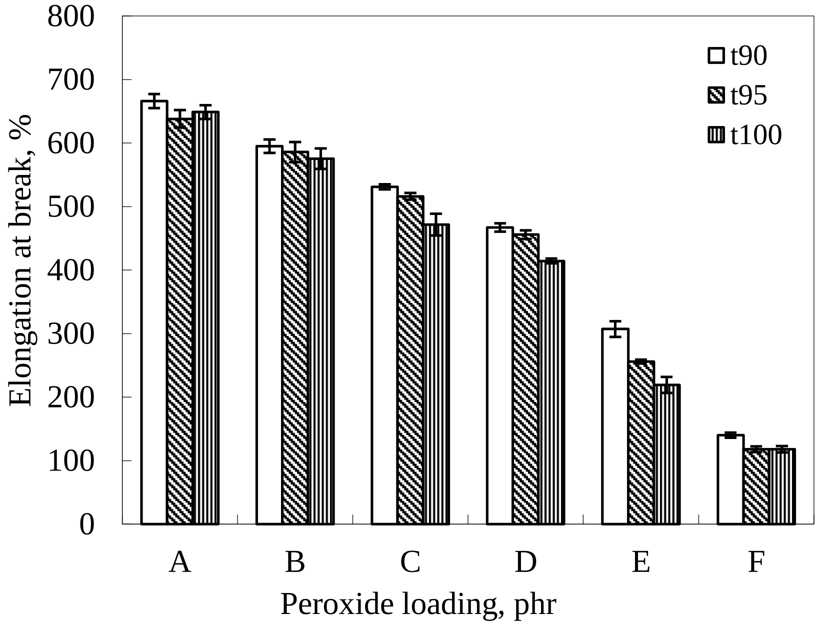

Figure 3.9 Variation of elongation at break as a function of concentration of peroxide

The variation of modulus for 100 per cent elongation with peroxide loading and cure-time (t_{90}, t_{95} and t_{100}) is shown in Figure 3.10. At t_{90}, modulus increases with increase in concentration of peroxide and showed slight increase at higher cure intervals (t_{95} and t_{100}). Modulus depends upon the extent of crosslinking.

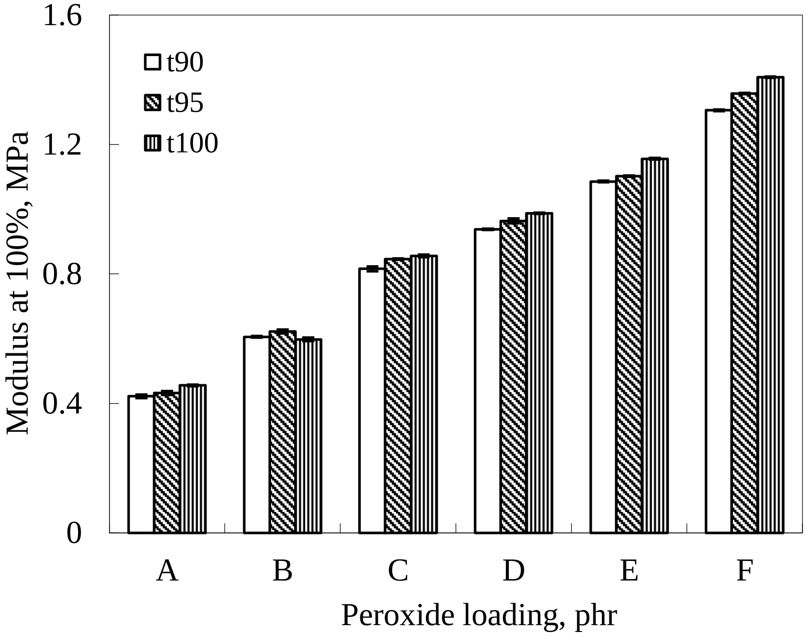

Figure 3.10 Variation of modulus (M_{100}) as a function of concentrationof peroxide

3.5.1 Compression set

Theoretically, set is the deformation that remains after an imposed strain has been removed. Thus, set measures the ability of elastomers to recover its original dimension after prolonged compressive stress at a given temperature and deflection. Variation of compression set at 70 and 100°C as a function of concentration of peroxide and cure temperature are shown in Figures 3.11 and 3.12 respectively.

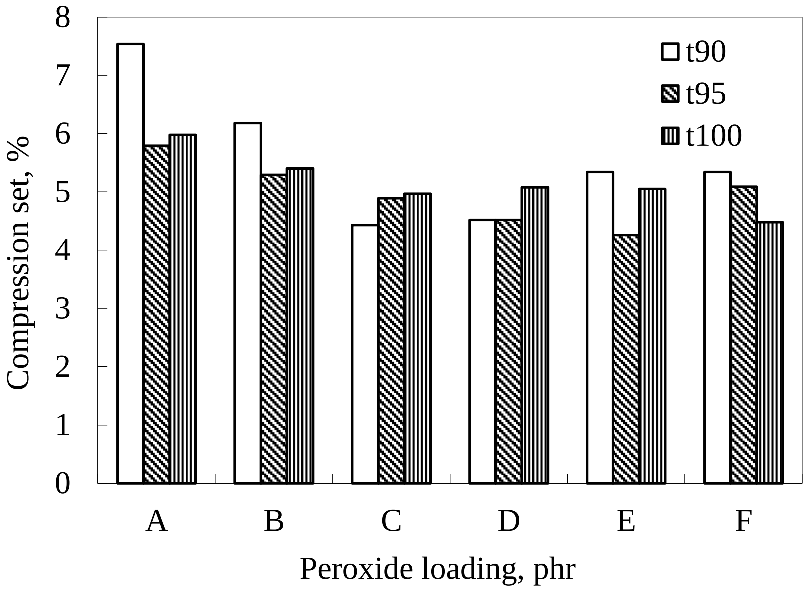

Figure 3.11 Variation of compression set (70°C for 22h)

Comparison of set values at t_{90}, t_{95} and t_{100} shows that, at 70°C, the set was not that much influenced by the peroxide level. In all the cases, there is a slight improvement (decrease) in set values as the concentration of peroxide increases and it remains more or less constant at or above 5 phr. This due to the fact that rigid C-C bond, having excellent thermal stability do not undergo any cleavage or deformation in the compressed state.

At elevated temperature (100°C) set values were mostly influenced by cure-time as shown in Figure 3.12. Irrespective of the concentration of peroxide high set values are observed for t_{90} and minimum at t_{100}. At t_{90} and t_{95}, as the peroxide loading increases set values increases reaches a maximum (sample D), then decreases. It is to be noted that for mixes A and B there is insufficient crosslinking whereas for D, E and F the residual peroxide contributes to high set. For t_{100} lowest set values are obtained with optimum peroxide loading (mix C).

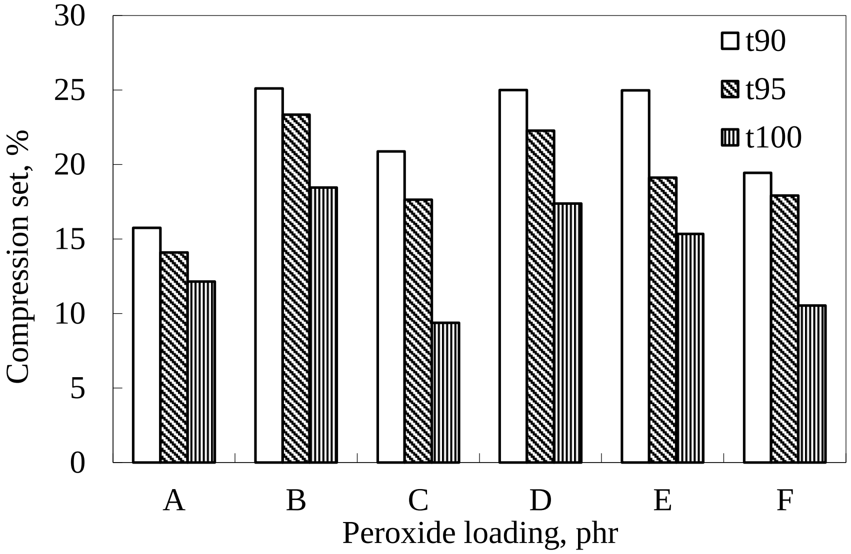

Figure 3.12 Variation of compression set (100°C for 22h)

Improved compression set with prolonged cure was related to network modifications [18]. Therefore, at elevated temperatures there is no need to carefully control optimum cure-time. For microcellular sheets were compression set is an essential service parameter, it is better to cure the material longer times (t_{95} or t_{100}) so as to have minimum residual peroxide content in the product.

3.5.2 Crosslink density

According to the theory of swelling of crosslinked polymers, strong bonds such as chemical crosslinks prevent rubber molecules to become completely surrounded by fluids, but cause swelling [19, 20]. The degree of equilibrium swelling provides additional information regarding the crosslink density of the vulcanized material. Table 3.6 represents the variation of crosslink density with cure-time as well as with the concentration of peroxide. The increase in torque during rubber curing is a measure of the number of crosslinks formed per unit volume of the rubber. The maximum torque increases with temperature and also with the concentration of peroxide. It can be seen from the table that, as the concentration of peroxide increases, in all cases (t_{90}, t_{95} and t_{100}), crosslink density remains more or less same. Further heating will not result in a considerable decomposition of peroxide as indicated in Table 3.4. At higher peroxide level there is also the possibility of the formation of clusters due to non-homogeneous distribution of crosslinks [10] which also results a higher crosslink density.

Table 3.6 Variation of crosslink density with concentration of peroxide

Sample	Crosslink density, x 10^{-5} mol/cm^3	Sample	Crosslink density, x 10^{-5} mol/cm^3	Sample	Crosslink density, x 10^{-5} mol/cm^3
A t_{90}	5.65	A t_{95}	5.85	A t_{100}	6.01
B t_{90}	8.36	B t_{95}	8.67	B t_{100}	8.69
C t_{90}	11.37	C t_{95}	11.79	C t_{100}	12.25
D t_{90}	13.33	D t_{95}	13.75	D t_{100}	14.27
E t_{90}	16.14	E t_{95}	16.26	E t_{100}	16.46
F t_{90}	18.60	F t_{95}	19.26	F t_{100}	19.77

3.6 CONCLUSIONS

The kinetics and cure characteristics of peroxide vulcanization of natural rubber with dicumyl peroxide have been studied. The ideal temperature for the peroxide vulcanization of NR is 160^{o}C and the optimum level is 5 phr (40 % DCP). Residual peroxide has no significant effect on tensile strength, elongation at break, modulus and low temperature compression set. However, high temperature set increases with residual peroxide in the vulcanizate. For rubber products with set is a critical parameter the consumption of entire peroxide must be ensured. The crosslinking efficiency of peroxide depends on the number of completed half-lives which in turn depends upon the initial concentration of peroxide. The peroxide concentration is the dominant factor which controls the final crosslink density and properties of the vulcanizates.

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CHAPTER 4

ROLE OF COAGENTS IN PEROXIDE VULCANIZATION OF NATURAL RUBBER

The drawbacks of peroxide vulcanization can be overcome to a great extent by introducing suitable co-curing agents (coagents) in the formulation. The role of various coagents such as zinc diacrylate (ZDA), trimethylolpropane trimethacrylate (TMPTMA) and triallyl cyanurate (TAC) in the peroxide vulcanization of natural rubber (NR) was studied by Fourier Transform infrared spectroscopy. Crosslink density was measured by equilibrium swelling technique. Crosslinking mechanism of peroxide in natural rubber was interpreted by comparing the spectra of cured and uncured vulcanizates. The predominance of hydrogen abstraction over radical addition was established (at 160°C). Coagent ZDA produces ionic as well as covalent crosslinks in the vulcanizate. Ionic crosslinks have the ability to slip along the hydrocarbon chains and thus resembles polysulphidic crosslinks. Hence, ZDA can be chosen for applications where good mechanical properties are required. Coagent TMPTMA produces covalent crosslinks between polymer chains, and is suitable for high modulus applications. TAC is not a suitable coagent for highly unsaturated rubbers like NR.

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4.1 INTRODUCTION

As new technologies emerge and develop in rubber industry, compounders realised that sulphur cure systems cannot fully achieve physical and chemical properties or meet the critical specifications of the new application demand. A well-known alternative to sulphur vulcanization is peroxide vulcanization. The mechanism of peroxide vulcanization of rubbers is an area of debate for many years and has been studied by a number of researchers [1-17]. Generally two mechanisms, hydrogen abstraction and radical addition are proposed for peroxide vulcanizates. For saturated rubbers the only possible mechanism is hydrogen abstraction and in unsaturated rubbers both hydrogen abstraction and radical addition are possible. The homolytic cleavage of organic peroxide produces highly reactive odd electron fragments called free radicals, which can abstract allylic hydrogen from polymer chain (route I) or undergo addition reaction with the unsaturated double bond of the polymer (route II) resulting in the formation of highly reactive macro free radicals as shown in Figure 4.1.

The polymer macro-radical produced by abstraction/addition further undergo coupling reaction and form C-C crosslink between polymer chains. Predominance of abstraction/addition is decided by a number of factors like vulcanisation temperature, peroxide loading [12, 13] etc. The peroxide cure systems generally results in slow cure rates and low crosslink density. Introduction of coagents overcomes most of the deficiencies associated with peroxide cure systems. Coagents are multi-functional organic molecules and are highly reactive towards free radicals [18]. Depending upon their chemical reactivity, coagents are classified into two types.

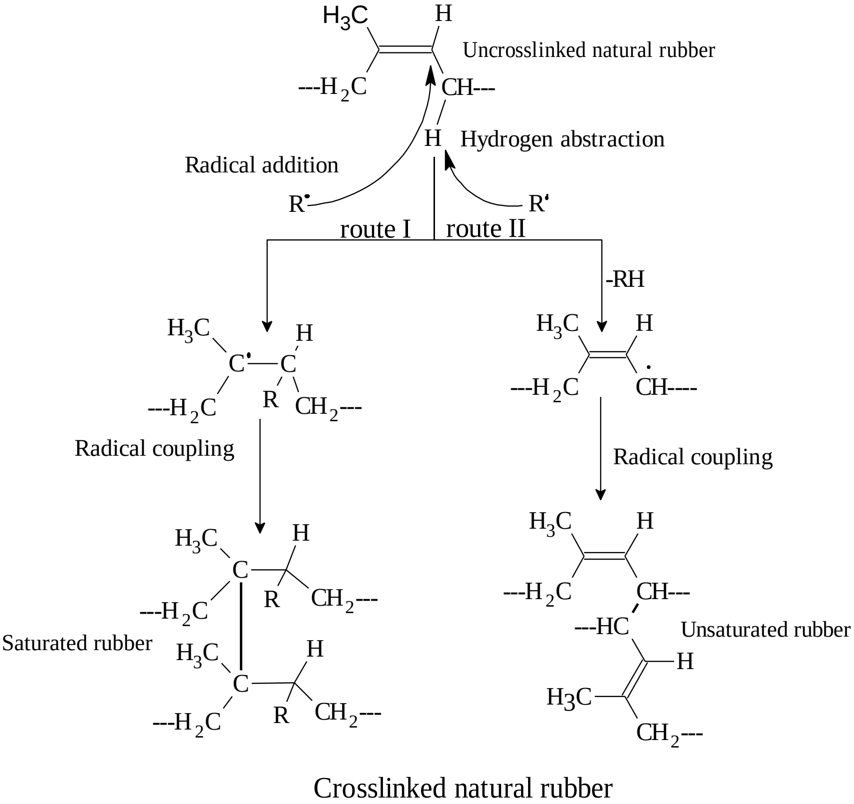


Figure 4.1 Abstraction and addition mechanism of peroxide cured natural rubber

The mechanism of incorporation of coagents and property improvement of several synthetic rubbers like EPDM, EPM, NBR, SBR etc. has been extensively investigated [19-42]. Very little work has been done to study the effect of these coagents on the network structure and properties of peroxide cured natural rubber.

The objective of this study was to understand the role of different coagents in the peroxide vulcanisation of natural rubber. In this study metallic coagent, zinc diacrylate (ZDA, SR 633) methacrylic and allylic coagents such as trimethylolpropane trimethacrylate (TMPTMA, SR 350) and triallyl cyanurate (TAC, SR 507) were selected for the peroxide vulcanization. The reactions were followed by FT IR spectroscopy and crosslink density was measured by equilibrium swelling technique. FT IR spectroscopy was successfully used to analyse and predict the mechanism of peroxide cure in the presence of various coagents [28, 29, 43, 44]. The mechanism of peroxide vulcanization of natural rubber was investigated by comparing the spectra of cured and uncured vulcanizates.

4.2 EXPERIMENTAL

4.2.1 Materials

The detailed specification of materials used is given in section 2.1

4.2.2 Methods

The composition of mixes used was given in Table 4.1. Preparation of the compounds and experimental procedures are presented in sections 2.2.1, 2.5 and 2.6 respectively.

Table 4.1 Composition of mixes

Ingredients	A	B	C	D	E
NR	100	100	100	100	100
DCP[a]	5	5	5	5	5
ZDA[b]	-	5	-	-	-
TMPTMA[c]	-	-	10	-	-
TAC[d]	-	-	-	5	10

a-dicumyl peroxide (40% activity), b- zinc diacrylate, c- trimethylolpropane trimethacrylate, d-triallyl cyanurate.

4.2.3 FT IR analysis of the vulcanizates

The role of coagent ZDA was studied by asymmetric and symmetric stretching of strongly coupled C-O group of carboxylate ion (1536 and 1593 cm^{-1}), C=C in conjugation with C=O group (1647 cm^{-1}) and α, β-unsaturated carboxylate (1276 cm^{-1}) and coagent TMPTMA was followed by terminal $=CH_2$ groups, having absorbance at 2986 cm^{-1} and ester group in conjugation with double bond (1718 cm^{-1}). The behaviour of coagent TAC was studied by the reactions of allyl moieties, vinylic C-H waging vibration (933 cm^{-1}), triazine quadrant stretching (1560 cm^{-1}) , triazine out of plane bending (817 cm^{-1}) and C-O stretch of ether (1139 cm^{-1}).

4.2.4 Controlled network degradation

In order to establish the existence of coagent bridges attempts were made for the selective cleavage of ester linkages in the vulcanizates whilst carbon-carbon bond remains unaffected. For the cleavage of the ester linkages of coagent TMPTMA, the vulcanized samples were immersed in a solution of tetrahydrofuran (THF), ethanol (C_2H_5OH) and 10M sodium hydroxide (NaOH) in the ratio 100:10:1 at room temperature for 72 h [43]. The samples were then washed with THF and vacuum dried (60°C) and FT IR experiments were carried out.

4.2.5 Determination of ionic crosslink density of ZDA

The quantification of relative amount of ionic crosslinks [44] in peroxide-metallic coagent cured networks has been carried out. Equilibrium swelling technique was used to calculate the total crosslink density (ionic and covalent). The sample system was then subjected to swelling in a mixture of chloroacetic acid (5%) and toluene (hydrolyses ionic crosslinks), followed by swelling in fresh toluene for 72h (only covalent crosslinks). The ionic crosslink density can be calculated using following equation.

Total crosslinks = Covalent crosslinks + Ionic crosslinks……….(4.1)

4.3 RESULTS AND DISCUSSION

4.3.1 FT IR spectroscopy

FT IR spectrum of natural rubber is shown in Figure 4.2 and the important peaks resolved are given in Table 4.2. The spectrum was scanned in the frequency range 700-1700 cm^{-1}. The spectra of unvulcanized and vulcanized (peroxide cured) natural rubber vulcanizates are given in Figure 4.3. The important peaks under consideration are 838 (=CH out-of-plane bending), 1025 and 1141 (C-C stretch) and 1654 cm^{-1} (C=C stretch).

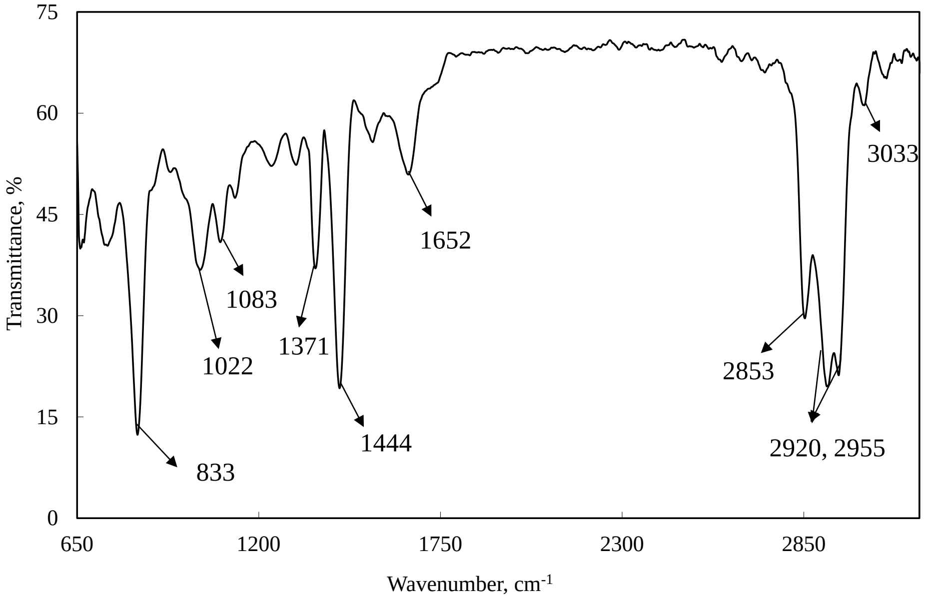


Figure 4.2 FT IR spectrum of pure natural rubber

The abstraction mechanism does not yield a reduction in unsaturation whereas if the addition reaction predominates there will be considerable reduction in the intensity of absorption bands corresponds to the -C=C- stretch/deformations of polyisoprene. Comparison of the FT IR spectra of vulcanized and unvulcanized films showed that the absorption band at 838 cm^{-1} in both the spectra nearly overlapped and the intensity of absorption bands due to C=C stretch (1664 cm^{-1}) and $–CH_3$ rock (1091 cm^{-1}) are also comparable in both cases.

Table 4.2 FT IR spectroscopic data for important peaks in natural rubber

Absorption bands (cm^{-1})	**Assignment**
833	=CH- out-of- plane bending
1023,1141	-C-C- stretching
1084	$-CH_3$ rocking
1371	CH_3 asymmetric deformation
1444	$-CH_2$ deformation
1652	-C=C- Stretching
2853, 2925	$-CH_2$ asymmetric stretching
2955	$-CH_3$ stretching
3033	=C-H stretching

This suggests the predominance of abstraction route over radical addition in the peroxide vulcanization of natural rubber at 160°C. Further there is a considerable increase in the intensity of absorption band due to C-C stretch (1141 and1025 cm^{-1}) in the cured vulcanizate compared to the uncured one, which further confirmed the formation of new C-C bond (crosslinks) during vulcanization. The absorption bands at 1373 (–CH_3 asymmetric deformation) and 1450 cm^{-1} (-CH_2 deformation) almost overlap as shown in Figure 4.3.

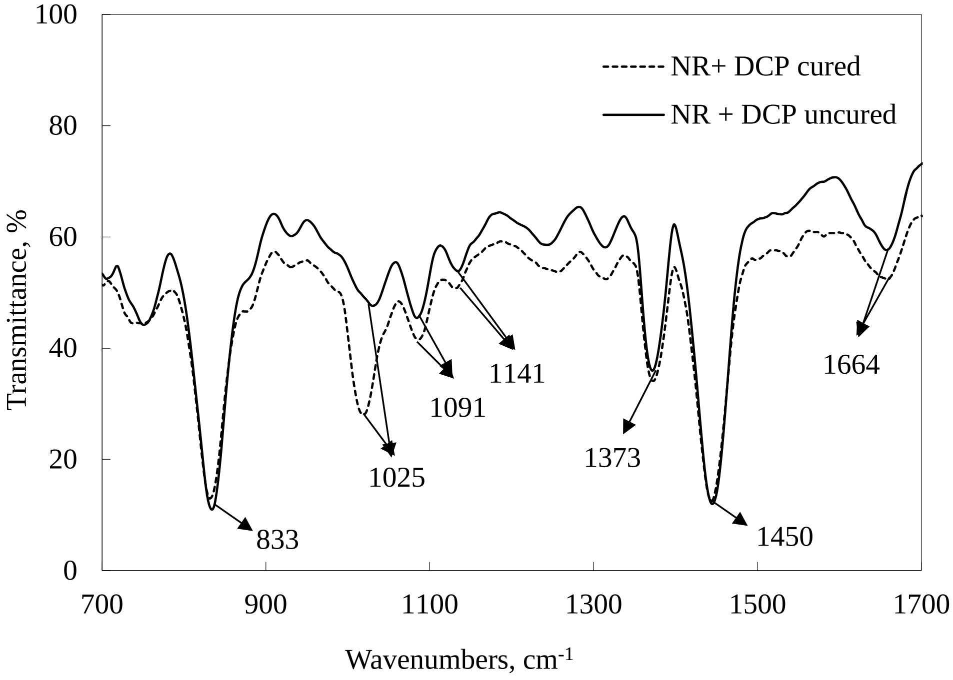


Figure 4.3 FT IR (ATR) spectra of peroxide cured and uncured natural rubber vulcanizates

4.3.2 Role of coagents in peroxide vulcanization of natural rubber

4.3.2.1 Zinc diacrylate (ZDA)

Zinc diacrylate is a metallic coagent (type I) and it produces ionic as well as covalent crosslinks in the vulcanizate. It has two highly reactive acrylic groups and undergoes addition reaction followed by abstraction with the rubber. When ZDA is incorporated, additional bands appear in the spectrum. Comparison of FT IR spectra of DCP cured NR and that with coagent ZDA is shown in Figure 4.4.

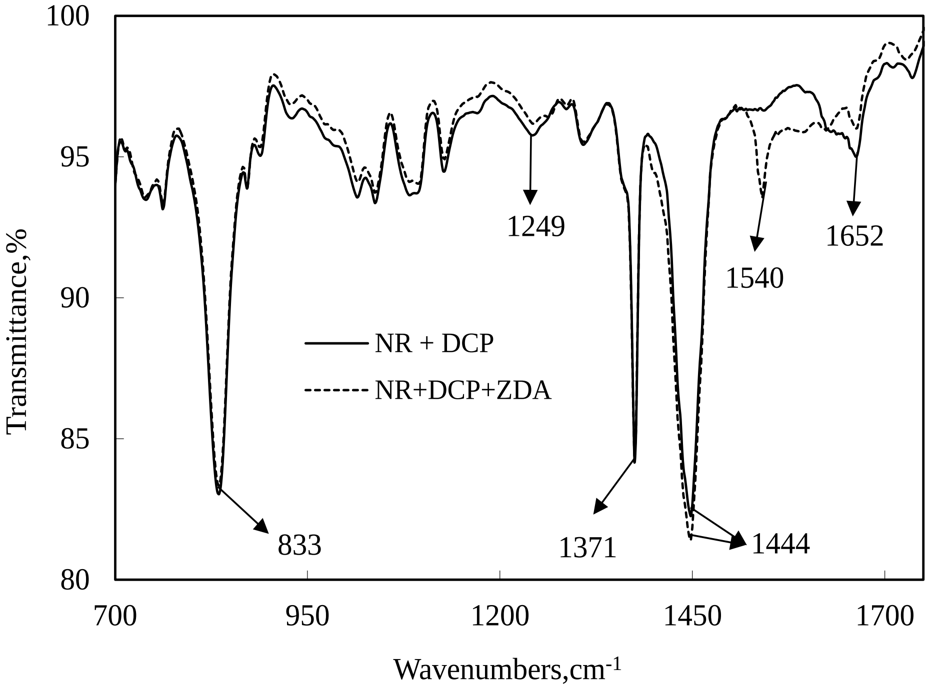
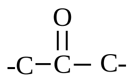


Figure 4.4 FT IR spectra of peroxide vulcanized NR and its vulcanizate with ZDA

The intensity of absorption band due to C=C stretch (1654 cm^{-1}) in the spectrum of cured vulcanizate is reduced when compared with the spectrum of vulcanizate containing coagent ZDA. This confirms the addition of coagent in to the vulcanizate. After peroxide cure, the intensity of band at 1444 cm^{-1} (-CH_2 deformation) is enhanced and new band appears at 1540 cm^{-1} (asymmetric stretching of strongly coupled C-O group of carboxylate anion). FT IR spectral data of coagent ZDA (pure) is given in Table 4.3. Important peaks are compared with the cured vulcanizate containing ZDA. The strong absorption band at 1647 cm^{-1} (C=C group in conjugation with C=O) and at 826, 969 cm^{-1} in the spectrum of ZDA (pure) are absent in the spectrum of vulcanizate with coagent ZDA. All these conforms the grafting of coagent ZDA in to the vulcanizate.

Table 4.3 Significant peaks of coagent ZDA and peroxide vulcanized NR containing coagent ZDA

Absorption bands ofpure ZDA (cm^{-1})	**Peak assignment**	**Peak assignment in NR+DCP+ZDA**
1536 and 1593	asymmetric and symmetric stretching of strongly coupled C-O group of carboxylate anion	only 1536 band is present and is shifted to 1540 cm^{-1} but with lower intensity.
1647	C=C in conjugation with C=O group	absent
826 and 969	out of plane C-H bending vibration from =CH_2	absent
1276	α, β- unsaturated carboxylate  $-C-\overset{\overset{O}{\|}}{C}-C-$	shifted to 1249 cm^{-1} with reduced intensity

4.3.2.2 Trimethylolpropane trimethacrylate (TMPTMA)

The rate of peroxide vulcanization of natural rubber in the presence of TMPTMA at 160°C was calculated from kinetic data [45] (1.67 x 10^{-3} s^{-1}) and was found to be relatively low compared with the high reaction rate of methacrylic groups. This indicates that the reactions of methacrylic group of coagent are of radical addition type. Comparison of FT IR spectra of cured (NR- DCP) vulcanizate and those with coagent TMPTMA (Figure 4.5) showed that, during vulcanization coagent molecules are incorporated into the network.

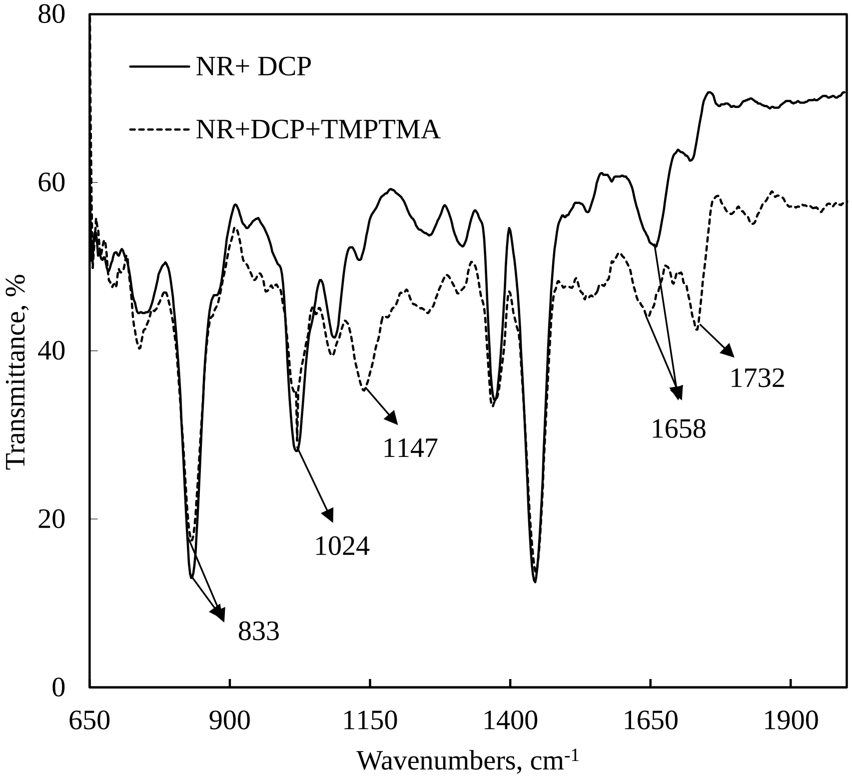


Figure 4.5 FT IR spectra of peroxide vulcanized NR and that of vulcanizate with TMPTMA (10 phr)

The broad and the intense absorption band present in the FT IR spectrum of pure TMPTMA at 1718 cm^{-1} (ester group in conjugation with double bond) is shifted to 1732 cm^{-1}(ester linkage without conjugation) in the spectrum of NR- DCP vulcanizates containing coagent (Table 4.4).

Table 4.4 Significant peaks of coagent TMPTMA and peroxide vulcanized NR containing coagent TMPTMA

Absorption bands of pure TMPTMA (cm^{-1})	**Peak assignment**	**Peak assignment in NR+DCP+TMPTMA**
2968 and 812	Terminal =CH$_2$ group	Absent
1718	Ester group in conjugation with double bond	Shifted to 1732 cm^{-1} (ester linkage without conjugation)
1633	C=C stretching vibration	Absent

During peroxide vulcanization of NR in the presence of coagent, the polymer macro- radical produced by abstraction (Figure 4. 1) is added to the terminal C=C of coagent. This is confirmed by the absence of intense absorption band at 1633cm^{-1} (C=C stretch) of pure TMPTMA and absorption band at 2962 and 812 cm^{-1} (terminal =CH$_2$ group of the coagent) in the spectrum of cured natural rubber containing coagent.

The intensity of the absorption band at 836 cm^{-1} (=CH- out-of- plane bending) was reduced and the band at 1658 cm^{-1} (C=C stretch) was shifted to lower frequency in the spectrum of NR – DCP containing TMPTMA. This may be due to the incorporation of coagent to the C=C bond of polymer. Further it was confirmed that the intensity of absorption peak at 1147 cm^{-1} (C-C stretching) was enhanced in the spectrum of the mix containing the coagent compared with the mix without coagent. Comparison of FT IR spectra of vulcanizates before and after controlled cleavage of ester linkages is shown in Figure 4.6.

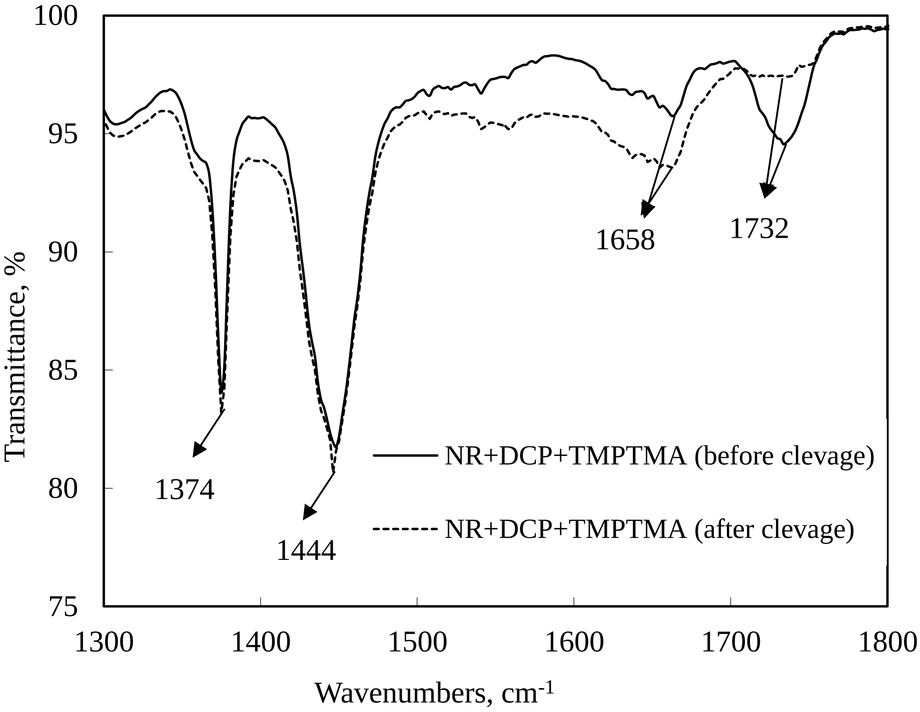


Figure 4.6 FT IR spectrum of vulcanized NR containg TMPTMA before and after ester linkage cleavage

The intensity of absorption band at 1732cm^{-1} (ester linkage without conjugation) is considerably reduced after controlled cleavage of ester linkage. There are slight increase in intensity of absorption band at 1658 cm^{1}(C=C stretch), 1444cm^{-1}(-CH_2 deformation) and 1374cm^{1}(CH_3

asymmetric deformation), which might be due to some rearrangement of molecules after cleavage.

4.3.2.3 Triallyl cyanurate (TAC)

The mechanism of peroxide vulcanization of saturated polymer in the presence of TAC has been studied by a number of researchers [28, 29]andit was concluded that grafting of TAC molecule occurs exclusively *via* intramolecular cyclisation. The cure kinetic data [46] showed that as the concentration of the coagent increased from 5 to 10 phr, the rate of peroxide decomposition decreased from 1.92 x10^{-3} to 1.69 x$10^{-3}s^{-1}$.

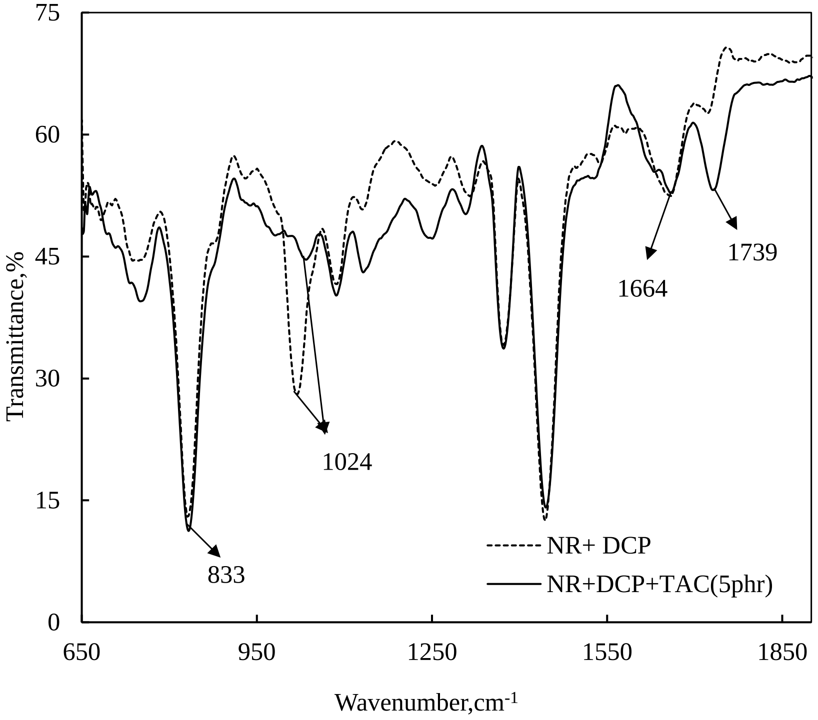


Figure 4.7 FT IR ATR spectrum of peroxide vulcanized NR and peroxide vulcanized NR containing 5 phr TAC

Since the rate is low compared to the high reaction rate of allyl groups, radical addition is expected in both cases. Comparison of FT IR spectrum of DCP cured NR vulcanizate containing 5 phr coagent TAC is shown in Figure 4.7. During vulcanization with TAC the absorption band at 833 and 1664 cm^{-1} (=CH- out-of- plane bending and C=C stretching respectively) almost overlapped and the intensity of absorption band at 1024 cm^{-1} (C-C stretch) is considerably reduced. If the coagent is grafted into the polymer network, there should be an increase in the intensity of absorption band due to C-C stretch.

The free radicals produced by homolytic fission of peroxide may abstract hydrogen from polymer to form polymer macro-radical or at the same time it can facilitate the isomerization of coagent triallyl cyanurate to triallyl isocynurate (Figure 4.8).

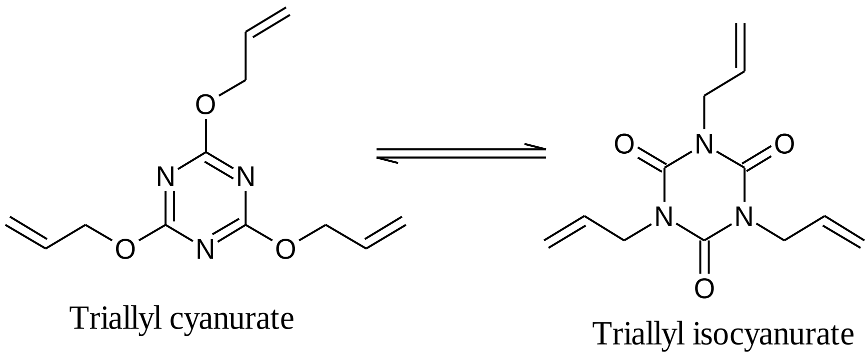


Figure 4.8 Isomerisation of triallyl cyanurate to triallyl isocyanurate

Since most of the radicals are consumed for isomerization, even though C-C bonds are formed by the recombination of polymer radical, the percentage of C-C formed and consequently the intensity was less compared to the vulcanizate without coagent.This was further supported by a peak at 1739 cm^{-1} (C=O group) in the spectrum of vulcanizate containing TAC. Details of FT IR spectra of vulcanizate containing coagent TAC (5 and 10 phr) and pure coagent is given in Table 4.5.

Table 4.5 FT IR spectroscopic data of pure TAC and peroxide vulcanized NR with TAC

Absorption bands of pure TAC (cm^{-1})	**Peak assignment**	**Peak assignment in NR+DCP+TAC (5phr)**	**Peak assignment in NR+DCP+TAC (10phr)**
1560	triazine quadrant stretching	Almost absent	Broad peak narrowed and medium intensity
1139	C-O stretch of ether	Intensity reduced	Intense than peak at 5phr
933	vinylic C-H waging vibration	Almost absent	Intensity reduced
817	triazine out of plane bending	Almost absent	Intensity reduced

The effect of varying concentration of coagent TAC in peroxide vulcanization of natural rubber was studied and the corresponding spectra were shown in Figure 4.9. Cure characteristics and crosslink density measurements showed that as the concentration of TAC increased from 5 to 10 phr, (Table 4.1) crosslink density is decreased considerably (Figure 4.9). Comparison of absorption spectra of coagent (Figure 4.9) showed that, the absorption bands due to triazine ring stretching and bending (1560 and 817 cm^{-1}) are absent in vulcanizate with 5 phr TAC and an less intense bands are observed in sample with 10 phr TAC. Similarly, the absorption band due to ether linkage and terminal vinyl group (1139 and 933 cm^{-1}) are almost completely disappeared in sample containing 5 phr coagent and low intensity band is appeared in the 10phr sample.

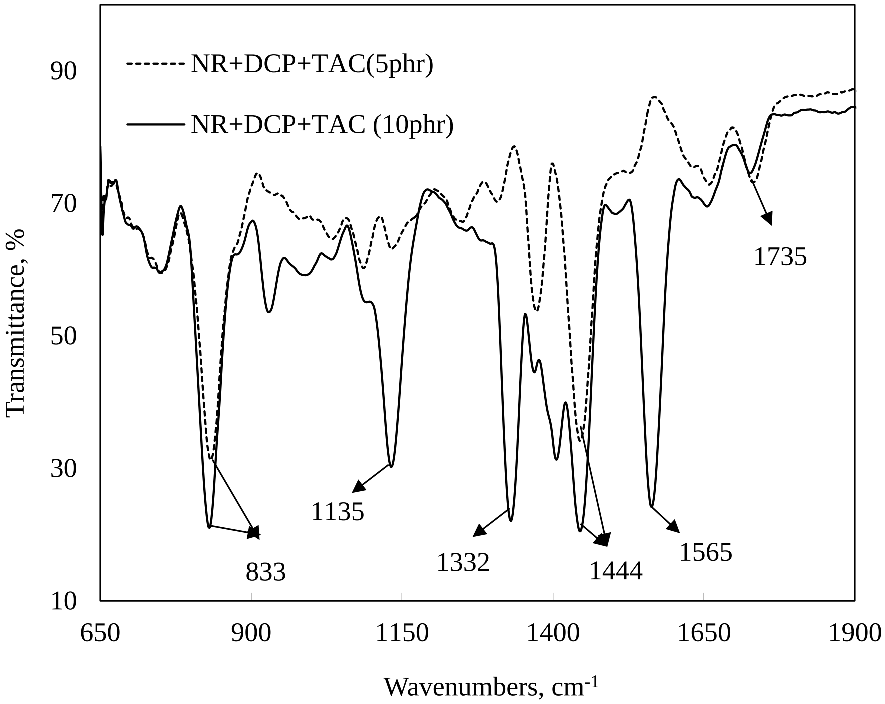


Figure 4.9 FT IR spectra of peroxide vulcanized NR containing 5 and 10phr TAC

When the concentration is low (5 phr) TAC is completely consumed either by cyclisation or isomerization as is evident from spectral data. When the concentration increased, homopolymerization predominates and TAC form a dispersed phase and it is incompatible with natural rubber. At higher concentration, tendency of the coagent to rearrange to isocyanurate is also very small. This is confirmed by the existence of absorption bands at 1565 cm^{-1} (triazine quadrant stretching) and 1135 cm^{-1} (C-O stretch of ether) in the spectrum of vulcanizates containing 10phr cogent (Figure 4.9 and Table 4.5).

4.4 Coagent selection for peroxide vulcanization of natural rubber

Since a wide range of coagents are available the selection of coagents for achieving optimum properties is of paramount importance [47]. The reactivity of coagents also depends on the elastomer [48] and the nature of the crosslinks formed determines the properties of the resulting network. Crosslink density of NR-DCP system with different coagents was measured using equilibrium swelling studies in toluene. Comparison of crosslink density and tensile strength of various coagents with control (gum vulcanizate) is given in Figure 4.10.

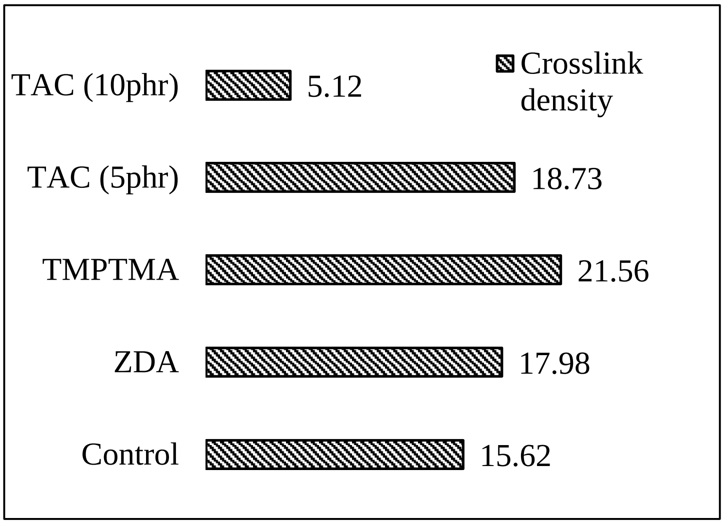


Figure 4.10 Comparison of crosslink density of various coagents with control

The swelling studies showed coagent TMPTMA produced maximum crosslink density. Being highly reactive, when coagent TMPTMA is added to natural rubber, a very fast reaction is expected to occur between methacrylic groups of the coagent and the macro radical of the polymer. The resulting polymer macro radical may undergo addition reaction with the coagent (further confirmed by FT IR studies) and new radicals were produced. This may undergo further reaction using the second and third methacrylic groups of the same coagent molecule which results a coagent bridge or star like network between the polymer chains [49]. At the same time the coagent can undergo homopolymerization and subsequent grafting to polymer chains. Both reactions increase crosslink density of the vulcanizate.

The effect of TAC as a coagent in the peroxide vulcanization of natural rubber is somewhat different. Crosslink density is higher for sample containing 5phr coagent and as the concentration of TAC increased (10 phr) crosslink density decreased. For highly unsaturated rubbers, usually type II coagents provide no increase in crosslink density due to the relative ease of allylic hydrogen abstraction from the polymer chain compared to the vinylic group of coagent. The polymer macro-radical formed by allylic hydrogen abstraction may either added to the coagent generating new radical, combine with another polymer radical to form C-C crosslink or abstract hydrogen from coagent. Some peroxide radicals may also initiate isomerization of TAC to TAIC (Figure 4.8). The former two reactions will increase crosslink density. This might be the reason for increased crosslink density at lower concentration of TAC. The share of ionic crosslinks with coagent ZDA was calculated (equation 4.1) and is found to be 20 per cent. The characteristic of ionic bond have been discussed in literature [50].

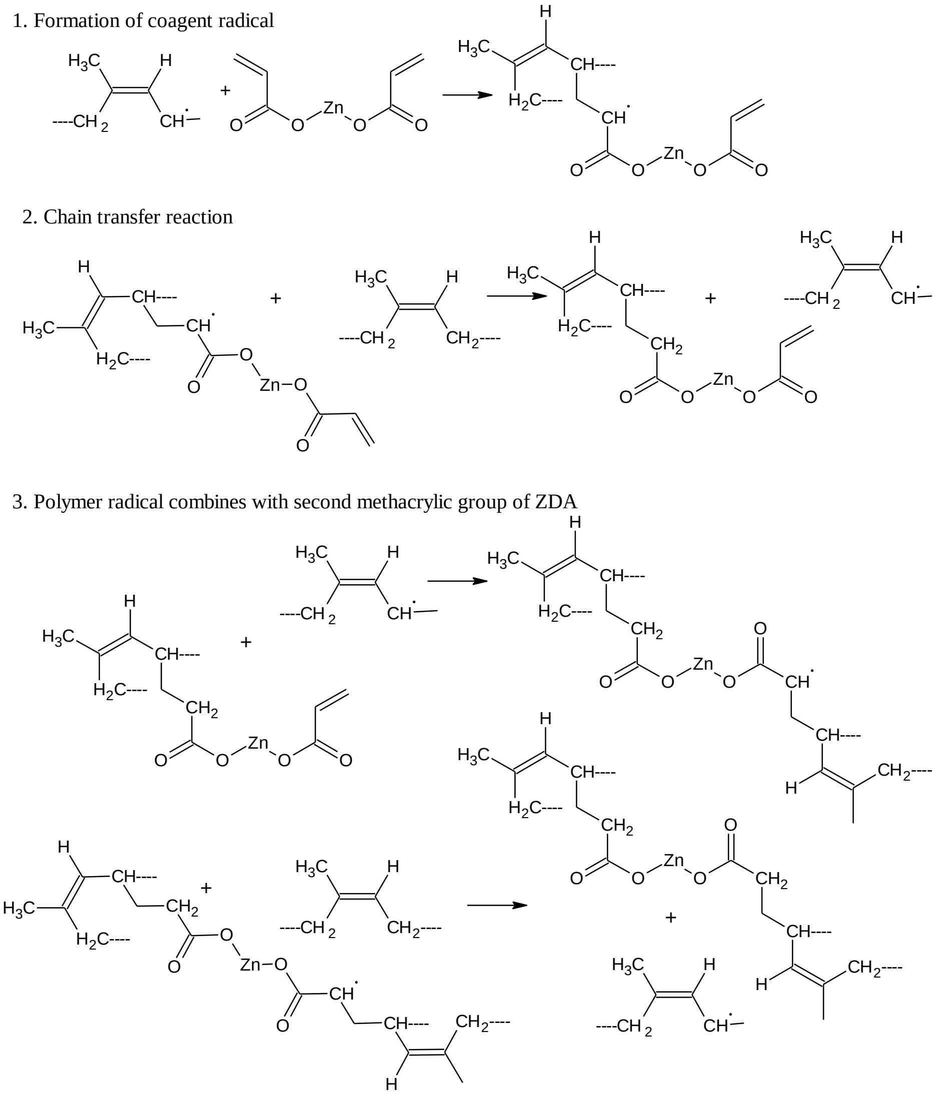


Figure 4.11 Proposed crosslinking mechanism of coagent ZDA with natural rubber

Ionic bonds exhibit both good heat stability and the ability to slip along the hydrocarbon chain. It can reform after break, like poly-sulphidic crosslinks in sulphur vulcanization. Therefore coagent ZDA is expected to provide good dynamic properties in peroxide cured rubber. A suitable crosslinking mechanism is proposed for natural rubber with coagent ZDA and is given in Figure 4.11.

4.5 CONCLUSIONS

FT IR spectroscopy along with swelling studies successfully explained the role of different coagents*viz* metallic coagent ZDA, methacrylic coagent (TMPTMA) and allylic coagent (TAC) in the peroxide vulcanization of natural rubber. ZDA and TMPTMA are being Type I coagents, increased delta torque, favour addition reaction leading to homopolymerization and subsequent grafting to polymer chains. They increased crosslink density of the vulcanizates. Allylic coagent TAC (type II) increased the crosslink density of the vulcanizate at lower concentration. As the concentration of coagent increased from 5 to 10 phr, cyclisation predominated and TAC forms a dispersed phase and it is incompatible with natural rubber resulting in a considerable reduction in crosslink density. ZDA impart ionic and covalent crosslinks in the vulcanizates and is a unique system having the best characteristics of both peroxide and sulphur cure systems.

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CHAPTER 5

EFFECT OF COAGENTS ON THE MECHANICAL PROPERTIES OF PEROXIDE CURED NATURAL RUBBER VULCANIZATES

The effect of different coagents like trimethylolpropane trimethacrylate (TMPTMA), triallyl cyanurate (TAC) zinc diacrylate (ZDA) and n-butyl acrylate (nBA), on the mechanical properties of peroxide cured natural rubber vulcanizate has been studied. Dicumyl peroxide (DCP) was used as the crosslinking agent. Mechanical properties like tensile strength, elongation at break and 100% modulus were measured. ZDA offered ionic bridges which behave like polysulphidic crosslinks and it can be used for applications where good mechanical properties are required. TMPTMA increases the modulus of the vulcanizates and is suitable for high modulus applications. Even though, nBA and TAC improved elongation at break, they have a detrimental effect on other mechanical properties.

5.1 INTRODUCTION

Since the discovery in 20th century [1], peroxide cure has been extensively used for the vulcanization of both saturated (EPM, EVM, CM, Q, FM etc.) and unsaturated (EPDM, SBR, NBR and NR) rubbers. The peroxide cure of natural rubber is an area of research for many years [2-15]. The factors determining the predominance of abstraction/addition has been investigated [13, 16]. However, peroxide cure results in the formation of C-C crosslinks between the polymer chains [17]. The properties of peroxide vulcanizates largely depend on the nature of C-C crosslinks [10, 18, 19]. Since the bond is not flexible as polysulphidic crosslinks, the crosslinked vulcanizates has inferior mechanical properties and poor scorch time in contrast to the inherent advantages. In order to overcome the problems associated with peroxide vulcanization, a wide range of coagents are available [20-24]. There are many benefits in using coagents in peroxide vulcanization, these include vulcanizates with higher resilience, modulus and hardness. Coagent system displays a lower initial viscosity, more rapid torque increase (high delta torque) and crosslink density than peroxide alone. It is possible to produce rubber having very high hardness as sulphur cured, but does not have the sulphur blooming problem [22]. Proper selection of coagents is critical in achieving optimum performance. Coagents can improve the peroxide cure efficiency by suppressing the side reactions like chain scission and disproportionation. This is, according to some authors, the main reason why coagents increase crosslink efficiency [13]. The mechanisms of incorporation of coagents and property improvement of several synthetic rubbers have been extensively investigated [25-31]. Very little work has been done to study the effect of these coagents on the mechanical properties of peroxide cured natural rubber [15, 16].

In this study metallic coagents, zinc diacrylate (ZDA) methacrylic and allylic coagents such as trimethylolpropane trimethacrylate (TMPTMA), triallyl cyanurate (TAC) and n-butyl acrylate (nBA) were selected for the peroxide vulcanization of natural rubber. The effect of these coagents on the mechanical properties of peroxide cured natural rubber vulcanizate was investigated. Mechanical properties like tensile strength, elongation at break, modulus (100 per cent elongation) were measured.

5.2 EXPERIMENTAL

5.2.1 Materials

Detailed material description is given in section 2.1 (Chapter 2).

5.2.2 Methods

The formulation used is given in Table 5.1. Preparation of the compounds and experimental procedures are presented in sections 2.2.1 and 2.5 respectively.

Table 5.1 Composition of mixes (phr)

Ingredients	A	B	C	D	E	F	G	H	I	J	K	L	M
[a]NR	100	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5
HAF black	50	50	50	50	5	50	50	50	50	50	50	50	50
Paraffinic oil	4	4	4	4	4	4	4	4	4	4	4	4	4
[b]DCP	5	5	5	5	5	5	5	5	5	5	5	5	5
[c]TMPTMA	-	5	10	15	-	-	-	-	-	-	-	-	-
[d]TAC	-	-	-	-	2	5	10	-	-	-	-	-	-
[e]ZDA	-	-	-	-	-	-	-	5	7	10	-	-	-
[f]nBA	-	-	-	-	-	-	-	-	-	-	2	5	7

a: natural rubber, b:dicumyl peroxide (40%), c: trimethylolpropane trimethacrylate, d: triallyl cyanurate, e: zinc diacrylate, f: n-butyl acrylate

5.3 RESULTS AND DISCUSSION

5.3.1 Peroxide cure of NR in the presence of coagents

Peroxide cure usually produces vulcanizates with good heat-ageing stability and low compression set due to the thermal stability of C-C covalent crosslinks. Synergistic use of multifunctional coagents can improve these properties by increasing the crosslink density of the vulcanizates and by altering the crosslink composition. The critical factor associated with peroxide cure is the selection of coagents for achieving optimum properties, since a wide range of coagents is available. The reactivity of coagents also depends on the type of elastomer and the nature of the crosslinks formed determines the properties of the resulting network. Further, the final physical properties of the vulcanizates are dependent to a large extent on the number of effective crosslinks. Increasing the crosslink density increases modulus and hardness, while decreasing elongation and permanent set of vulcanizates.

5.3.2 Peroxide cure of NR in the presence of TMPTMA

Trimethylolpropane trimethacrylate (TMPTMA) is a commonly used coagent belonging to methacrylate type. Its effect on peroxide cured NR was studied by varying concentration of coagent. The rheographs recorded with different coagent concentrations and variation of delta torque with time at 160°C is given in Figures 5.1 (a) and 5.1(b) respectively.

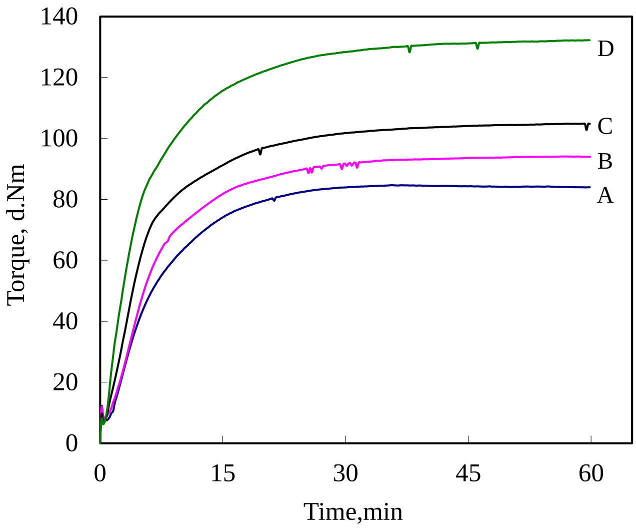

Figure 5.1(a) Variation of torque with time at 160ºC

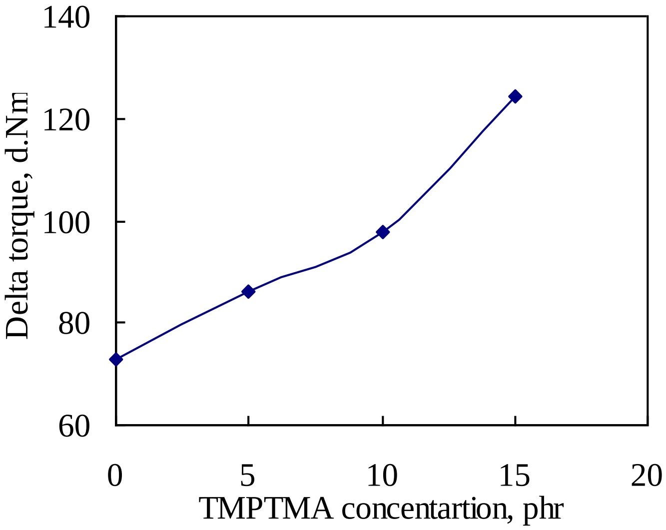

Figure 5.1(b) Variation of delta torque with coagent concentration at 160ºC

It can be seen that as the concentration of coagent increases, torque increases gradually. Since the coagents are multifunctional organic molecules, which contain highly reactive side groups, they can undergo very fast reaction with polymer macro-radicals and can form additional crosslinks or 'coagent bridges' between polymer chains. At the same time the coagent can undergo homopolymerization, cyclisation etc. All these reactions increase the crosslink density of the vulcanizates.

This is further supported by the increase in delta torque with coagent concentration. The mechanical properties of peroxide cured vulcanizates containing TMPTMA are shown in Figures 5.2(a) to5.2(c).When TMPTMA is used as a coagent, the tensile strength and elongation were found to decrease and modulus (100 % elongation) was found to increase with coagent concentration. The mechanical properties, elongation at break and modulus are directly related to the crosslink density of the vulcanizates.

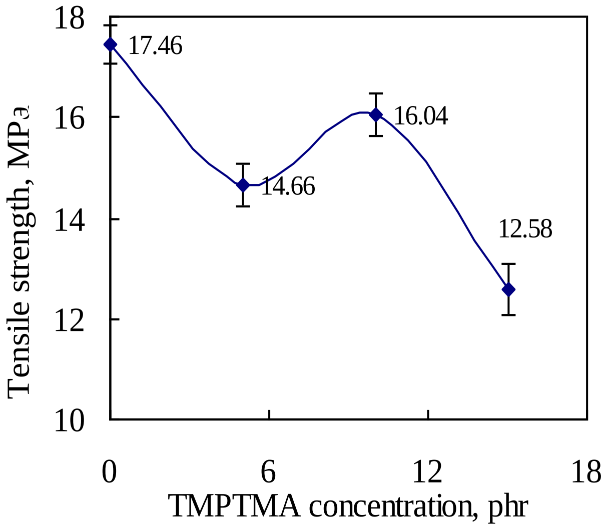

Figure 5.2(a) Variation of tensile strength with coagent concentration

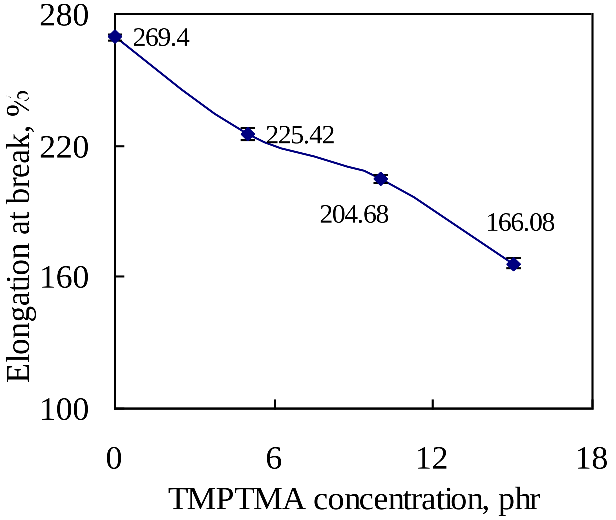

Figure 5.2(b) Variation of elongation at break with coagent concentration

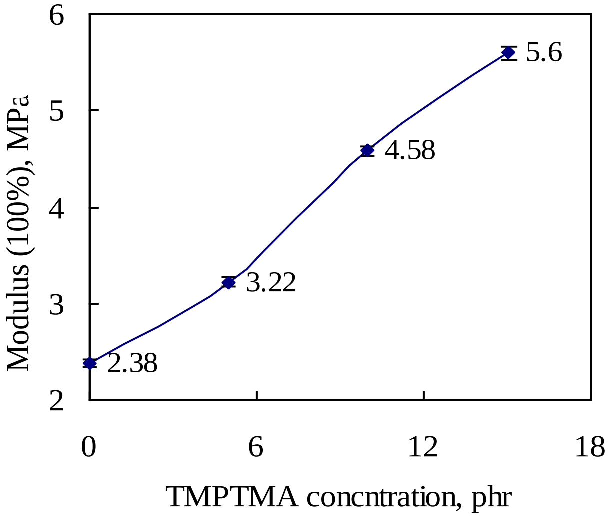

Figure 5.2(c) Variation of modulus (100%) with coagent concentration

Therefore, the decrease in elongation and increase in modulus with increase in coagent concentration was attributed to an increase in crosslink density of the vulcanizates. The maximum tensile strength was observed with 10phr coagent concentration.

5.3.3 Peroxide cure of NR in the presence of TAC

Triallyl cyanurate (TAC) is an allylic coagent (type II) which is expected to increase the state of cure at the expense of scorch safety. The variation of torque with time and delta torque with coagent loading are shown in Figures 5.3 (a) and 5.3 (b) respectively.

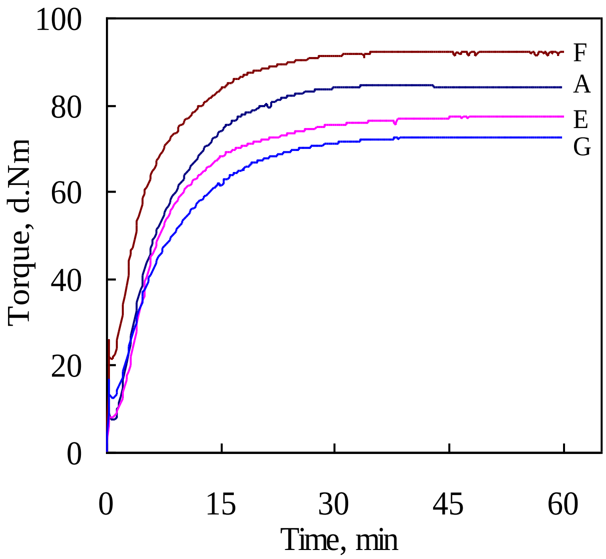

Figure 5.3(a) Variation of torque with time of coagent TAC at 160°C

The coagent triallyl cyanurate (TAC) exhibit an anomalous behaviour in natural rubber. TAC was found to be very effective as coagents in most of the synthetic rubbers including EPDM and its mechanism of action has extensively been investigated [21]. At very low (2 phr) and very high concentrations (10 phr), both the torque and delta torque values were found to be lower than that of control and a comparatively high torque and crosslink density values are obtained with 5 phr TAC. At lower concentration there may not be sufficient coagent to react to give an increase in crosslink density. At intermediate concentration (5phr) TAC is completely consumed either by cyclisation or isomerization.

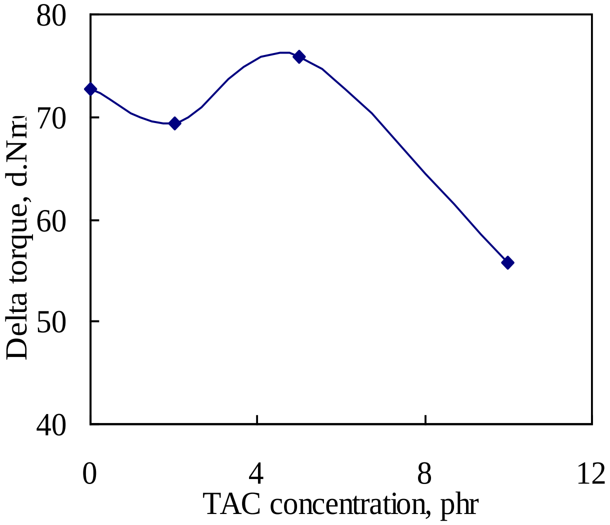

Figure 5.3(b) Variation of delta torque with coagent concentration at 160°C

When the concentration increased, homopolymerization may predominates and TAC form a dispersed phase and it is incompatible with natural rubber [16]. The mechanical properties of peroxide cured vulcanizates containing coagent TAC are shown in Figures 5.4 (a) to 5.4 (c). It can be seen that addition of coagent (TAC) does not improve the tensile strength of natural rubber vulcanizates. The maximum tensile strength is observed at 5phr coagent.

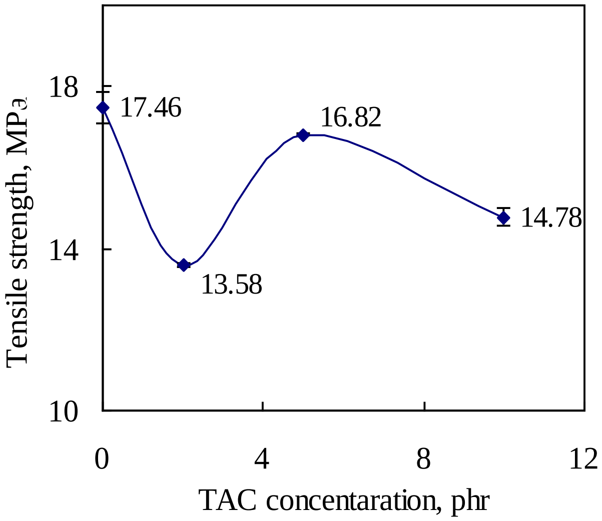

Figure 5.4(a) Variation of tensile strength with coagent concentration

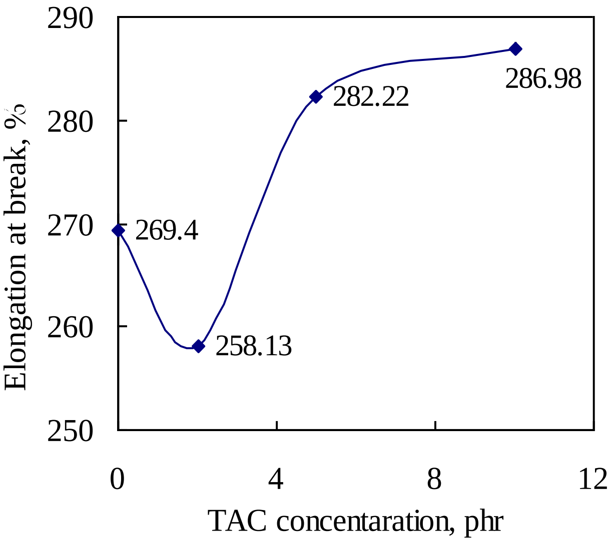

Figure 5.4(b) Variation of elongation at break with coagent concentration

The elongation at break was increased at higher coagent concentration (5 and 10phr) than the control compound. Similarly, the modulus at 100 per cent elongation was decreased by the addition coagent. Further, as the concentration of coagent increased, modulus decreased regularly.

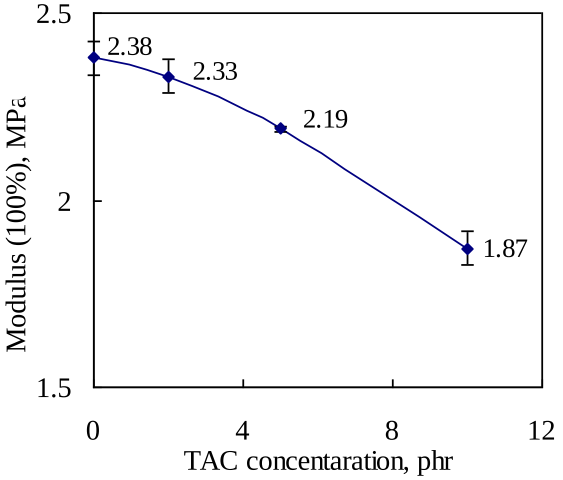

Figure 5.4(c) Variation of modulus (100%) with coagent concentration

Therefore, for highly unsaturated rubbers, usually type II coagents provide no increase in crosslink density due to the relative ease of allylic hydrogen abstraction from the polymer chain compared to the vinylic group of coagent [10]. This is responsible for decreased elongation at break and modulus of the vulcanizates.

5.3.4 Peroxide cure of NR in the presence of ZDA

Zinc diacrylate (ZDA) is a metallic coagent which produces ionic as well as covalent crosslinks between polymer chains. The variation of torque with time and delta torque with coagent loading is shown in Figures 5.5(a) and 5.5(b) respectively. As observed in Figure 5.5 (a), the concentration of ZDA has a big influence on the final torque level achieved. As the concentration of ZDA increases the torque and delta torque increases regularly due to an increase in crosslink density of the vulcanizates. The mechanical properties of peroxide cured vulcanizates containing coagent ZDA are shown in Figures 5.6(a) to 5.6(c).

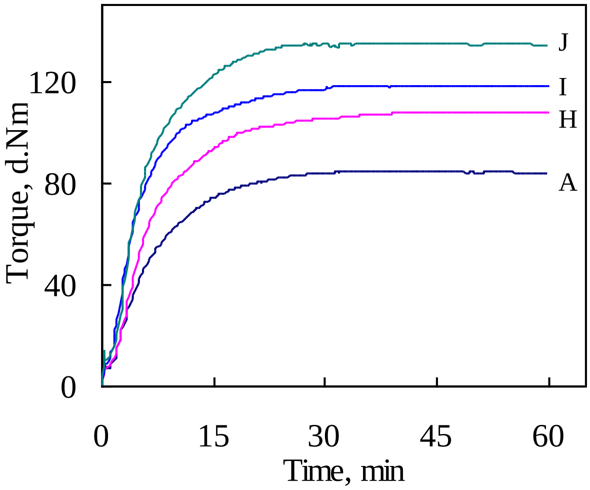

Figure 5.5 (a) Variation of torque with time of coagent ZDA at 160°C

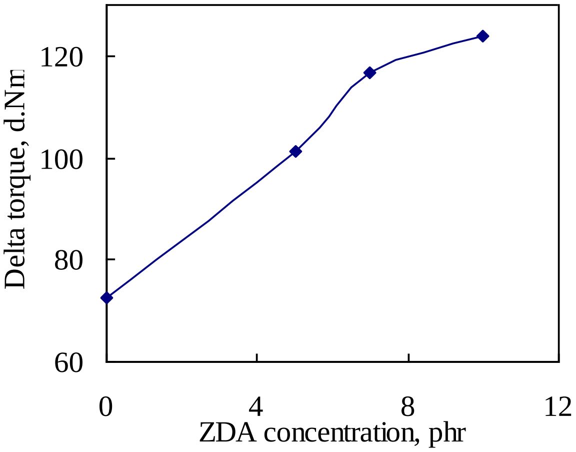

Figure 5.5(b) Variation of delta torque with time of coagent ZDA at 160°C

Peroxide vulcanization generally results in the formation of C-C crosslink between polymer chains. Since the C-C crosslink is quite rigid and stable, the peroxide cured vulcanizates generally have lower tensile strength than sulphur cured vulcanizates.

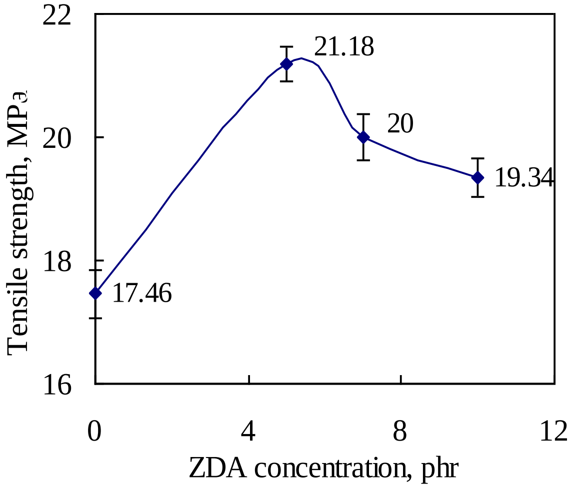

Figure 5.6(a) Variation of tensile strength with coagent concentration

Thus, from Figure 5.6 (a),it can be seen that the tensile strength of vulcanizates containing coagent ZDA is higher than that of control. The maximum tensile strength and elongation at break are observed with 5 phr ZDA loading. The 100% modulus increases continuously with coagent concentration as expected.The good heat stability of this covalent bond also explains the superior ageing characteristics of peroxide cured systems.In contrast, polysulfide crosslinks formed in sulphur cure are thermally weak but are mobile under stress and can slip along the hydrocarbon chain[24].

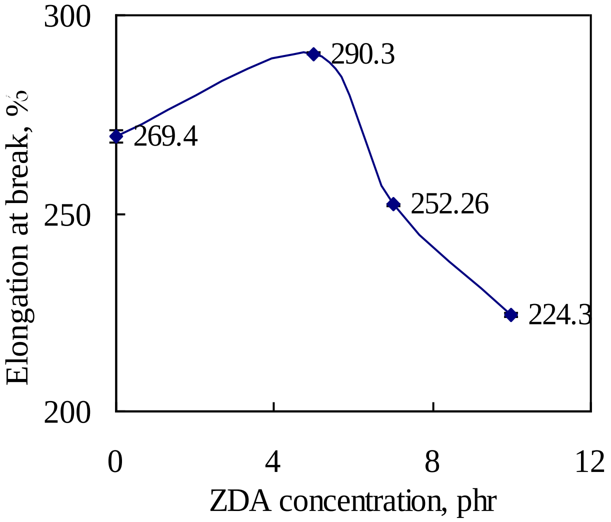

Figure 5.6 (b) Variation of elongation at break with coagent concentration

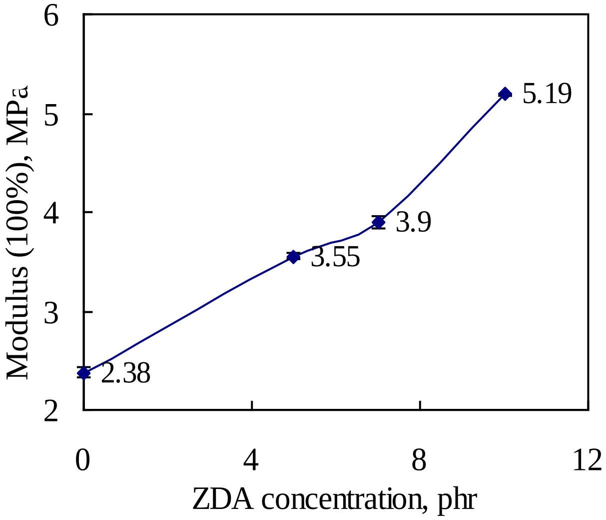

Figure 5.6(c) Variation of 100% modulus with coagent concentration

This mobility has been used to explain the superior tensile and tear strength in sulphur cured vulcanizates. Coagents are added to peroxide cure formulations to improve the crosslink density and hence vulcanizate properties (Figure 5.7).

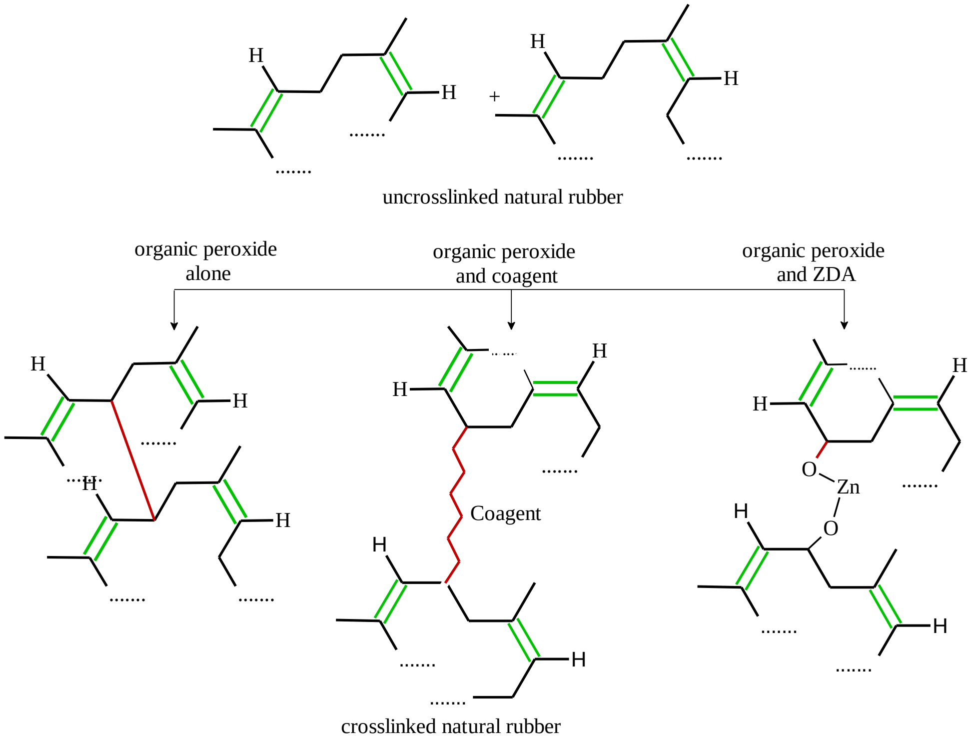

Figure 5.7 Crosslink networks of peroxide and coagents

The ionic crosslinks of coagent ZDA can exhibit both thermal stability and the ability to slip along the hydrocarbon chain and reform. Thus, this unique system couples the best characteristics of both peroxide and sulphur crosslink systems, giving high tensile and tear strength and excellent thermal properties.

5.3.5 Peroxide cure of NR in the presence of nBA

n-butyl acrylate (nBA) is widely used as a sensitizer in radiation vulcanization of natural rubber latex. Here, an attempt was made to study its role as a coagent in peroxide vulcanization of natural rubber. The variation of torque with time and delta torque with coagent loading is shown in Figures 5.8(a) and 5.8(b) respectively.

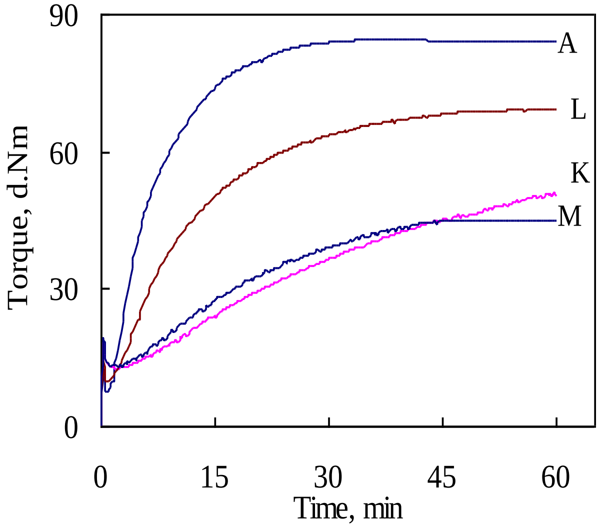

Figure 5.8(a) Variation of torque with time at 160°C

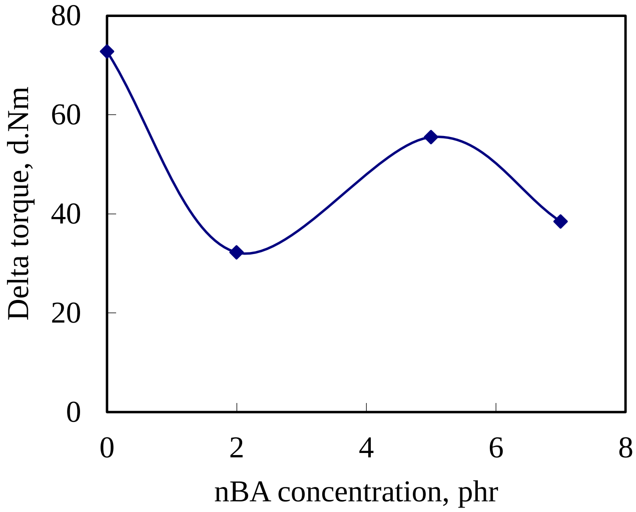

Figure 5.8(b) Variation of torque with time of coagent at 160°C

The rheometric curves of vulcanizates containg coagent nBA are lower than that of control. Similar to TAC, torque and delta torque values are lower at low (2 phr) and high (7phr) concentrations of nBA. At lower concentration nBA follows marching cure behaviour and there may not be sufficient coagent to give sufficient crosslinks. At higher levels it may undergo cyclisation or homopolymerization. The mechanical properties of peroxide cured vulcanizates containing nBAare shown in Figures 5.9 (a) to 5.9 (c).

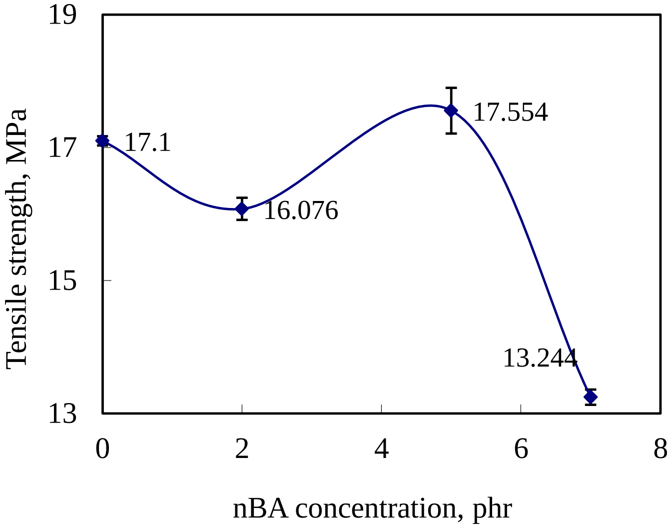

Figure 5.9 (a) Variation of tensile strength with coagentconcentration

The tensile strength of vulcanizates containing nBA initially decreases then reaches a maximum which is slightly higher than the control and then decreases. The maximum tensile strength is observed at 5phr. The elongation at break of vulcanizates containing nBA exhibits an anomalous behaviour as shown in Figure 5.9(b).As the tensile strength, the elongation at break increases, first reaches a maximum at 5 phr and then decreases.

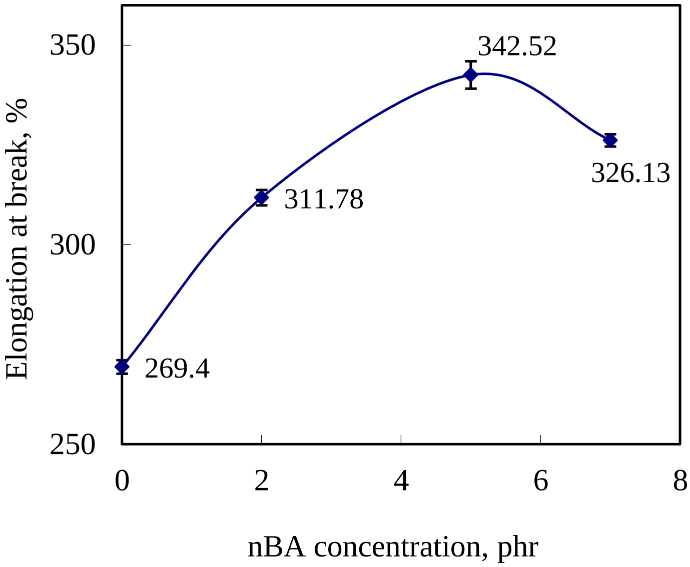

Figure 5.9 (b) Variation of elongation at break with coagent concentrations

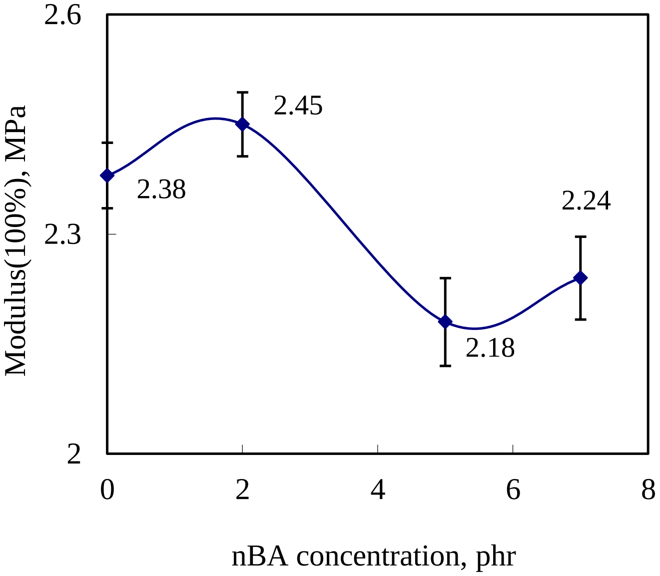

Figure 5.9 (c) Variation of modulus (100%) with coagent concentration

nBA provides vulcanizates with highest elongation at break among other coagents and control. However, 100% modulus showed a decrease with nBA concentration.

5.4 Comparison between different coagents

In this study, four different commercially available coagents in the peroxide vulcanization of natural rubber have been evaluated. Three of them (TMPTMA, TAC and ZDA) have already been used as effective coagents in various types of rubbers in industry and nBA is used as an initiator in radiation vulcanization of latex. Except the system containg TAC as coagent, in all cases the rheometric torque as well as the final mechanical properties of the vulcanizates has been significantly improved. For each coagent, concentration plays an important role. The mechanical properties of vulcanizates with various coagents are shown inFigures 5.10(a) to 5.10(c).When different coagents are compared on the basis of performance, it can be seen that the coagent ZDA and TMPTMA gives an optimum balance of properties. Coagent ZDA gives highest tensile strength good elongation at break and modulus. However, highest modulus was observed for TMPTMA. For a highly unsaturated rubber like natural rubber, TAC is not a suitable coagent as it deteriorates most of the performance properties of the vulcanizates. A disadvantage of coagent nBA is that it produces vulcanizates with an unacceptable odour.

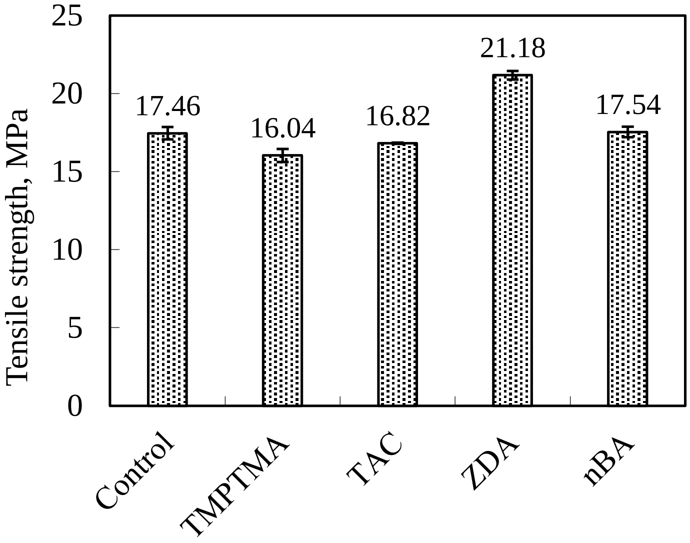

Figure 5.10 (a) Variation of tensile strength with coagents

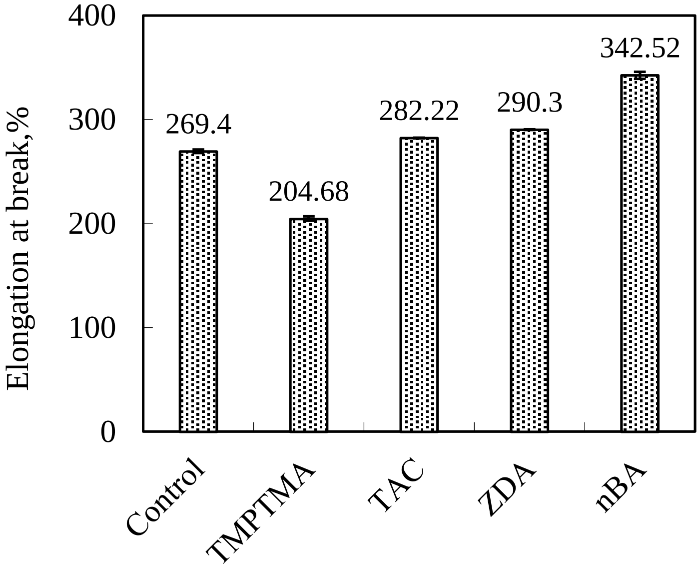

Figure 5.10 (b) Variation of elongation at break with coagents (loading corresponding to optimum tensile strength)

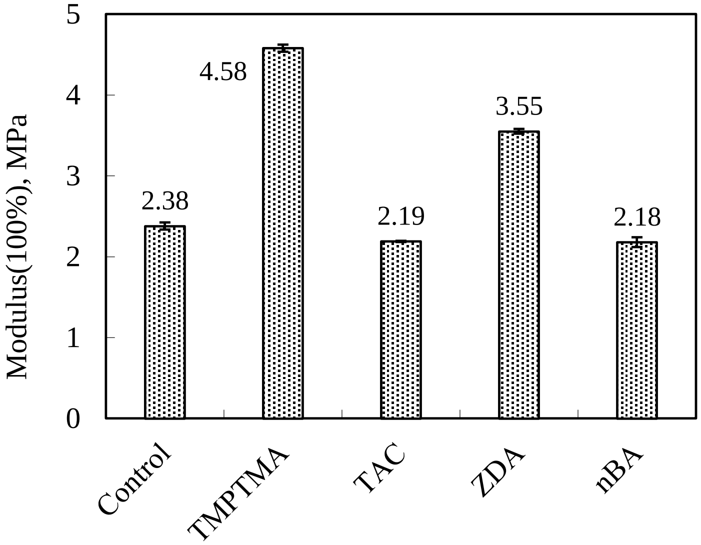

Figure 5.10 (c) Variation of modulus (100%) with coagents (loading corresponding to optimum tensile strength)

5.5 CONCLUSIONS

Comparison of mechanical properties of peroxide cured vulcanizates with those of coagents showed that all coagents enhanced the crosslink density of the vulcanizates. Coagent ZDA is capable of introducing both ionic and covalent crosslinks in the vulcanizate. The ionic crosslinks behave like polysulphidic crosslinks which is responsible for improved mechanical properties but it provides poor compression set. Coagent TMPTMA is suitable for applications where high modulus and ageing resistance are required. nBA enhances the elongation at break values of vulcanizates with an unpleasant odour. In a highly unsaturated rubber like NR, TAC undergoes predominantly cyclisation and forms coagent domains in the vulcanizates which is unfavourable as far as mechanical properties are concerned.

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CHAPTER 6

RESPONSE SURFACE METHODOLOGY: A TOOL FOR ASSESSING THE ROLE OF COMPOUNDING INGREDIENTS IN PEROXIDE VULCANIZATION OF NATURAL RUBBER

Response surface methodology was used for assessing the role of various compounding ingredients like zinc oxide, antioxidant, coagent, oil and filler in peroxide vulcanization of natural rubber. A Face Centred Central Composite Design (FCCD) with four factors at three different levels was used to obtain the relationship between vulcanizate properties and the level of ingredients. The four factors selected were filler/oil ratio and the amount of zinc oxide, antioxidant and coagent. The filler/oil ratio was kept at constant throughout the experiment. The vulcanizates were evaluated for their mechanical properties like tensile strength, elongation, modulus (M100), tear strength, hardness, compression set (70 and 100^{o}C) and crosslink density. Regression equations were generated to model the propertiesof interest and response surfaces and contour diagrams were plotted.

The contents of this chapter has been published in Rubber Chem. Technol., 89(2), 211-226, 2016

6.1 INTRODUCTION

Manufacturing of rubber products requires the use of many additives. Therefore, mixing the additives is a very important step in the processing of rubber. There has been extensive research to understand the relationships between the contents of formulation and the properties of the final product [1]. Since the discovery of vulcanization in the nineteenth century, rubber has been a major industrial product. From its inception, the use of vulcanizing agents, reinforcing fillers and other additives has been a major feature of the rubber industry. The effect of compounding ingredients on peroxide vulcanization has been reviewed [2-5].Metallic oxides like zinc oxide (ZnO) and stearic acid accelerate sulphur vulcanization. The mechanism of these additives in peroxide vulcanization is not yet known completely.

Fillers are usually added to reduce the cost and improve the properties of rubber products. Presence of acidic fillers in the peroxide formulation reduces the overall efficiency of peroxides by the ionic cleavage of peroxides [2]. All oils [6], plasticizers and antioxidants reduce the efficiency of peroxides because some of the radicals generated are transferred to the oil and do not lead to crosslinking [7, 8]. The degree to which these materials reduce cure efficiency is dependent on the level of addition and type of oil or plasticizer used. There are many explanations for the deteriorating effect of mineral oils on peroxide cure efficiency [9, 10]. However, the relative importance of the various effects is not yet known. For the development of cost- effective products, it is essential to incorporate considerable amount of filler and oil, in such circumstances free radical loss can be compensated by increasing the level of peroxide content in the formulation. Since the driving force behind peroxide vulcanization is free radicals, the use of antioxidants is a critical issue. Antioxidant selection needs to be made by considering the antioxidant activity and interference with peroxide crosslinking. It has been reported that the most effective antioxidant are also the most potent inhibitors of peroxide curing [3, 11]. Role of various coagents in the peroxide vulcanization of natural rubber has been reported [12].However, proper selection of coagents and its concentration is critical in achieving optimum performance.

In a conventional experimentation technique, the experimental procedure was to hold all but one variable as constant while methodologically changing one variable at a time. In the case of rubber vulcanizates, the properties are influenced by a number of parameters. In such cases, the one factor at-a-time approach is not only time consuming, but also does not give any information on interaction effects of variables on the vulcanizate properties. Design of experiment (DOE) is a statistical technique, which increases the productivity of the experiments by minimizing the number of experiments involving multiple parameters and maximizing the accuracy of results [13]. Now-a- days, this technique has been widely used in polymer industry for the optimization of processing parameters, [14-22]polymer formulations [23-26]and to model mechanical properties [27-31]. Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques used in DOE. When the combined effect of various parameters is required, RSM is a good choice for modeling, analyzing and optimizing responses [32, 33]. In RSM, a second order polynomial equation that contains the significant factors affecting the responses and interaction between the parameters is obtained for each property. This method involves identification of the objective functions, selection of the influencing factors and determination of the main and interaction effects of the factors on the responses. RSM also provides surface and contour plots that aid in visualizing the interactions [13].

The objective of the present study was to investigate the effect of various compounding ingredients on the mechanical properties of peroxide cured natural rubber vulcanizates using response surface methodology. The use of many of theadditives in peroxide vulcanization has been an area of debate for many years. A Face Centered Central Composite design (FCCD) with four factors (zinc oxide content, coagent content, filler/ oil ratio and antioxidant content) with three levels was used for the analysis. The effect of these factors on the properties of the vulcanizates can be predicted by generating mathematical models. Surface and contour diagrams were plotted to optimize the properties.

6.2 EXPERIMENTAL

6.2.1 Materials

Detailed material description is given in section 2.1 (Chapter 2).

6.2.2 Methods

The formulation used for the study included natural rubber, zinc oxide (variable), stearic acid (1 phr), HAF black (variable), paraffinic oil (variable), antioxidant TMQ (varied), dicumyl peroxide (5 phr) and coagent ZDA (variable). The independent factors selected along with their low, medium and high levels are given in Table.6.1. Preparation of the compounds and experimental procedures are presented in sections 2.2.1 and 2.5 respectively.

Table 6.1 Factors in Face Centred Central Composite design (FCCD) for peroxide vulcanization

Factor, phr	Low (-1)	Medium (0)	High (+1)
ZnO	2	5	8
Antioxidant	0	1	2
Coagent	0	5	10
Filler*	20	40	60
Oil*	4	8	12

*Filler to oil ratio is selected as 5:1

6.2.3 Selection of design

Since there are four variables, a Face Centred Central Composite Design (FCCD) was chosen considering its efficiency in the number of required runs [34]. An FCCD design consists of axial points placed on the face centres of the cube and each factor has three levels. It consists of all combinations of the factors at three levels, seven centre points and eight points at the face of the cube portion of the design as shown in Figure 6.1[35].

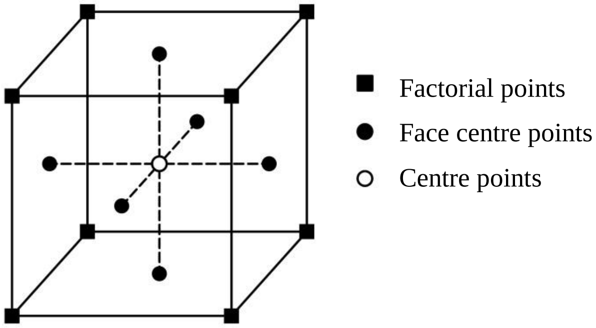

Figure 6.1 Geometry of FCCD for three variables

The FCCD design permits the response to be modeled by a second order polynomial equation which allows estimation of the main, quadratic and interactive effects of the factors on the properties under study [34].The number of experiments required in FCCD design is given by 2^k+2k+n, where k is the factors and n is the number of centre points [34]. In this study there are 31 experiments (k=4, n=7) with zinc oxide (A), antioxidant (B), coagent (C) and filler/oil ratio (D) as the independent variables. Multiple centre points were used in order to have substantial degrees of freedom for estimating pure error. The analysis was done using normalized centred representations, called “coded values” were adopted for the factor levels; -1, 0 and +1 corresponding to minimum, central point and maximum levels of the factors respectively. The reason for coded values is to ensure orthogonality, which is a desired statistical property of any DOE.

6.3 RESULTS AND DISCUSSION

Here an attempt was made to study the effect of various compounding ingredients *viz,* ZnO, antioxidant (AO), coagent, filler and oil (Filler: oil = 5:1) in natural rubber vulcanizates cured with organic peroxide. The experiments were performed in the run order to minimize noises in the measured responses. The vulcanizates were prepared as per the FCCD design and were evaluated for mechanical properties *viz.* tensile strength (TS), elongation at break (EB), modulus (M100), tear strength (TR), hardness, compression set (70 and 100^{o}C) and crosslink density (υ). The cure parameters that are drawn from the rheographs are given in Table 6.2 and results are shown in Table 6.3.

Table 6.2 Rheometric properties of the vulcanizates at 160^{o}C

Mix	M_H, d.Nm	M_L, d.Nm	M_H-M_L, d.Nm	t_{90}, min	t_{s2},min
1	100.02	6.16	93.86	16.48	1.01
2	75.87	12.82	63.05	11.56	1.30
3	75.87	15.35	60.52	12.36	1.94
4	92.76	10.28	82.48	14.25	1.40
5	59.59	1.37	58.22	15.87	0.53
6	91.98	8.72	83.26	17.57	1.07
7	64.47	11.75	52.72	12.83	1.46
8	62.07	9.74	52.33	14.02	1.23
9	82.61	4.61	78.00	20.31	1.34
10	115.87	5.87	110.00	16.21	1.15
11	96.32	5.82	90.50	15.27	1.25
12	82.24	7.44	74.80	19.22	1.89
13	113.79	5.19	108.60	15.84	0.86
14	67.63	7.28	60.35	22.59	1.86
15	94.94	6.06	88.88	18.47	1.06
16	96.33	8.40	87.93	22.29	2.11
17	95.01	11.47	83.54	14.59	1.84
18	69.18	14.28	54.90	18.25	1.58
19	88.46	12.09	76.37	16.39	1.42
20	65.61	17.42	48.19	18.13	2.23
21	90.96	12.80	78.16	16.37	1.66
22	116.63	14.75	101.88	14.70	1.51
23	87.17	5.21	81.96	15.28	1.22
24	85.53	9.75	75.78	15.39	1.52
25	85.78	7.71	78.07	14.50	1.38
26	115.75	6.87	108.88	17.45	1.09
27	58.14	9.06	49.08	18.86	1.70
28	94.17	12.55	81.62	11.61	1.79
29	86.96	7.38	79.58	15.64	1.23
30	108.67	10.54	98.13	13.60	1.46
31	85.74	10.22	75.52	13.42	1.32

Table 6.3 Four factor FCCD with mechanical properties of peroxide cured NR

order	ZnO, phr	AO, phr	Coagent, phr	Filler, phr	TS, MPa	EB, %	M100, MPa	TR, kN/mm	Hardness, Shore A	Set, 70ºC, %	Set, 100ºC, %	υ x10^{-5} mol/cm^3
1	-1	+1	+1	-1	12.62	292.3	2.09	29.39	56	19.6	36.82	25.1033
2	-1	-1	-1	+1	17.61	353.1	1.84	27.84	54	13.34	49.21	6.1095
3	+1	-1	-1	+1	17.8	327.9	2.26	22.27	54.5	13.83	43.2	7.3196
4	-1	0	0	0	19.15	337.7	2.27	23.82	58	17.25	40.49	19.5313
5	-1	+1	-1	-1	17.3	510.3	0.81	16.66	39.5	12.24	53.9	9.6769
6	0	+1	0	0	20.17	360.9	2.12	26.81	60	19.47	50.79	22.0183
7	+1	+1	-1	+1	18.55	413.1	1.51	21.82	58.5	14.88	52.94	15.5654
8	-1	+1	-1	+1	17.25	391.6	1.45	20.24	54	14.31	48.79	14.6754
9	0	0	0	0	18.89	332.1	2.29	29.69	59	18.07	41.31	25.0175
10	-1	-1	+1	+1	17.95	229.6	4.49	19.19	70	18.59	50.52	33.1024
11	-1	+1	+1	+1	18.34	253.4	3.8	18.85	68	21.25	49.32	34.6766
12	0	0	0	-1	18.17	374.2	1.75	29.94	52	17.56	38.25	22.1235
13	+1	-1	+1	-1	15.18	264.7	3.19	28.89	61	18.59	47.55	24.0713
14	+1	-1	-1	-1	11.91	360.1	1.22	21.53	44	12.24	35.09	7.9279
15	0	-1	0	0	15.3	243.5	3.18	16.82	62	14.97	40.46	18.3771

16	+1	+1	+1	-1	18.05	319.4	2.73	30.31	59	20.09	39.17	26.7096
17	0	0	0	+1	18.18	288.5	2.9	23.67	63	17.97	50	15.3127
18	-1	-1	-1	-1	17.26	434.9	1.18	19.47	44	9.51	33.69	3.9406
19	0	0	0	0	17.54	302.9	2.52	27.88	59	17.17	38.32	19.4209
20	0	0	-1	0	18.35	378.3	1.58	30.7	50	11.04	33.55	10.1414
21	+1	0	0	0	16.66	304.3	2.62	26.54	60	18.43	52.35	20.2939
22	+1	-1	+1	+1	15.73	195.5	5.12	18.07	71	19.47	44.69	28.8339
23	0	0	0	0	17.49	312.6	2.37	23.35	59	15.42	51.98	20.6048
24	0	0	0	0	19.21	344.3	2.27	22.68	59	16.16	50.59	22.5757
25	0	0	0	0	14.51	281.2	2.47	21.79	59	16.24	49.24	20.6361
26	-1	-1	+1	-1	12.36	212.2	3.65	23.59	62	14.27	41.58	22.63649
27	+1	+1	-1	-1	14.18	493.5	0.84	21.29	41	12.14	38.53	10.38821
28	+1	+1	+1	+1	17.88	247.4	4.03	24.47	67	17.71	51.08	30.05115
29	0	0	0	0	16.41	306.4	2.23	20.19	60	16.59	46.66	21.13282
30	0	0	+1	0	18.76	274.4	3.35	25.88	64	20.77	43.7	30.03605
31	0	0	0	0	18.18	316.1	2.51	31.84	60	19.32	47.95	30.03605

6.3.1 Regression Analysis

The MINITAB software package was used for regression analysis. General form of the second order polynomial equation used to analyze the experimental data by response surface regression procedure is [34],

$$y = \beta_0 + \Sigma\beta_i\chi_i + \Sigma\beta_{ii}\chi_i^2 + \underset{i<j}{\Sigma\Sigma}\beta_{ij}\chi_i\chi_j$$

where, y is the response, and χ_i and χ_j are the coded independent variables. When normalized centred representations (coded levels) are used to represent factor levels, β_0, β_i, β_{ii} and β_{ij} are the mean values of responses, linear, quadratic and interaction coefficients respectively. Each coefficient (except interactions) allowed estimation of the change in the mean response per unit increase in χ when all other factors were held constant. The different notations used for generating regression equations for various properties are given in Table 6.4.

Table 6.4 Notations used to generate regression equations

Term	Notation	Term	Notation
ZnO	A	Filler*Filler	DD
Antioxidant	B	ZnO*Antioxidant	AB
Coagent	C	ZnO*Coagent	AC
Filler	D	ZnO*Filler	AD
ZnO*ZnO	AA	Antioxidant*Coagent	BC
Antioxidant*Antioxidant	BB	Antioxidant*Filler	BD
Coagent*Coagent	CC	Coagent*Filler	CD

The response surface regression analysis for the tensile strength of peroxide cured vulcanizates is given in Table 6.5. The p- value quantifies the significance of each term in the polynomial model. If the p- value of a coefficient is less than a chosen level of significance α, the relationship between the factor and response is statistically significant [13].

Table 6.5 Regression analyses for tensile strength of NR- peroxide vulcanizates.

Term	Coefficient	p-value
Constant	17.93	0.000
ZnO (A)	-0.21	0.615
Antioxidant (B)	0.73	0.096
Coagent (C)	-0.18	0.666
Filler (D)	1.23	0.008
ZnO*coagent (AC)	0.78	0.094
R^2 (53.87 %)	$R^2_{(adj)}$(13.54%)	

In this analysis, the significant level of α was chosen to be 0.1. It may be noted that only one interaction term is significant in addition to the linear term of factors. All other quadratic and interaction terms were found to be statistically insignificant in the case of tensile strength. R^2 is the percentage of variation of response variable that is explained by its relationship with one or more predictor variables [13].A higher R^2 value implies that the polynomial model is a very good predictor of the response [32, 36]. An R^2 value of 53.87 per cent (and adjusted R^2 value 13.54per cent) indicates that only 53.87 per cent of the variation in the response can be explained by a combination of factors. A lower value of R^2 indicates that some factors are not considered in this experimental design which affects the tensile strength. The regression equation for tensile strength was obtained as

$$TS = 17.93 - 0.2167\,A + 0.7356\,B - 0.1856\,C + 1.2367\,D + 0.7844\,AC$$

Factors with positive coefficients must be kept at high levels and those with negative coefficients at low levels to maximize the tensile strength of vulcanizates. It was observed that increasing the content of ZnO or coagent alone had a deteriorating effect on tensile strength while the interaction between these two had a positive effect. The use of ZnO in formulations with peroxide as crosslinking agent is limited as it deteriorates the properties of vulcanizates [2].The coagent selected for the study was zinc diacrylate; it is a metallic coagent which produces ionic as well as covalent crosslinks in the vulcanizates [37-39]. The main effect plot for tensile strength is shown in Figure 6.2. It was observed that as the concentration of coagent increased, tensile strength increased, reached a maximum at 5phr and then decreased. Ionic bonds exhibit both good heat stability and the ability to slip along the hydrocarbon chain. Like polysulphidic crosslinks (sulphur vulcanization) they reform after break and are responsible for an increase in tensile strength [12]. However, high loading of coagent leads to a decrease in tensile strength [40]. The addition of filler increased the tensile strength of vulcanizates. In a carbon black-rubber system the rubber that fills the void space [41] within each aggregate is occluded (occluded volume fraction of rubber) and immobilized, and thus acts as a part of filler rather than as a part of deformable matrix [42]. At a lower occluded volume fraction, multiple layers of rubbers are adhered to the carbon black particles along with the embedded rubbers through the coupling action of processing oil. Thus, an effective volume fraction of carbon black is higher at a lower occluded volume. This leads to higher tensile strength [43].

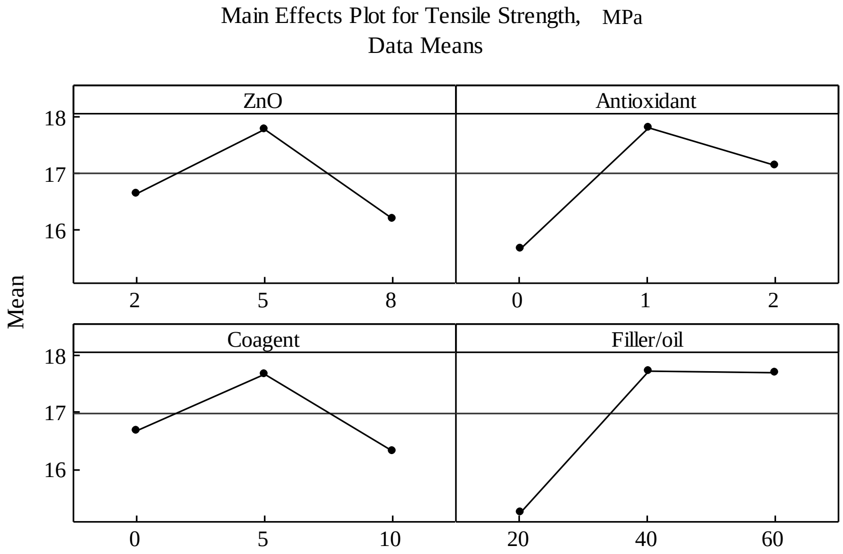

Figure 6.2 Main effect plots for tensile strength

Most of the antioxidants interfere with peroxide vulcanization by consuming the free radicals generated by homolytic fission of peroxides in a non-productive manner [2, 44-46]. Peroxide cured compounds can be stabilized by adding a maximum of 1 phr antioxidant TMQ (2, 2, 4-trimethyl-1,2-dihydroquinoline). It does not scavenge radicals rapidly and provides ageing stability to the vulcanizates [44].Hence, in this study antioxidant TMQ was found to have little effect on mechanical properties of the vulcanizates.

Similarly, the regression equations for elongation at break, tensile modulus (100 per cent elongation), tear strength, hardness, compression set (70 and 100^{o}C) and crosslink density were generated. The equation for elongation at break is given below.

$$EB = 324.40 - 4.947A + 36.684B - 76.327C - 31.201D + 8.429AC - 9.009BD + 9.394CD$$

As mentioned earlier, only statistically significant terms (p value ≤ 0.10) are included in this equation. An R^2 value of 91.68 per cent (and adjusted R^2 value 89.15per cent) indicates that 91.68 per cent of the variation in the response can be explained by a combination of factors. Elongation at break is the ultimate tensile stretch at which failure occurs. The elongation at break decreases with increasing ZnO content; this may be due to the fact that as the concentration of ZnO increases, the reinforcing capacity increases consequently elongation at break decreases [47]. Eventhough antioxidant TMQ enhances elongation at break of the vulcanizates; it has a deteriorating effect when interact with filler and oil. Similarly, coagent and filler alone do not contribute to increase in elongation but interaction of two has a positive effect. It was expected that at higher levels, coagent provides higher crosslink density, which would naturally lead to lower elongations [48].As the concentration of filler increases, stiffness of the vulcanizates increases resulting in lower elongations.

Generally, modulus is a measure of stiffness and is also a measure of the degree of vulcanization of a rubber compound. The increase in stiffness imparted by the filler particles involves a hydrodynamic effect which depends on the volume fraction of the filler. The occlusion of rubber by the aggregate and the rubber trapped within the filler agglomerates may increase the effective filler volume. Thus, volume fraction of the filler is an important parameter which determines the stiffness as well as modulus of a rubber compound. The regression equation for tensile modulus (M100) is given below.

$$M_{100} = 2.3946 + 0.1078A - 0.3750B + 1.0978C + 0.5522D + 0.137BB0.1194BC + 0.1731CD \ (R^2 = 97.44\%, R^2_{adj} = 96.66\%)$$

Regression equation for M_{100} shows that ZnO, coagent and filler/oil ratio has a positive effect on modulus. The increase in modulus is attributed to increase in crosslink density of vulcanizates. Table 6.3 shows that crosslink density increases with ZnO content, coagent and filler level.

Tear strength is the ultimate failure property at which the rubber chains are teared under stretch. This is due to the initiation of cracks developed by friction mainly at the rubber-carbon black interfaces as well as at the rubber -rubber interfaces [49]. The regression equation for tear strength is given below

$$\text{Tear strength} = 25.9977 + 0.6761\,B + 0.9344\,C - 1.3694\,D - 3.3582\,BB + 1.5238\,BC - 2.8013\,CD \ (R^2 = 52.44\%, R^2_{adj} = 40.55\%)$$

Regression equation shows that the addition of antioxidant and coagent improves tear strength. Generally, crosslinking with peroxide results in vulcanizates with inferior tear strength due to the rigid and stable carbon – carbon crosslinks. Tear strength can be improved by the addition of coagents, particularly coagents which are capable of forming ionic as well as covalent crosslinks (ZDA) in the formulation [44].

Hardness is typically defined as resistance to indentation under specific conditions. Hardness in moulded rubber articles is a function of crosslink density and hence the amount of filler and coagent. The hardness was found to obey the equation

$$\text{Hardness} = 59.2872 + 0.5833\ A - 1.0833\ B + 7.6944\ C + 5.6389\ D + 1.5666\ BB - 2.4334\ CC - 1.9334\ DD + 0.4688\ AB - 0.6562\ BC + 0.8438\ BD - 0.9062\ CD \quad (R^2 = 98.98\% \text{ and } R^2_{adj} = 98.39\%).$$

The above equation shows that ZnO, coagent and filler has a positive effect on hardness of the vulcanizates. Higher crosslinking in a given material, the harder the vulcanizates will be.

Compression set is the steady decline in sealing force that results when an elastomer is compressed over a period of time. One of the major advantages of peroxide cured rubber vulcanizates is the low compression set value of finished product. This is due to the fact that rigid carbon-carbon bond, having excellent thermal stability do not undergo any cleavage or deformation in the compressed state [50]. In practice, compression set was chosen as a criteria for the peroxide demand since compression set is directly influenced by crosslink density which itself will be determined by the amount of peroxide available to crosslink the polymer. The regression equations for compression set at 70 and 100°C are;

Compression set (70^{o}C) = 17.2785 + 0.3900 A + 0.9378 B + 3.1561 C + 0.8394 D - 1.5079 CC - 0.6875 AB - 0.5650 AD (R^2 = 86.95% and R^2_{adj} = 82.98%).

Compression set (100^{o}C) = 44.8942 + 1.9639 B + 0.8628 C + 4.1761 D - 2.5575 BC (R^2 = 43.60% and R^2_{adj} = 34.92%).

Crosslink density of a rubber is defined as the number of crosslink points per unit volume. Most of the mechanical properties of rubber depend on the crosslink density of the vulcanizates. The regression equation for crosslink density is;

Crosslink density (x 10^{-5}) = 23.993 + 1.922 B + 7.155 C + 1.160 D - 2.696 CC - 1.467 BC BC (R^2 = 93.46% and R^2_{adj} = 92.15%)

The addition of antioxidant, coagent and filler enhances the crosslink density of the vulcanizates.

6.3.2 Interaction plots

Interaction plots are used to visualize the interaction effects of factors on the responses. When the interaction effects are significant, the main effect plots are misleading and all inferences must be drawn from the interaction plots [51]. If the change in the mean of the response form one level of a factor to another level depends on the level of another factor, the two factors are said to have interaction effects. If the interaction plot has parallel lines, there is no interaction between two factors. As the deviation form parallel lines increases, the interaction between factors also increases [34, 52, 53]. The interaction plot for tensile strength is shown in Figure 6.3.

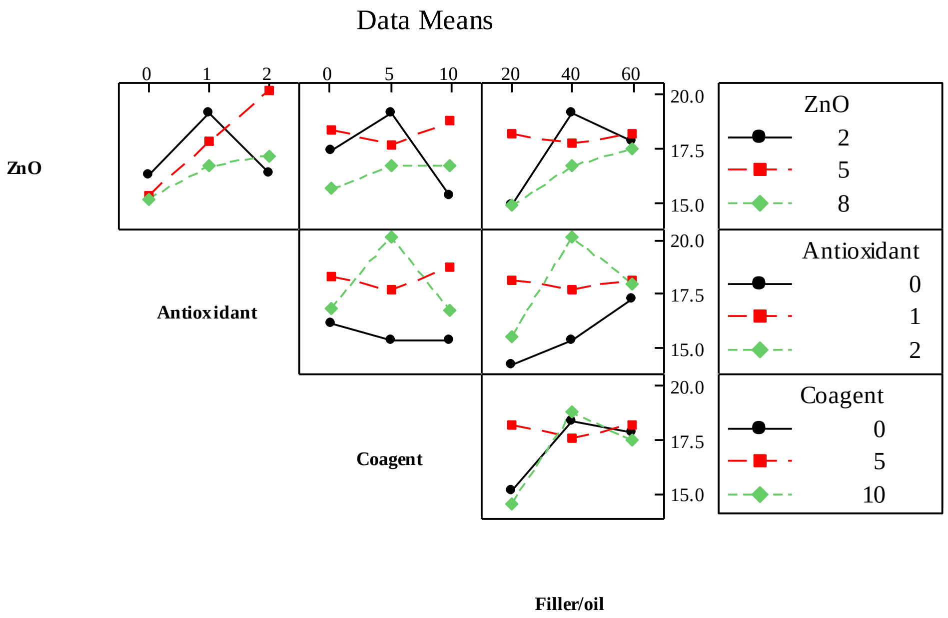

Figure 6.3 Interaction plot for tensile strength

The factor labelled underneath each individual plot is the X- axis, while the factor on the right most boxes given as a legend represents the levels of the second factor captured in the individual plot. In each such plot, the response was plotted on the Y- axis and here the response is tensile strength.

From Figure 6.3, it was observed that the interaction between antioxidant and ZnO has a significant effect on tensile strength. At mid-level of ZnO, as antioxidant level increases, tensile strength also increases. This effect was not significant at low or high level of ZnO. Similarly, if the interaction between ZnO and coagent are considered maximum tensile strength can be attained at low ZnO level and mid coagent level or mid ZnO level and high coagent level. This may be due to the fact that as ZnO is an ionic compound it may activate the formation of ionic crosslinks which leads to an increased tensile strength. Interaction effects are also observed in the case of antioxidant content and filler/oil ratio. In order to maximize tensile strength; the ZnO content should be mid, antioxidant content - high, coagent content and filler/oil ratio-mid.

Similarly, interaction plots were plotted for all the properties considered. Interaction plots for tear strength (Figure 6.4) and compression set (70 and 100°C) (Figure 6.5 and 6.6 respectively) shows that, there is significant interaction between the parameters.

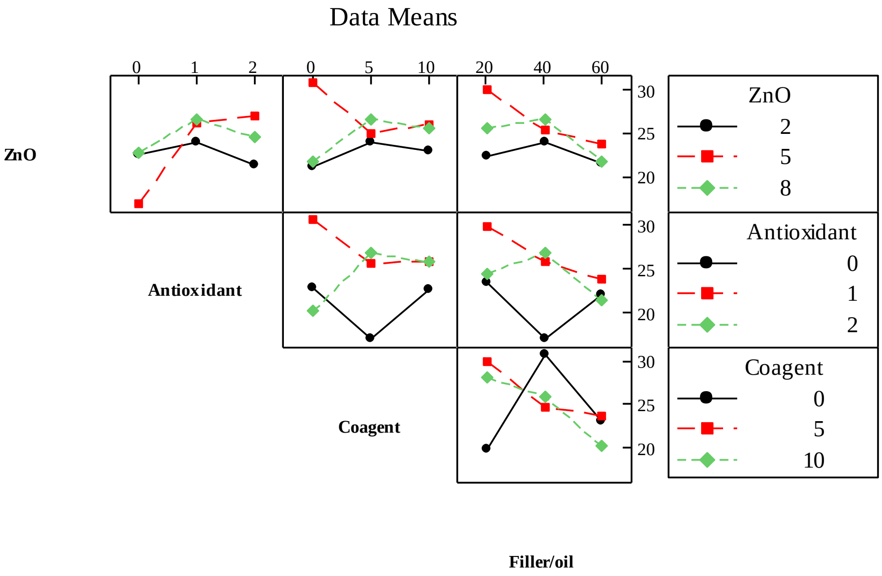

Figure 6.4 Interaction plots for tear strength

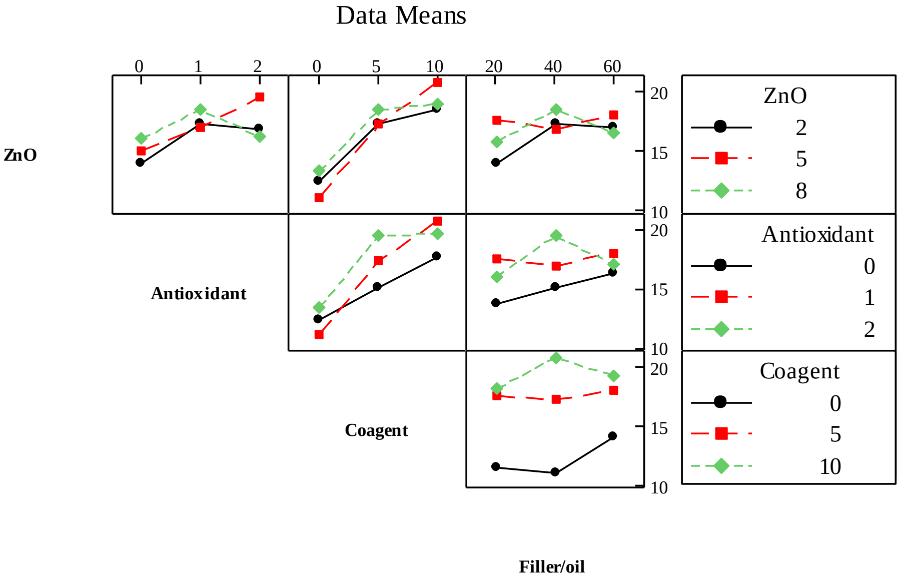

Figure 6.5 Interaction plots for compression set (70ºC)

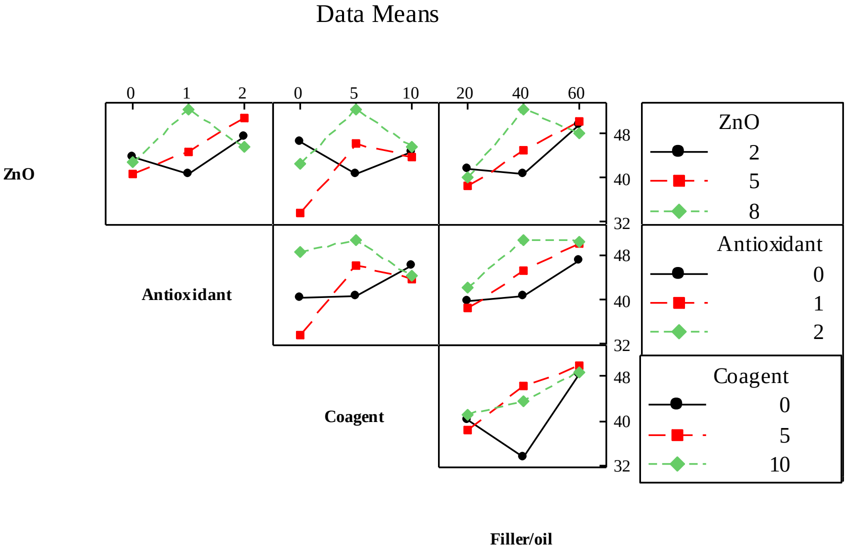

Figure 6.6 Interaction plots for compression set (100ºC)

For other properties like, elongation at break (Figure 6.7), modulus (100 %) (Figure 6.8), hardness (Figure 6.9) and crosslink density (Figure 6.10) the interaction effects between parameters seems to be insignificant.

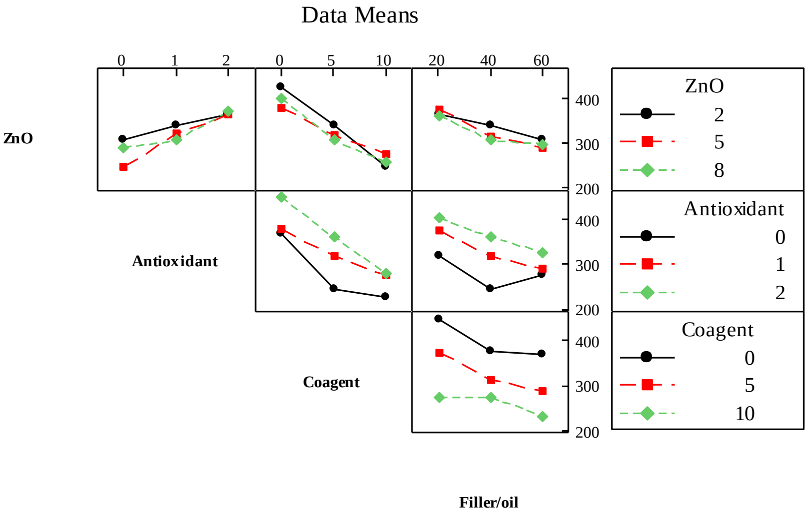

Figure 6.7 Interaction plots for elongation at break

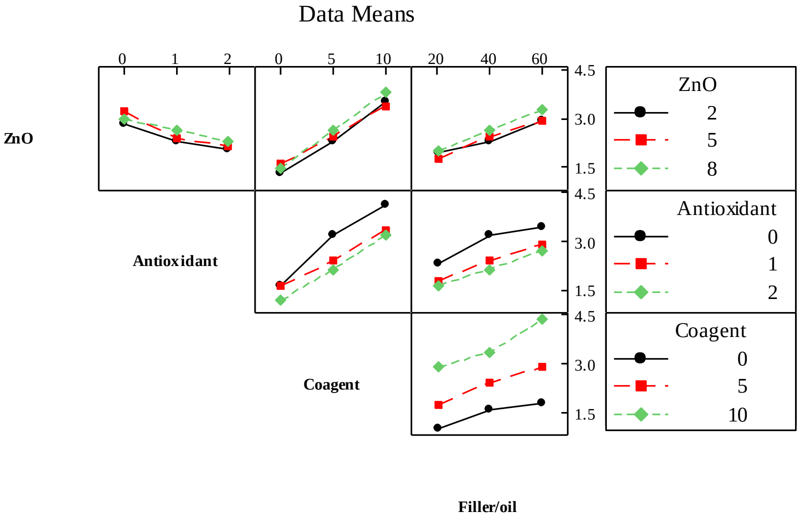

Figure 6.8 Interaction plots for M100

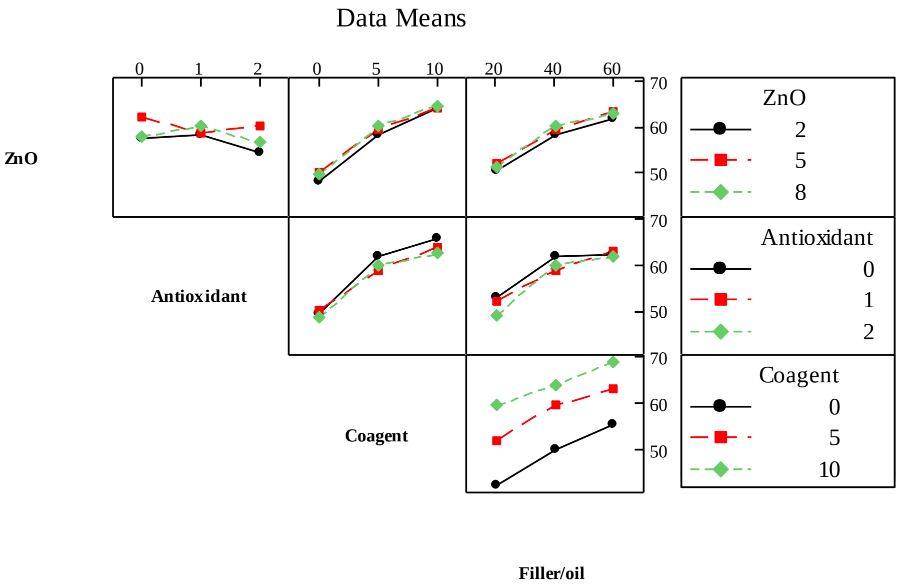

Figure 6.9 Interaction plots for Hardness

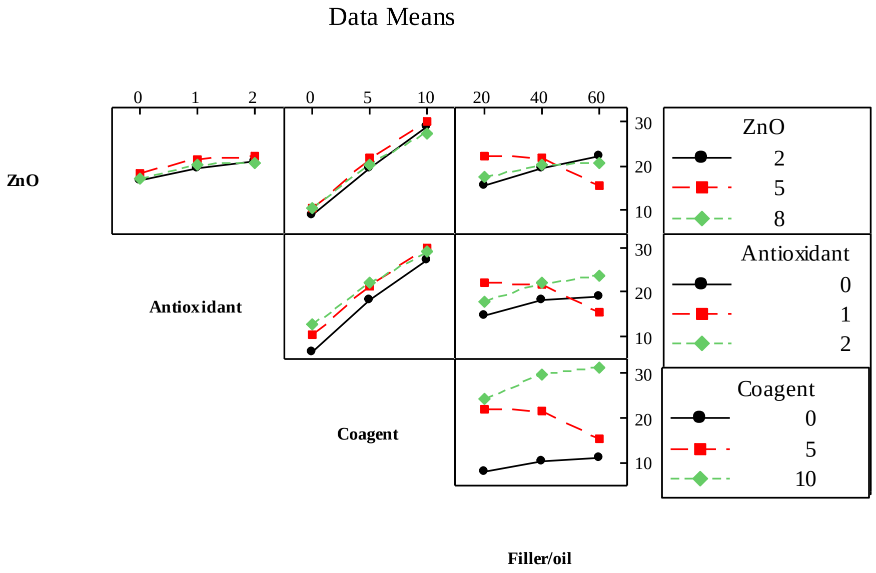

Figure 6.10 Interaction plots for crosslink density

To obtain maximum tensile strength with appreciable elongation, modulus (100%), hardness, tear strength, crosslink density and low compression set (70 and 100^{o}C); the following conclusions (Table 6.6) can be drawn from interaction plots.

Table 6.6 Factor ranges for peroxide cured natural rubber

Response	**Factors ranges**			
	ZnO	**Antioxidant**	**Coagent**	**Filler/oil**
Tensile strength	low-mid	high	Mid	mid
Elongation at break	mid-high	high	Low	low
Modulus (100%)	low	low	High	high
Hardness	mid-high	low	High	low-mid
Tear strength	mid	mid-high	Low	Mid
Crosslink density	low	high	High	High
Set (70^{0}C)	low	low-mid	Mid	Low
Set (100^{0}C)	mid	low-mid	Low	mid

6.3.3 Response surface plot

The response surface plot is a three dimensional graph showing the empirical functional relationship between the response and two factors, while the remaining factors being held at constant levels. Figures 6.11(a) and 6.11 (b) show the response surface plot for tensile strength of peroxide cured natural rubber. These plots show how antioxidant content and filler/oil ratio are related to tensile strength of peroxide cured natural rubber vulcanizates. In both cases, to maximize the tensile strength, antioxidant content should be selected between 1-2 phr and filler/oil ratio between 40-60 phr. Similarly, response surface plots were plotted for all the properties considered.

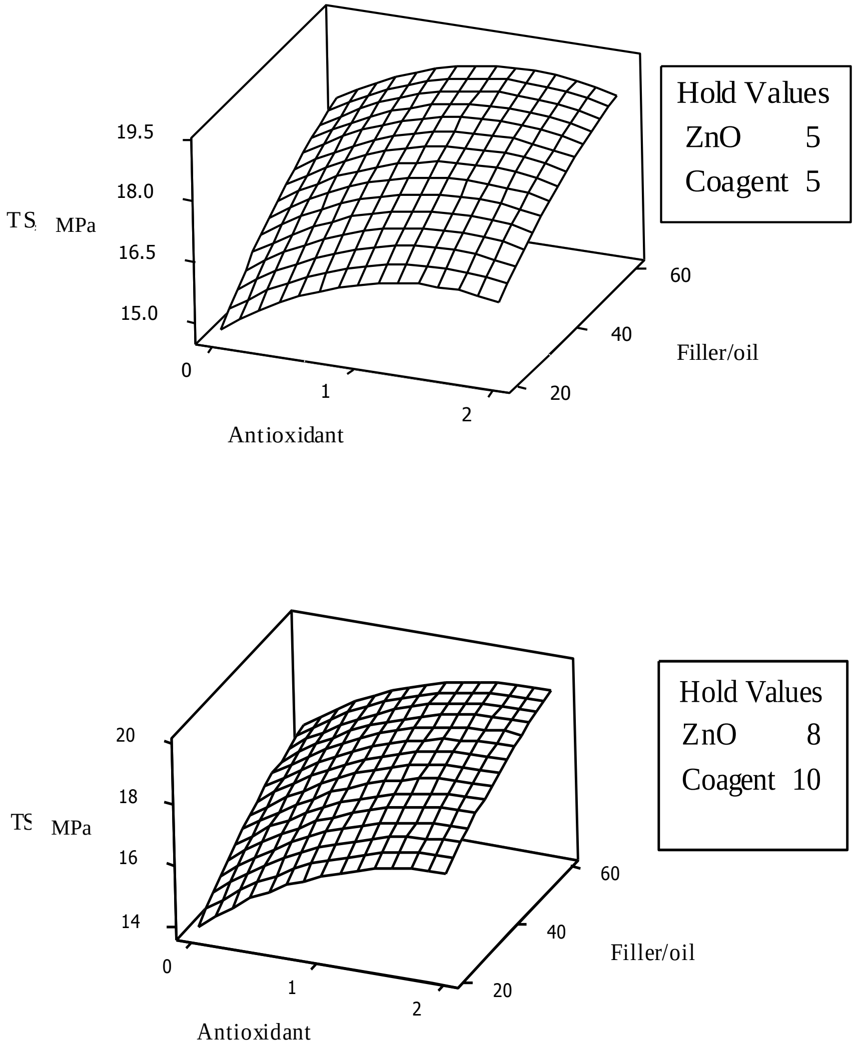

Figure 6.11(a) and 6.11 (b) Response surface plots for tensile strength

6.3.4 Contour plots

Contour plots are two dimensional graphs showing a series of curves of constant response for different combinations of factor levels. Such diagrams illustrate the change in properties when two or more variables change together and allow predictions to be made for combinations not actually run in the experiment. The contour plots for the response tensile strength with different factors are given in Figure 6.12. Analysis of Figure 6.12 shows that a high tensile strength (>19) can be obtained at a number of combinations. These combinations are based on high values of the hold variables when the other two factors are varied. Other combinations based on low and mid values of hold variables are also possible.

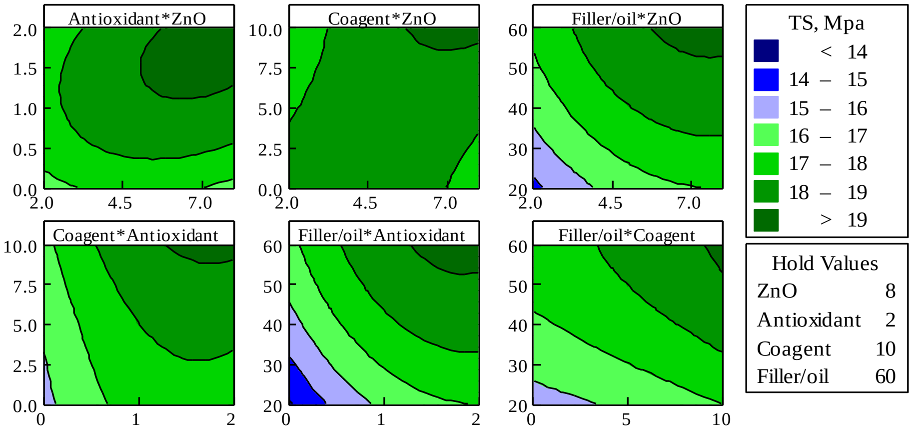

Figure 6.12 Contour plots for tensile strength of peroxide cured NR

Similar plots can be generated for all the properties of interest.The contour plot for elongation at break (Figure 6.13), 100% modulus (Figure 6.14), tear strength (Figure 6.15), hardness (Figure 6.16), compression set at 70 and

100^{o}C (Figure 6.17 and 6.18) and crosslink density (Figure 6.19) are given below.

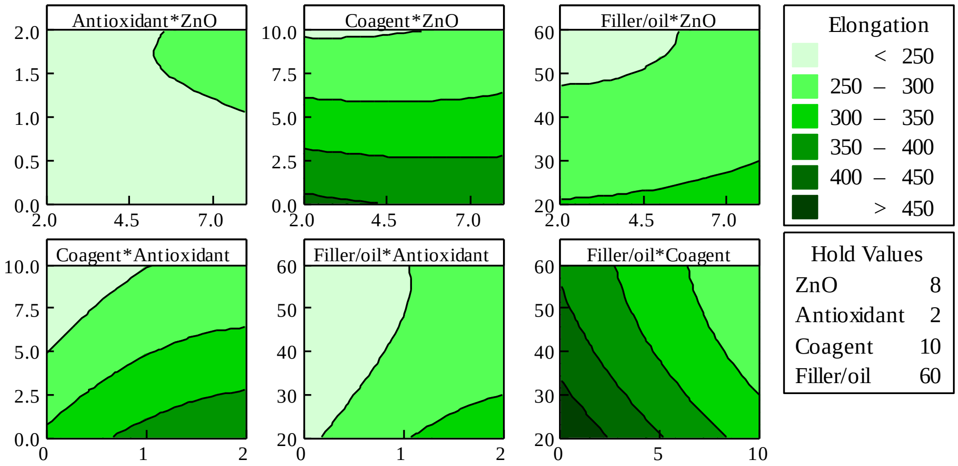

Figure 6.13 Contour plots for elongation at break

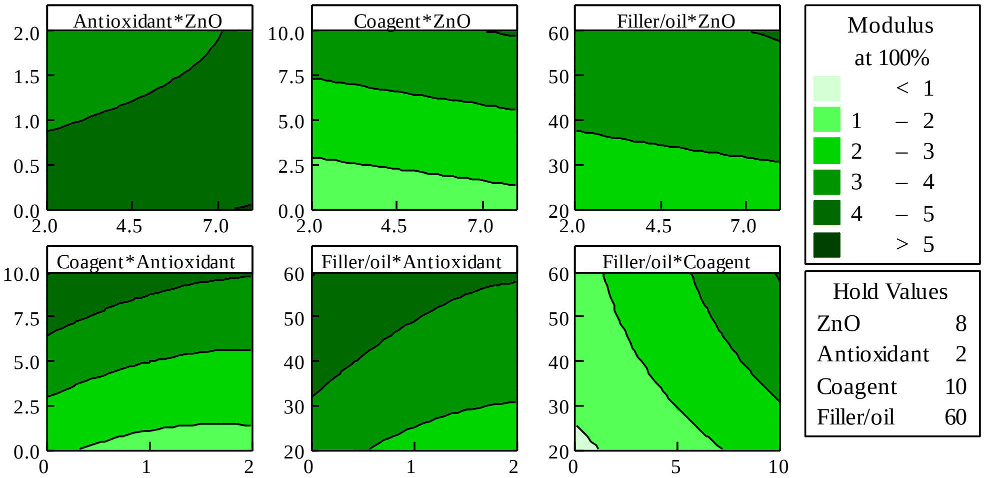

Figure 6.14 Contour plots for modulus (100% elongation)

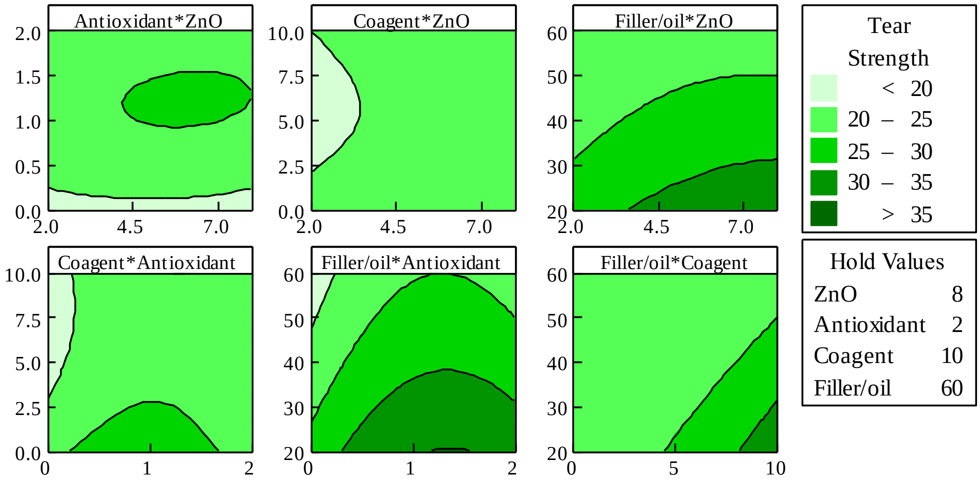

Figure 6.15 Contour plots for tear strength

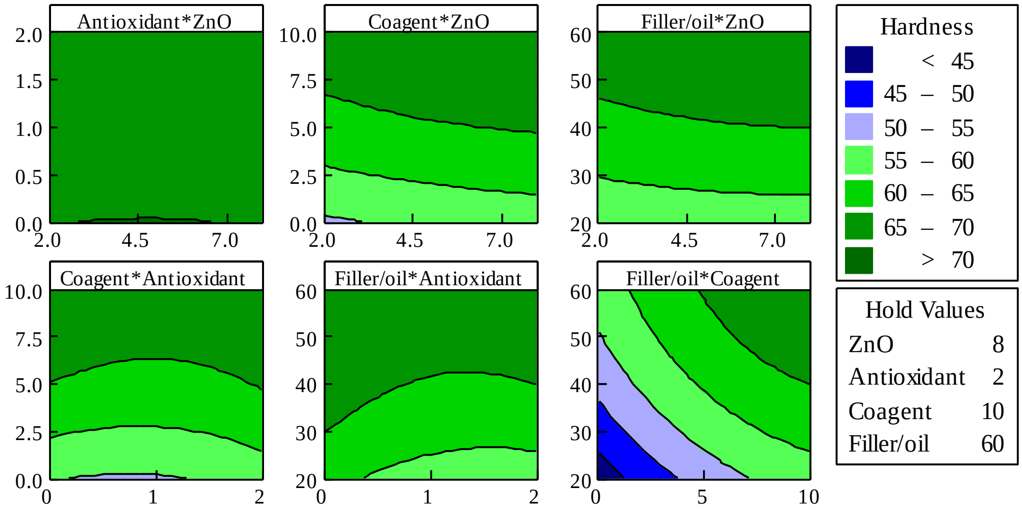

Figure 6.16 Contour plots for hardness

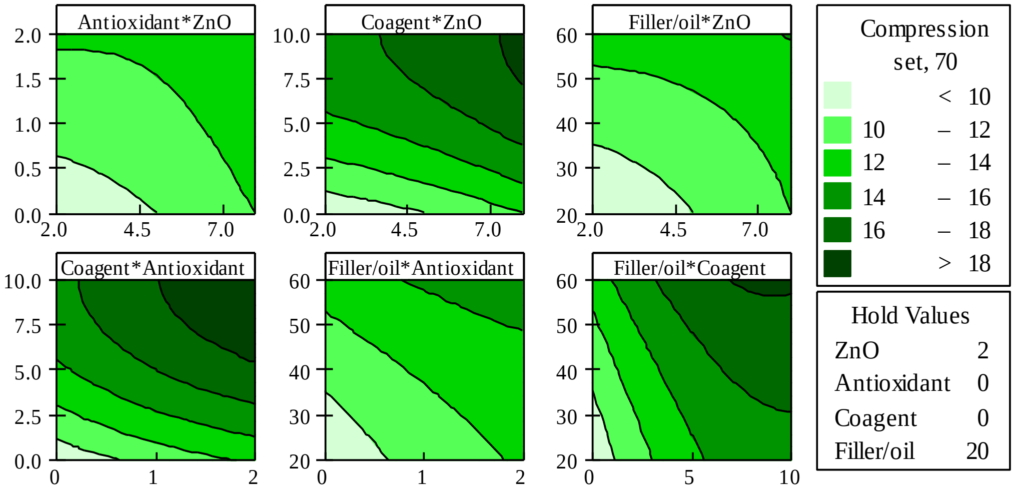

Figure 6.17 Contour plots for compression set (70ºC)

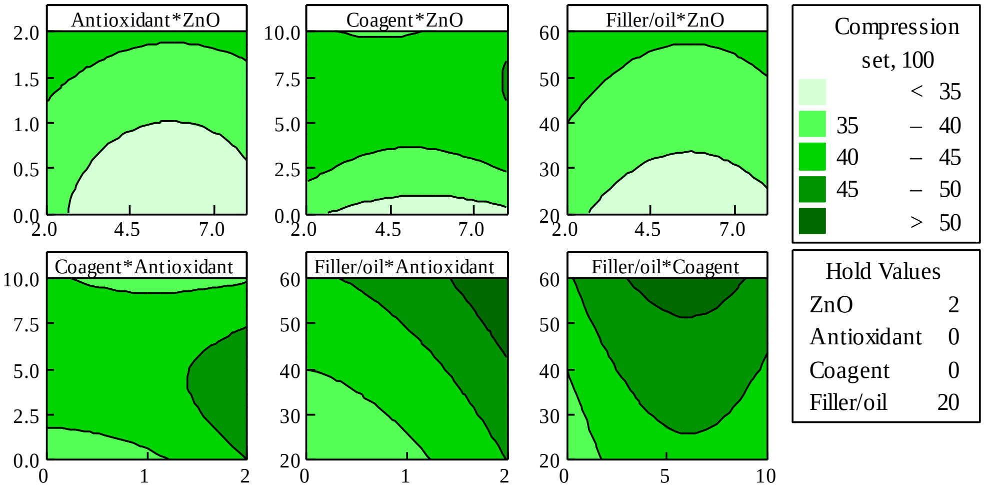

Figure 6.18 Contour plots for compression set (100ºC)

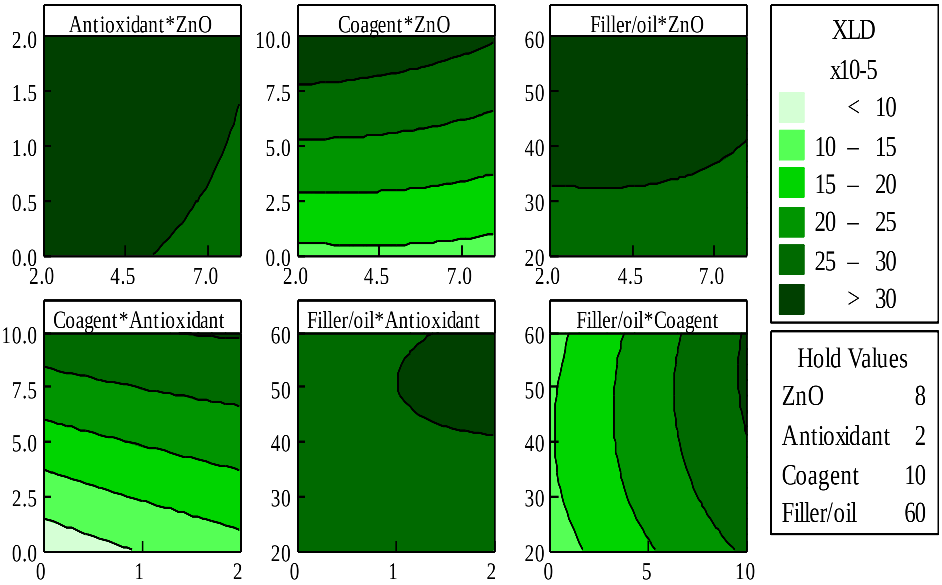

Figure 6.19 Contour plots for crosslink density

6.3.5 Verification experiments

Verification experiments were carried out to validate the empirical model based on predictions using combinations of independent variables which were not part of the original experimental design but were within the experimental region. The actual values of the variables used in verification experiments were ZnO-3phr, antioxidant-1.5phr, coagent - 5phr and filler - 50phr and oil -10phr. The predicted and experimental values for mechanical properties are given in Table 6.7 were in good agreement. These validations confirmed the suitability of the design chosen, method of sample preparation and property evaluation.

Table 6.7 Comparison of predicted and observed values for verification experiments

Properties	Predicted	Observed	% change
Tensile strength, MPa	18.1	19.2	6.07
Elongation at break, %	327	324	-0.91
Modulus (100%), MPa	2.5	2.7	8.00
Hardness, Shore A	62	60	-3.22
Tear strength, kN/mm	24.8	24.1	-2.82
Crosslink density x10^{-5}, g/cm^3	25.5342	25.0175	-2.02
Compression set (70^{o}C)	18.32	18.07	-1.36
Compression set (100^{o}C)	47.96	46.31	-3.44

6.3.6 Optimization of formulation of peroxide cured natural rubber

In this study the role of various compounding ingredients in the peroxide vulcanized natural rubber was investigated. Peroxide cured formulations usually suffer from inferior mechanical properties like low tensile strength, tear strength, hardness, modulus etc. However, better ageing resistance and compression set values compared to sulphur cured vulcanizates are observed. The constraints applied to the responses are given in Table 6.8. The individual contour plots were generated for each of the property and then simultaneous optimization of properties were carried out by overlaying the individual plots to obtain the overlaid contour plots. The desired values of all these properties can be obtained at any given combination within the optimized (white coloured region in the figure).

Table 6.8 Constraints on responses for finding the optimum formulation

Name	Goal	Lower limit	Upper limit
ZnO	in range	2	8
Antioxidant	in range	0	2
Coagent	in range	0	10
Filler	in range	20	60
Oil	in range	4	12
Tensile strength	maximize	18	20
Elongation at break	maximize	200	500
Modulus (100%)	maximize	1	4.5
Hardness	maximize	50	72
Tear strength	maximize	16	32
Compression set (70^{o}C)	minimize	8	21
Compression set(100^{o}C)	minimize	30	52
Crosslink density x10^5	maximize	6.1095	34.6766

The overlaid contour plots for optimum properties of peroxide cured natural rubber with ZnO and antioxidant as variables keeping the values of coagent and filler/oil ratio constant at high levels and vice versa are shown in Figures 6.20 and 6.21 respectively. The desired values of all these properties could be obtained at any given combination within the optimal region.

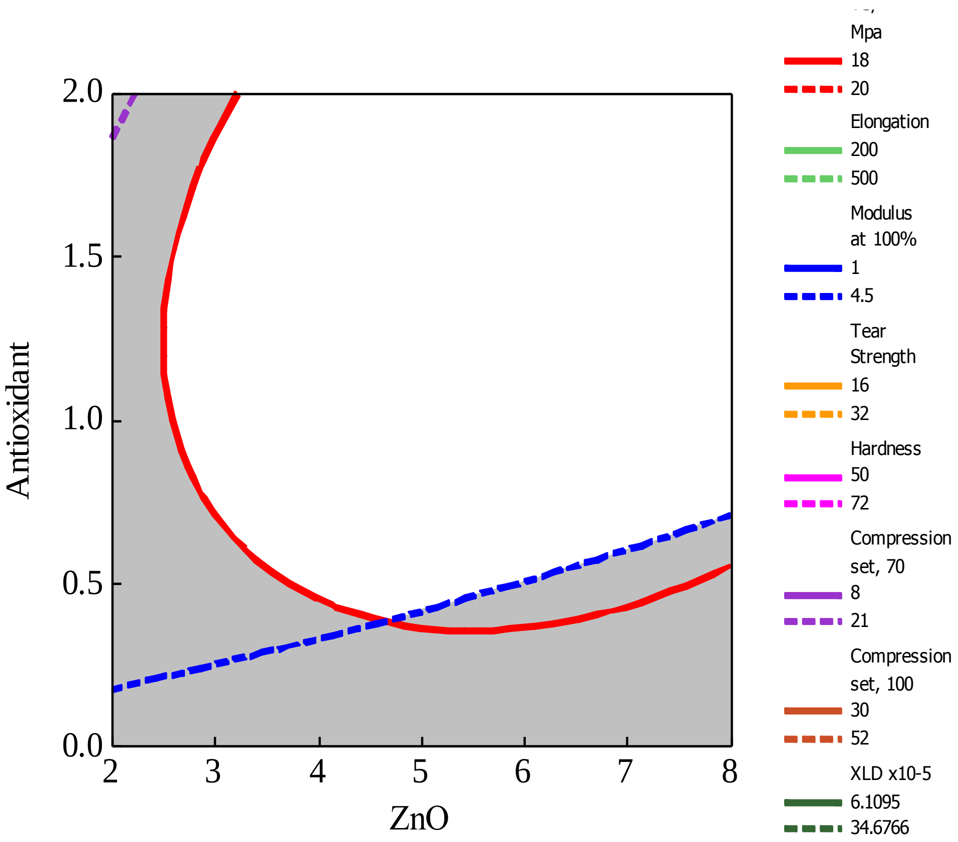

Figure 6.20 **Overlaid contour plots for optimum properties with ZnO and antioxidant content as variables at constant coagent (high) and filler/oil ratio (high)**

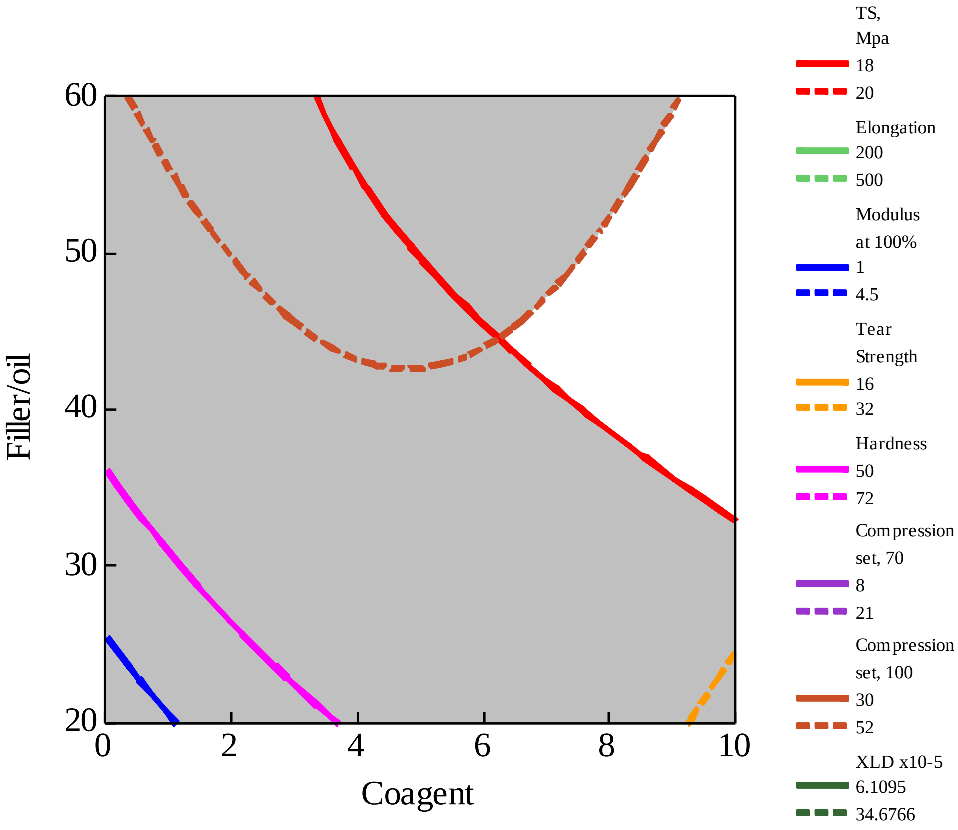

Figure 6.21 Overlaid contour plots for optimum properties with coagent and filler/oil ratio content as variables at constant ZnO (high) and antioxidant (high)

6.4 CONCLUSIONS

The levels of different ingredients in the peroxide vulcanization system were optimized using a Face Centred Central Composite Design (FCCD). Tensile strength, elongation at break, modulus (M100), tear strength, hardness, compression set (70 and 100°C) and crosslink density were chosen as the responses for generating model equations by regression analysis using MINITAB software. The mechanical properties like tensile strength, tear strength, compression set (70 and 100°C) were influenced by all the factors as well as the interaction effect between factors. The interaction effect was found to be insignificant for properties like elongation at break, modulus (M100), hardness and crosslink density. An increase in mechanical properties with a reduction in compression set can be achieved when antioxidant content selected was in between 1-2 phr and filler/oil ratio between 40-60 phr. Coagent content increases the low and high temperature compression set values of the vulcanizates. The contour plots for all properties were overlaid to obtain an optimum region for a desired set of specifications. The verification experiment confirmed the predictions of mechanical properties and the suitability of FCCD for optimizing the formulations of peroxide cured natural rubber vulcanizates.

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CHAPTER 7(A)

PEROXIDE CURED NATURAL RUBBER/ LAYERED SILICATE NANOCOMPOSITES: PREPARATION, CHARACTERIZATION AND MECHANICAL PROPERTIES

Natural rubber/organoclay nanocomposites were prepared and cured using peroxide system. Dicumyl peroxide was used as the crosslinking agent. The effect of four different types of nanoclays (layered silicates) viz, cloisite Na$^+$, cloisite 10A, cloisite 15A and cloisite 93A on cure characteristics, mechanical properties, hardness and swelling behaviour of NR/organoclay nanocomposites were studied. Commercial clay- (English Indian clay) a non-layered version was included in the study for comparison and the filler loading was kept at 10 phr in all the mixes. The composites were characterized by XRD. Properties such as mechanical, thermal, barrier and dynamic mechanical behaviour were discussed. Layered silicates registered superior properties compared to the reference material (commercial clay) in all aspects. This was attributed to the intercalation/exfoliation of the silicates in the NR matrix.

7.1 INTRODUCTION

Polymer nanocomposites represent a new alternative to conventionally filled polymer systems. Because of their nanometer size and dispersion they exhibit markedly improved properties at very low volume fractions and therefore, in recent years, these nanocomposites have generated much research interest [1-10]. Layered silicate/polymer nanocomposites exhibit superior mechanical [11-14], barrier properties [15, 16], heat resistance, reduced flammability,[17, 18] abrasion [19] and chemical resistance compared to the neat or traditionally filled resins. The property improvement results from only a 0.1-10 volume per cent addition of dispersed nanophase. Generally, polymer/clay nanocomposites are prepared by melt intercalation, solution blending and latex compounding. Melt processing is the simplest way to incorporate nanoclays in the polymer matrix [20]. In this process nanocomposite with structures varying from intercalated to exfoliated can be obtained, depending on the depth of penetration of the polymer chains within the clay interlayers [21]. Reviews on polymer/ layered silicate nanocomposites have been published [22, 23]. The nanoscale dispersion of the filler in the polymer matrix leads to significantly enhanced interfacial contact of the nanoparticles with the polymer matrix and this leads to synergistic improvements in the composite properties [24]. The larger specific surface area and smaller particle size of organoclay was believed to provide better rubber-filler interaction [25-26].

Among different organo- clays montmorillonite clay has been extensively used for the preparation various polymer nanocomposites. Each platelet of montmorillonite clay consists of Al-octahedral sheets sandwiched between two Si-tetrahedral sheets. Isomorphic substitution in the sheets creates deficit of positive charge which is balanced by the Na^+ ions present at the interlayer or d-spacing region. It is well established that layered silicates (e.g., montmorillonite (MMT)) are hydrophilic [27, 28] and they do not have chemical affinity with hydrophobic organic polymers. Therefore, the modification of montmorillonite with different compounds to make it compatible with polymer has been extensively investigated [29-32]. The startling property of montmorillonite is its ability to expand and contract its interlayer structure while maintaining two-dimensional crystallographic integrity. By this means, a large amount of active surface area (700-800 m^2/g) is generated, allowing an enormous range of rubber molecules to be intercalated [33].

In this study, natural rubber/ organo clay composites were prepared using four different organoclays, *viz*. cloisite Na^+, cloisite 10A, cloisite 15A and cloisite 93A. Inert non- layered filler (English Indian clay) was used for comparison. Cure characteristics, mechanical properties, hardness and swelling behaviour of NR/clay nanocomposites were studied. The composites were characterized by XRD. Properties such as barrier, thermal and dynamic mechanical behaviour are also discussed.

7.2 EXPERIMENTAL

7.2.1 Materials

The detailed specification of materials used is given in section 2.1.

7.2.2 Methods

The composition of mixes used was given in Table 7.1. The filler loading was kept at 10 phr in all mixes. Preparation of the compounds and experimental procedures are presented in sections 2.2.3, 2.5, 2.6 and 2.8.

Table 7.1 Composition of mixes

Ingredients	phr
Natural rubber	100
DCP (40%)	5
*Filler (variable)	10

* MMT, MMT – 2MBHT, MMT- 2M2HT, MMT – M2HT, CC

7.3 RESULTS AND DISCUSSION

7.3.1 Cure characteristics

The cure characteristics of the compounds are given in Table 7.2. The maximum toque, M_H, is a measure of crosslink density of the vulcanizates. Organically modified clays shows the highest M_H values and M_H-M_L values compared to commercial clay (CC) and unmodified clay (MMT) indicating higher degree of crosslinking, which is also confirmed by swelling measurements. The minimum torque, M_L measures the viscosity and hence stiffness of the compound before vulcanization. Except MMT-2M2HT, the minimum torque is almost similar and comparable in all the cases. The increase in viscosity with the addition of filler suggests a reduced mobility of the rubber chains caused by the incorporation of fillers. The cure time (t_{90}) values indicate that both unmodified clay (MMT) and modified clays (MMT-2MBHT, MMT-2M2HT and MMT-M2HT) accelerate the vulcanization compared to commercial clay (CC). The lowest cure time is observed for MMT- M2HT with highest cure rate index and this may be due to the action of modifiers present in the clay. Therefore, organo MMT-

M2HT behaves as an effective accelerating agent in the peroxide vulcanization of natural rubber.

Table 7.2 Cure characteristics of the mixes at 160°C

Parameters	**MMT**	**MMT-2MBHT**	**MMT-2M2HT**	**MMT-M2HT**	**CC**
Maximum torque, M_H (dNm)	59.27	60.16	62.46	65.94	60.12
Minimum torque, M_L (dNm)	13.92	10.39	7.80	12.83	11.08
M_H-M_L, d.Nm	41.35	49.77	54.66	53.11	49.04
Optimum cure time, t_{90} (min)	18.21	20.07	19.86	16.65	21.84
Scorch time, t_2 (min)	1.40	2.08	1.73	2.09	1.08
CRI, %	5.49	4.99	5.03	6.01	4.57
Crosslink density, x10^{-5} mol/cm^3	9.5779	11.5821	11.7130	11.6348	9.2276

Scorch time is a measure of the processing safety of the rubber compound. Scorch time is lowest for commercial clay and organic modifiers improve the scorch time compared to the unmodified clay. It may be due to the intercalation of nanofiller between the polymer matrix, which restricts the polymer macro-radical to combine and form crosslinks [34].

7.3.2 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis measures the response of a given material to a cyclic deformation as a function of temperature. The main results obtained from DMA analysis are (a) the storage modulus (*E'*), corresponding to elastic response to the deformation, (b) the loss modulus (*E''),* corresponding to the plastic response to deformation and (c) mechanical loss factor, tan δ, that is the (*E''/E'*) ratio, useful for determining the occurrence of molecular mobility transitions such as the glass transition temperature [35].

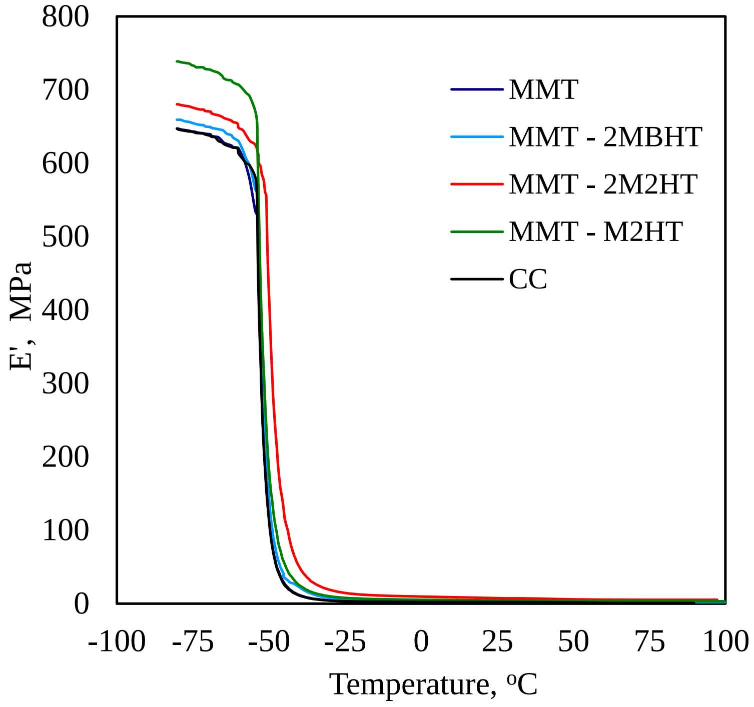

Figure 7.1 (a) Storage modulus (E') as a function of temperature

Extend of intercalation and exfoliation of layered silicates in polymer can be obtained from the storage modulus and glass transition temperature. The dynamic mechanical properties of polymer layered silicate nanocomposites depend on the d-spacing of silicate layers. As the spacing between the silicate layers increases the storage modulus increases and the damping peak corresponding to the glass transition temperature broadens. Figure 7.1(a) and 7.1(b) represents the temperature dependence of storage modulus (E') and tan δ respectively.

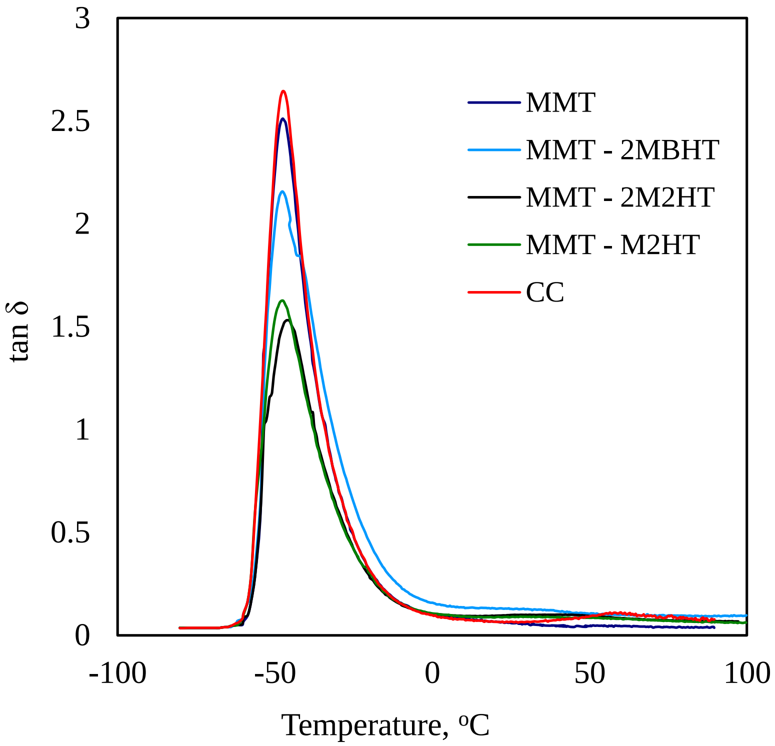

Figure 7.1(b) Mechanical loss factor (tanδ) as a function of temperature

Figure 7.1 (a) shows that there is an increase in the storage modulus of organically modified clay compared to unmodified clay and commercial clay. The order of fillers with respect to the stiffness below the glass transition temperature (Tg) is: CC≈ MMT< MMT-2MBHT < MMT-2M2HT < MMT- M2HT. In Figure 7.1(b) the mechanical loss factor tanδ is shown for commercial clay, unmodified and modified clay filled vulcanizates. Compared to commercial clay and unmodified clay (MMT) the height of the tanδ peak of all organically modified clays are reduced to a greater extent. This can be interpreted in terms of restricted mobility of polymer chains due to the confinement in the layers of silicates. It is well known that the reduction in tanδ peak reflects a strong adhesion between polymer and nanoclay [36, 37]. Therefore, the nanoclays MMT- 2M2HT and MMT-M2HT exhibits strong filler polymer coupling.

7.3.3 Thermal stability of NR/layered silicate nanocomposites

The thermal decomposition behaviour of NR/ layered silicate nanocomposites are given in Table 7.3. Compared to commercial clay and unmodified clay, at 400°C, the percentage of weight retained is higher for NR/modified layered silicate nanocomposites.

Table 7.3 Thermal decomposition behaviour of NR/layered Silicate nanocomposites by TGA

Temperature, °C	Weight retained, %				
	MMT	MMT-2MBHT	MMT-2M2HT	MMT-M2HT	CC
300	96.63	94.42	95.34	99.39	96.67
350	93.18	91.17	91.62	95.60	92.98
400	40.49	47.05	44.16	51.41	36.46
450	11.25	10.77	8.59	13.17	9.80
500	6.76	3.94	3.82	7.14	6.18
550	6.54	3.61	3.62	6.56	5.37
600	5.97	3.05	2.94	5.72	4.61

In an exfoliated rubber-nanoclay system, the rubber hydrocarbons are surrounded by clay layers (Since nanoclays are characterized by large surface area (800 m^2/g), exfoliation of a part of 10 phr is enough for improved properties and thermal stability). As silicate layers have high themal stability, the exfoliated system register high hydrocarbon deposit at elevated temperature.

At 450°C, MMT- M2HT is more thermally stable than other composites indicating the dispersion state of clay in rubber. Therefore, it can be concluded that among the modified layered silicates, the better rubber filler interaction is for MMT –M2HT at 400°C.

7.3.4 X -ray diffraction studies (XRD)

X-ray diffraction was used to study the nature and extent of dispersion of the clay in NR/clay nanocomposites. Figure 7.2 shows the XRD diffractograms of NR composites containing nanoclays MMT, MMT-2MBHT, MMT- 2M2HT and MMT-M2HT.

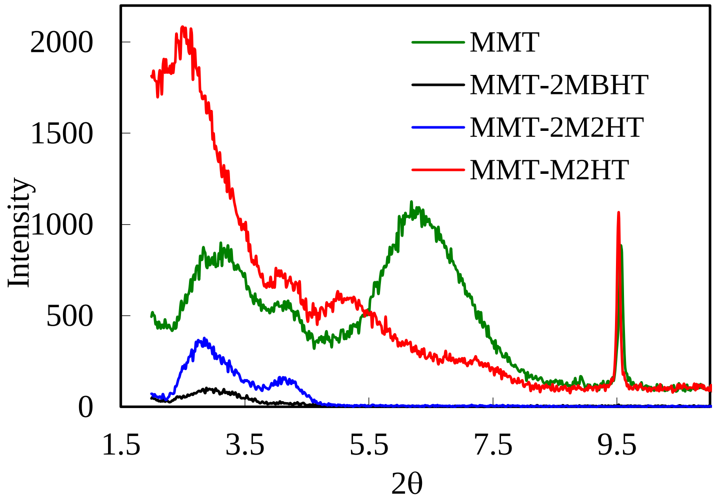

Figure 7.2 XRD spectra of NR/layered silicate nanocomposites

Compared to the unmodified clay (MMT), all the vulcanizates containg modified clays showed a peak at lower diffraction values. This might be due to the intercalation of rubber chains into the gallery spaces of the silicates. As the intercalation of the polymer chains increases, the interlayer spacing of the clays increases, this leads to the shifting of diffraction peak towards lower 2θ values in the XRD spectrum.

7.3.5 Gas barrier properties

The oxygen permeability of nanoclay filled and commercial clay filled vulcanizates are given in Table 7.4. It is clearly seen that the oxygen permeability decreased substantially by the incorporation of organically modified layered silicate. While commercial clay (CC) and unmodified montmorillonite (MMT) exhibits the same oxygen permeation behaviour the organically modified clay follows the order MMT-2MBHT<MMT-M2HT<MMT-2M2HT. Generally, clays are believed to increase the barrier properties by creating a ‘tortuous path’ that retards the progress of the gas molecules through the polymer matrix [38]. The barrier mechanism of clay layers has been discussed in detail [39, 40].

Table7.4 Oxygen permeability of nanoclay filled and commercial clay filled vulcanizates

Material	Permeability, mL x m^2/24hrs
MMT	1658.50
MMT-2MBHT	1016.44
MMT-2M2HT	1044.34
MMT-M2HT	1030.20

It was assumed that the movement of the gas molecule to enter or pass through the polymer material was prolonged due to the existence of nanodispersed clay layers, which will reduce the number of molecules that can passed through the membrane. This is because the nanodispersed silicate layers cause hindrance to gas molecules which will improve the barrier properties of the material.

7.3.6 Mechanical properties

The mechanical properties of NR/layered silicate nanocomposites are given in Table 7.5. It can be seen that when compared to commercial clay, addition of unmodified clay as well as modified clays improve the mechanical properties on vulcanizates.

Table 7.5 Mechanical properties of NR/layered silicate nanocomposites

Properties	MMT	MMT-2MBHT	MMT-2M2HT	MMT-M2HT	CC
Tensile strength, MPa	9.98	13.62	12.87	14.13	8.34
Elongation at break, %	491.79	483.99	476.58	463.75	489
100% Modulus, MPa	0.99	1.27	1.35	1.52	0.97
200% Modulus, MPa	1.69	1.89	1.95	2.27	1.56
300% Modulus, MPa	2.56	3.4	3.9	4.2	2.7
Tear strength, kN/m	19.75	21.88	23.59	25.77	18.60
Hardness, Shore A	40	43	46	46	38

Intercalation/exfoliation of silicates resulted in enhanced strength and reduced elongation at break [41]. Tensile strength follows the order MMT-M2HT > MMT- 2MBHT > MMT -2M2HT > MMT > CC. The enhancement in properties by the incorporation of fillers is due to better polymer-filler interaction than filler-filler interaction. Therefore, intercalation of rubber chains into the clay layers resulted in the increased tensile strength.MMT-M2HT filled composites showed the lowest elongation at break followed by MMT-2M2HT, MMT- 2MBHT CC and MMT. The decrease in elongation can be accounted by an increase in rigidity of the material. The tensile modulus of vulcanizates has been improved when nanocomposites are formed with layered silicates. The ranking of fillers according to the moduli of elongations 100, 200 and 300% are fairly matched with stiffness derived from that of dynamic mechanical analysis (Figure 7.1(a)). The tear strength of the vulcanizates, proven to be a measure of the clay dispersion [42], follows the order CC < MMT < MMT-2MBHT < MMT-2M2HT< MMT-M2HT. Hardness, a measure of low strain elastic modulus, is higher for MMT- M2HT and MMT- 2M2HT. This may be due to the fact that as more rubber get into the gallery spacing of the clays, the elasticity of rubber nanocomposites is reduced and the interlayer distance increased resulting in more rigid vulcanizates.

7.4 CONCLUSIONS

Natural rubber/layered silicate nanocomposites exhibited remarkable improvement in thermal, mechanical and barrier properties compared to their virgin polymers or microcomposites. Among the four different nanoclays used, MMT-M2HT showed overall balance in all properties. When compared to the commercial clay, both unmodified clay and modified clays accelerated the rate of vulcanization. The dynamic mechanical properties were found to depend highly on extent of delamination of silicate layers. As the spacing between silicate layers increased, the storage modulus increased and consequently, the height of the damping peak corresponding to Tg decreased. The nanoclays MMT-2M2HT and MMT-M2HT exhibited strongest filler-polymer coupling. XRD analysis confirmed the intercalation of rubber chains into the gallery spaces of the layered silicates. All the nanoclays improved the gas barrier properties of the composites compared to commercial clay. The enhancement in mechanical properties by the incorporation of fillers was due to better polymer-filler interaction than filler-filler interaction.

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CHAPTER 7(B)

KINETIC ANALYSIS OF PEROXIDE CURED NATURAL RUBBER/LAYERED SILICATE NANOCOMPOSITES USING THERMOGRAVIMETRY

The thermal stability and kinetics of thermal degradation of natural rubber/layered silicate nanocomposites were studied by thermogravimetric analysis (TGA). The activation energy for the degradation of NR/layered silicate nanocomposites was determined by applying Liu and Fan method. Results showed that the thermal degradation is a first order reaction and organically modified clays exhibited highest thermal stability.

7.5 INTRODUCTION

Natural rubber is a general purpose polymer and its unique combination of properties has made it an elastomer of choice for many sophisticated industrial applications. Although natural rubber has excellent mechanical properties, these may interfere with its low thermal stability. Generally, thermal stability of polymer materials can be improved by the introduction of inorganic nanoparticles into the polymer matrix. The thermal stability and thermal degradation kinetics of polymer nanocomposites has been the subject of interest for many years [1-14]. In general, it has been reported that the polymer/clay nanocomposites are thermally more stable than pure polymers [15-19]. The effect of clay layers had been more explained as superior insulation and mass transport barrier against the volatile compounds generated during the decomposition of polymer under thermal conditions [20]. Also it has been reported that clays assist in the formation of layered carbonaceous char during degradation of polymer/clay nanocomposite [21-23]. Thereby, in the beginning stage of thermal decomposition, the clay could shift the decomposition temperature to higher values. The stacked silicate layers could hold the accumulated heat that could be used as a heat source to accelerate the decomposition process in conjunction with the heat flow from the source. Clay minerals are inorganic materials and are almost stable in the temperature ranges that organic polymers are degraded in to volatile compounds. Therefore in TGA experiments the clay content of nanocomposites remains as residue during thermal decomposition [24].

Good information about the thermal stability of polymer nanocomposites can be obtained from thermogravimetric analysis (TGA). The technique is particularly useful for the compositional analysis of multi-component materials or blends, thermal/oxidative stability, estimation of shelf-lives decomposition kinetics, effect of reactive atmosphere on materials and filler, moisture and volatile content of the materials. Dynamic thermogravimetry has been widely used to study the kinetics of thermal decomposition reactions during the past several decades [25]. It measures the changes in weight as a function of increasing temperature. Several integral and differential methods are available to study the kinetics of thermal decomposition of polymer layered silicate nanocomposites from thermogravimetric data. The integral method utilizes weight loss versus temperature data directly and most widely used methods are those developed by Doyle [26], Coats and Redfern [27], Zsako [28], Broido [29], Reich and Stivala [30], and Ozawa *et al*., [31]. The differential methods for kinetic analysis uses the rate of weight loss versus temperature data and the differential methods in common use are those derived by Freeman and Caroll [32], Newkirk [33], Achar *et al*., [34] Vachuska and Voboril [35] and Friedman *et al.*,[36]. For most of these methods the prior knowledge of reaction mechanism is essential for calculating the kinetic data. In fact, the techniques to obtain the kinetic parameters when the reaction mechanism is unknown have been a subject of concern over the past several decades.

The objective of the present study is to analyze the thermal stability of natural rubber layered silicate nanocomposites by thermogravimetric analysis (TGA). The organoclays selected were cloisite Na^+, cloisite 10A, cloisite 15A and cloisite 93A. Gum and commercial clay (English Indian clay) were used as reference materials. Liu and Fan method [25] was used to derive kinetic parameters like activation energy (E) and order of the reaction (n) from TGA data.

7.6 Materials

The detailed specification of materials used is given in section 2.1 (Chapter 2).

7.6.1 Methods

The composition of mixes used was given in Table 7.1 (Chapter 7(A)). Preparation of the compounds and experimental procedures are presented in sections 2.2.3 and 2.7.

7.6.2 Kinetic analysis

Kinetic analysis of thermogravimetric data from the weight loss curve is based on the formal kinetic equation,

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \text{.............}(7.1)$$

Where, α is the fraction of material decomposed at time t, n is the order of the reaction and k is the rate constant. The combination of this equation and the empiric Arrhenius equation along with the heating rate β gives the following relationship,

$$\frac{d\alpha}{dt} = \frac{A}{\beta} e^{-E/RT}(1-\alpha)^n \text{.............}(7.2)$$

Where, A is the Arrhenius frequency factor, E is the activation energy of the reaction, R is the gas constant and T is the absolute temperature in Kelvin.

This is the fundamental expression of analytical methods to calculate kinetic parameters on the basis of TGA data. This expression is the base of all the above said methods to derive kinetic parameters *E, n* and *A*. The most widely used method for kinetic analysis of TGA data was that developed by Freeman and Caroll [32](FC method), and the major advantage is that the method can be used without any prior knowledge of the reaction order. According to FC method, the reaction order *n* and activation energy *E* can be calculated using the equation

$$\frac{-\left(E/R\right)\Delta\left(1/T\right)}{\Delta\ln\left(1-\alpha\right)} = \frac{\Delta\ln\left(d\alpha/dt\right)}{\Delta\ln\left(1-\alpha\right)} - n \text{ ....(7.3)}$$

By plotting a graph of $\Delta ln\ d\alpha/dt/\Delta ln(1\text{-}\alpha)$ versus-$\Delta(1/T)\ /\Delta ln(1\text{-}\alpha)$, activation energy *E* and order *n* can be calculated from intercept and slope of the regression line respectively. However, the major problem associated with FC method in most practical instances is the difficulty of obtaining reliable values for reaction order, n [37]. Sharp and Wentworth [38] showed that the obtained reaction order values sensitively fluctuated with the number of the points selected for fitting the straight line.

Therefore Liu and Fan [25] developed a new method for deriving kinetic parameters E and n accurately from the slopes rather than the intercepts, of the regression lines of two equations which were derived based on Freeman and Caroll [32]method. The two equations are

$$\frac{\Delta\ln\left(d\alpha/dT\right)}{\Delta\ln\left(1-\alpha\right)} = -E\,\frac{\Delta\left(1/T\right)}{R\ln\left(1-\alpha\right)} + n \text{ ....(7.4)}$$

$$\frac{\Delta \ln(1-\alpha)}{\Delta \ln\left(\frac{d\alpha}{dt}\right)} = \frac{E}{n}\,\frac{\Delta\left(\frac{1}{T}\right)}{R\ln\left(\frac{d\alpha}{dt}\right)} + \frac{1}{n} \quad \ldots\ldots\ldots.(7.5)$$

Equation (7.4) is the proposed new method to determine activation energy (*E*) from slope; similarly, the slope term (*E/n*) of equation (7.5) can be effectively used to calculate the reaction order value by substituting activation energy (*E*) from equation (7.4).

7.7 RESULTS AND DISCUSSION

7.7.1 Thermal stability

Thermal stability indicates the ability of a material to maintain the required properties such as strength, toughness or elasticity of a material at a given temperature. TGA measures the weight change of a material when it is heated in an inert atmosphere or in the presence of oxygen. Under an inert gas flow, a non-oxidative degradation occurs, while the use of air or oxygen allows oxidative degradation of the samples.When a compound is heated, the polymer part will get degraded first. Further heating will remove all organic matter, leaving inorganic components in the compound. Generally, the incorporation of clay into the polymer matrix was found to enhance the thermal stability by acting as a superior insulator or mass transport barrier to the volatile products generated during decomposition [20]. The TGA and DTG curves for NR/ layered silicate nanocomposites are given in Figures 7.3(a) and 7.3(b). Figure 7.3(a) shows that all composites degrades in a single step and major weight losses are observed in the range 300-500^{o}C which corresponds to structural decomposition of the polymer.

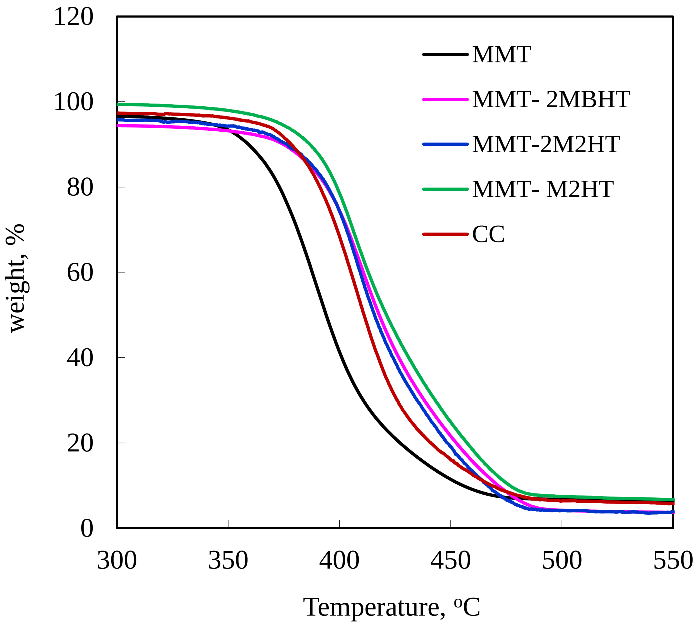

Figure 7.3(a). TGA curves of NR/layered silicate nanocomposites

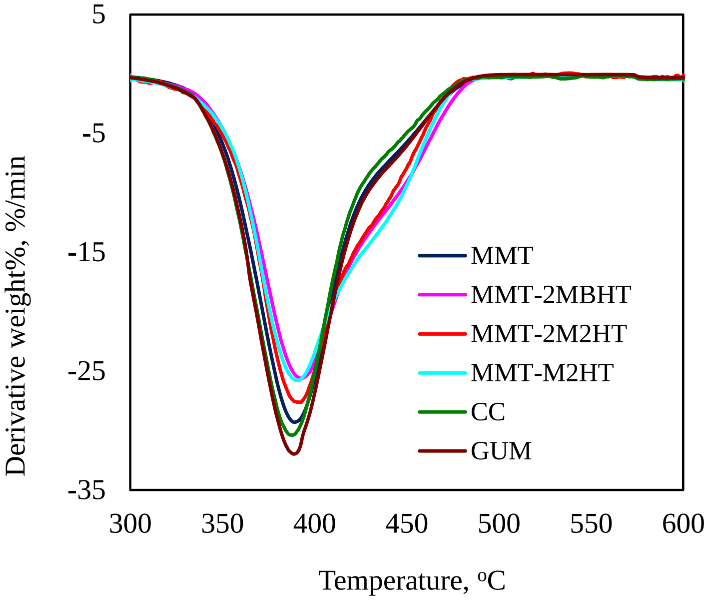

Figure 7.3(b). DTG curves of NR/layered silicate nanocomposites

The temperature of onset of decomposition (Ti), the maximum decomposition temperature (T_{max}), the peak degradation rate (R_{max}) and the residue weight at 800°C are given in Table 7.6.

Table 7.6 Thermal degradation characteristics of NR/layered silicate nanocomposites

Sample	Onset decomposition temperature T_i, °C	Maximum decomposition Temperature Tmax, °C	Percentage degraded, %/min	Residue at 800°C (%)
MMT	308	389.6	43.1	5.24
MMT-2MBHT	310	392.9	42.1	2.11
MMT-2M2HT	312	390.3	41.6	1.58
MMT-M2HT	322	390.9	36.9	3.05
CC	304	388.2	44.5	2.67
GUM	302	388.3	46.1	-

The degradation of unfilled NR compound (GUM) started at 302°C with maximum rate of degradation 53.8 per cent/minute without leaving any residue at 800°C. By the introduction of 10 phr filler, the temperature of onset of degradation was shifted to higher values in the case of nanocomposites. The onset decomposition temperature is an index of thermal stability of polymer layered silicate nanocomposites [39]. Table 7.6 shows that the onset decomposition temperature of modified MMTs are higher than that of unmodified MMT and from the DTG curve (small shoulder/peak in the temperature range 410-500°C) it can be observed that the decomposition of organically modified nanoclays follows a different mechanism [39]. The maximum decomposition temperature is slightly improved with nanoclay filled vulcanizates compared to gum and commercial clay filled vulcanizates. The rate of decomposition is highest for MMT-M2HT and residue at 800^{o}C is lowest for MMT-2M2HT. Therefore, it can be concluded that the thermal stability of NR/layered silicate nanocomposites follows the order MMT-M2HT > MMT-2M2HT > MMT-2MBHT > MMT > CC > GUM.

7.7.2 Kinetics of thermal degradation

Here an attempt was made to study the kinetics of decomposition of NR/layered silicate nanocomposites based on TGA data by a modified method proposed by Liu and Fan [26]. Several data points were selected randomly from the weight loss curve and fitted in equations (7.4) and (7.5) respectively. The corresponding regression lines for MMT are shown in Figures 7.4 and 7.5. Similar regression lines were plotted for all other vulcanizates and kinetic parameters were calculated and are given in Table 7.7.

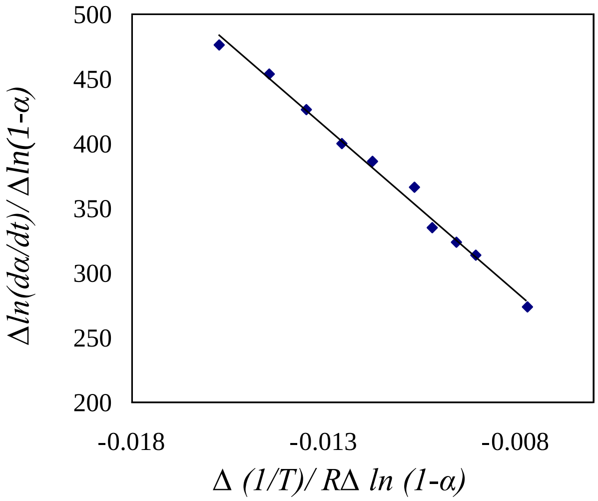

Figure 7.4 Plot of $\Delta(1/T)/R\Delta ln(1-\alpha)$ versus $\Delta ln(d\alpha/dt)/\Delta ln(1-\alpha)$

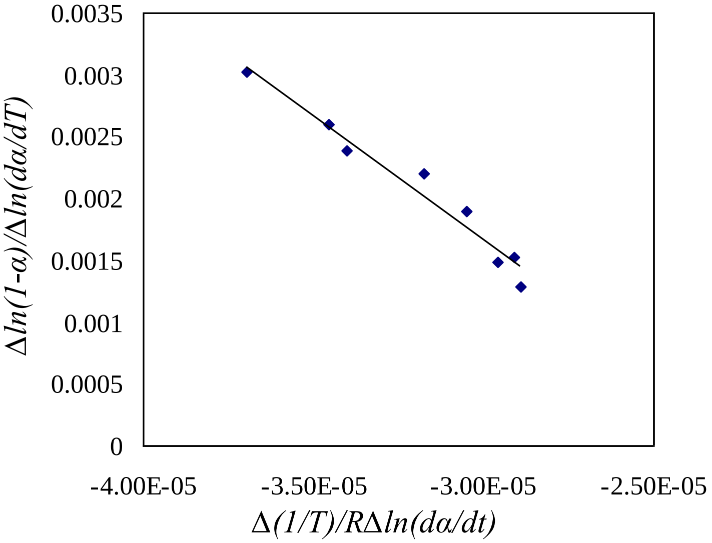

Figure 7.5 Plot of Δ*(1/T)/R*Δ*ln(dα/dt)* versus Δ*ln(1-α)*/ Δ*ln(dα/dt)*

Table 7.7 Activation energy (E) and order (n) of thermal decomposition of NR layered silicate nanocomposites

Samples	Equation (4) E, kJ/mol	Equation(5) E/n, kJ/mol	n
MMT	25.63	25.31	1.03
MMT-2MBHT	26.47	23.28	1.13
MMT-2M2HT	31.64	31.00	1.02
MMT-M2HT	35.81	34.36	1.04
CC	22.36	23.60	1.11
GUM	16.61	14.54	1.14

Table 7.7 shows that thermal degradation of unfilled vulcanizates and natural rubber layered silicate nanocomposites follow first order kinetics. The higher the activation energy of the decomposition of the composite, the

better will be the thermal stability of the composite [40]. Addition of nanofiller enhanced the thermal stability of the composites as expected. The activation energy and hence stability is highest for MMT-M2HT followed by MMT- 2M2HT, MMT-2MBHT, MMT, CC and GUM.

7.8 CONCLUSION

The thermal stability and thermal degradation kinetics of natural rubber layered silicate nanocomposites have been analyzed by thermogravimetric analysis. Among the different organoclays selected, the highest thermal stability is exhibited by MMT-M2HT. The kinetics of decomposition was investigated by a modified method (Liu and Fan [25]). The thermal decomposition was found to be a first order reaction in both unfilled and filled vulcanizates. The organoclay MMT-M2HT showed highest activation energy which supports the improved thermal stability of the vulcanizate.

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CHAPTER 8

THERMAL OXIDATIVE BEHAVIOUR OF PEROXIDE CROSSLINKED NATURAL RUBBER

Peroxide vulcanization of natural rubber was carried out with four chemically different peroxides, namely 2,5-dimethyl-2,5-bis(tert-butylperoxy) hexane (DHBP), 1,1'-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane (TMCH), 1,3 1,4-bis (tert-butyl peroxy isopropyl) benzene (DIPP) and dicumyl peroxide (DCP). Fourier transform infrared spectroscopy (FTIR) and Thermo gravimetric analysis (TGA) were used to characterize the byproducts formed as a result of the thermal oxidative degradation. Tensile strength, elongation at break, modulus at different elongations was tested before and after ageing. The vulcanizates were also evaluated for hardness, crosslink density and compression set. The reactivity of different peroxides towards the crosslinking of natural rubber was rated based on the properties of the respective vulcanizates.

8.1 INTRODUCTION

In rubber industry, organic peroxides are useful as curing agents for both saturated and unsaturated rubbers [1-7]. The reactivity of the organic peroxides depends on the peroxide group configuration and type of substituents [8, 9]. In peroxide vulcanization, the curing agent does not enter into polymer chains but form carbon-carbon linkages between adjacent polymer chains. Organic peroxides that can be used for crosslinking polymers mainly include diacyl peroxides (benzoyl peroxide and its derivatives), dialkyl or diaralkyl peroxides (di *tert* butyl peroxide, dicumyl peroxide, etc.) and peresters (*tert*- butyl perbenzoate) [10]. Diacyl peroxides and peroxyesters are more vulnerable to acid-catalyzed decomposition than dialkyl peroxides [10, 11]. The first reported organic peroxide for the vulcanization of rubber was benzoyl peroxide [1]. Disadvantage associated with benzoyl peroxide crosslinking is the surface blooming of vulcanizates due to benzoic acid produced from the decomposition of peroxide [10]. The vulcanizates obtained have poor physical properties and poor resistance to heat ageing when compared to sulphur cured vulcanizates. Brandon and Fletcher[12]reported the use of dicumyl peroxide for the vulcanization of natural rubber. A variety of dialkyl peroxides and *t*- butyl perbenzoate lead to high efficiency crosslinking reactions in gum rubber but only *t*-butyl peroxide and dicumyl peroxide are capable of curing compounds having reinforcing black fillers. Of these two peroxides, *t*-butyl peroxide is a highly volatile liquid and dicumyl peroxide, being a non-volatile solid are the generally used peroxides [13]. Its decomposition in rubber has been extensively studied [14-16].

Dicumyl peroxide covers around 30 per cent of the total peroxide consumed by the polymer industry. One of the major disadvantages of dicumyl peroxide is the unpleasant odour of the vulcanizates due to the formation of acetophenone as a by-product. Di (tert-butylperoxyisopropyl) benzene can be used as an alternative to dicumyl peroxide, but the blooming phenomena can take place by the formation of dihydroxy isopropyl benzene due its limited solubility in the rubber [17]. In order to overcome the difficulties associated with peroxide vulcanization several other organic peroxides and their scorch retarding grades have been developed and are commercially available [18, 19]. These new generation peroxides contain unsaturatedfunctional groups,in addition to peroxide group, therefore, part of the decomposition products is no longer volatile, nor will give rise to smell or blooming phenomena [17].The use of structurally different peroxides for the vulcanization of natural rubber, synthetic rubber and their blends has been investigated extensively [20 - 27]. Very little work has been done to study the effect of different peroxides on the ageing resistance and mechanical properties of peroxide cured natural rubber.

The objective of this study was to understand the role of different peroxides in the vulcanization of natural rubber. In this study, four different peroxides, namely 2, 5-bis (*tert*-butylperoxy)-2, 5-dimethylhexane, 1, 1’-di (*tert*-butylperoxy)-3, 3,5trimethyl cyclohexane, 1, 3 1,4-bis (*tert*-butylperoxyisopropyl) benzene and dicumyl peroxide were selected for the peroxide vulcanization of natural rubber. The thermal oxidative degradation behaviour of peroxide cured vulcanizates was characterized by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA).

8.2 EXPERIMENTAL

8.2.1 Materials

Detailed material description is given in section 2.1 (Chapter 2).

8.2.2 Methods

The composition of mixes used was given in Table 8.1. Peroxide loading is fixed after evaluating each peroxide for their optimum properties in natural rubber. Preparation of the compounds (section 2.2.1) and experimental procedures (2.5, 2.5.5 and 2.6) are given in chapter 2.

Table 8.1 Composition of mixes

Ingredients	**A**	**B**	**C**	**D**
NR	100	100	100	100
HAF black	50	50	50	50
Paraffinic oil	4	4	4	4
Peroxide	1.5[ai]	4[bi]	2.6[ci]	2.5[di]

ai- 2, 5-bis (*tert*-butylperoxy)-2, 5-dimethylhexane, bi- 1, 1'-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane, ci- 1, 3 1, 4-bis (*tert*-butylperoxyisopropyl) benzene, di- dicumyl peroxide

8.3 RESULTS AND DISCUSSION

8.3.1 Cure characteristics

In order to study the curing of natural rubber with different peroxides, it is necessary to understand the efficiency and reactivity of these peroxides. Even though thermally induced homolytic cleavage of all peroxides produces highly reactive free radicals, the efficiency of these radicals may vary considerably [8]. Free radical produced by the homolytic cleavage of peroxides may be either alkoxy radicals or alkyl radicals. The primary radicals produced by thermal decomposition readily undergo rearrangements in order to form a stable radical [8, 28] which decreases the crosslinking efficiency. Another important factor which determines the reaction efficiency is the energy level of radicals. The active free radical will react with polymer only if the energy level of the radicals is reduced in the process [8, 29, 30]. Reactivity of peroxides depends on a number of factors viz. type and concentration of peroxide, nature of the polymer, presence of other compounding ingredients in the formulation etc. [31].The cure characteristics and crosslink density of natural rubber vulcanizates are given in Table 8.2.

Table 8.2 Cure characteristics of the mixes at 160°C

Sample	$M_{H,}$ d.Nm	M_L,d.Nm	t_{90},min	$t_{2,}$min	CRI,%
A(DHBP)	16.08	1.59	33.26	1.29	3.13
B(TMCH)	11.55	1.86	2.00	0.22	56.17
C(DIPP)	13.9	1.65	27.38	1.38	3.84
D(DCP)	18.82	1.48	16.26	1.02	6.57

The maximum torque (M_H) generally represents the crosslink density and the minimum torque ($M_{L)}$ measures the viscosity of the vulcanizates. DCP shows the maximum torque values followed by DHBP, DIPP and TMCH whereas considering the cure rate index (CRI), TMCH is the fastest followed by DCP, DIPP and DHBP. Minimum torque, M_L of all compounds shows only marginal difference in the values. TMCH yields a rapid cure under typical vulcanization conditions, but it is more prone to premature crosslinking than other peroxides. Scorch time, $t_{2,}$ is comparatively high for DHBP, but requires long cure times. DIPP provides an intermediate cure that is less vulnerable to scorch than DCP. Crosslink density (Table 8.5) is highest for DCP, TMCH was found to give lowest crosslink densities whereas DHBP and DIPP show almost similar crosslink densities. Homolytic cleavage of DCP produces both cumyloxy radicals and methyl radials, both have sufficient energy to react with polymer backbone and this is responsible for the higher crosslink density. For other peroxides, alkoxy radicals are the predominant species and due to the energy considerations, these are less able to abstract hydrogen from polymer backbone than cumyloxy and methyl radicals, hence low crosslink densities [7].

8.3.2 Fourier transform infrared spectroscopy studies

An attempt was made to study the oxidative degradation behaviour of natural rubber cured with four different peroxides by analyzing the FT IR (ATR) spectrum of samples.

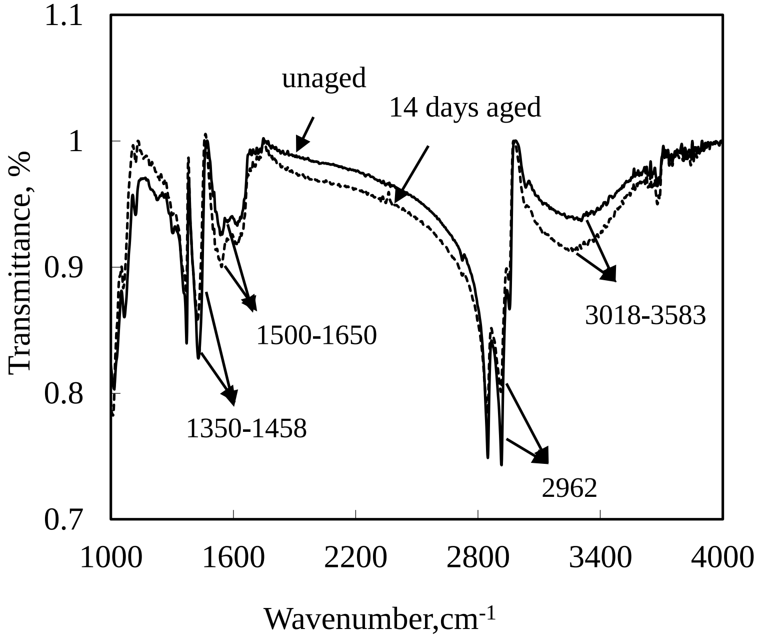

Figure 8.1 FT IR spectra of natural rubber cured withDHBP before and after thermal ageing

FT IR spectra of vulcanizates cured with different peroxides before and after ageing (14 days) at 70°C were shown in Figures 8.1- 8.4.

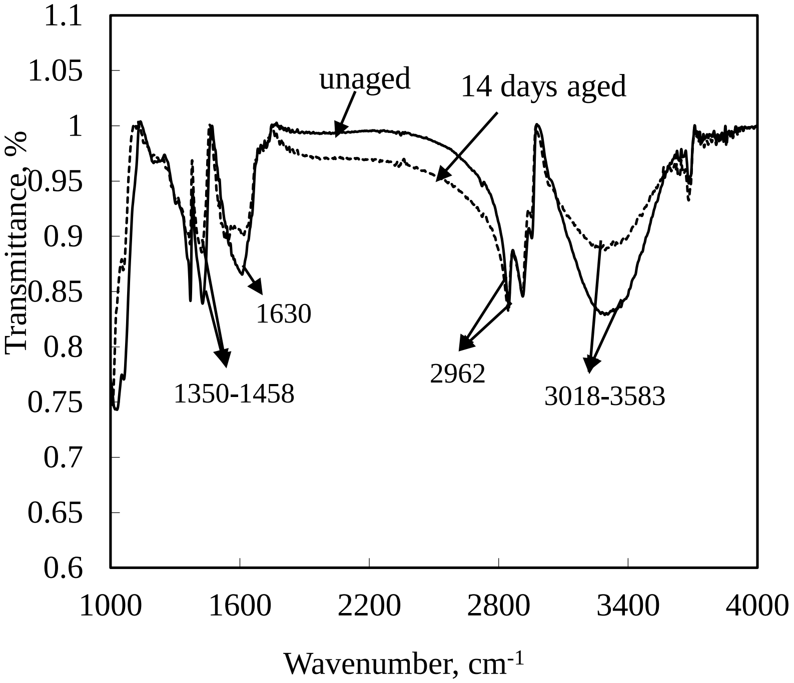

Figure 8.2 FT IR spectra of natural rubber cured with TMCH beforeand after thermal ageing

One of the major decomposition products of all the peroxides used in this study is an alcohol (Table 2.2), therefore, FT IR spectra of all the unaged vulcanizates contains a broad absorption band in the range 3583-3018 cm^{-1} due to –OH stretching vibration. The FT IR spectra of natural rubber cured with DHBP (Figure 8.1) showed that after 14 days of ageing, there is a considerable increase in the intensity of absorption due to –OH stretching vibrations with a significant reduction in the intensity of absorption due to –

CH_3 asymmetric stretch (2962, 2956 cm^{-1}). Chain scission was further confirmed by the broad and intense absorption band at 1500-1650 cm^{-1} due to C=O stretching mode. In addition, strong bands in the range 1428-1369 cm^{-1} are attributed to chain scission (C-H bond) [33].

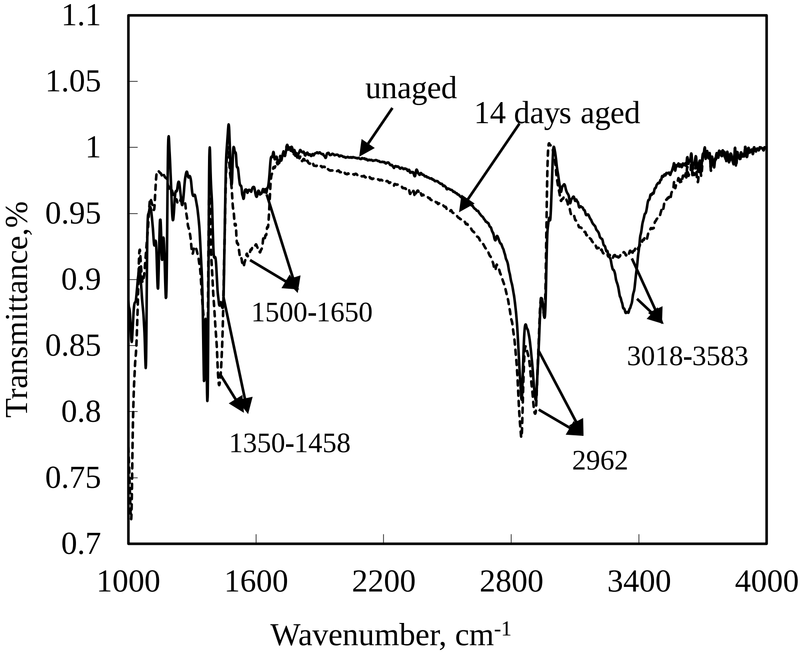

Figure 8.3 FT IR spectra of natural rubber cured with DIPP before and afterthermal ageing

Natural rubber vulcanizates cured with TMCH exhibits a different behaviour towards oxidative degradation (Figure 8.2). Here, upon ageing, the intensity of absorption band due to –OH stretching vibrations is considerably reduced without any change in the absorption band due to –CH_3 asymmetric stretch. After ageing, chain scission occurs as evident from the considerable decrease in the intensities of the absorption band at 1660 cm^{-1} (C=C stretch) and also at 1428-1368 cm^{-1} (scission of C-H bond).

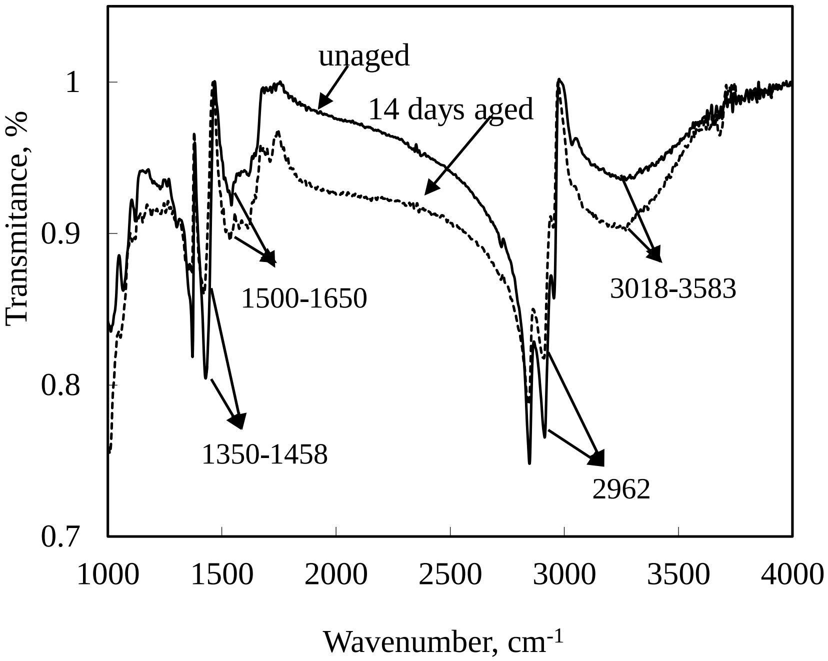

Figure 8.4 FT IR spectra of natural rubber cured with DCP before and after thermal ageing

The oxidative degradation behaviour of DIPP cured natural rubber vulcanizate is still different. The narrow absorption band at 3273 cm^{-1} (-OH stretch) in the unaged vulcanizate was converted into a less intense broad peak in the absorption spectrum of vulcanizate after ageing. Further, there is no change in the intensity of absorption band due to $-CH_3$ asymmetric stretch (2962, 2956 cm^{-1}). However, chain scission can be confirmed by the broad absorption bands in the range 1490- 1666 cm^{-1} and 150-1650 (C=O stretching mode).

For DCP, intensity of absorption band for –OH is enhanced while with $-CH_3$ is considerably reduced. For all vulcanizates, especially after ageing, the absorption band in the range 1800-1600 cm^{-1} (corresponding to C=O group) was enhanced due to the oxidation of main polymeric chain.

8.3.3 Thermogravimetric Analysis

The thermal stability of natural rubber vulcanizates cured with four different peroxides were analyzed by thermogravimetric analysis (TGA). The TGA(mass loss) curves and derivative curves (DTG) were shown in Figure 8.5. The onset decomposition temperature was calculated from the TGA curve by extrapolating the initial mass loss of the natural rubber vulcanizates. The maximum decomposition temperature was deduced from the derivative thermogravimetry curves.

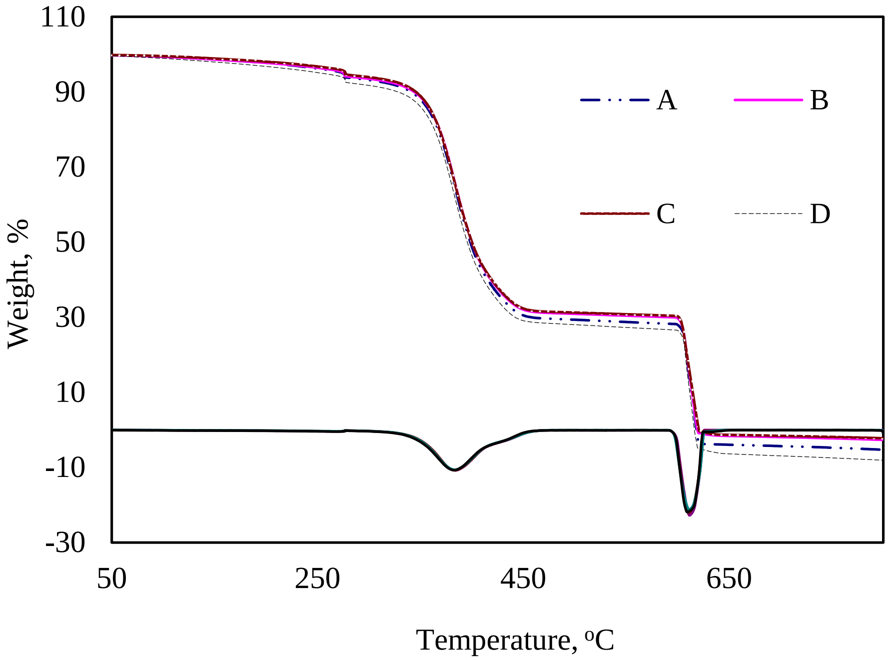

Figure 8.5 TGA and DTG curves of natural rubber vulcanizates cured with different peroxides

It can be observed that (Figure 8.5) all the vulcanizates undergo two step decomposition process. The first decomposition corresponds to the degradation of natural rubber and the second one is due to the loss carbon black (filler). Further, since all the peroxide cured vulcanizate produce thermally stable C-C crosslinks, thermal stability of all the vulcanizates are similar. Table 8.3 shows the initial (or onset, Ti) and the final (maximum) decomposition temperatures (Tmax) of the vulcanizates. The initial decomposition temperature is used to predict the thermal stability of rubber vulcanizates. DCP is found to have slightly lower Ti than other peroxides. The maximum decomposition temperatures of all the vulcanizates were similar as they contain the same type of elastomer and the nature of crosslinks is also same. A better understanding of the thermal stability of the vulcanizates can be deduced from the percent of weight retained at different temperatures.

Table 8.3 Ti and Tmax of peroxide cured natural rubber vulcanizates

Samples	**Ti, ^oC**	**Tmax, ^oC**
A	314.15	383.78
B	316.20	383.78
C	316.85	384.43
D	293.80	384.43

The thermal decomposition behaviour of peroxide cured vulcanizates was shown in Table 8.4. It can be seen that at 450^{o}C, among the four different types of peroxides used for the study, the thermal stability follows the order DIPP> TMCH> DHBP> DCP.

Table 8.4 Thermal decomposition characteristics of peroxide cured vulcanizates

Temperature, ^oC	Weight retained, %			
	A	B	C	D
100	99.13	99.37	99.56	98.91
200	97.75	97.76	98.09	96.77
300	93.16	93.53	93.96	91.71
350	88.09	88.73	89.01	86.06
400	48.84	50.09	50.26	46.51
450	30.50	32.06	32.38	29.08
500	29.33	30.90	31.28	28.01
550	28.72	30.41	30.82	27.27
600	28.00	29.74	30.31	26.51

8.3.4 Mechanical properties

One of the major disadvantages of peroxide cure is the poor mechanical properties of the vulcanizates owing to the rigid carbon - carbon crosslinks. Mechanical properties can be increased to great extent by the addition of fillers. The tensile properties of filled vulcanizates are generally governed by filler dispersion, particle size or specific surface area of filler and rubber -filler interaction [34, 35]. The tensile strength values of all vulcanizates are greatly improved by the addition of HAF black.The unaged mechanical properties of vulcanizates are given in Table 8.5. The rate of decomposition of organic peroxide depends on the strength of peroxide (-O-O-) bond, which in turn depends on the chemical nature of the alkyl group and hence the free radicals derived from it. The resonance stabilization, inductive effect and steric effect of free radicals play an important role in determining the final vulcanizates properties [22, 36].

Table 8.5 Physical properties of natural rubber vulcanized with different peroxides

Parameters	**DHBP**	**TMCH**	**DIPP**	**DCP**
Tensile strength, MPa	23.6	19.9	23.2	22.1
Elongation at break, %	368.5	350.8	398.6	320
100% modulus, MPa	2.1	1.78	1.84	2.92
200% modulus, MPa	7.38	6.68	6.60	11.36
300% modulus, MPa	16.1	14.18	13.68	19.8
Hardness, Shore A	51	50	52	58
Compression set 22h at 70°C,%	5.99	15.55	8.77	5.66
Compression set 22h at 100°C,%	14.46	52.27	18.97	16.34
Crosslink density, x10^{-5} mol/cm^3	5.34236	3.38295	4.89557	10.4925

The major decomposition products, which are indicative of the types of radicals generated form the thermal decomposition of various peroxides are shown in Table 2.2. DHPB, DIPP and DCP are dialkyl peroxides whereas TMCH is a peroxy ketal. DHBP, TMCH and DIPP primarily produce highly reactive t- butyloxy radicals, which further decomposes in to methyl radicals. However, the amount of t – butyl and methyl radicals vary among peroxides. In the case of DCP, since natural rubber is a highly unsaturated polymer, the approach of least sterically hindered methyl radical is preferred than t –butyloxy or cumyloxy radicals. Among the samples, highest tensile strength is observed for DHBP followed by DIPP, DCP and TMCH. The variation in tensile strength of vulcanizates can thus be accounted by the type and amount of reactive radicals generated during vulcanization.

Elongation is defined as the length at the breaking point expressed as a percentage of its original length. Usually, for peroxide cured vulcanizates suffers from lower elongation at break (EB) due to the strong and rigid carbon-carbon bond between the polymer chains. EB depends on the peroxide loading and hence crosslink density of rubber vulcanizates. As the peroxide loading increases more crosslinks are formed and EB decreases. Among the four different peroxides used, the vulcanizates cured with DCP showed the lowest EB owing to its high crosslink density. Among other peroxides, vulcanizates cured with DIPP shows a relatively higher value compared to others. From Table 8.5, it can be seen that both moduli (100, 200 and 300% elongations) and hardness followed the same trend as that of crosslink density.

Compression set is the measure of the vulcanizates ability to recover its original dimensions after being compressed under specified conditions. As peroxide vulcanization produces covalent crosslinks (C - C), which is thermally stable, and do not undergo any cleavage under compressed state. Therefore, peroxide cure results in vulcanizates with improved set resistance compared to suphur or other vulcanizing systems. At low temperature say 70^{o}C, DHBP and DCP shows lowest set values followed by DIPP. TMCH shows highest set value. At high temperature (100^{o}C), lowest set values were observed for DHBP followed by DCP, DIPP and TMCH. Further, the set value shown by TMCH is abnormally high. The variation in compression set values can be accounted by the nature and type of free radicals generated by thermal decomposition of peroxides. Therefore, for vulcanizates, were compression set is a critical parameter, DCP can be replaced with DHBP. Further, vulcanizates cured with DHBP has comparatively higher tensile strength and elongation at break than those cured with DCP, but it requires prolonged curr time (Table 8.2). As the CRI of TMCH is very high and optimum cure time and crosslink density are very low, therefore, generally it is not recommended for curing NR.

8.3.5 Mechanical properties after ageing

Ageing is the process of deterioration of desirable properties during storage or on service. The service life or shelf- life of rubber compounds is usually determined by ageing the samples at an elevated temperature and measuring the mechanical properties there after [37]. Here an attempt was made to study the thermal oxidative behaviour of the vulcanizates by analyzing the mechanical properties. The tensile strength, elongation at break and modulus (100% elongation) values of natural rubber cured with four different types of peroxides before and after ageing for 1, 3, 5, 7 and 14 days at 70°C are shown in Figures 8.6-8.8.All the properties were found to decrease gradually with increasing ageing periods. As all these properties are related to crosslink density of the vulcanizates, the decrease can be attributed to the chain scission during ageing in presence of oxygen.

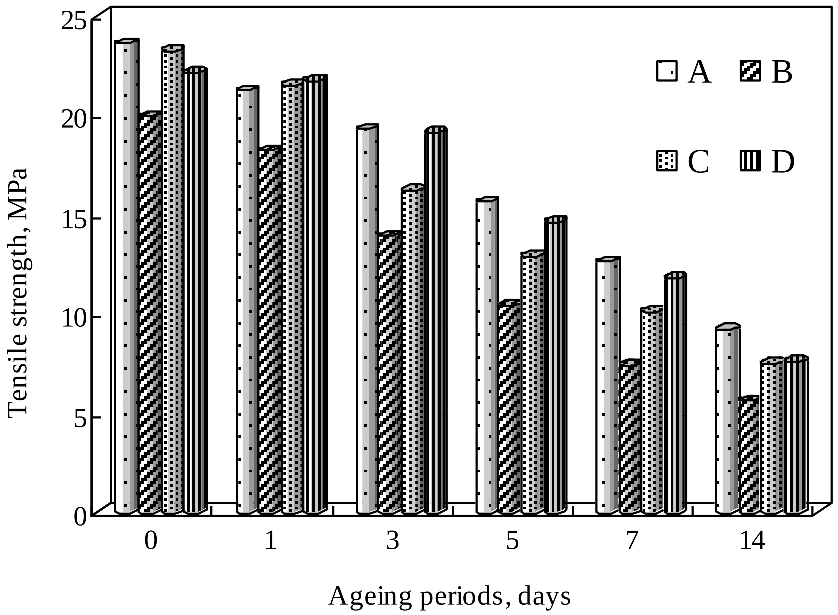

Figure 8.6 Tensile strength values of NR vulcanizates before and after ageing at 70^0C

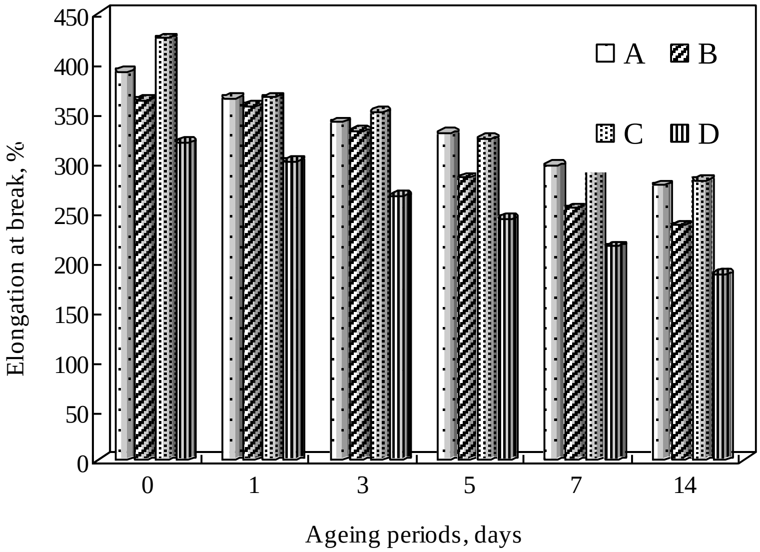

Figure 8.7 Elongation at break values of NR vulcanizates before and after ageing at 70^{0}C

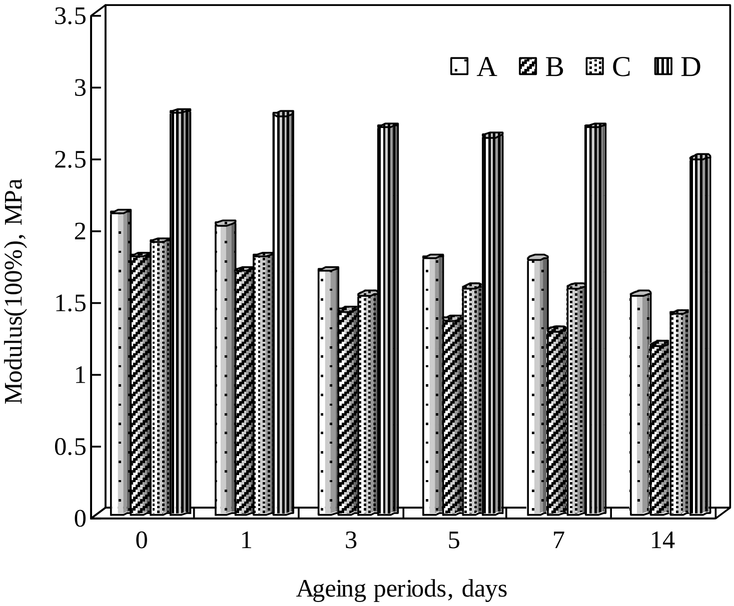

Figure 8.8 Modulus (100%) values of NR vulcanizates before and after ageing at 70^{0}C

The percentage retention in properties before and after ageing is shown in Table 8.6.It can be seen that among the four peroxides used, the highest percentage retention in tensile strength is observed for TMCH followed by DIPP, DCP and DHBP.

Table 8.6 Percentage retention in properties after ageing for 14 days

Parameters*	DHBP	TMCH	DIPP	DCP
Tensile strength, %	61.01	71.85	67.67	65.61
Elongation at break, %	29.34	34.71	33.64	41.56
100% Modulus, MPa	27.14	34.44	26.31	11.42

* after 14 days of ageing

8.4 CONCLUSION

The thermal oxidative behaviour of natural rubber cured with four different peroxides *viz* 2,5– dimethyl-2,5-*bis* (tert -butylperoxy) hexane (DHBP), 1,1'-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane (TMCH), 1,3 1,4-*bis* (*tert*-butyl peroxy isopropyl) benzene (DIPP) and dicumyl peroxide (DCP) were studied. The reactivity of the decomposition products of peroxides formed during vulcanization and accordingly the crosslinking efficiency of various peroxides was rated. Mechanical properties like tensile strength, elongation at break, modulus and compression set (70^o and 100^{o}C) of the vulcanizates cured with different peroxides were measured. The FTIR data revealed clear understanding of the nature of the by-products formed during vulcanization. Thermogravimetric studies revealed that the degradation behaviour of all vulcanizates were similar. The choice of the peroxide for natural rubber depends on the requirements of the application. Among the four peroxides, DHBP and DIPP registered the best mechanical properties, however the prolonged vulcanization time of DHBP is a constraint. However unlike DCP, DHBP imparted odour free vulcanizates. Out of the four different peroxides used DIPP showed the best overall balance of properties and thermal stability.

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CHAPTER 9

SUMMARY AND CONCLUSIONS

A detailed description on the major findings of the work done is reported in this chapter. The scope of future work is also mentioned.

The crosslinking of elastomers with peroxide has been known for more than 90 years and now-a-days it is widely accepted in polymer industry. Peroxides are commonly used as an alternative to sulphur in the vulcanization of elastomers and plastics. Although both peroxides and sulphur can crosslink most of the rubber/plastics, the chemistry behind their crosslinking reaction and properties of the cured material are entirely different. The peroxide crosslinked vulcanizates have very good heat resistance and hence the technique is important in automotive applications. Sulphur cure systems are also associated with a number of short comings. These include poor heat ageing properties, high compression set, reversion, high stress relaxation and blooming. There are many types of vulcanizing systems, deciding which system is optimal for a given application depends on the required curing conditions, the elastomer or elastomers blend employed and the desired physical properties of the final vulcanizates.

Peroxides are capable of vulcanizing most polymer types including unsaturated and saturated elastomer grades, flouroelastomers and silicones. Most of the peroxides that are commonly used in rubber formulations are very stable and require high temperature for decomposition. Emerging trends for improved performance and longer service life, particularly in the transportation industry, have prompted a renewed interest and acceptance for peroxide vulcanization. Property improvements including high temperature resistance, low compression set, potential for process safety (scorch), non-staining, non- discolouring systems and covulcanization with highly unsaturated elastomers are just a few of the benefits obtainable from peroxides. Though peroxide vulcanization can be performed very easily, this technique has not yet gained wide industrial importance. Low mechanical properties, residual smell of vulcanizates and higher curing time are some of the reasons for this lack of interest in industry. Moreover, a wide range of coagents are available and proper selection of coagents is critical in achieving optimum performance.

In this study, peroxide vulcanization of natural rubber is carried out mainly with dicumyl peroxide. The kinetics has been studied at various temperatures viz 150,155,160 and 165°C. Dicumyl peroxide (DCP) was used as the crosslinking agent. Thermal decomposition of peroxide followed a first order free radical decomposition reaction. The percentage of residual peroxide was calculated from the cure kinetic data. The effect of residual peroxide on mechanical properties was studied at various peroxide levels and also by extending the cure time (from t_{90} to t_{95} and then to t_{100}). It was found that residual peroxide has no significant effect on tensile strength, elongation at break, modulus and low temperature compression set. Excess peroxide was found to cause high compression set at elevated temperature.In such cases the cure time was selected in such a way so as to get minimum residual peroxide in the product. Results indicated that peroxide concentration is the dominant factor which controls the crosslink density and hence the properties of the vulcanizates.

Co-curing agents or coagents are used widely in industry to overcome the problems associated with peroxide cure. Therefore, the role of various coagents such as zinc diacrylate (ZDA), trimethylolpropane trimethacrylate (TMPTMA) and triallyl cyanurate (TAC) in the peroxide vulcanization of natural rubber (NR) was followed by Fourier Transform infrared spectroscopy. Crosslinking mechanism of peroxide in natural rubber was interpreted by comparing the spectra of cured and uncured vulcanizates. The predominance of hydrogen abstraction over radical addition was established (at 160°C). A crosslinking mechanism was proposed for coagent ZDA in natural rubber.

The effect of various coagents like zinc diacrylate (ZDA), Trimethylolpropane trimethacrylate(TMPTMA), Triallyl cyanurate (TAC) and n- butyl acrylate (nBA) on the mechanical properties of peroxide cured natural rubber vulcanizates were analyzed. Comparison of mechanical properties showed that all coagents enhanced the crosslink density of the vulcanizates. Coagent ZDA is capable of introducing both ionic and covalent crosslinks in the vulcanizates and is a unique system having the best characteristics of both peroxide and sulphur cure systems. Coagent TMPTMA is suitable for applications where high modulus and ageing resistance are required. nBA enhances the elongation at break values of vulcanizates with an unpleasant odour. In a highly unsaturated rubber like NR, TAC undergoes predominantly cyclisation and forms coagent domains in the vulcanizates which is unfavourable as far as mechanical properties are concerned.

A statistical method, Response surface methodology, is ued for assessing the role of various compounding ingredients in peroxide vulcanization of natural rubber. A Face Centred Central Composite Design (FCCD) with four factors at three different levels was used to obtain the relationship between vulcanizate properties and the level of ingredients. The four factors selected were filler/oil ratio and the contents of zinc oxide, antioxidant and coagent. The vulcanizates were evaluated for their mechanical properties like tensile strength, elongation, modulus (M_{100}), tear strength, hardness, compression set (70 and 100°C) and crosslink density. Regression equations were generated to model the properties of interest and response surfaces and contour diagrams were plotted. The contour plots for all properties were overlaid to obtain an optimum region for a desired set of specifications. The verification experiment confirmed the predictions of mechanical properties and the suitability of FCCD for optimizing the formulations of peroxide cured natural rubber vulcanizates.

The thermal stability and thermal degradation kinetics of natural rubber layered silicate nanocomposites have been analyzed by thermogravimetric analysis. Among the different organoclays selected, the highest thermal stability is exhibited by MMT-M2HT. The kinetics of decomposition was investigated by Liu and Fan method. The thermal decomposition was found to be a first order reaction in both unfilled and filled vulcanizates. The organoclay MMT-M2HT showed highest activation energy which supports the improved thermal stability of the vulcanizate.

The thermal oxidative behaviour of natural rubber cured with four different peroxides *viz* 2,5-dimethyl-2,5- bis (tert -butylperoxy) hexane (DHBP), 1,1’-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane (TMCH), 1,3 1,4-bis (tert-butyl peroxy isopropyl) benzene (DIPP) and dicumyl peroxide (DCP) were studied. The reactivity of the decomposition products of peroxides formed during vulcanization and accordingly the crosslinking efficiency of various peroxides was evaluated. Mechanical properties like tensile strength, elongation at break, modulus and compression set (70^o and 100^{o}C) of the vulcanizates cured with different peroxides were measured. The FTIR data revealed clear understanding of the nature of the by-products formed during vulcanization. Thermogravimetric studies revealed that the degradation behaviour of all vulcanizates were similar. The choice of the peroxide for natural rubber depends on the requirements of the application. Among the four peroxides, DHBP and DIPP registered the best mechanical properties, however the prolonged vulcanization time of DHBP is a constraint. However unlike DCP, DHBP imparted odour free vulcanizates. Out of the four different peroxides used DIPP showed the best overall balance of almost all properties and thermal stability.

Future scope

In polymer industry, organic peroxides are used in a wide range of applications including crosslinking elastomers, silicones, thermosetting polymers, thermosetting resins, polymerization of numerous monomers, polymer modifications, curing optical polymers etc. 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. Compared to sulphur vulcanization, organic peroxide cured elastomers exhibit superior physical properties such as low compression set, improved heat resistance, and rapid vulcanization without reversion. By using various organic peroxide-coagent systems to various synthetic rubbers a large database can be generated on fundamental and application aspects. Scorch safety (premature crosslinking) is another important problem associated with peroxide cure system. A cost-effective peroxide-coagent system to overcome the present difficulties is an area, were interest can be put into.

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ABBREVIATIONS AND SYMBOLS

ABS	Acrylonitrile styrene vinyl copolymer
ACM	Polyacrylate rubber
AEM	Poly ethylene co-methacrylate
AO-1010	*tetrakis* (3-(3, 5-di-tert-butyl-4-hydroxy phenyl) propionate)
AO-445	4, 4’-*bis* (α, α- dimethyl benzyl) diphenyl amine
AO-ZMTI	Zinc-2- mercaptotoluimidazole
ASTM	American Society for Testing and Materials
AU/EU	Polyurethane rubber
BHT	2, 6-di-tert-butyl-p-cresol
BIS	Bureau of Indian Standards
BMI-MP	N, N’-m- phenylene dimaleimide
BR	Polybutadiene rubber
CC	Commercial clay
CIIR	Chlorobutyl rubber
CO	Epichlorohydrin rubber
CPE	Chlorinated polyethylene
CR	Polychloroprene rubber
CRI	Cure rate index

CSM	Chlorosuphonated polyethylene
d	Interplanar distance
DAP	Diallyl phthalate
DCP	Dicumyl peroxide
DEG	Diethylene glycol
Dw	Deswollen weight
FCCD	Face centred central composite design
DHBP	2, 5- dimethyl-2, 5- *bis* (tert -butylperoxy) hexane
DIPP	1, 3 1,4-*bis* (*tert*-butyl peroxy isopropyl) benzene
DMA	Dynamic mechanical analysis
DOTG	Diorthotolyl guanidine
DPG	Diphenyl guanidine
DSC	Differential scanning calorimetry
DTG	Differential thermogram
E’	Storage modulus
E’’	Loss modulus
Ea	Activation energy
EB	Elongation at break
EBA	Ethylene butylacrylate copolymer
ECO	Epichlorohydrin copolymer
ENB	Ethylidenenorbornene

EOM	Poly ethylene co-octene
EPDM	Ethylene propylene diene rubber
EPM	Ethylene propylene rubber
EVA	Ethylene vinyl acetate copolymer
FKM	Fluoro elastomers
FTIR	Fourier Transform infrared
HAF	High abrasion furnace
HLT	Half-life temperature
HNBR	Hydrogenated acrylonitrile butadiene rubber
HNR	Hydrogenated natural rubber
HTE	High throughput experimentation
IIR	Butyl rubber
IR	Polyisoprene rubber
ISNR	Indian Standard Natural Rubber
K	Kelvin
k	Rate constant
LDPE	Low density polyethylene
M_{100}	Modulus at 100% elongation
Mc	Molar mass between crosslinks
m-EPDM	Maleated Ethylene propylene Rubber
M_H	Maximum torque

M_L	Minimum torque
MMT	Montmorillonite
MMT-2M2HT	dimethyl, dihydrogenated tallow quaternary ammonium chloride modified montmorillonite
MMT-2MBHT	dimethyl, benzyl, hydrogenated tallow quaternary ammonium chloride modified montmorillonite
MMT-M2HT	methyl, dihydrogenated tallow ternary ammonium modified montmorillonite
ρr	Density of rubber
ρs	Density of solvent
MPa	Mega Pascal
n	order
NBR	Acrylonitrile butadiene rubber
NMR	Nuclear magnetic resonance
NR	Natural rubber
P	Permeation coefficient
PB	1, 2-Polybutadiene
PE	Polyethylene
PEG	Polyethylene glycol

PIB	Polyisobutene
Po	Initial plasticity
PP	Polypropylene
PRI	Plasticity retention index
PVC	Polyvinylchloride
Q	Silicone rubber
R	Universal gas constant
SBR	Styrene butadiene rubber
Sw	Swollen weight
T	Polysulphidic rubber
$t_{½}$	Half-life
t_{90}	Optimum cure time
TAC	Triallyl cyanurate
TAIC	Triallyl isocyanurate
tan δ	Mechanical loss factor
TBC	4-*tert*-butylcatechol
Tg	Glass transition temperature
TEMPO	(2, 2, 6, 6-Tetramethylpiperidin-1-yl) oxyl, or (2, 2, 6, 6-tetramethylpiperidin-1-yl) oxidanyl
TGA	Thermogravimetric analysis

TMCH	1, 1’-di (*tert*-butylperoxy)-3, 3, 5-trimethylcyclohexane
TMPTMA	Trimethylolpropane trimethacrylate
TMQ	2, 2, 4-trimethyl -1,2-dihydroquinoline
TPVs	Thermo plastic vulcanizates
t_{s2}	Scorch time
UTM	Universal testing machine
UV	Ultra violet
V	Molar volume of the solvent
XRD	X-ray diffraction
ZDA	Zinc diacrylate
ϕ	Volume fraction of rubber in the swollen gel
θ	Incident angle
λ	Wavelength
χ	Interaction parameter
υ	Crosslink density

LIST OF PUBLICATIONS AND PRESENTATIONS

Publications in International/National Journals

1. **Rejitha Rajan**, Siby Varghese, K. E George,*"Kinetics of peroxide vulcanization of natural rubber"*, Journal of Rubber Plastic and Recycling Technology, Volume 28, No. 4, 201-220, 2012.
2. **Rejitha Rajan**, Siby Varghese, K. E George,*"Cure kinetics and coagent selection in peroxide vulcanization of natural rubber"* Rubber Science, Volume 25, No.2 , 307-314, 2012.
3. **Rejitha Rajan**, Siby Varghese, K. E George, *"Role of coagents in peroxide vulcanization of natural rubber"* Rubber Chemistry and Technology, Vol. 86, No. 3, pp. 488–502, 2013.
4. **R. Rajan**, S. Varghese, K. E. George,"*Die Rolle von Coagenzienbei der Peroxidvulkanisation von Naturkautschuk"*GAK 5, 300-307, 2014.
5. **Rejitha Rajan**, Siby Varghese, K. E George,*"Peroxide vulcanization of polymers",* Rubber Science, Volume 27, No.1 , 98-126, 2014.
6. **Rejitha Rajan**, Siby Varghese, Meera Balachandran, K. E George, *"Response Surface Methodology: A Tool for Assessing the Role of Compounding Ingredients in Peroxide vulcanization of Natural rubber"* (Rubber Chemistry and Technology, Vol. 89, No. 2, pp. 211–226, 2016.).

7. **Rejitha Rajan**, Siby Varghese, K. N. Madhusoodanan, M.A. Fancy, K. E George, *“Kinetic analysis of peroxide cured natural rubber/layered silicate nanocomposites using thermogravimetry”* (Communicated to Thermochimica Acta).

8. **Rejitha Rajan**, Siby Varghese, K. E George,‘Effect of coagents on the mechanical properties of peroxide cured natural rubber vulcanizates” (Communicated to Rubber Science).

9. **Rejitha Rajan**, Siby Varghese, M.A. Fancy, Reethamma Joseph, K. E George, *“Thermal oxidative behaviour of peroxide crosslinked natural rubber”* (Communicated to Polymer Degradation and Stability).

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1. **Rejitha Rajan**, Siby Varghese, K. E George,*“Kinetics of peroxide vulcanization of natural rubber”*, Advances in Polymer Technology, (APT’10), Rubber Park, Irapuram, February 2010.

2. **Rejitha Rajan**, Siby Varghese, K. E George, *“Role of coagents in peroxide vulcanization of natural rubber”* 24th Kerala Science Congress, Rubber Research Institute of India, Kottayam, January 29-31, 2012.

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