NEW ACCELERATOR SYSTEM FOR LOW TEMPERATURE CURING OF ELASTOMERS

WITH SPECIAL REFERENCE TO NR, NBR AND NR/BR BLENDS

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……to my husband

Certificate

*This is to certify that the thesis entitled "**New accelerator system for low temperature curing of elastomers with special reference to NR, NBR and NR/BR blends**" is based on the original work carried out by **Ms. Shiny Palaty** under my supervision in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi-22, and no part of this thesis has been presented for any other degree from any other institution.*

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DECLARATION

*I hereby declare that the thesis entitled "**New accelerator system for low temperature curing of elastomers with special reference to NR, NBR and NR/BR blends**" is the original work carried out by me under the supervision of Dr. Rani Joseph, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi-22, and no part of this thesis has been presented for any other degree from any other institution.*

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Shiny Palaty

CONTENTS

Chapter 1

INTRODUCTION

Rubbers or elastomers constitute an important class of engineering materials, like metals and ceramics, without which modern technology would be unthinkable. It has such remarkable and desirable properties that it is being put to many engineering applications like bearings, springs and seals in addition to the manufacture of bulk products like tyres, tubes, belts, hoses etc. Rubber, in its raw state, is not suitable for such engineering applications. In 1839 Charles Goodyear[1] discovered that rubber heated with sulphur gave products, which were far superior to the original material and were not so sensitive to temperature changes. Goodyear[2] patented the process in 1844 and in 1843 Thomas Hancock independently patented a similar process. The word vulcanization had been suggested to this process by William Brockedan, who derived it from 'Vulcan', the God of fire and volcanoes to signify that both heat and sulphur were involved in the reaction. Vulcanization is the process of conversion of rubber, by any treatment, from a plastic substance of very low strength and breaking elongation into a resilient, highly elastic material of considerable strength. From the chemical point of view, vulcanization is the process whereby the flexible, discrete rubber chains are joined together by crosslinking reactions giving a three dimensional network.

Studies on the chemistry of vulcanization[3] play a central role in the efforts to achieve better product performance from natural and synthetic rubbers. The oldest method of vulcanization consisted of heating rubber with sulphur. But this form of 'sulphur only' vulcanization is a very slow process and takes several hours or even days to reach optimum curing depending on the temperature of vulcanization and the nature of the rubber used. This yields vulcanizates of very low physical and mechanical properties. Also, they have a strong tendency to revert and their resistance to ageing is poor. Vulcanization with sulphur alone is therefore of no technological importance at all. The ultimate goal of vulcanization is to obtain the desired vulcanizate properties. These properties to a great extent depend on the network structure of the cured elastomer, which in turn, depends on the chemistry of vulcanization. Therefore an understanding of the vulcanization chemistry and its relationship with the resulting network is important to achieve the desired properties.

There are two tendencies towards the interpretation of the general nature of chemical reaction of sulphur with rubber. Farmer and co-workers [4-7] proposed a free radical chain mechanism whereas Bateman [8-15] and co-workers favoured a polar mechanism for the structural changes in rubber during vulcanization.

1.1. Accelerated vulcanization

The addition of certain organic compounds greatly accelerate the vulcanization reaction. These substances, known as 'accelerators', can reduce the cure time from hours to minutes or even seconds at higher temperatures. Furthermore, in the presence of an accelerator, the amount of sulphur required to get a vulcanizate of desired properties is significantly less. In addition to the organic compounds, some basic salts were also initially used to accelerate the sulphur vulcanization. They were litharge, lime, magnesium oxide and zinc oxide. Organic accelerators were first utilized in the rubber industry in the beginning of the twentieth century[16-21]. Oenslager[19] found that the addition of small amounts of aniline, the first organic accelerator used, greatly increased the rate of vulcanization and also improved the final vulcanizate properties. Later it was discovered that a wide variety of amines function similarly[22]. Thus organic bases were the first vulcanization accelerators for rubber[23-25]. Other accelerators such as diphenyl guanidine, di-orthotolyl guanidine and hexamethylene tetramine came into use around 1910 and were a great relief for the people in the rubber industry because of their relative non-toxic character compared to the former ones[26-27].

The mixing of rubber with various ingredients generally known as compounding is an essential step before vulcanization. The main objectives of compounding are to facilitate processing and fabrication, to achieve the required balance in vulcanizate properties and provide durability, all at the lowest possible cost. The various ingredients generally added to rubber during compounding include processing aids, accelerators, activators, fillers, antidegradants, vulcanizing agents and a variety of other materials which are compiled into a recipe[28]. Each ingredient in the recipe has a specific function either in the processing, vulcanization or end use of the product. Each ingredient added to maximize one property may reduce another. Thus compounding involves a compromise.

The accelerators require activators like zinc oxide and co-activators like stearic acid in all types of rubbers[29]. These activators develop the full potential of the accelerators thereby making vulcanization faster. Fillers are added to rubber compounds to modify its properties and to reduce cost. Reinforcement by a filler is the enhancement of one or more properties of an elastomer by the incorporation of that filler, thus making it more suitable for a given application[30-31]. Carbon blacks offers the most potential reinforcement[32-35]. The reinforcing effect of carbon black on rubber is well known[36-41]. Earlier workers have studied the reinforcement of silica filler in NR, in the presence of silane coupling agents[42]. Fillers like calcium carbonate and clay are found to reduce the tensile properties but, silane coupling agent treated clays are found to show improved tensile properties[43-44].

Various processing aids are added to rubber during compounding to make the processing easy. These processing aids include plasticizers, peptizers, factices, tackifiers etc. which improve the elasticity and tackiness of rubber. Rubbers are protected against oxidative degradation by incorporating antioxidants[45]. These antioxidants or protective agents, oppose oxidation and in many cases, suppress many undesirable reactions promoted by oxygen or peroxides. Vulcanizing agents are substances which bring about the actual crosslinking. The most important vulcanizing agent for rubber is elemental sulphur[46]. Other vulcanizing agents include sulphur donors like tetramethyl thiuram disulphide, peroxides, metal oxides, resins etc. Selection of the vulcanizing agent primarily depends on the rubber to be vulcanized. Diene rubbers like natural rubber (NR), polybutadiene rubber (BR), styrene butadiene rubber (SBR), nitrile rubber (NBR) etc. can be easily vulcanized with sulphur. Sulphur vulcanization is preferred for several reasons - (1). high flexibility during compounding (2).better mechanical properties for the vulcanizates (3). easier onset of vulcanization etc. In the case of saturated rubbers like EPM and silicone rubber, peroxide vulcanization is preferred. Neoprene rubber (CR) can be vulcanized with metal oxides like magnesium oxide and zinc oxide which form bridge type crosslinks.

The actual compounding or mixing of the various ingredients of the recipe is done on a two roll mill or internal mixers like the Banbery mixer. The compounded stock is then vulcanized using heat and pressure under specified conditions. The practical aspects of compounding and vulcanization vary from rubber to rubber depending on whether it is saturated or unsaturated, natural or synthetic etc.

1.2. Natural and synthetic rubbers

Rubbers are broadly classified into natural and synthetic. Synthetic rubbers are further classified into two categories namely, general purpose rubbers – like SBR, BR etc which are intended for the manufacture of tyres and general mechanical products and special purpose rubbers – NBR, CR etc. which have special properties and are in consequence, intended for specialized applications.

NR is made up of cis 1,4 isoprene units arranged in a highly stereo regular manner. The molecular weight of the polymer ranges from 10^5 to 10^6 and it varies widely[47]. Due to the high structural regularity, NR tends to crystallize on stretching. This strain induced crystallization gives high tensile strength for its gum vulcanizates. NR is preferred in many areas of application because of its superior building tack, green stock strength, better processibility, high resilience and excellent dynamic properties.

Nitrile rubber is a co-polymer of butadiene and acrylonitrile. NBR has good resistance to a wide variety of oils and solvents[48] and hence is widely used in products like oil seals, pipe protectors, blow out preventors etc. Major properties of NBR depend on the acrylonitrile content (ACN) and usually it varies from 20 – 50 % by weight. NBR shows no self reinforcing effect, as there is no crystallinity[49]. NR and NBR differ in the degree of unsaturation, polarity etc.[50]. So the nature and amount of the compounding ingredients are different for NR and NBR. The elastomer should have a certain viscosity in order to incorporate fillers and other compounding ingredients easily and to disperse them uniformly. NR has got a high viscosity. The viscosity can be reduced by mastication. Compared to NR, synthetic rubbers are more uniform in quality and compounds are more consistent in both processing and product properties. They are also supplied at viscosity ranges, which facilitate good dispersion of ingredients. Since NBR contains lesser unsaturation than NR, it requires higher concentration of accelerators with a corresponding reduction in the amount of sulphur.

Polybutadiene comes under general purpose rubbers[51]. However, one type of rubber may not possess all the physical properties desired in a finished product. Polymers are conveniently and economically modified by combination of two or more of them[52]. Much attention is currently being devoted to the simplest route for combining the outstanding properties of different existing polymers, ie., the formation of polymer blends[53-54]. For example, in tread compounds, the high abrasion resistance conferred by the use of BR is desirable but the poor road holding and rib tearing properties are not. Hence, blends of BR with NR and SBR are employed.

1.3. Mechanism of rubber vulcanization

In general, vulcanization processes are not simple chemical reactions, but involves complex mechanisms. The unaccelerated sulphur formulation consists of rubber and sulphur while the accelerated sulphur system contains rubber, accelerator and sulphur. In addition to this, both the types include zinc oxide- stearic acid activator system also. There is a third category also in which elemental sulphur is not present, instead, the accelerator provides the sulphur for vulcanization. These sulphurless systems are generally referred to as sulphur donor formulations.

The mechanism of unaccelerated or the sulphur only vulcanization involves reactions such as double bond migration, isomerization, chain cleavage, cyclisation, formation of vicinal crosslinks etc.[55-62]. The mechanism was studied using radical scavengers[63] and electron paramagnetic resonance techniques[64]. These studies revealed a polar (ionic) mechanism in these systems. However, the possibility of the S_8 ring undergoing homolytic ring opening, producing a radical reaction also is possible[69]. Although certain experimental results would be explained by a radical process, the general consensus is that sulphur only vulcanization occurs via polar mechanism.

Although the mechanism of accelerated vulcanization has been extensively studied over last few decades, there is still much disagreement as to its exact mechanism. Crag[11], Dogadkin[12-13], Bevilacqua[14], Scheel[15], Blokh[65], Tsurugi and Fukuda[66-67] and their co- workers have advanced free radical mechanism to explain the results of accelerated sulphur vulcanization whereas Bateman[3], Porter[68], and Allen[69] suggested polar mechanism as a logical extension of their proposed mechanism for unaccelerated sulphur vulcanization. On the other hand, Shelton, McDonel[63] and Coran[70] proposed mechanism involving both free radical and ionic species. In fact, it is now believed that in a complex mixture of rubber, ZnO, sulphur, fatty acids and accelerators, both free radical and ionic reactions may occur simultaneously at different stages of the overall vulcanization reaction depending on the system used[71].

In the vulcanization process, sulphur form crosslinks between, the long rubber chains to form a three-dimensional net work. In this network, sulphur is combined in a number of ways as shown below[72].

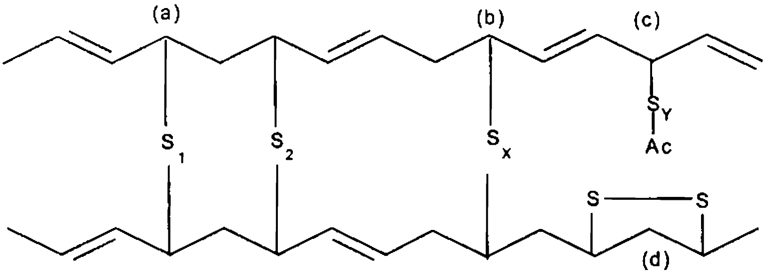


Fig. 1. 1. A diagrammatic representation of the network structure of a rubber vulcanizate

It may be present as monosulphidic or disulphidic crosslinks as shown in (a), as polysulphidic crosslinks as shown in (b), as pendent sulphides as shown in (c) or as cyclic sulphides as shown in (d).

The ratio of accelerator to sulphur determines the efficiency with which S is converted into crosslinks and also the nature of crosslinks. Based on the sulphur accelerator ratio, the sulphur vulcanizing system can be classified as[73]

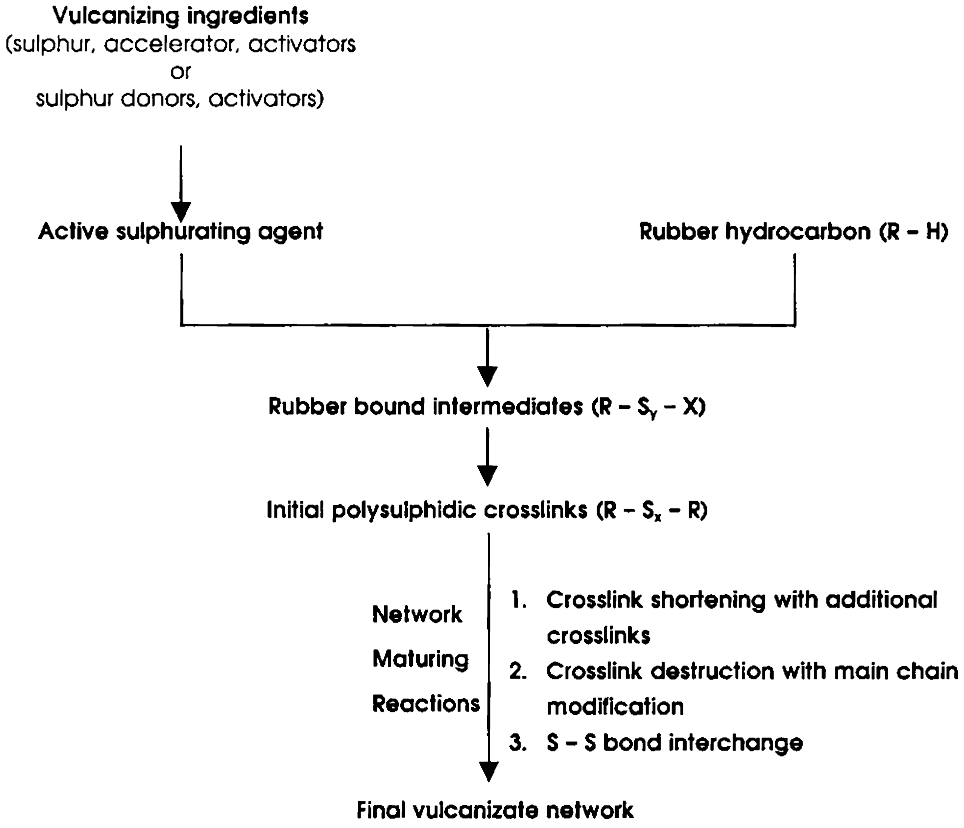
(a) the conventional or high sulphur vulcanizing (CV) system in which the level of sulphur is in the range of 2–3.5 phr and the corresponding level of accelerator is in the range of 1–0.4 phr

(b) the efficient vulcanizing (EV) system consisting of 0.3 - 0.8 phr sulphur and 6.0 - 2.5 phr accelerator.

(c) the semi efficient vulcanizing (SEV) system with the level of sulphur lying between 1.0 - 2.0 phr.

Structural characterisation of sulphur vulcanized rubber networks were done by B.Savilla et.al.[74]. In EV systems, the network will contain an abundance of mono sulphidic crosslinks, usually accounting for at least eighty percent of the total. As a measure of the improved crosslinking efficiency, the number of sulphur atoms combined for every chemical crosslink is unlikely to exceed five and can be as low as two[75]. These systems are usually suitable for products that need improved reversion resistance during vulcanization and those which are exposed to higher temperatures. But these systems are comparatively expensive. Owing to the increased number of polysulphidic crosslinks, the CV systems find use in products that do not require substantial heat resistance during manufacture and service. These systems are comparatively less expensive. SEV system is usually a compromise between EV and CV systems.

The vulcanization properties are not functions of crosslink density only, but they are affected by the type of crosslink, nature of polymer, type and amount of filler etc[76-77]. The overall course of accelerated sulphur vulcanization can be represented as follows[78].



Scheme 1.1 – Generalised mechanism of vulcanization

In the scheme, R-H denotes the rubber hydrocarbon, H being an allylic hydrogen in a methyl or methylene group. The active sulphurating agent is the species that reacts with rubber hydrocarbon to form C – S bonds. It is produced by a sequence of reactions from sulphur, accelerator and activator or from a sulphur donor such as TMTD and activator. The active sulphurating agent reacts directly with the rubber molecule to give a rubber bound pendent group, in which a fragment derived from the accelerator or sulphur donor, is linked through two or more sulphur atoms to the rubber chain. These pendent groups form crosslinks either by direct reaction with another rubber molecule or by disproportionation with a second pendent group of a neighbouring rubber chain. The polysulphidic crosslinks are formed first. These are thermally unstable and chemically reactive and undergo a number of competing reactions, which are termed network maturing reactions, leading to the final network structure.

1.4. Classification of accelerators

Accelerators play an important role in the vulcanization of rubber and they affect the scorch safety, the rate of cure and the length and the number of the crosslinks formed[79]. Accelerators are used in a rubber compound because of the following reasons[80].

(a) They reduce the cure time and increase the aging resistance of the vulcanizates.
(b) They increase the rate of vulcanization.
(c) They help to reduce the amount of sulphur, thereby achieving optimum vulcanizate properties.

According to reactivity, accelerators are classified as (1). Ultra accelerators, (2). Semi ultra accelerators, (3). Medium fast accelerators, (4). Slow accelerators.

According to their chemical composition, accelerators are classified as

(a) Dithiocarbamates
(b) Thiurams
(c) Xanthates
(d) Thiazoles
(e) Aldehyde amine accelerators
(f) Basic accelerators
(g) Sulphenamide accelerators

Organic compounds were not used as accelerators until 1906 when the effect of aniline and its derivatives (thiocarbanilides) on sulphur vulcanization was discovered by Oenslager[19]. Later several other organic compounds were shown to have accelerating activity and majority of them were nitrogen containing organic bases[81-83]. Earlier it was believed that the basicity of these substances, rather than chemical constitution, primarily governs its effectiveness. But it was subsequently established that the accelerating activity of organic bases is not proportional to their basicity[84-85]. The discovery of nitrogen free accelerators such as zinc alkyl xanthates[86] and zinc thiophenols[87] rejected the theory that the element nitrogen was responsible for the accelerating activity.

During the first two decades of the last century, a large variety of accelerators were developed. Molony[88] introduced a reaction product of amines from beet molasses with carbon disulphide which was later identified as tetramethyl thiuram disulphide (TMTD). Granski and co-workers made a detailed study of the vulcanization of NR with TMTD[89-90]. Investigations on the effects of zinc oxide led to the discovery of two most important accelerators, diphenyl guanidine (DPG) and mercapto benzothiazole (MBT)[91]. Around 1920, organic accelerators came into common use and it was discovered that thiuram disulphide enable vulcanization to proceed without sulphur[80]. In 1925, Sebrell[92-93] and Bruni[94] discovered independently that 2- mercapto benzothiazole, its homologues, its disulphides[95-96] and its metal salts are very effective accelerators, which yields vulcanizates of improved physical properties. Chatterjee and Sircar made a detailed study of the reaction between MBT and rubber[97]. Mercaptodibenzothiazyl disulphide (MBTS) was the first delayed action accelerator, which give great scorch safety at higher processing temperatures. With the introduction of synthetic elastomers and the use of fine furnace blacks, delayed action accelerators like sulphenamide type (eg. Benzothiazyl derivatives of sulphenamide) were developed for long processing safety and satisfactory cure rates. Attempts to modify the extra ordinary fast ammonium dithiocarbamate resulted in zinc dialkyl dithiocarbamates.

Several workers have studied the effect of amines on vulcanization[98-101]. The most studied amine was hydrofuramide which is a reaction product of furfural and ammonia. It is found to increase the cure percentage, decrease the scorch time and increase the vulcanization rate.

1.5. Single accelerator systems

The most common vulcanization systems used in industrial applications are the accelerated sulphur formulations. The accelerated sulphur systems can further be classified into single accelerator systems and binary accelerator systems. A schematic representation of a typical cure curve for the accelerated sulphur system is shown in fig 1.2.[102].

The curve illustrates three main regions of cure. The first region is the scorch delay period or the induction period in which majority of the accelerator chemistry takes place. During this period, various accelerator complexes are formed which are the active sulphurating agents. The extend of this region varies with different accelerators. For example, there is very little scorch time in thiuram types and very long scorch time in sulphenamide types. The second region is the crosslinking period, where the initial network structures are formed and the accelerator intermediates are consumed. The final stage is the overcure or reversion period, during which the property deterioration occurs.

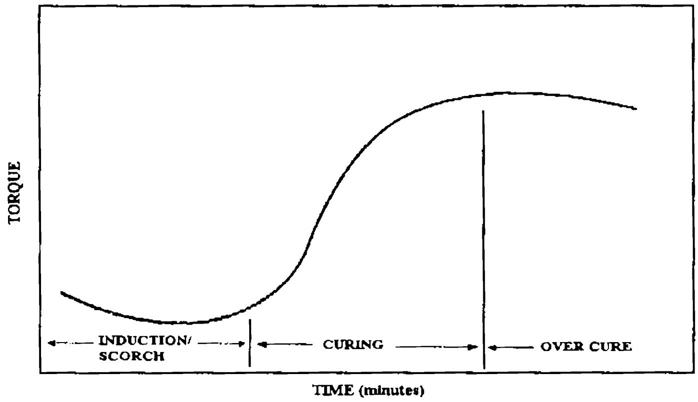


Fig. 1.2. Typical cure curve for the accelerated sulphur system

From the mechanistic point of view of accelerated sulphur vulcanization, the single accelerator systems are the most widely studied. This is mainly due to their widespread use and simplicity of the mechanism. However, the amount of research in the fundamental chemistry of binary accelerator system is also rapidly growing.

1.6. Binary accelerator system

The use of vulcanization systems composed of two or more accelerators finds wide technological applications in recent years. There is no ideal accelerator ie., one that is absolutely safe at processing temperature and fast curing at vulcanizing temperatures. Use of suitable binary accelerator system has been found to approach this ideal behavior to some extend[103-105]. Such binary systems have the following advantages.

(1) They prevent premature vulcanization

(2) Permit the vulcanization to be carried out at lower temperature in lesser time

(3) Produce vulcanizates with superior physical and mechanical properties compared to those cured with single accelerator.

In the binary system, the accelerator present at a reasonably high level is called primary accelerator and that present in smaller amounts is called the secondary accelerator. A large number of binary systems have been developed for practical applications. It has been known for a long time that amines are powerful activators of thiazole type accelerators. Many amines like diphenyl guanidines are used in combination with other accelerators such as MBT or sulphenamides to activate the vulcanization reactions. However, present day binary accelerator systems mainly consists of benzothiazole and thiocarbamate derivatives. To increase the scorch delay of thiuram systems, usually MBT and sulphenamides are added additionally[106].

Eventhough, great deal of work has been done on elucidating the mechanism of vulcanization with single accelerator, work on binary systems is less. Jones[107] suspected that the action of bases was similar to that of fatty acids and reported that diphenyl guanidine (DPG), like a fatty acid, could act as a transmitter of zinc by forming a zinc diphenyl guanidine compound. His theory can be applied in principle to all accelerators having amine bases soluble in rubber. But it could not satisfactorily interpret the action of all the known binary systems used for the vulcanization of rubbers. Misatoya and Aoe[108-110] explained the higher activity of binary systems by the formation of either eutectic mixture or salt forming compound having better solubility in rubber and greater chemical reactivity. Skinner and Watson[111-112], Dogadkin and collaborators[113-115] investigated a number of accelerator combinations and found mutual activity with many of them. They classified the binary systems into three groups.

(1) Systems with synergistically active accelerators

(2) Systems with a pair of accelerators in which the activity of the pair does not exceed the activity of the more active accelerator.

(3) Systems with additive action of accelerators.

The first group of accelerators includes mixtures of disulphides (MBTS, TMTD etc.) or mercaptans (MBT) with nitrogen containing organic bases and disulphides with sulphenamides. The second system consists of sulphenamides with nitrogen containing organic bases. The third category exhibiting additive effect involves sulphenamides in combination with TMTD and those containing combination of accelerators belonging to the same chemical class.

Dogadkin and collaborators[116-117] suggested that, in the initial stage of vulcanization, the accelerators interact with one another to form an active complex, which then disintegrates with the formation of active free radicals responsible for initiating the interaction of rubber with sulphur. Further investigations[118-119] with binary accelerator systems have provided more valuable informations regarding the mechanism of action. Zamyslov[120] showed that sulphenamide – tetramethyl thiuram accelerator system exhibits synergistic activity. Corinberg found that salts of MBT combined with DPG and piperidine have activities similar to those of the sulphenamides; the activity of the latter being dependent on the basicity of the amine group attached to the sulphenamide N-atom. MBT salts when used along with strong organic bases as accelerators were found to produce high strength vulcanizates. To determine the synergistic effect and the effectiveness of different binary accelerator systems, Kemperman[121] investigated many pairs of vulcanization accelerators in NR and SBR compounds. Out of these, majority of combinations showed strongly positive, few slightly positive and very few of them did not show observable synergism. Amidino thiourea and its derivatives were found to be effective secondary accelerators and they were found to increase the accelerator activity of MBTS and TMTD[122-125].

1.7. Low temperature vulcanization

Vulcanization temperature is very important in determining the quality of the rubber product. Optimum properties are obtained when curing is done at the lowest possible temperature. Linear rubbers like NR, NBR etc. are degraded when temperature is raised[126]. Low temperature curing results in products of good quality and fine appearance. The modulus developed decreases as cure temperature is raised[127].

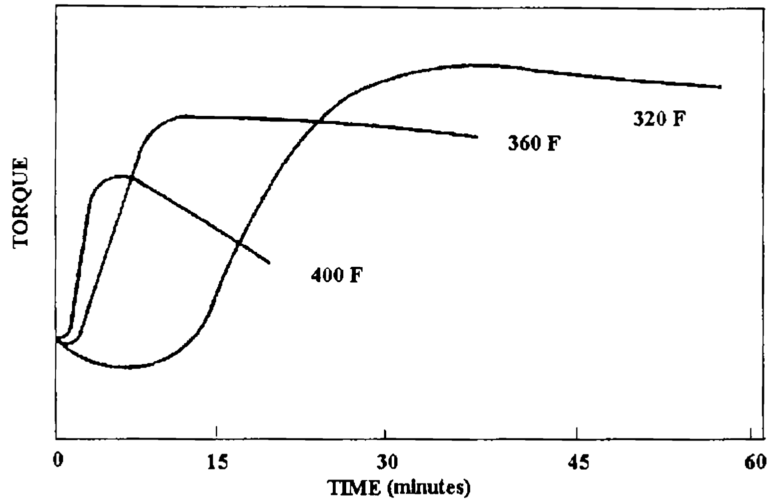


Fig. 1.3. Variation of torque with time at different temperatures

Natural and synthetic rubbers are mainly used in the manufacture of articles like automobile tyres and tubes, beltings, retreading materials, foot wear etc. In rubber product manufacture, direct plant energy is involved in the following steps : (a). mastication and mixing (b). shaping and curing.

In the rubber industries, in order to increase production, the rubber products are moulded at very high temperatures (160°C and above) where the energy consumption is very high. The need for conserving energy is being felt now more than ever before mainly on account of the enhanced cost of mineral fuels.

In addition to the high energy consumption, there are many other disadvantages for the high temperature curing. For example, in a tyre industry, high temperature moulding leads to the following drawbacks.

1. *High energy consumption*: - In a tyre industry, the average fuel used per kg. of product is approximately 0.25 litre. Fuel cost / litre is approximately Rs. 8/-. For a 100 tonnes per day plant, cost for fuel will come to Rs. 2 lakhs per day. A reduction of 20% in heat input can reduce the cost by as much as Rs. 40,000/- per day.

2. *Less safety* :- The mould is heated from outside by circulating superheated steam which is under high pressure. In case of leaks, there are chances for accidents.
3. *Higher insulation costs* :- High temperature moulding requires thick insulation for pipelines and curing press.
4. *Less flexibility in designing the compound for each component at high temperature.*
5. *Inconveniences in the curing room* :- Curing rooms are usually hot and not comfortable to work in. Reduction in curing temperature can improve the conditions in the curing room.
6. *Chances of overvulcanization* :- A tyre having surface defects, after repair is revulcanized at high temperature. This will result in the overvulcanization of the rubber compound and shrinkage of the nylon cord inside the tyre. So repairing at a lower temperature can prevent deterioration in the quality and life time of the repaired product.

So if the shaping and curing of a rubber product is done at a lower temperature, the above problems can be avoided in addition to getting a better quality product with a longer lifetime.

OBJECTIVES AND SCOPE OF THE WORK

The primary objective of this work is to develop an efficient accelerator system for low temperature vulcanization of rubbers. Although xanthates are known to act as accelerators for low temperature vulcanization, a systematic study on the mechanism of vulcanization, the mechanical properties of the vulcanizates at varying temperatures of vulcanization, cure characteristics etc are not reported. Further, xanthate based curing systems are not commonly used because of their chance for premature vulcanization during processing. The proposed study is to develop a novel accelerator system for the low temperature vulcanization of rubbers having enough processing safety. It is also proposed to develop a method for the prevulcanisation of natural rubber latex at room temperature.

As already mentioned the manufacture of rubber products at low temperature will improve its quality and appearance. Also, energy consumption can be reduced by low temperature vulcanization. In addition, low temperature vulcanization will be extremely useful in the area of repair of defective products, since subjecting finished products to high temperatures during the process of repair will adversely affect the quality of the product. Further, room temperature curing accelerator systems will find extensive applications in surface coating industries.

Prevulcanized latex is a convenient form of latex for the dipped goods manufacturing industries since it can be used directly for product manufacturing, eliminating the product curing step. Prevulcanisation of the NR latex can be done at room temperature, keeping its colloidal stability unaffected and it can result in high amount of energy saving.

The specific objectives of the work are

1. To prepare zinc salts of methyl, ethyl, isopropyl, butyl and ethylene glycol xanthates.
2. To characterise the prepared xanthates by IR, NMR and TGA techniques.
3. To develop a low temperature curing system for NR, NBR and NR/BR blends.
4. To study the effect of the different xanthates on the curing and mechanical properties of the NR, NBR and NR/BR blends.
5. To develop a technique for the prevulcanization of NR latex at room temperature.

This thesis is divided into the following chapters

Chapter 1 : Introduction

Chapter 2 : Experimental techniques

Chapter 3 : Preparation, characterization and use of zinc xanthate accelerators in natural rubber

Part 1 : Preparation and characterisation of zinc salts of different xanthates.

Part 2 : Cure characteristics of NR gum compounds containing zinc salts of different xanthates.

Chapter 4 : Studies on the use of zinc xanthate accelerators alone and in combination with ZDC for the curing of NR at different temperatures

Part 1 : Use of zinc xanthate accelerators in NR gum and black filled compounds.

Part 2 : Effect of zinc xanthate accelerators in combination with ZDC in the vulcanization of NR.

Part 3 : Room temperature vulcanization of NR and NR latex

Chapter 5 : Use of zinc xanthate accelerators in combination with dithiocarbamate for the curing of NBR at different temperatures

Part 1 : Effect of carbon black on the vulcanization of NBR using zinc xanthate/ ZDC accelerator combination.

Part 2 : Use of zinc xanthate/ ZDC accelerator combination for the vulcanization of NBR.

Part 3 : Effect of silica filler on the vulcanization of NBR using zinc xanthate/ZDC accelerator combination.

Part 4 : Room temperature vulcanization of NBR.

Chapter 6 : Use of zinc xanthate/ ZDC accelerator combination for the vulcanization of NR/BR blends at different temperatures

Chapter 7 : Summary and conclusion

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Chapter 2

EXPERIMENTAL TECHNIQUES

In this chapter, a detailed description of the experimental procedures adopted and the materials used are given

2.1. Elastomers

2.1.1. Natural rubber (NR)

Natural rubber used was solid block rubber conforming to ISNR – 5 grade of Mooney viscosity ML (1+4) at 100°C equal to 85, obtained from Rubber Research Institute of India, Kottayam. In a particular experiment, rubber from the same lot has been used. This is because the molecular weight, molecular weight distribution and non-rubber constituents of natural rubber are affected by clonal variation, season, method of preparation etc[1-2]. Specifications of the ISNR-5 used are given below:

Parameters	**Limit**
Dirt content, % by mass, max.	0.05
Volatile matter, % by mass, max.	1.00
Nitrogen, % by mass, max.	0.70
Ash, % by mass, max.	0.60
Initial plasticity, P_0, min.	30.00
Plasticity retention index (PRI) min.	60.00

2.1.2. Polybutadiene rubber (BR)

Polybutadiene rubber (BR) was obtained from Indian Petrochemicals Corporation Ltd., Baroda. The grade used was Cisamer 1220 having Mooney viscosity ML (1+4) at 100°C 45.

2.1.3. Acrylonitrile- butadiene rubber (NBR)

Nitrile rubber used in this study was Aparene-N 553 supplied by Apar Polymers Ltd. Gujarat, India. It had the following specifications

Acrylonitrile content (% by weight)	34
Mooney Viscosity ML (1+4) at 100°C	42

2.2. Compounding ingredients

2.2.1. Zinc oxide (activator)

Zinc oxide supplied by M/s. Meta Zinc Ltd., Bombay, had the following specifications:

Specific gravity (g/cm^3)	5.5
Zinc oxide content (% by mass)	98.0

2.2.2. Stearic acid (co-activator)

Stearic acid was supplied by Godrej Soaps (pvt.) Ltd., Bombay and the specifications are given below:

Melting point	65°C
Acid number	200

2.2.3. Zinc diethyl dithiocarbamate (accelerator)

Zinc diethyl dithiocarbamate (ZDC) used in the present study was supplied by ICI India Ltd., Calcutta, the specifications are given below:

Specific gravity (g/cm^3)	1.47
Melting point	178°C

2.2.4. Tetramethylthiuram disulphide (accelerator)

Tetramethylthiuram disulphide (TMTD) supplied by Polyolefins Industries Ltd., Bombay, had the following specifications:

Melting point	138°C
Specific gravity (g/cm^3)	1.3

2.2.5. Sulphur (crosslinking agent)

Supplied by M/s. Standard Chemicals Co. Pvt. Ltd., Madras. The specifications are:

Specific gravity (g/cm^3)	2.05
Ash (%)	0.10
Solubility in CS_2 (% by mass)	98

2.2.6. Fillers

a) High Abrasion Furnace Black (N 330) was supplied by M/s. Philips Carbon Black Ltd., Cochin. It had the following specifications:

DBP absorption	102 ± 5 cc/100g
Iodine number	82

b) Precipitated silica used was of commercial grade supplied by Minar chemicals, Alwaye. The specifications of this are given below:

Specific gravity (g/cm^3)	2.03

SiO_2 hydrate on dried sample, min.	90%

2.2.7. Process oils

a) Aromatic Oil

Supplied by Hindustan Organic Chemicals, Cochin. It had the following specifications:

Specific gravity (g/cm^3)	0.98
Aniline Point (°C)	43.00
Viscosity gravity constant	0.96

b) DOP

DOP was commercial grade and was supplied by Rubo Synthetic Impex Ltd., Bombay.

Specific gravity (g/cm^3)	0.986
Viscosity (cps)	60

2.2.8. Antioxidants

a) Vulkanox 4020

Vulkanox 4020 N (1,3-dimethyl butyl-N'- phenyl-p-phenylenediamine) was supplied by Bayer India Ltd., having specific gravity of 1.1.

b) Vulkanox SP

Vulkanox SP (mixture of styrenated phenols) was supplied by Bayer India Ltd, had a density of 1.08 g/cc.

c) Vulkanox HS

Commercial antioxidant vulkanox HS (1,2-dihydro-2,2,4-trimethyl quinoline, polymerised) was obtained from Bayer India Ltd, having specific gravity of 1.1.

2.2.9. Other reagents used

Other reagents such as toluene, methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohol, ethylene glycol, potassium hydroxide and carbon disulphide were of analar grade. Zinc sulphate used for precipitation was commercial grade.

Propane-2-thiol and piperidine used for network structure elucidation were analytical grade reagents supplied by Fluka, Germany.

2.3. Experimental methods

2.3.1.Mixing and homogenization using mixing mill

Mixes were prepared on a laboratory size two roll mixing mill (6 x12 inch) as per ASTM D 3182-89. The mixing was carried out at a friction ratio of 1:1.25. The mill opening was set at 0.2 mm and the elastomer was passed through the rolls twice without banding. This was then banded on the slow roll with mill opening at 1.4 mm and was increased to 1.9 mm as the band became smooth. The temperature of the rolls was maintained at 70±5°C. The compounding ingredients were added as per procedure given in ASTM D 3184-89 and ASTM D 3182-89 in the following order: activator, filler, accelerator and curing agents. Before the addition of accelerator and sulphur the batch was thoroughly cooled.

After the completion of mixing, homogenization of the compound was carried out by passing the rolled stock endwise six times at a mill opening of 0.8 mm. The mill was opened to give a minimum stock thickness of 6 mm and the stock was passed through the rolls four times folding it back on itself each time.

2.3.2. Determination of cure characteristics of rubber compounds

Goettfert elastograph, model 67.85, was used for the determination of the cure characteristics of the mixes. It uses two directly heated, opposed biconical disc that are designed to achieve a constant shear gradient over the entire sample chamber. The specimen was kept in the lower die, which is oscillated through a small deformation angle (±0.2°) at a frequency of 50 oscillations per minute. The torque transducer on the upper die senses the force being transmitted through rubber.

i) Minimum torque, M_L

Torque obtained by mix after homogenizing at the test temperature, the onset of cure.

ii) Maximum torque, M_H

Maximum torque recorded after the curing of the mix is completed.

iii) Torque, M_T

Torque at any time T

iv) Optimum cure time, T_{90}

It is the time taken to attain 90% of the maximum torque.

v) Scorch time, T_{10}

This is the time taken to attain 10% of the maximum torque.

vi) Cure rate index

It is calculated as: $100/(T_{90}-T_{10})$ where T_{90} and T_{10} respectively are the time corresponding to optimum cure time and scorch time.

2.3.3. Moulding of test specimen

The test specimens for determining the physical properties were prepared in standard moulds by compression moulding on an electrically heated hydraulic press having 18x18 inch platens at a pressure of 200 kg/cm^2 on the mould. The rubber compounds were vulcanized upto their respective optimum cure times at 150°C. Moulding were cooled quickly in water at the end of the curing cycle and stored in a cool and dark place for 24 hrs and were used for subsequent physical tests. For samples having thickness more than 6 mm (compression set, abrasion resistance etc) additional time based on the sample thickness was given to obtain satisfactory mouldings.

2.4. Compounding of latex

2.4.1. Preparation of dispersions

The compounding ingredients were added to rubber latex as aqueous solution, dispersion or emulsion according as they are water soluble solid, water insoluble solid or water immiscible liquids. Aqueous dispersions were made by grinding action and the materials were made to disperse in water. Dispersing agents were used to prevent the dispersed particles from reaggregation.

A ball mill consists of a cylindrical container in which the slurry is placed together with a charge of porcelain balls. When the mill is working, the balls are carried round with the container a short way and then cascade. It is this process of cascading which causes the particles of the slurry to be pulverized. The efficiency of the ball mill depends on the speed of rotation of jar, size and material of the ball, viscosity of slurry, period of ball milling etc.

In the present study, the following dispersions were made using a ball mill. Dispersol F was used as the dispersing agent.

a) Zinc oxide dispersion (50%)

Zinc oxide	100.00
Dispersol F	2.00
Water	98.00
Ball milled for	48 hrs

b) ZDC dispersion (50%)

ZDC	100.00
Dispersol F	2.50
Water	97.50
Ball milled for	48 hrs

c) Sulphur dispersion (50%)

Sulphur	100.00
Dispersol F	3.00
Water	97.00
Ball milled for	72 hrs

d) Zinc xanthate dispersion (50%)

Zinc xanthate	100.00
Dispersol F	2.00
Water	98.00
Ball milled for	48 hrs

2.4.2. Latex compounding

Mixing of ingredients to natural rubber latex was done in the following order : stabilising agents, sulphur, accelerators, fillers and zinc oxide. Stabilisers were added as solution. Mixing was carried out in a glass vessel and stirred for homogenization using a laboratory stirrer. It was occasionally stirred during storage in order to prevent settling of the ingredients.

2.4.3. Preparation of latex film

After completion of mixing, the latex compound was matured at ambient temperature for 24 hours. Latex films were then casted in glass cells as described in ASTM D 1076-88. The size of the glass cell was 15 x 15 cm and about 30-35 ml of the latex compound was poured and distributed so that a film of thickness 1 – 1.5 mm was obtained upon drying. The glass cells with the latex compound were placed in a leveled table. The film will undergo vulcanization at room temperature. The time required for vulcanization is determined by testing the tensile strength at regular intervals. The time taken for attaining maximum tensile strength was taken as the optimum cure time.

2.5. Evaluation of physical properties

For each property studied, at least three specimens per sample were tested and the mean values are reported.

2.5.1. Tensile properties: tensile strength and elongation at break

The tensile properties of the vulcanizates were determined on a 'Zwick' Universal testing machine, model 1445, using a crosshead speed of 500 mm/ min as per ASTM D 412-87 (method A). All the tests were carried out at 28±2°C. Dumbbell specimens for the test were punched out of the moulded sheet along the mill grain direction, using a dumbbell die (C-type). The thickness of the narrow portion was measured using a bench thickness gauge. The sample was held tight by two grips, the upper grip being fixed. The tensile strength and elongation at break were evaluated and printed out after each measurement by the microprocessor.

2.5.2. Tear resistance

Angular test specimens were used to measure the tear resistance on a Zwick universal testing machine model 1445, according to ASTM D 624-86. The samples were cut from the moulded sheets parallel to the mill grain direction. The speed of extension was 500 mm min^{-1} and the test temperature was 28±2°C.

2.5.3. Compression set

Samples (6.25 mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hrs in the air oven at 70°C. After the heating period the samples were taken out, cooled to room temperature for half an hour and the final thickness was measured. The compression set was calculated using the following expression:

$$\text{Compression set (\%)} = \frac{t_0 - t_1}{t_0 - t_s} \times 100$$

where, t_0 = initial thickness of the specimen, t_1 = final thickness of the specimen,

t_s = the thickness of the spacer bar. The procedure adopted was in accordance with ASTM D 395-86 (method B).

2.5.4. Abrasion resistance

The abrasion resistance of the samples were tested using a DIN 53516. Cylindrical samples having diameter 15 mm and length 20 mm was kept on a rotating sample holder and 10N load was applied. Initially a pre-run was given for the sample and its weight was taken. The sample was then given a complete run and the final weight was noted. The difference in weight is reported as the abrasion loss. It is expressed as the volume of the test piece getting abraded by its travel through 42 m on a standard abradant surface. The abrasion loss was calculated as follows:

$$V = \frac{m}{\rho}$$

where V = abrasion loss, m = mass loss, ρ = density of the sample.

2.5.5. Heat build-up

The heat build-up was measured using the Goodrich flexometer conforming to ASTM D 623-78 (Method A). Cylindrical samples of height 25 mm and 19 mm diameter were used to carry out the test. The oven temperature was kept constant at 50°C. The stroke was adjusted to 4.45 mm and the load to 10.9 kg. The sample was preconditioned to the oven temperature for 20 minutes. The heat development at the base of the sample was sensed by a thermocouple and relayed to a digital temperature indicator. The temperature rise (ΔT°C) at the end of 20 minutes was taken as the heat build-up.

2.5.6. De Mattia flex resistance

The De Mattia flex resistance of the vulcanizates were determined using a Wallace De Mattia flexing machine as per ASTM D 430-57 T.

2.5.7. Ageing studies

Ageing studies were carried out in air oven as per ASTM D 573-88. Dumb bell samples were punched out from the vulcanized sheets and kept in the air oven at predetermined temperatures for specified periods. Physical properties like tensile strength, elongation at break etc. were measured before and after ageing. The percentage retention of these properties was evaluated for assessing the effect of ageing.

2.5.8. Testing of the latex film

The tensile properties of the latex film were determined as per ASTM D 412-87 (method A) using a Zwick Universal Testing machine. The chemical crosslink density was determined by equilibrium swelling method.

2.6. Chemical test methods

2.6.1. Determination of the concentration of crosslinks of the vulcanizates

The chemical crosslink density of the vulcanizates was evaluated as follows. Samples of approximately 10 mm diameter and 2 mm thickness and 0.2 g weight were punched out from the central portion of the vulcanizates and allowed to swell in toluene for 24 hrs. The swollen samples were taken out and weighed. The solvent was removed in vacuum and the samples weighed again. The volume fraction of rubber, V_r, in the swollen network was then calculated by the following equation.[3-4]

$$V_r = \frac{(D-FT)\rho_r^{-1}}{(D-FT)\,\rho_r^{-1} + A_0\,\rho_s^{-1}}$$

where,

T = the weight of the test specimen

D = the weight of the deswollen test specimen

F = the weight fraction of insoluble components

A_0 = the weight of the absorbed solvent corrected for the swelling increment.

ρ_r = density of the rubber

For NR, ρ_r = 0.92 g/cm^3 ; For NBR, ρ_r = 1.0118

ρ_s = density of the solvent

For toluene, ρ_s = 0.886g/cm^3 ; For Methyl ethyl ketone ρ_s = 0.804

Knowing the value of V_r, the total chemical crosslink density $1/2M_c$ was calculated using Flory-Rehner equation[5-6].

$$-(\ln(1-V_r)+V_r+\chi V_r^2) = \frac{\rho_r V_s (V_r)^{1/3}}{M_c}$$

where,

V_s = molar volume of solvent

χ = the parameter characteristic of the interaction between rubber and solvent

M_c = the number average molecular weight of the rubber chains between crosslinks

The values of the parameter χ taken for calculation were the following[7]

For NR – toluene, χ = 0.42

For NBR – MEK, $\chi = 0.21$

Although natural rubber gum vulcanizates have received much attention, less details are available on network structure of filled vulcanizates. This is because of the uncertainities introduced by the filler-rubber interactions. The volume fraction of rubber (V_r) is calculated assuming that the filler does not swell. It is then converted to V_{r0} (the value V_r would have in the absence of filler) according to Cunneen and Russel[8].

$$\frac{V_{r0}}{V_r} = ae^{-z} + b$$

Here a and b are constants characteristic of the system and z is the weight fraction of the filler in the vulcanizate. The values for a and b for HAF black filled systems are; a = 0.56 and b = 0.44. The corresponding values for silica filled systems are[9]; a = 1.41, b = -0.41

The values of V_{r0} were then substituted in the Flory-Rehner equation in place of V_r to obtain the crosslink density $1/2M_c$.

2.6.2. Determination of concentration of polysulphidic crosslinks[10-12]

The concentration of polysulphidic crosslinks was estimated from the change in the crosslink density of the vulcanizate before and after treatment with propane-2-thiol and piperidine which cleaves the polysulphidic crosslinks in the network. Vulcanizate sample weighing about 0.2-0.3. gm was allowed to stand in excess of the solvent (toluene/benzene) containing 0.1% PBN for 24 hours at room temperature. Then the solvent was replaced by a solution (100 ml) of 0.4 M propane –2-thiol and piperidine in the solvent containing 0.5% PBN for 2 hours. On completion of reaction, the sample was removed from the reagent solution, washed with petroleum ether four times, surface dried on filter paper as quickly as possible and dried in vacuum to constant weight at room temperature. The specimen was then kept in excess of the solvent with 0.1% PBN for 24 hours and finally extracted for 2 hours in pure solvent. The swollen sample was weighed, solvent removed in vacuum and the sample weighed again. The volume fraction of rubber (V_r) was then determined as before and the crosslink density was determined.

2.7. Morphology studies

2.7.1. Using scanning electron microscope

Scanning electron microscopic studies were found to be a very powerful tool in polymer research for studying morphology[13-14]

Scanning electron microscope model (H-6010A Hitachi) was used to investigate the morphology of fractured surfaces. In this technique an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors (photo multiplier tube) and magnified. An image of the investigated microscopic region of the specimen is thus observed in cathode ray tube (CRT) and photographed using 120 roll black and white film.

The SEM observations reported in the present study were made on the fracture surface of tensile test specimen. A thin specimen of the samples was prepared and mounted on a metallic stub with the help of a silver tape and conducting paint in the upright position. The stub with the sample was placed in an ion sputter (Eiko IB-3 ion coater-Hitachi) for gold coating of the sample to make it conducting. Gold coated sample was observed in the SEM.

2.8. Characterisation of the xanthates

The xanthates were characterized by IR, NMR and TGA techniques.

2.8.1. Infrared Spectroscopy:- IR spectra of the samples were taken on a Perkin-Elmer model 377 IR spectrometer.

2.8.2. ^{1}H NMR Spectroscopy:- The proton NMR spectra of the samples were recorded from a solution of $CDCl_3$ using a dpx300 model spectrometer.

2.8.3. Thermogravimetric Analysis:- The TGA was carried out using a V5. IA Du Pont 2000 model in air.

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Chapter 3

PREPARATION, CHARACTERISATION AND USE OF XANTHATE ACCELERATORS IN NATURAL RUBBER

Introduction

Xanthates are ultra accelerators and the activity of these accelerators is so high that compounds containing xanthates vulcanize even at room temperature[1]. They can be prepared as their zinc, sodium and potassium salts. Sodium and potassium salts are water soluble and are used in latex compounds, while zinc salts are used in dry rubber compounds[2]. Xanthates can be prepared by the reaction of carbon disulphide with alcohols in the presence of alkali[3-8].

Natural rubber latex is obtained mainly from *Hevea Brasiliensis.* The raw rubber contains approximately 94% rubber hydrocarbon, 3% proteins and 3% of other materials including fatty acids and resins[9]. The conversion of raw rubber to useful products needs compounding and vulcanization. During vulcanization, the long chain rubber molecules become crosslinked by reaction with the vulcanizing agents to form three dimensional structures. This reaction transforms the weak plastic like material to a strong elastic product. The properties of the latter, in particular, the modulus, hardness, elastic properties, resistance to swelling etc are considerably influenced by the course of vulcanization[10]. The extent of changes in properties is governed by the choice of vulcanizing agents added to rubber to bring about the vulcanization process and also by the vulcanization conditions. Therefore, to obtain rubber products with best possible properties, it is always necessary to use the most suitable combination of vulcanizing agents and vulcanization conditions.

NR is usually vulcanized at 140°C - 160°C with a combination of sulphur, accelerators, zinc oxide and a fatty acid. Sulphur vulcanization of NR is widely studied by a number of researchers[10-15]. In ultra accelerated compounds, smaller quantities of sulphur can be used to produce optimum physical properties in a shorter curing time than can be obtained with other classes of accelerators[16]. The vulcanizates so obtained have the best overall combination of physical properties for many applications; but at the same time the aging properties deteriorate even when antioxidants are present. This deficiency is largely due to the low thermal stability of the network and is characterized by a rapid reversion in properties when the vulcanizate is subjected to overcure. Low temperature vulcanization can result in products of good quality and fine appearance.

In this chapter we describe the preparation of five different xanthate accelerators, their characterization and the cure characteristics in NR gum compounds.

Part 1

3.1. Preparation and characterisation of xanthates

3.1.1. Experimental

Materials

Methyl alcohol, ethyl alcohol, isopropyl alcohol, n-butyl alcohol, ethylene glycol, potassium hydroxide and carbon disulfide were reagent grade and were used as supplied. Zinc sulphate used for precipitation was commercial grade.

Preparation

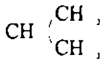
Potassium methyl, potassium ethyl, potassium isopropyl, potassium butyl and potassium ethylene glycol xanthates were prepared in the laboratory by mixing equimolar amounts of the corresponding alcohol, potassium hydroxide and carbon disulfide. These xanthates were then precipitated as their zinc salts by adding zinc sulphate solution. They were purified by reprecipitation using methanol as solvent.

Analysis of xanthates

Analysis of zinc salts of xanthates were carried out using IR spectroscopy, proton magnetic resonance spectroscopy (H-NMR) and thermogravimetric analysis (TGA). IR spectra of the samples were taken on a Perkin-Elmer model 377 IR spectrometer. The proton NMR spectra of the samples were recorded from a solution of $CDCl_3$ using a dpx300 model spectrometer. The TGA was carried out using a V5. IA Du Pont 2000 model in air.

The melting points of the xanthates were also determined using capillary melting point apparatus.

3.1.2. Results and discussion

Figures 3.1.1 – 3.1.5 show the IR spectra of zinc methyl xanthate (Zn $(mext)_2$), zinc ethyl xanthate(Zn$(ext)_2$), zinc isopropyl xanthate(Zn$(ipxt)_2$), zinc butyl xanthate(Zn$(bxt)_2$), zinc ethylene glycol xanthate(Zn$(egxt)_2$) respectively. The IR spectrum of Zn $(mext)_2$ shows sharp peaks at 1385.1 cm^{-1} corresponding to C = S stretching (str.), at 2878 cm^{-1} due to C – H str. in methyl group, at 659 cm^{-1} corresponding to C – S stretching. The IR spectrum of $Zn(ext)_2$ shows sharp peaks at 1385.1cm^{-1} corresponding to C = S stretching, at 868.1cm^{-1} corresponding to C – C stretching in n-alkanes, and at 657.8cm^{-1} corresponding to C – S stretching. The IR spectrum of $Zn(ipxt)_2$ shows peaks at 1385.1cm^{-1} corresponding to C = S stretching at 1371cm^{-1} due to  $CH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$ group and at 652cm^{-1} due to C – S stretching. The IR spectrum of $Zn(bxt)_2$ shows sharp peaks at 1385.1cm^{-1} corresponding to C = S stretching, at 902.8cm^{-1} corresponding to C – C stretching in n-alkanes, at 663.6cm^{-1} corresponding to C – S stretching. The IR spectrum of $(Zn(egxt)_2)$ shows peaks at 1384.42 cm^{-1} corresponding to C = S str., at 661cm^{-1} corresponding to C – S str., at 1466.26 cm^{-1} due to C – H str. in – CH_2 –, at 872cm^{-1} due to C – C str. and a sharp peak at 3642 cm^{-1}showing the presence of a free – OH group. These show the presence of C = S bond and C – S bond in all the five xanthates[17]. In $Zn(egxt)_2$, only one – OH group of ethylene glycol reacts and the second – OH group is free.

Figures 3.1.6 - 3.1.10 show the thermograms of $Zn(mext)_2$, $Zn(ext)_2$, $Zn(ipxt)_2$, $Zn(bxt)_2$ and $Zn(egxt)_2$ respectively. From the figures it is clear that the decomposition of all the xanthates starts at about 150°C. The changes in weight percentages suggest that the xanthates finally decompose to zinc oxide[18].

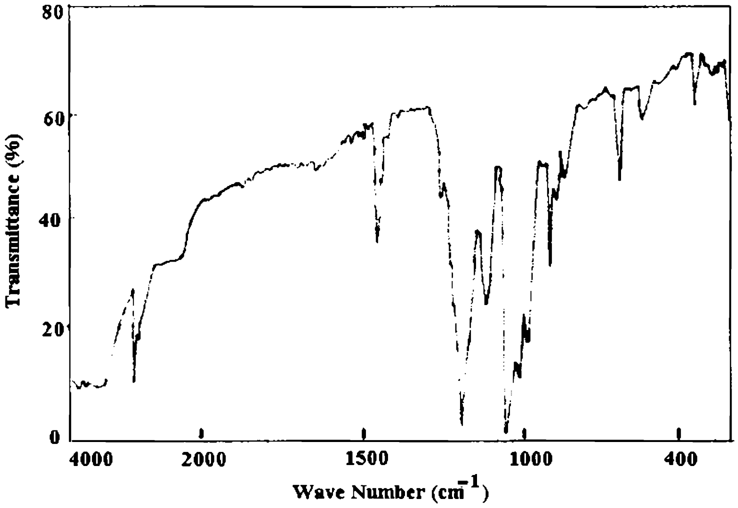


Fig. 3.1.1. IR spectrum of $Zn(mext)_2$

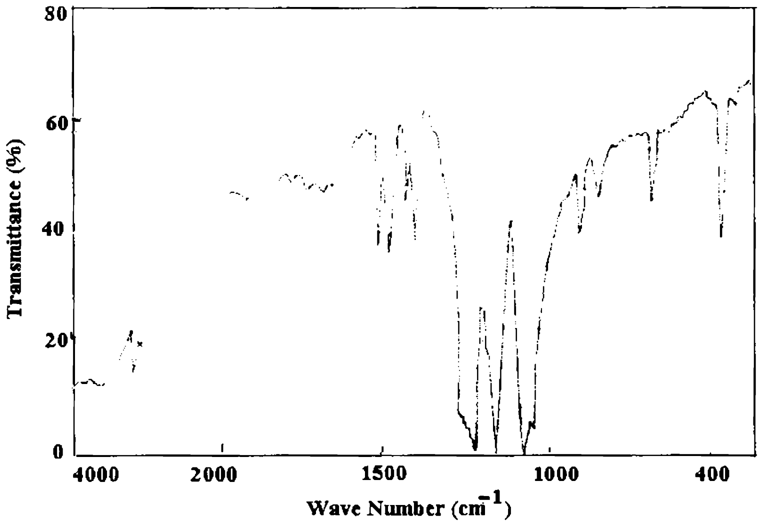


Fig. 3.1.2. IR spectrum of $Zn(ext)_2$

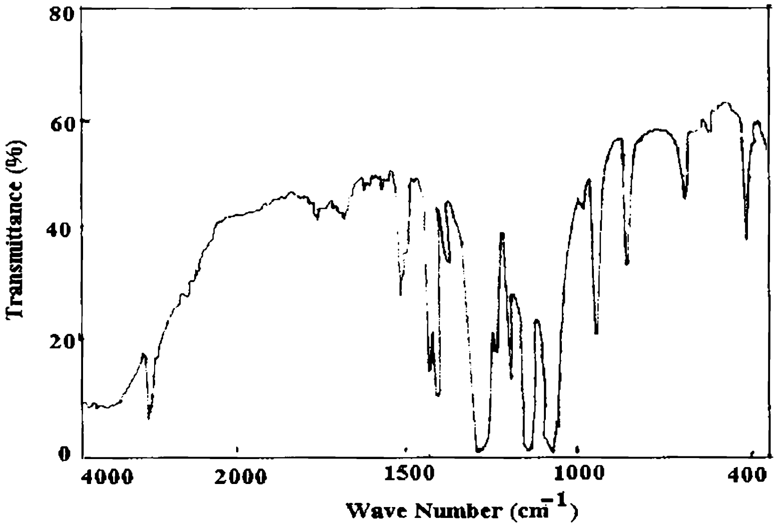


Fig. 3.1.3. IR spectrum of $Zn(ipxt)_2$

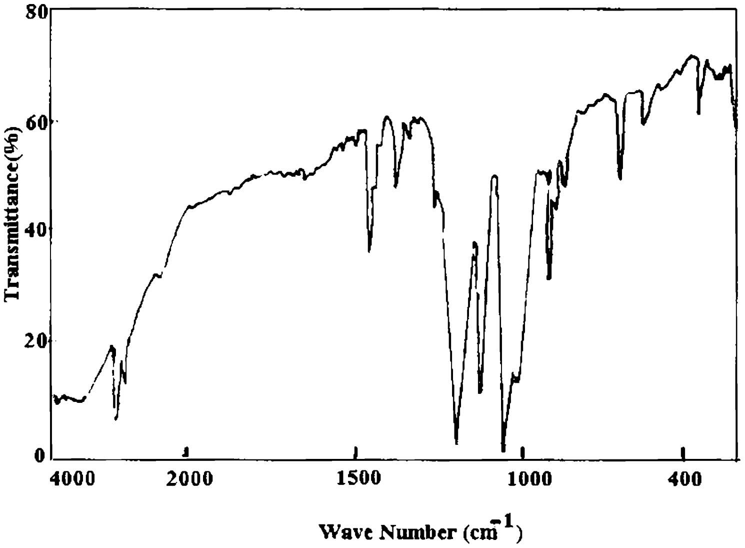


Fig. 3.1.4. IR spectrum of $Zn(bxt)_2$

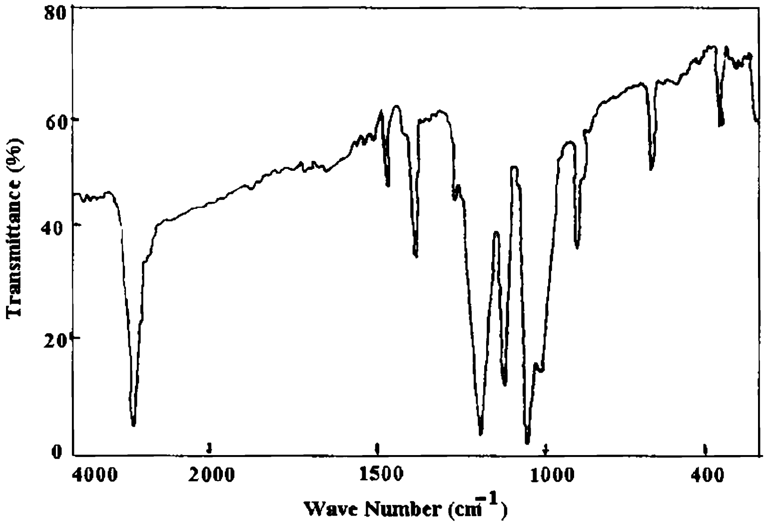


Fig. 3.1.5. IR spectrum of $Zn(egxt)_2$

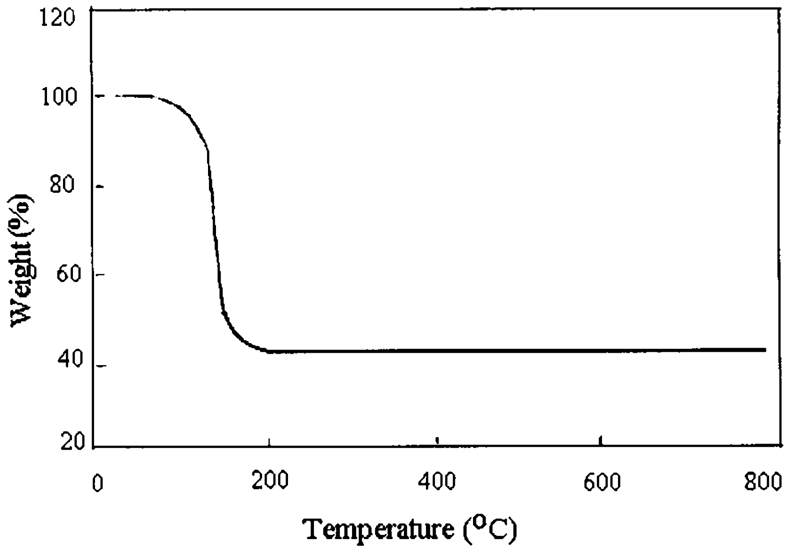


Fig. 3.1.6. Thermogram of Zn $(mext)_2$

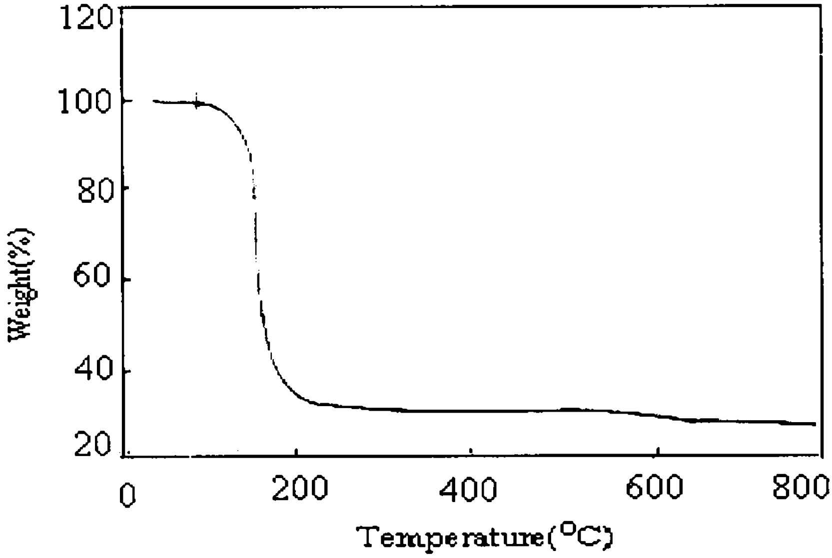


Fig. 3.1.7. Thermogram of Zn$(ext)_2$

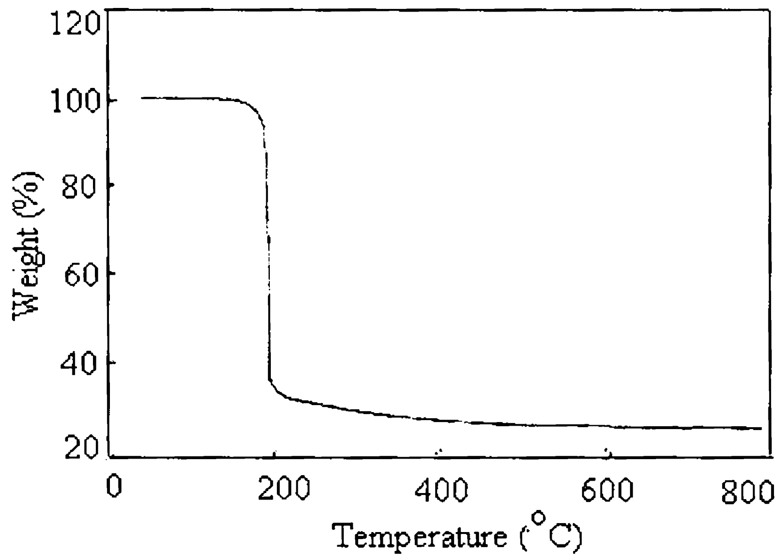


Fig. 3.1.8. Thermogram of Zn(ipxt)$_2$

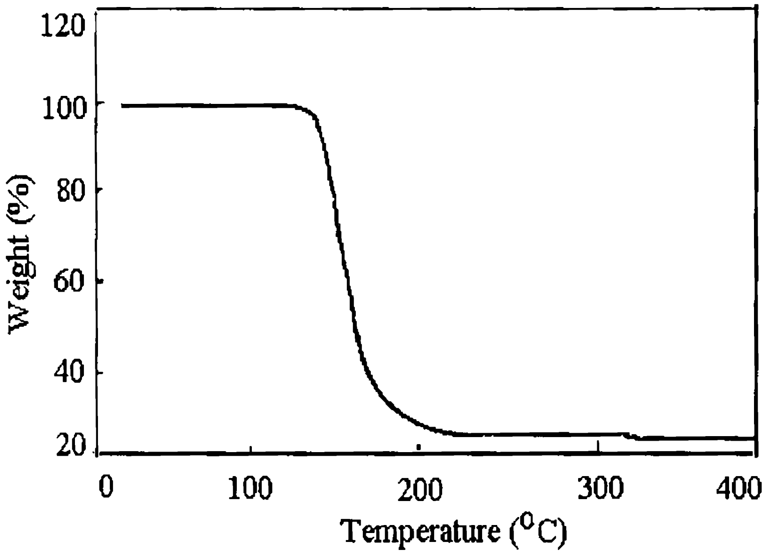


Fig. 3.1.9. Thermogram of Zn (bxt)$_2$

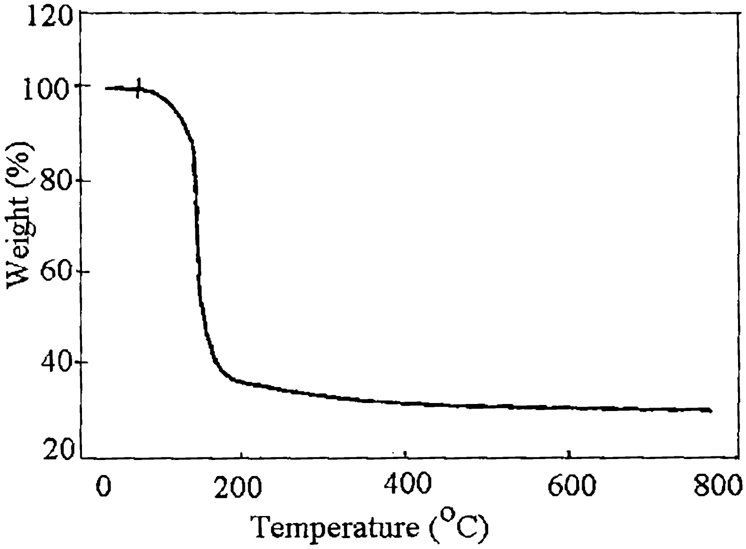


Fig. 3.1.10. Thermogram of Zn $(egxt)_2$

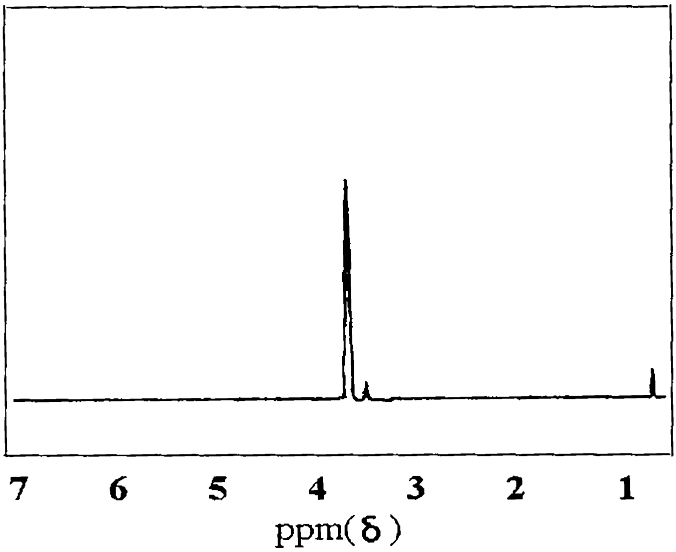


Fig. 3.1.11. ^{1}HNMR spectrum of Zn$(mext)_2$

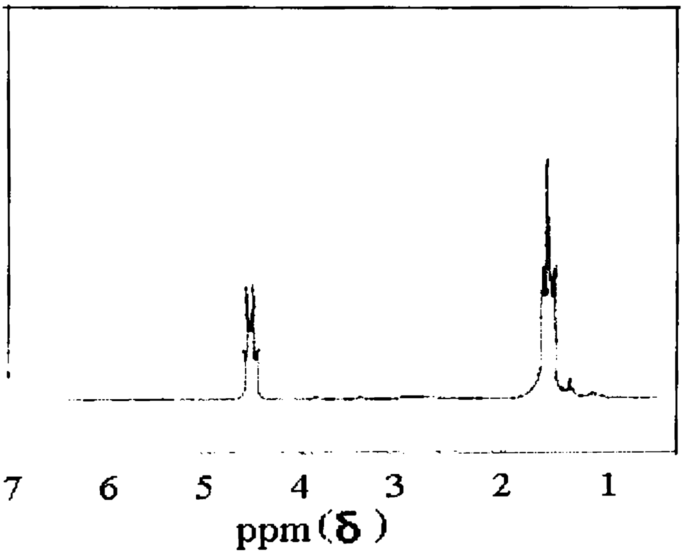


Fig. 3.1.12. ¹HNMR spectrum of $Zn(ext)_2$

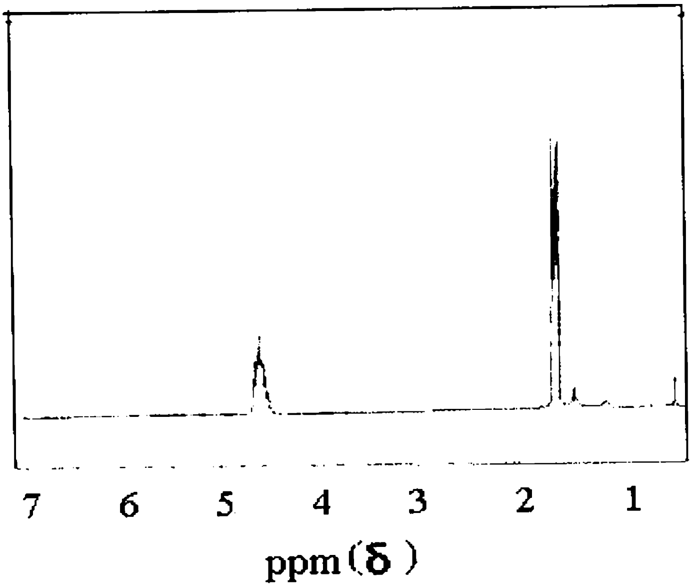


Fig. 3.1.13. ¹HNMR spectrum of $Zn(ipxt)_2$

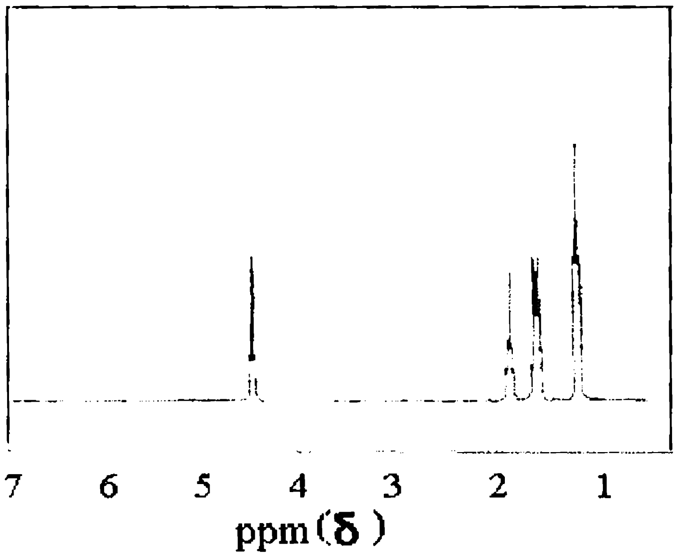


Fig. 3.1.14. ^{1}HNMR spectrum of Zn(bxt)$_2$

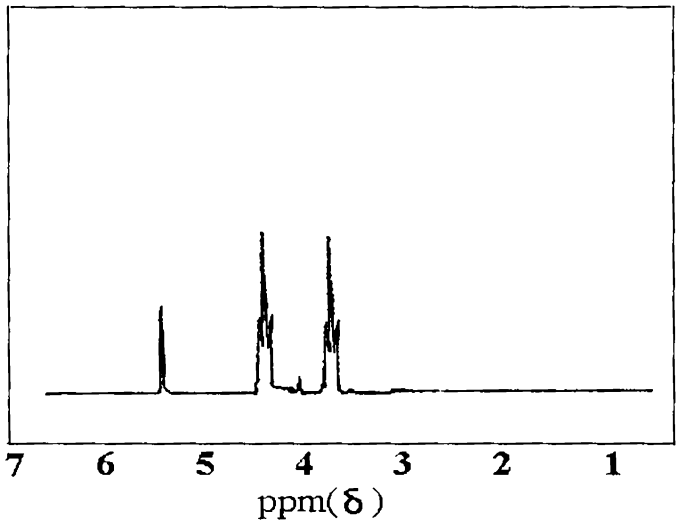
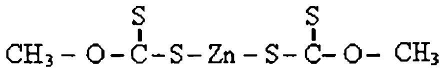


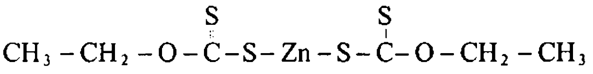
Fig. 3.1.15. ^{1}HNMR spectrum of Zn(egxt)$_2$

Figures 3.1.11 – 3.1.15 show the ^1H NMR spectra of $Zn(mext)_2$, Zn $(ext)_2$, Zn $(ipxt)_2$, $Zn(bxt)_2$ and $Zn(egxt)_2$ respectively. In fig.3.1.11, there is a three proton singlet at $\delta = 3.4$ showing the presence of a $-CH_3$ group attached to an oxygen atom in $Zn(mext)_2$. Fig.3.1.12 shows the ^1H NMR spectrum of $Zn(ext)_2$. There is a triplet at $\delta = 1.6$ and a quartet at $\delta = 4.5$ showing the presence of $-CH_2-CH_3$ group in Zn $(ext)_2$. Fig.3.1.13 shows the ^1H NMR spectrum of $Zn(ipxt)_2$. There is a six proton doublet (up field) and a one proton septet (down field), showing the presence of $-CH\begin{smallmatrix}/CH_3\\ \backslash CH_3\end{smallmatrix}$ group in Zn $(ipxt)_2$. Fig.3.1.14 shows the ^1H NMR spectrum of Zn $(bxt)_2$. There is a three proton triplet at $\delta = 1$, a two proton sextet at $\delta = 1.5$, a two proton pentet at $\delta = 2$ and a two proton triplet at $\delta = 4.5$ showing the presence of $CH_3-CH_2-CH_2-CH_2-$ group in Zn $(bxt)_2$. In fig.3.1.15, there is a two proton triplet at $\delta = 4.2$ (due to the $-O-CH_2-$ group), a two proton triplet at $\delta = 3.6$ and a one proton singlet at $\delta = 5.3$ showing the presence of $-CH_2-CH_2-OH$ group in $Zn(egxt)_2$[19].

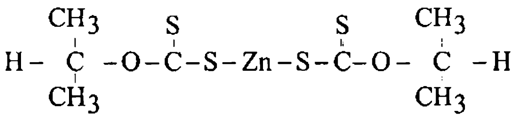
From the above data, the structures of $Zn(mext)_2$, $Zn(ext)_2$, $Zn(ipxt)_2$, $Zn(bxt)_2$ and $Zn(egxt)_2$ can be written as



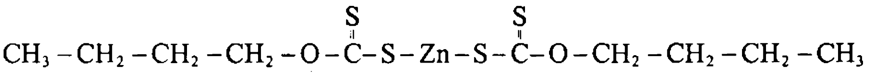
$$CH_3-O-\overset{S}{\overset{|}{C}}-S-Zn-S-\overset{S}{\overset{|}{C}}-O-CH_3$$



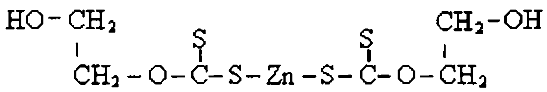
$$CH_3-CH_2-O-\overset{S}{\overset{|}{C}}-S-Zn-S-\overset{S}{\overset{|}{C}}-O-CH_2-CH_3$$



$$H-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-\overset{S}{\overset{|}{C}}-S-Zn-S-\overset{S}{\overset{|}{C}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-H$$



$$CH_3-CH_2-CH_2-CH_2-O-\overset{S}{\overset{\|}{C}}-S-Zn-S-\overset{S}{\overset{\|}{C}}-O-CH_2-CH_2-CH_2-CH_3$$



$$\overset{\overset{HO-CH_2}{|}}{CH_2}-O-\overset{S}{\overset{|}{C}}-S-Zn-S-\overset{S}{\overset{|}{C}}-O-\overset{\overset{CH_2-OH}{|}}{CH_2}$$

The melting points are found to be

1. $Zn(mext)_2$ - 115°C
2. $Zn(ext)_2$ - 120°C
3. $Zn(ipxt)_2$ - 148°C
4. $Zn(bxt)_2$ - 107°C
5. $Zn(egxt)_2$ - 156°C

3.1.3. Conclusions

1. Zinc salts of methyl, ethyl, isopropyl, butyl and ethylene glycol xanthates can be prepared in the laboratory using the procedure described.
2. The structure of zinc xanthates can be elucidated by IR, NMR and TGA techniques.

Part 2

3.2. Cure characteristics of NR gum compounds containing zinc xanthates

3.2.1. Experimental

Materials

The NR (ISNR - 5, Mooney viscosity ML (1+4) 100°C- 82) was supplied by rubber research institute of India, Kottayam. The compounding ingredients ie., zinc oxide, stearic acid, and sulphur were commercial grade. Zinc salts of different xanthates were prepared in the laboratory.

Compounding

Natural rubber was compounded on a 6 x 12 inch laboratory mixing mill. In order to optimize the amount of accelerator for vulcanization, the concentration of the zinc butyl xanthate was varied from 0.5 to 3.0 phr (formulations are given in table 3.1). The optimum cure times (time to reach 90% of the maximum torque) of the mixes A to D given in table 3.1 were determined on a Goettfert elastograph (model 67.85) as per ASTM D 1646 (1981) at 150°C and are shown in fig. 3.1.

NR gum compounds were prepared using different xanthates as per the formulations given in table 3.2. The cure characteristics of the mixes A_1 to E_1 given in table 3.2 were determined at 100°C on a Goettfert elastograph (model 67.85) as per ASTM D 1646 (1981) and were reported in table 3.3

Table 3.1 NR formulations containing different amounts of $Zn(bxt)_2$

Mix	A	B	C	D	E	F
NR	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
$Zn(bxt)_2$	0.5	1.0	1.5	2.0	2.5	3.0
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

Table 3.2. NR formulations containing different xanthates

Mix	A_1	B_1	C_1	D_1	E_1
NR	100	100	100	100	100
ZnO	5	5	5	5	5
Stearic acid	2	2	2	2	2
$Zn(mext)_2$	2.5	-	-	-	-
$Zn(ext)_2$	-	2.5	-	-	-
$Zn(ipxt)_2$	-	-	2.5	-	-
$Zn(bxt)_2$	-	-	-	2.5	-
$Zn(egxt)_2$	-	-	-	-	2.5
Sulphur	2.5	2.5	2.5	2.5	2.5

3.2.2. Results and discussion

Fig. 3.2.1. shows the optimum cure times of the mixes given in table 3.1. At concentrations 0.5 and 1.0 phr $Zn(bxt)_2$, the compound doesn't undergo curing even after 1 hour. At concentrations 1.5 and 2 phr, curing occurs, but there is a significant reduction in the cure time when the concentration of $Zn(bxt)_2$ is increased to 2.5 phr. After 2.5 phr $Zn(bxt)_2$, there is no appreciable change in the cure time. So 2.5 phr was taken as the optimum concentration of the xanthate in NR compounds.

Table 3.3 shows the cure characteristics of the mixes A_1 to E_1 given in table 3.2. The minimum torque, maximum torque, scorch time and cure rate index of the NR compounds increases and the optimum cure times decreases from $Zn(mxt)_2$ → $Zn(ext)_2$ → $Zn(ipxt)_2$ → $Zn(bxt)_2$, but the cure time increases for the compound containing $Zn(egxt)_2$. It may be due to the better solubility of the accelerator in NR when the size of the alkyl group in the accelerator increases. In the case of $Zn(egxt)_2$ containing compound, the cure time increases. This may be due to the presence of the free alcoholic group which decreases the polarity of the S – Zn bond.

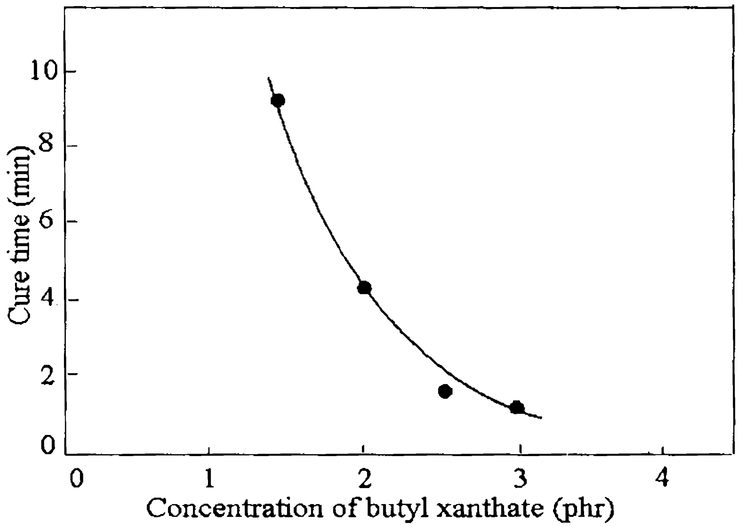


Fig.3.2.1. Optimum cure times of NR compounds containing different amounts of $Zn(bxt)_2$

Table 3.3 Cure characteristics of the mixes given in table 3.2 at 100°C.

Mix	A_1	B_1	C_1	D_1	E_1
Min. torque (Nm)	0.026	0.033	0.042	0.056	0.031
Max.torque (Nm)	0.321	0.339	0.374	0.386	0.317
Scorch time (min.)	1.83	1.76	1.62	1.59	1.75
Optimum cure time (min.)	11.32	9.51	8.10	7.24	14.62
Cure rate (Nm/min)	0.026	0.033	0.041	0.046	0.029

3.2.3 Conclusions

1. The cure time of the NR compound decreases as the size of the alkyl group in the accelerator increases.
2. The xanthate prepared by using a dihydric alcohol is found to contain a free alcoholic group which increases the cure time of the NR compound.

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Chapter 4

STUDIES ON THE USE OF ZINC XANTHATE ACCELERATORS ALONE AND IN COMBINATION WITH ZDC FOR THE CURING OF NR AT DIFFERENT TEMPERATURES

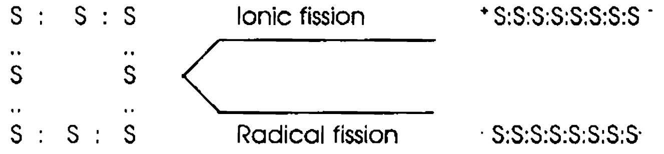
Introduction

Natural rubber hydrocarbon is made up of cis 1,4 poly isoprenoid units arranged in a highly stereoregular manner[1-2]. Due to the high structural regularity, NR crystallizes on stretching. This strain induced crystallization gives it the unique high tensile strength in gum and non-reinforcing filler vulcanizates[3]. The superior building tack, green strength, better processing, high resilience and excellent dynamic properties make it a preferred polymer in many applications.

Rubber products of desired properties are prepared by compounding rubber with selected ingredients. These ingredients include activators, accelerators, processing aids, vulcanizing agents, age resistors, fillers and miscellaneous ingredients like retarders, blowing agents, colorants etc[4]. Accelerators reduce the vulcanization time by increasing the rate of vulcanization. Activators form chemical complexes with accelerators and help in obtaining maximum benefits from the accelerators. Zinc oxide is the most commonly used activator. Stearic acid, which acts as the co-activator, also serve as lubricants and allow easier flow of the compound. Both ends of stearic acid molecule help processing. The paraffinic end provides the lubricating effect while the acid group, along with other functions absorbs the pigments on the surface. Although, stearic acid is by far the most common fatty acid, others like oleic acid may also be used.

Ageing is a collective term for changes in property of materials that occur on long term storage that lead to partial or complete degradation. These changes can occur in the form of degradation, embrittlement, rotting, softening and fatigue processes, static crack formation and the like. Antidegradents are used to reduce the degradation of rubber during ageing. Ageing is normally caused by chain scission, crosslinking or some form of chemical alteration of the polymer chain. The unsaturation in diene rubbers make it possible to cure with sulphur but at the same time present a sensitivity towards oxygen, ozone and other reactive substances. Since soft rubbers based on diene structure contain free double bonds, they remain sensitive to the above agents even after vulcanization. Higher temperatures makes these effects more noticeable. Substituted amines and phenols are the commonly used antioxidants.

Sulphur is the most commonly used vulcanizing agent in NR. Vulcanizing agents form crosslinks between rubber chains to give a three dimensional structure. Bressler and Co-workers have confirmed that sulphur dissolved in NR has an S_8 ring structure[5-6]. Pauling puts the amount of energy required to split the sulphur ring as 64 kcal/mol[7]. Splitting of sulphur ring can be in two ways – radical or ionic.



The nature of splitting of S_8 ring depends on the medium surrounding the sulphur and thus on the activity of accelerators. Thus in the presence of accelerators, smaller sulphur fragments are available for crosslinking reactions.

Processing aids are used to reduce the time and energy required in processing. Also, they help the dispersion of ingredients in rubber, improve extrusion rates and increase the homogeneity of blended rubber. A brief discussion of the action of various accelerators in NR is needed and is given below.

Vulcanizates of high heat resistance are obtained by using a high ratio of accelerator to sulphur. These systems consists of 0.3 to 0.8 phr sulphur and 2.5 to 6.0 phr accelerator[8] which are usually recommended for products which need improved reversion resistance during vulcanization and for products which are exposed to higher service temperatures. Conventional vulcanization system continue to find widespread general purpose use for the products that do not require sustained heat resistance during manufacture or service. The course of vulcanization, to a large extend, depends on the nature of the accelerators used. Among thiuram accelerators, tetramethyl thiuram disulphide (TMTD) is one of the safer and fastest accelerators. Thiurams act as ultra accelerators and impart relatively high modulus, good mechanical and aging properties to the vulcanizates[9]. Generally thiurams are used as secondary accelerators to raise the rate of vulcanization of mercaptans and sulphenamide accelerators. Another class of accelerators most widely used are thiazoles and sulphenamides. Compared to thiuram accelerators, thiazole accelerators give compounds with higher processing safety. Of the main accelerators of this type, mercapto benzothiazole (MBT) and zinc mercapto benzothiazole (ZMBT) have relatively fast onset of vulcanization and hence lowest processing safety. Compounds with thiazole accelerators that are activated by secondary accelerators have less tendency to overcure and give vulcanizates with excellent ageing properties. Thiurams and guanidines are the most frequently used secondary accelerators with thiazoles. Sulphenamide accelerators act slowly in the beginning of the vulcanization process and subsequently become very active. Such vulcanization behaviour is especially desirable in the case of multilayered and complex articles such as automobile tyres. Zinc diethyl dithiocarbamate (ZDC) is an ultra accelerator which ensures a rapid vulcanization in presence of small amount of sulphur. This is very active in latex mixes even in the absence of zinc oxide and activates thiazole accelerators.Zinc alkyl xanthates are also ultra accelerators and ensure low temperature vulcanization.

The use of vulcanization systems composed of two or more accelerators finds wide technological applications in recent years. Dogadkin and collaborators investigated a large number of accelerator combinations and found mutual activation with many of them[10-12].

Eventhough gum natural rubber vulcanizate shows high tensile strength, it is not suitable for many commercial applications. Fillers are generally incorporated for improved processability, reinforcement and cost reduction. Reinforcement by a filler is the enhancement of one or more properties of an elastomer by the incorporation of that filler, thus making it more suitable for a given application[13-14]. The effect of filler on rubber vulcanizates depends on its physical properties such as particle size, surface area, surface reactivity, electrical charge on the particle and chemical properties such as pH and reactivity with accelerators. The fundamental aspects of polymer filler interaction has been studied is detail in a number of polymers[15-18]. Studies on filled systems have also been reviewed by Kraus[19] and Voet[20]. In general, the best reinforcing fillers are those having the smallest particle size. Carbon blacks are the most effective reinforcing fillers used in rubber industry[21-24]. It is known that carbon black contains active functional groups such as phenolic, ketonic and carboxylic together with lactones[25-26].

During vulcanization, carbon black enters a chemical reaction with sulphur, accelerators etc., participating in the formation of vulcanized network. It is generally agreed that strong links exist between rubber chains and reinforcing filler particles[27-28]. The nature of polymer- filler attachments in vulcanizates has been investigated in great detail by Rehner[29]. The introduction of carbon black in the rubber mixture results is an additional consumption of accelerators because of the adsorption of accelerators on the surface of the carbon black particles[30-31]. So more accelerators or a combination of more active accelerators has to be employed in the compounds containing high dosage of carbon black.

We have prepared zinc salts of ethyl, isopropyl and butyl xanthates in our laboratory. The effect of these xanthates on the curing and mechanical properties of gum and black filled NR compounds at different temperatures are discussed in this chapter. This chapter also describes the effect of zinc xanthate /ZDC accelerator combination on NR vulcanizates.

Part 1

4.1. Use of zinc xanthate accelerators in natural rubber

4.1.1. Experimental

Materials

Natural rubber (NR) (ISNR- 5, Mooney Viscosity ML (1+4) 100°C value of 82) was supplied by the Rubber Research Institute of India, Kottayam. Compounding ingredients- zinc oxide, stearic acid, sulphur, aromatic oil, HS, vulcanox 4020 and carbon black (HAF N330) were of commercial grade. Denatured spirit, isopropyl alcohol, n-butyl alcohol, potassium hydroxide, carbon disulphide and toluene used for swelling studies were of reagent grade and were used as supplied. Zinc sulphate used for precipitation was commercial grade.

Zinc salt of ethyl, isopropyl and butyl xanthates were prepared in the laboratory as per the procedure described in chapter II. Gum and black filled NR compounds were prepared using $Zn(ext)_2$, $Zn(ipxt)_2$ and $Zn(bxt)_2$.

Compounding

Gum and black filled NR compounds were prepared on a (6x12 inch) laboratory mixing mill as per the formulations given in table 4.1.1 and 4.1.2. The optimum cure times of the compounds were determined using a Goettfert elastograph model 67.85 as per ASTM D 1646(1981) at different temperatures from 60°C - 150°C and are reported in table 4.1.3. The compounds were moulded in an electrically heated hydraulic press at various temperatures from 60°C - 150°C upto their optimum cure times at a pressure of $200 kg/cm^2$. The chemical crosslink density was estimated by swelling the samples in toluene as described in detail in chapter 2. The crosslink density values of the NR gum vulcanizates are given in table 4.1.4 and the values of the black filled NR vulcanizates are given in fig.4.1.1. The percentage of the polysulphidic linkages in the gum vulcanizates moulded at 150°C and 80°C were determined using propane 2-thiol in piperidine as per the procedure given in chapter II and the values are given in table 4.1.5. Thermograms of the NR gum vulcanizates containing $Zn(bxt)_2$ moulded at 150°C and 80°C were taken using a V5.IA Du Pont 2000 model in air and the results are shown in fig.4.1.2 and fig. 4.1.3. Dumb bell shaped tensile test pieces were punched out of the compression moulded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick universal testing machine using a cross head speed of 500 mm/minute according to ASTM D 2240. Angular test specimens were used to measure the tear resistance according to ASTM D 624.86.The tensile properties of the gum vulcanizates are given in table 4.1.4 and that of black filled vulcanizates are given in fig.4.1.4 to 4.1.6. SEM studies of the fractured tensile surfaces of the gum NR vulcanizates moulded at 150°C and 80°C were taken using a SEM model Hitachi-H.6010 A - scanning system. The SEM photographs are given in fig. 4.1.7 and fig. 4.1.8. The ageing resistance of the black filled vulcanizates containing $Zn(ipxt)_2$ moulded at different temperatures were determined by keeping the samples at 70°C for 24 hours in a laboratory air oven and then measuring the retention in properties and the results are given in table 4.1.6. Abrasion resistance of the samples were tested using a DIN abrader according to DIN 53516 and the values of the gum vulcanizates are given in table 4.1.7 and the values of the black filled vulcanizates are given in fig.4.1.9. Compression set was determined as per ASTM D 395-61(method B) and the values of the gum vulcanizates are given in table 4.1.7and that of black filled vulcanizates are given in fig.4.1.10. The heat build up of the samples were measured using Goodrich Flexometer conforming to ASTM D 623-78(method A). The heat build up values of the gum vulcanizates are given in table 4.1.7 and that of the black filled vulcanizates are given in fig.4.1.11.

Table 4.1.1. Formulations of NR gum compounds

Mix	**A**	**B**	**C**
NR	100	100	100
ZnO	5	5	5
Stearic acid	2	2	2
$Zn(ext)_2$	2.5	-	-
$Zn(ipxt)_2$	-	2.5	-
$Zn(bxt)_2$	-	-	2.5
Sulphur	2.5	2.5	2.5

Table 4.1.2. Formulations of black filled NR compounds.

Mix	A_1	B_1	C_1
NR	100	100	100
ZnO	5	5	5
Stearic acid	2	2	2
HAF N330	25	25	25
Aromatic oil	3	3	3
$Zn(ext)_2$	2.5	-	-
$Zn(ipxt)_2$	-	2.5	-
$Zn(bxt)_2$	-	-	2.5
Sulphur	2.5	2.5	2.5

4.1.2. Results and discussions

Table 4.1.3 shows the cure times of gum and black filled NR compounds given in table 4.1.1 and table 4.1.2 at different temperatures from 60°C - 150°C. The results show that xanthate accelerators can bring about the vulcanization of NR at high temperatures as well as low temperatures. As expected, cure time increases as the temperature of vulcanization decreases. At a particular temperature, the cure times of NR compounds decreases from $Zn(ext)_2 \rightarrow Zn(ipxt)_2 \rightarrow Zn(bxt)_2$. It may be due to the better solubility of the accelerator in NR when the size of the alkyl group in the accelerator increases. At a particular temperature, the cure time of the black filled NR compound is found to be more compared to that of the gum compound. It may be due to the adsorption of the accelerator on the surface of carbon black.

Table 4.1.3. Optimum cure times (in minutes) of the compounds given in table 4.1.1 and table 4.1.2 at different temperatures.

Temp (°C)	A	B	C	A_1	B_1	C_1
150	0.90	0.84	0.76	1.32	1.16	0.92
125	3.41	2.96	2.39	4.68	4.21	4.08
100	9.24	7.24	5.00	10.08	8.84	7.48
80	24.20	23.90	21.2	27.11	26.8	25.6
60	54.01	52.91	50.1	56.20	54.2	53.1

The crosslink density values of the NR gum vulcanizates are given in table 4.1.4 and fig. 4.1.1 gives the corresponding values of the black filled vulcanizates moulded at different temperatures. The results show that crosslink densities of NR vulcanizates increases as the temperature of vulcanization decreases. It may be due to the lesser degradation of rubber at lower temperatures and also due to the higher stability of the accelerator at lower temperatures. Again, more mono and disulphidic crosslinks are formed between NR chains at lower temperatures compared to the same compound moulded at higher temperatures. This is clear from the percentage of polysulphidic linkages present in the gum vulcanizates containing $Zn(bxt)_2$ moulded at 150°C and 80°C respectively which are given in table 4.1.5. This is supported by the thermograms of the same vulcanizates given in fig. 4.1.2 and 4.1.3. Since monosulphidic and disulphidic crosslinks are thermally more stable, the decomposition of the NR vulcanizate moulded at 80°C starts only at 329°C (fig.4.1.3) while the decomposition of the vulcanizate moulded at 150°C starts at 308°C (fig.4.1.2). This is attributed to the low Tea (effective commencing temperature of the accelerator) of the xanthates[32] which makes possible the release of small sulphur fragments from the xanthate - sulphur complex even at lower temperatures. But at higher temperatures, the xanthates undergo decomposition and its activity decreases.

The tensile properties of the gum vulcanizates moulded at different temperatures are given in table 4.1.4. Fig.4.1.4. to fig.4.1.6 give the tensile strength, tear strength and elongation at break respectively of the black filled vulcanizates moulded at different temperatures from 60°C to 150°C. It is seen that tensile properties increases as the temperature of vulcanization decreases. It may be due to the higher crosslinking at lower temperatures

Table 4.1.6 shows the ageing resistance of the black filled vulcanizates containing $Zn(ipxt)_2$ moulded at different temperatures from 60°C to 150°C. The ageing resistance increases as temperature of vulcanization decreases. This behaviour is expected since low temperature vulcanization using xanthates lead to a higher percentage of mono and disulphidic crosslinks. It is also reported that xanthates have antioxidant properties also which will be more pronounced at lower temperatures[33].

Fig. 4.1.7 and fig.4.1.8 show the SEM photographs of the tensile fracture surface of the NR gum vulcanizates moulded at 150°C and 80°C respectively. More tear marks are present in the vulcanizates moulded at 80°C. From the nature of the stretch marks, it is clear that the polymer is existing in a high molecular state when it is vulcanized at a lower temperature which clearly indicates that the degradation of rubber is prevented at low temperatures.

Table 4.1.4 Properties of NR gum vulcanizates containing different xanthates

Mix	**Temperature (°C)**	**Crosslink density (g/mol/cm^3)**	**Tensile strength (N/mm^2)**	**Tear strength (N/mm)**	**Elongation at break (%)**
A	150	1.29×10^{-5}	10.63	27.01	750
	125	2.36×10^{-5}	19.61	32.71	673
	100	3.26×10^{-5}	20.90	55.63	651
	80	4.48×10^{-5}	23.12	58.49	647
	60	5.62×10^{-5}	24.72	60.86	533
B	150	1.76×10^{-5}	12.82	31.20	671
	125	2.96×10^{-5}	17.98	39.46	652
	100	3.29×10^{-5}	24.01	59.70	635
	80	4.90×10^{-5}	26.31	68.80	541
	60	5.43×10^{-5}	28.04	78.47	472
C	150	1.62×10^{-5}	12.01	29.30	695
	125	3.01×10^{-5}	16.85	38.52	662
	100	4.64×10^{-5}	21.32	58.67	645
	80	5.26×10^{-5}	25.00	65.86	585
	60	6.13×10^{-5}	26.72	74.38	496

A - NR gum compound containing Zn $(ext)_2$

B - NR gum compound containing Zn $(ipxt)_2$

C - NR gum compound containing Zn $(bxt)_2$

Table 4.1.5. Percentage of polysulphidic linkages

Sample	Temperature of moulding(°C)	Polysulphidic linkages(%)
I	150	73.9
II	80	60.8

Table 4.1.6. Ageing resistance of filled NR vulcanizates containing $Zn(ipxt)_2$ moulded at different temperatures.

Temperature (°C)	Tensile strength (N/mm²)			Tear strength (N/mm)			Elongation at break (%)		
	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)	Before aging	After aging	Retention (%)
150	15.20	11.72	77.12	36.89	27.88	75.60	631	510	80.89
125	21.02	17.81	84.73	49.60	42.36	85.42	596	513	86.16
100	26.20	25.51	97.38	67.90	65.80	96.91	563	512	90.95
80	32.41	35.09	108.29	78.21	83.64	106.96	492	484	98.43
60	34.28	38.95	113.63	81.01	91.65	113.15	428	425	99.49

The abrasion resistance, compression set and heat build up values of the gum vulcanizates at different temperatures are given in table 4.1.7 and the corresponding values of the black filled vulcanizates are given in fig. 4.1.9 to fig.4.1.11. The mechanical properties are found to increase as the temperature of vulcanization decreases. It may be due to the lesser degradation of rubber at lower temperatures and also due to the higher crosslinking at lower temperatures. At 150°C, the crosslink density and mechanical properties of gum and black filled vulcanizates are found to be very low. This may be due to the decomposition of the xanthates at high temperatures. At a particular temperature, the mechanical properties of the black filled vulcanizates are found to be high compared to that of the gum vulcanizates. It may be due to the reinforcement by carbon black.

Table 4.1.7. Mechanical properties of NR gum vulcanizates containing different xanthates, moulded at different temperatures.

Mix	Temperature (°C)	Abrasion loss (cc/hr)	Compression set (%)	Heat build up (ΔT) °C
A	150	21.36	37.68	23
	125	18.25	33.04	18
	100	12.32	31.63	15
	80	7.98	28.65	13
	60	4.36	26.35	11
B	150	18.96	31.43	20
	125	14.56	28.32	16
	100	8.31	26.16	14
	80	5.41	24.81	11
	60	3.89	21.98	10
C	150	20.45	33.65	23
	125	16.99	30.15	17
	100	10.35	28.45	15
	80	6.13	25.96	12
	60	4.16	23.65	10

A - Vulcanizate containing $Zn(ext)_2$, B - Vulcanizate containing $Zn(ipxt)_2$

C - Vulcanizate containing $Zn(bxt)_2$

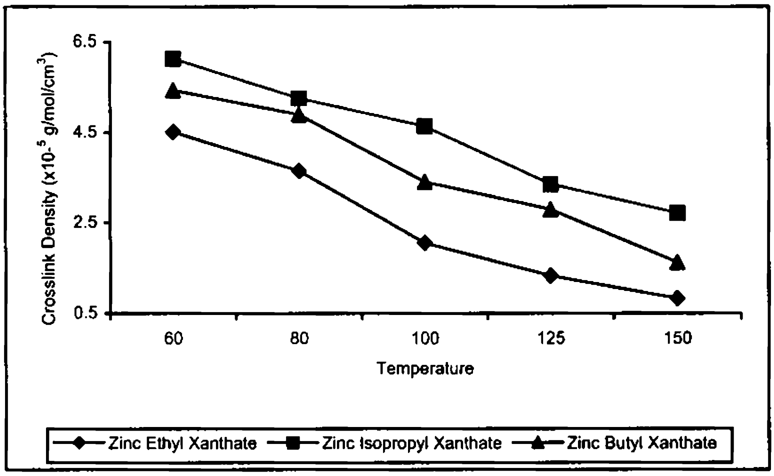


Fig.4.1.1. Crosslink densities of black filled NR vucanizates containing xanthates

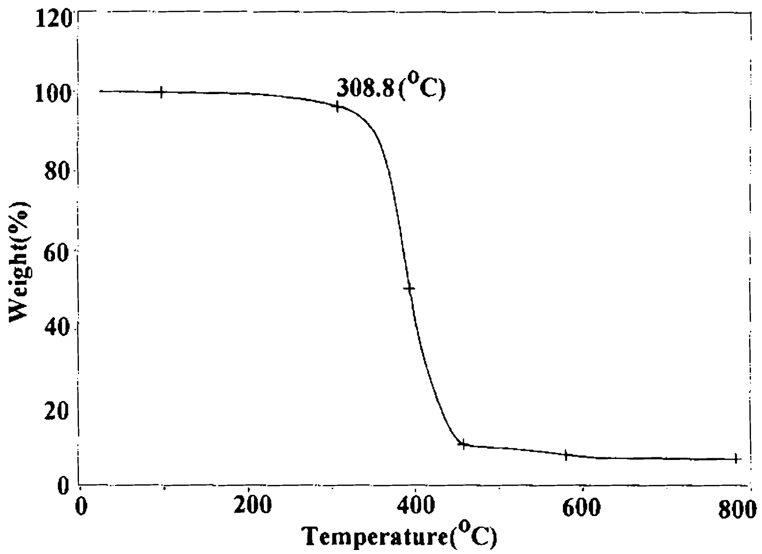


Fig. 4.1.2. Thermogram of NR vulcanizate moulded at 150°C

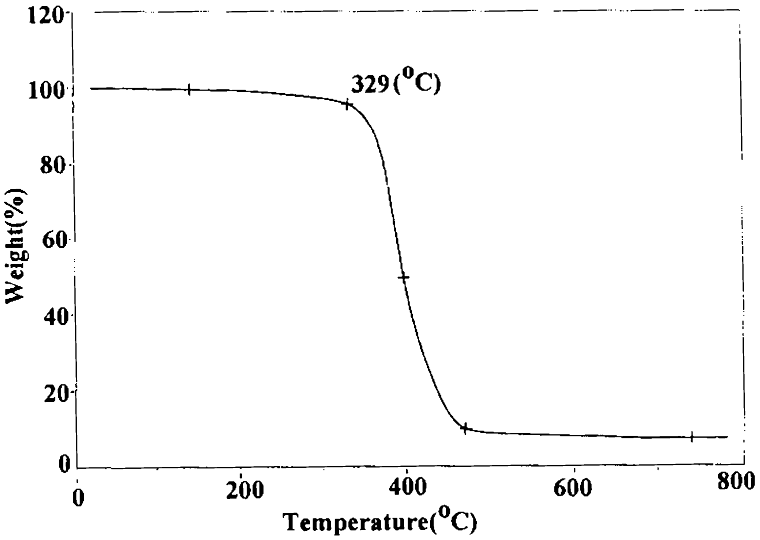


Fig. 4.1.3. Thermogram of NR vulcanizate moulded at 80°C

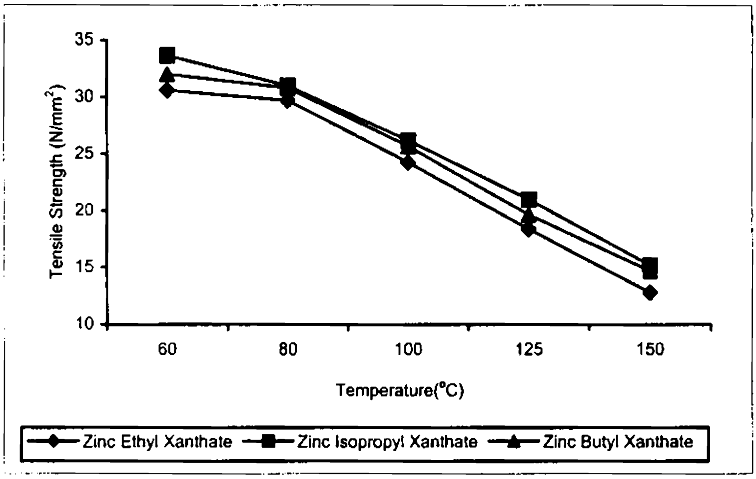


Fig.4.1.4. Tensile strength of black filled NR vucanizates containing xanthates

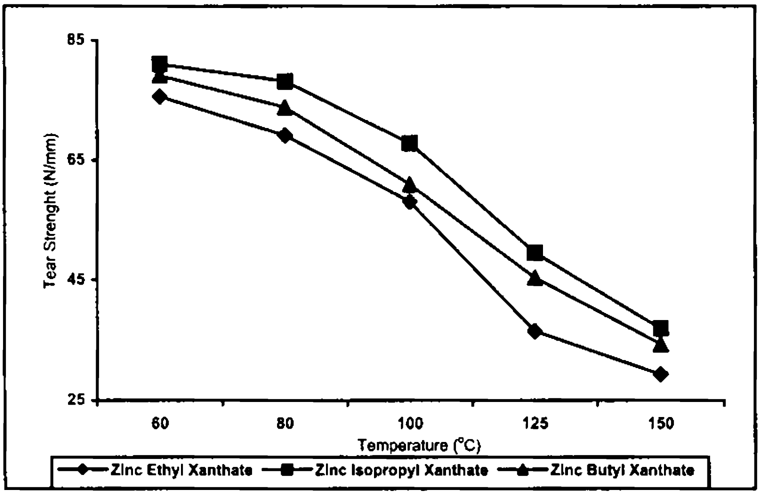


Fig.4.1.5. Tear strength of black filled NR vucanizates containing xanthates

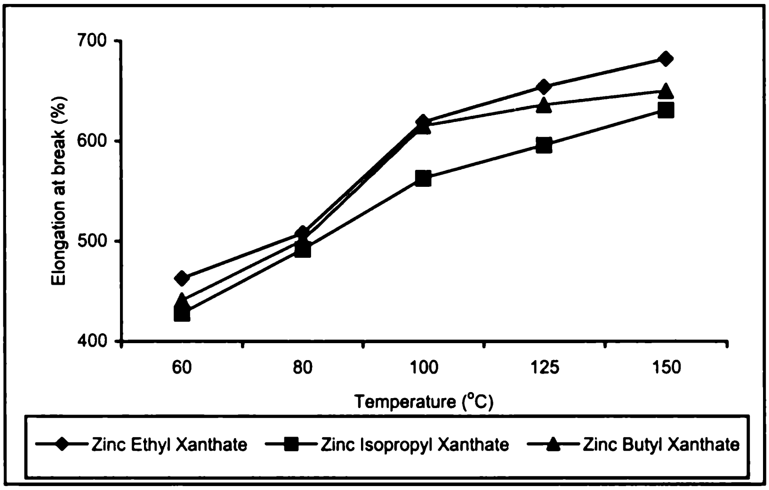


Fig. 4.1.6. Elongation at break of the black filled NR vulcanizates

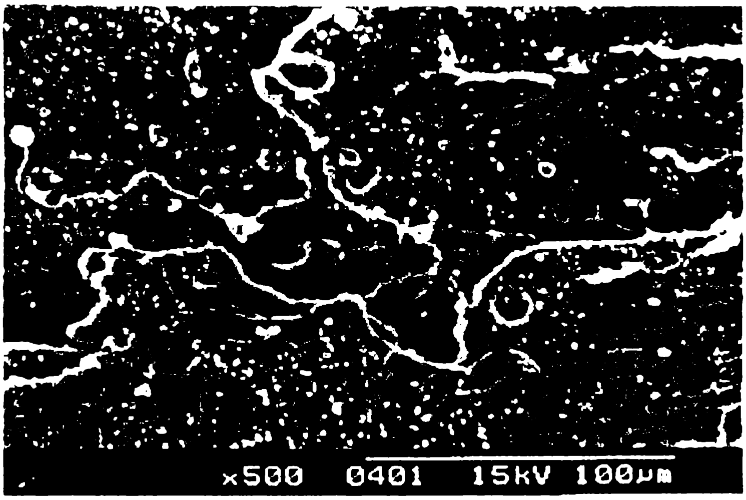


Fig. 4.1.7. SEM Photograph of NR vulcanizate moulded at 150°C

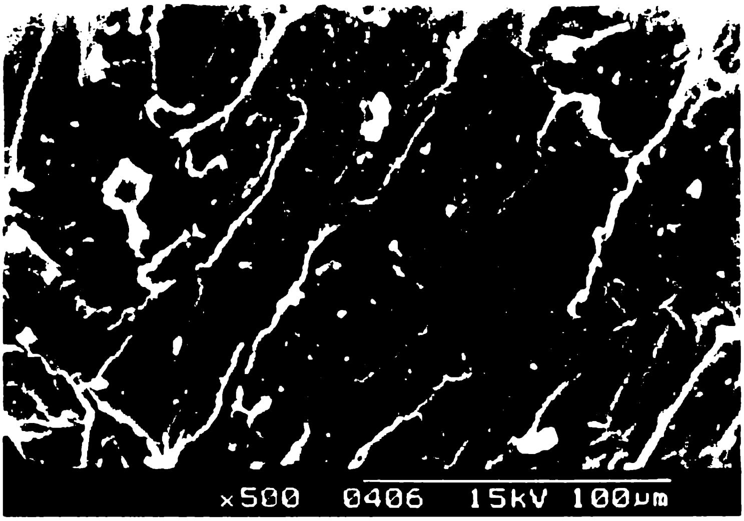


Fig. 4.1.8. SEM Photograph of NR vulcanizate moulded at 80°C

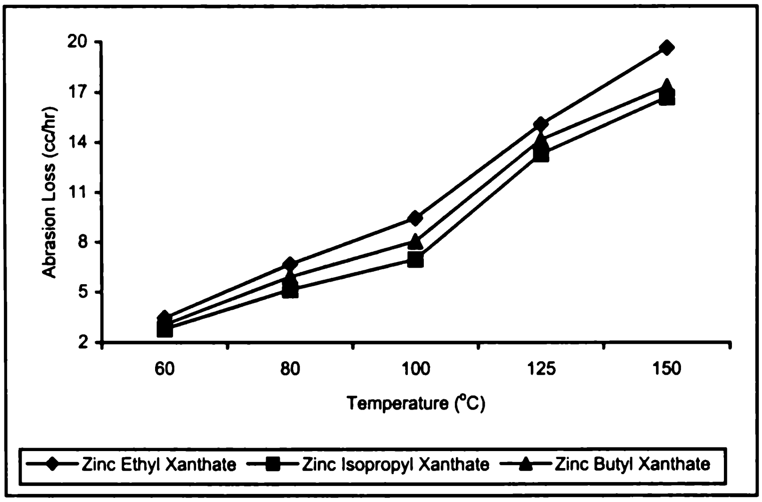


Fig. 4.1.9. Abrasion resistance of the black filled NR vulcanizates containing xanthates

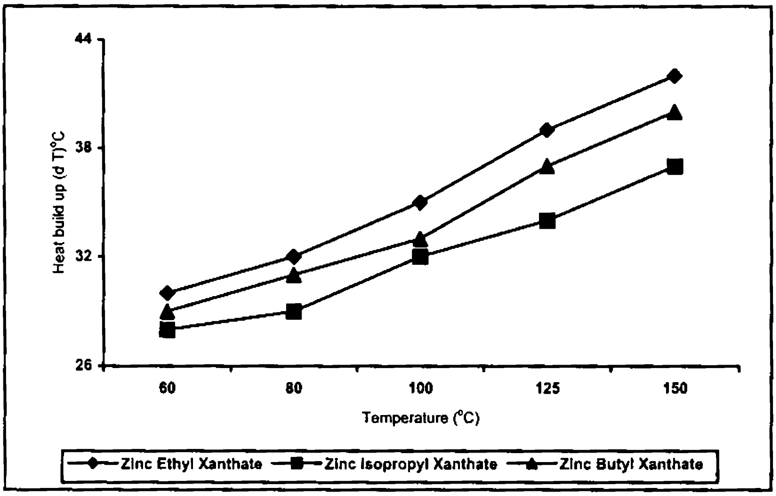


Fig. 4.1.10. Heat build up of black filled NR vulcanizates containing xanthates

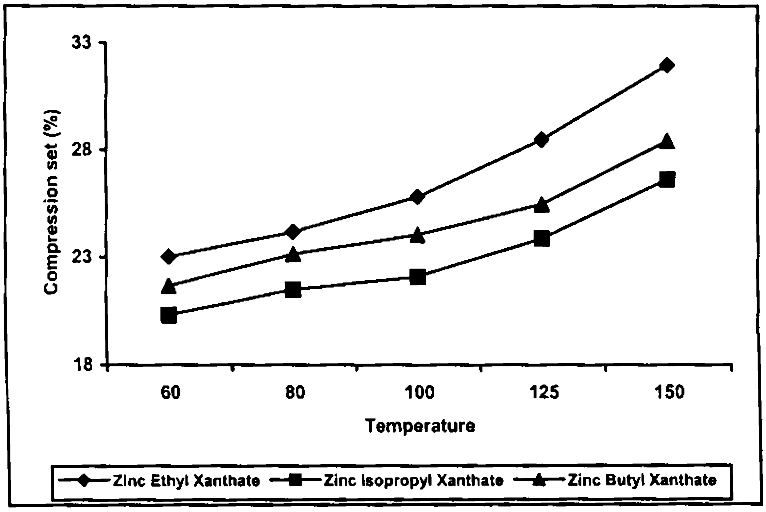


Fig. 4.1.11. Compression set of black filled NR vulcanizates containing xanthates

4.1.3. Conclusions

1. Zinc ethyl, zinc isopropyl and zinc butyl xanthates can be used as accelerators for the low temperature vulcanization of NR.
2. As the temperature of vulcanization decreases, cure time increases.
3. Crosslink density of the vulcanizates increases as the temperature of vulcanization decreases and more mono and disulphidic crosslinks are formed at lower temperatures.
4. All the mechanical properties of NR vulcanizates are found to increase as the temperature of vulcanization decreases.
5. At 150°C, the mechanical properties of the NR vulcanizates containing xanthate accelerators are very low.

Part 2

4. 2. NR vulcanizates containing zinc xanthate / ZDC

4.2.1. Experimental

Zinc salts of ethyl, isopropyl and butyl xanthates were prepared in the laboratory as per the procedure described earlier. Gum and black filled NR compounds were prepared using $Zn(ext)_2$/ZDC, $Zn(ipxt)_2$ /ZDC and $Zn(bxt)_2$/ZDC accelerator combinations.

In order to optimize the amount of xanthate / ZDC accelerator combination for the vulcanization of NR, the concentration of ZDC was varied from 0 to 1.25 phr as shown in table 4.2.1 and the concentration of zinc isopropyl xanthate was varied from 0 to 1.25 phr as shown in table 4.2.2. The cure characteristics of the mixes were determined using a Goettfert elastograph model 67.85 as per ASTM D 1646(1981) at 100°C. The optimum cure time (t_{90}) is calculated as the time taken for attaining 90% of the maximum torque. Scorch time (t_{10}) is the time taken for attaining 10% of the maximum torque. The cure rate index is calculated as $100/(t_{90} - t_{10})$. The cure characteristics are reported in table 4.2.7 and the different cure curves are given in fig. 4.2.1 and fig.4.2.2.

Gum and black filled NR compounds were prepared on a (6x12 inch) laboratory mixing mill as per the formulations given in table 4.2.3 and 4.2.4. The optimum cure times of these compounds were determined at different temperatures from 60°C – 150°C and are reported in table 4.2.8. The compounds were moulded in an electrically heated hydraulic press at various temperatures from 60°C – 150°C upto their optimum cure times at a pressure of 200kg/cm^2. Dumb bell shaped tensile test pieces were punched out of the compression moulded sheets along the mill grain direction. Angular test specimens were used to measure the tear resistance according to ASTM D 624.86. The tensile properties of the vulcanizates were evaluated on a Zwick universal testing machine using a cross head speed of 500 mm/minute according to ASTM D 2240. The tensile properties of the gum vulcanizates are given in table 4.2.9 and that of black filled vulcanizates are given in fig.4.2.3 to 4.2.5. Crosslink density of the samples were determined by equilibrium swelling method using toluene as the solvent and the degree of crosslinking was calculated using the Florey Rehner equation[34]. The crosslink density values of the NR gum vulcanizates moulded at different temperatures are given in table 4.2.9 and that of the black filled vulcanizates are shown in fig. 4.2.9. Abrasion resistance of the samples were tested using a DIN abrader according to DIN 53516. Compression set was determined as per ASTM D 395-61(method B). The heat build up of the samples were measured using Goodrich Flexometer conforming to ASTM D. 623-78(method A). Flex resistance of the samples were determined using a Wallace De Mattia flexing machine as per ASTM D 430-57 T. The mechanical properties of the NR gum vulcanizates moulded at different temperatures are given table 4.2.10 and that of the black filled vulcanizates are shown in figures 4.2.10 to 4.2.14.

Table 4.2.1. Formulation of Mixes

Mix	a_1	a_2	a_3	a_4	a_5
Natural rubber	100	100	100	100	100
ZnO	5	5	5	5	5
Stearic Acid	2	2	2	2	2
$Zn(ipxt)_2$	1.25	1.25	1.25	1.25	2.5
ZDC	1.25	1.0	0.75	0.50	-
Sulphur	2.5	2.5	2.5	2.5	2.5

Table 4.2.2. Formulation of Mixes

Mix	b_1	b_2	b_3	b_4	b_5
Natural rubber	100	100	100	100	100
ZnO	5	5	5	5	5
Stearic Acid	2	2	2	2	2
$Zn(ipxt)_2$	1.25	1.0	0.75	0.50	-
ZDC	0.75	0.75	0.75	0.75	1.75
Sulphur	2.5	2.5	2.5	2.5	2.5

Table 4.2.3. Formulation of Mixes

Mix	A	B	C	D	E
Natural Rubber	100	100	100	100	100
ZnO	5	5	5	5	5
Stearic acid	2	2	2	2	2
ZDC	0.75	0.75	0.75	-	1.75
$Zn(ext)_2$	1.0	-	-	2.5	-
$Zn(ipxt)_2$	-	1.0	-	-	-
$Zn(bxt)_2$	-	-	1.0	-	-
Sulphur	2.5	2.5	2.5	2.5	2.5

A – NR gum compound containing Zn $(ext)_2$/ZDC, B - NR gum compound containing $Zn(ipxt)_2$/ZDC, C - NR gum compound containing $Zn(bxt)_2$/ZDC, D-NR gum compound containing $Zn(ext)_2$, E- NR gum compound containing ZDC

Table 4.2.4 Formulation of mixes

Mix	F	G	H
Natural Rubber	100	100	100
Zinc Oxide	5	5	5
Stearic acid	2	2	2
HAF, N 330	40	40	40
Aromatic oil	5	5	5
HS	0.5	0.5	0.5
Vulcanox 4020	1.0	1.0	1.0
ZDC	0.75	0.75	0.75
Zn $(ext)_2$	1.0	-	-
Zn $(ipxt)_2$	-	1.0	-
Zn $(bxt)_2$	-	-	1.0
Sulphur	2.5	2.5	2.5

Table 4.2.5. Formulation of mixes

Mix	A_1	A_2	A_3	A_4	A_5	A_6
Natural Rubber	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2
HAF,N 330	-	5	10	20	30	40
Aromatic oil	-	-	-	2	4	5
HS	0.5	0.5	0.5	0.5	0.5	0.5
Vulcanox 4020	1.0	1.0	1.0	1.0	1.0	1.0
Zn $(bxt)_2$	1.0	1.0	1.0	1.0	1.0	1.0
ZDC	0.75	0.75	0.75	0.75	0.75	0.75
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

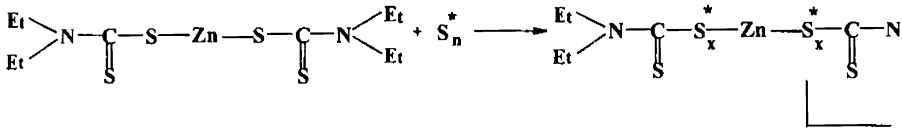
Table 4.2.6. Formulation of mixes

Mix	B_1	B_2	B_3	B_4	B_5	B_6
N. Rubber	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2
HAF, N 330	-	5	10	20	30	40
Aromatic Oil	-	-	-	2	4	5
HS	0.5	0.5	0.5	0.5	0.5	0.5
40.20	1.0	1.0	1.0	1.0	1.0	1.0
ZDC	0.75	0.85	0.95	1.15	1.35	1.55
Zn $(bxt)_2$	1	1.1	1.2	1.4	1.6	1.8
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

When the cure times of the mixes given in table 4.2.4 were determined, it is seen that curing becomes slow in black filled NR compounds compared to the curing of NR gum compounds. It is made clear by gradually increasing the concentrations of HAF from 5 phr to 40 phr as shown in table 4.2.5. It can be seen that the cure time of HAF filled NR compounds, containing different amounts of carbon black can be made equal to the cure times of NR gum compounds by gradually increasing the concentration of the accelerator as shown in table 4.2.6.

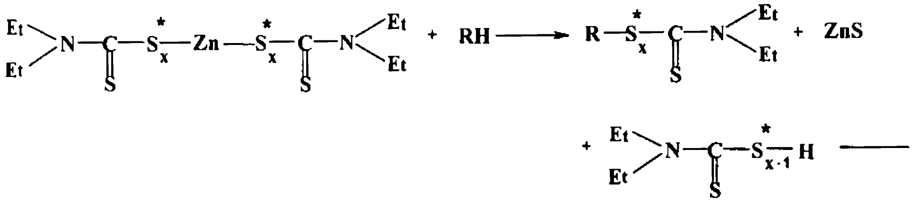
4.2.2. Results and discussion

The reaction of ZDC with NR may be in the following [35-36] manner. (equations 1-4). Sulphur rich complexes of ZDC are formed by inserting sulphur atoms in the zinc - dithiocarbamate bond.



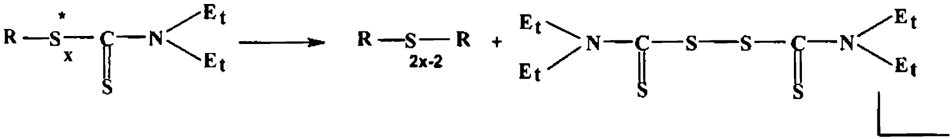
(1)

This polythio complex can act as an active sulphurating agent. This reacts with the rubber molecules in the presence of activators to give the rubber bound intermediate.



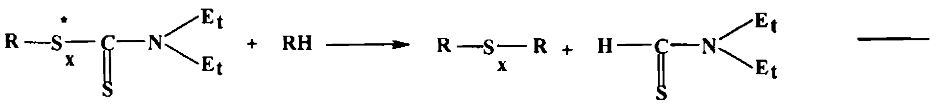
(2)

Then the crosslinking reaction starts giving the initial polysulphidic crosslinks



(3)

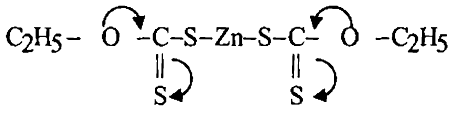
or



(4)

As the crosslinking reaction proceeds, the initial polysulphidic crosslinks changes to mono or disulphidic crosslinks.

In xanthates, oxygen donates its lone pair as follows:



$$C_2H_5-O-\underset{\underset{S}{\|}}{C}-S-Zn-S-\underset{\underset{S}{\|}}{C}-O-C_2H_5$$

But the nitrogen of the dithiocarbamate will donate its lone pair more readily than oxygen. So, in ZDC, the positive charge on the carbon atom of the C=S bond will be less thereby decreasing the polarity of the S - Zn bond. As a result, the breaking of the S - Zn bond will be difficult in ZDC compared to xanthate. Hence, xanthates are much more active accelerators compared to dithiocarbamates.

When two ultra accelerators are combined together, a synergistic effect may appear. Misatoya et al. and Aoe et al[37,38] explained the higher activity by the formation of either eutectic mixture or salt forming compounds having better solubility in rubber and greater chemical reactivity. Figure 4.2.1 and Figure 4.2.2 are the cure curves of the various mixes given in table 4.2.1 and 4.2.2 respectively at 100°C.

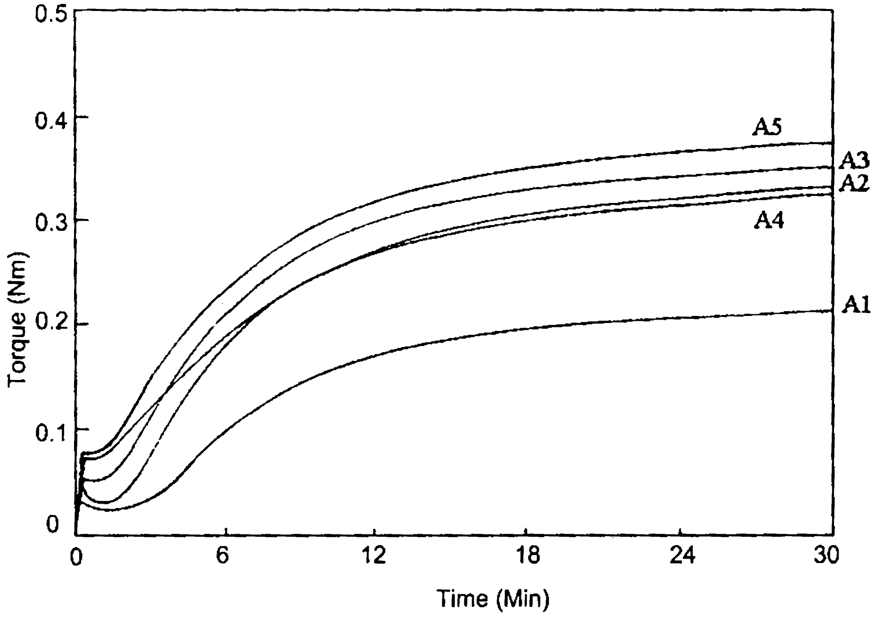


Fig. 4.2.1. Cure curves of the mixes given in table 4.2.1. at 100°C

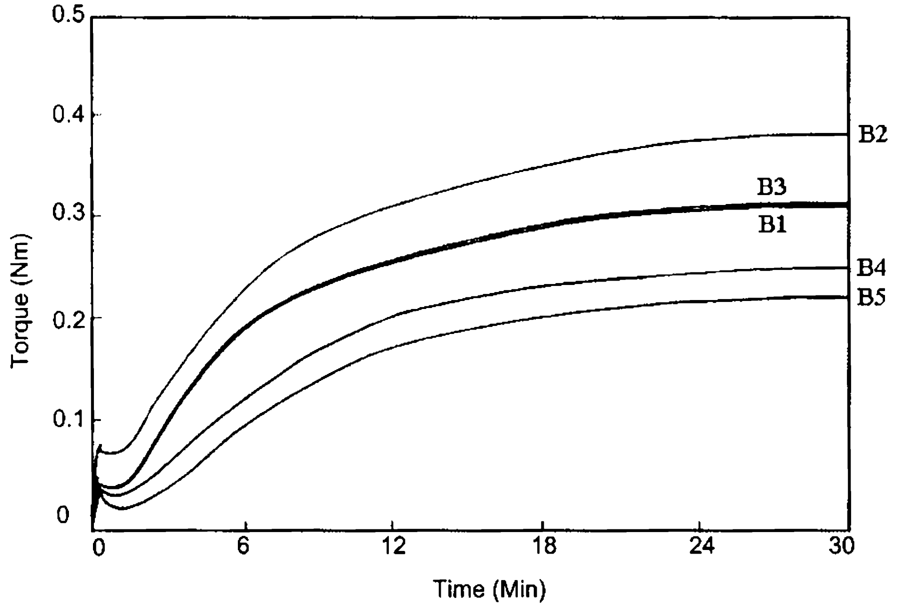


Fig. 4.2.2. Cure curves of the mixes given in table 4.2.2 at 100°C

The cure characteristics given in table 4.2.7 shows that among the zinc xanthate/ZDC compounds the maximum torque and cure rate index are highest and the optimum cure time is minimum for the compound containing 0.75 phr ZDC and 1.0 phr xanthate. This compound is having enough scorch time as not to cause processing problems. So 0.75 phr ZDC and 1.0 phr xanthate was taken as the optimum dosage for NR compounds. When zinc xanthate is used as the single accelerator (compound a_5), 2.5 phr is necessary, eventhough the compound has got a shorter cure time. The ZDC compound (b_5) has got a longer cure time compared to xanthate/ZDC compounds. So zinc xanthate/ZDC accelerator combination has got a positive synergistic effect on the curing of NR compounds.

Table 4.2.7. Cure Characteristics of mixes containing Zn(ipxt)$_2$/ZDC at 100°C

Mix	Min torque (Nm)	Max torque (Nm)	Scorch time (min)	Optimum cure time (min)	Cure rate Nm/min
A_1	0.022	0.209	2.85	9.98	0.028
A_2	0.026	0.319	2.33	9.50	0.044
A_3	0.048	0.339	2.12	8.93	0.047
A_4	0.070	0.310	1.83	11.32	0.032
A_5	0.077	0.371	1.98	8.65	0.050
B_1	0.040	0.336	2.10	8.90	0.047
B_2	0.071	0.384	1.84	8.55	0.052
B_3	0.042	0.337	2.11	8.92	0.048
B_4	0.031	0.258	2.30	9.45	0.034
B_5	0.020	0.227	2.50	12.12	0.030

Table 4.2.8 shows the optimum cure times of the gum and black filled NR compounds given in table 4.2.3 and 4.2.4 at different temperatures. The results show that the cure time increases as the temperature of curing is changed from 150°C to 60°C. Again, it is clear that at a particular temperature, the cure times of the NR compounds decreases from Zn (ext)$_2$ /ZDC $\rightarrow$ Zn(ipxt)$_2$/ZDC $\rightarrow$ Zn(bxt)$_2$/ZDC. As explained earlier, it may be due to the better solubility of the accelerator in NR when the size of the alkyl group in the accelerator increases. Zinc xanthate alone can cure NR compounds at all temperatures from 60°C to150°C in a shorter time, but the amount of xanthate needed is 2.5 phr. ZDC can cure NR compounds only upto 100°C; below 100°C, curing of NR compounds is not possible if ZDC alone is used as the accelerator.

At any temperature, when the cure time of the black filled compound is compared with their corresponding gum compounds, it is seen that curing becomes slow when carbon black is added. It is made clear by gradually increasing the amount of carbon black from 0 to 40 phr as shown in table 4.2.5. Fig. 4.2.3 & 4.2.4 are the cure curves of the mixes given in table 4.2.5 at 150°C and 125°C respectively. It is seen that there is a proportionate increase in cure time with the amount of carbon black present in the compound. This may be due to the adsorption of accelerator on the surface of carbon black. But it can be shown that the cure times of the compounds, containing any amount of carbon black can be made equal to that of the corresponding gum compounds by gradually increasing the accelerator concentration as shown in table 4.2.6. Fig. 4.2.5 &4.2.6 are the cure curves of the mixes given in table 4.2.6 at 150°C and 125°C respectively. Thus in HAF filled NR compounds, the cure time is influenced by the accelerator concentration.

Table 4.2.8. Optimum cure times of the compounds given in tables 4.2.3 and 4.2.4

Temp. (°C)	A	B	C	D	E	F	G	H
150	0.98	0.86	0.79	0.76	1.98	1.81	1.42	1.26
125	4.42	3.27	3.01	2.39	10.31	8.01	7.20	7.11
100	9.38	8.70	7.01	5.00	24.38	30.12	25.31	21.24
80	35.86	32.76	29.68	21.20	-	78.16	72.41	63.62
60	59.75	55.32	50.41	50.10	-	92.65	90.42	88.31

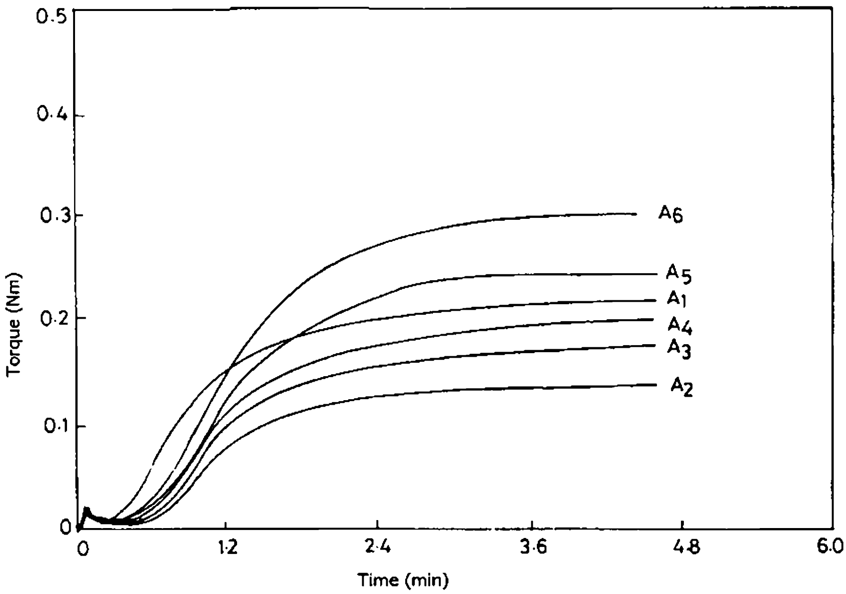


Fig. 4.2.3. Cure curves of the compounds given in table 4.2.5. at 150°C

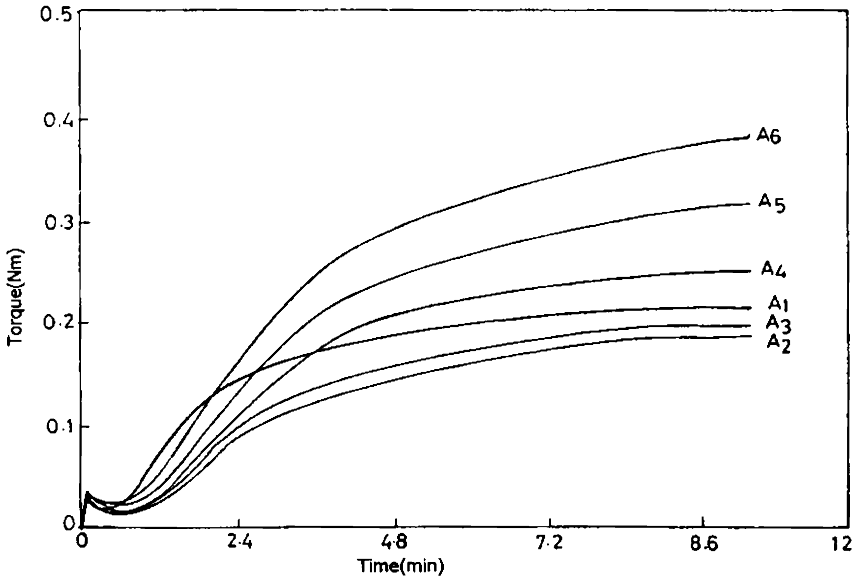


Fig. 4.2.4. Cure curves of the compounds given in table 4.2.5. at 125°C

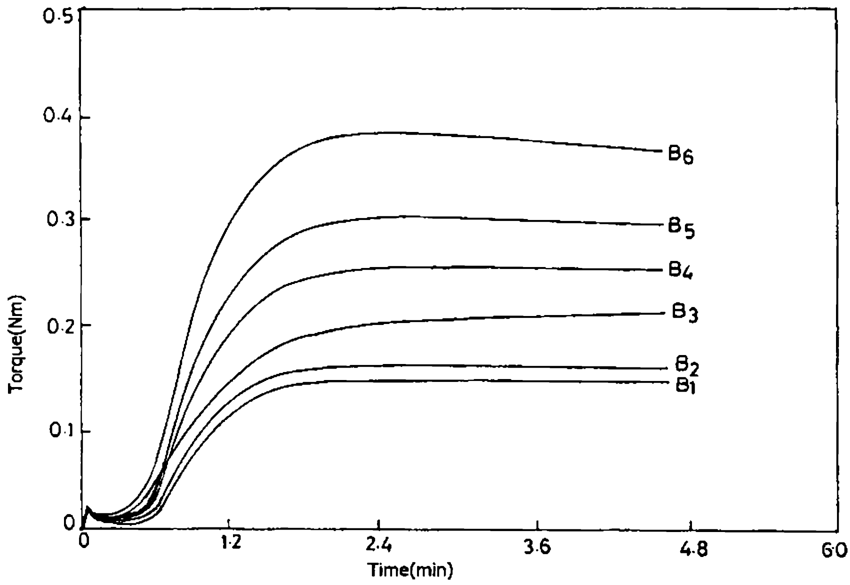


Fig. 4.2.5. Cure curves of the compounds given in table 4.2.6. at 150°C

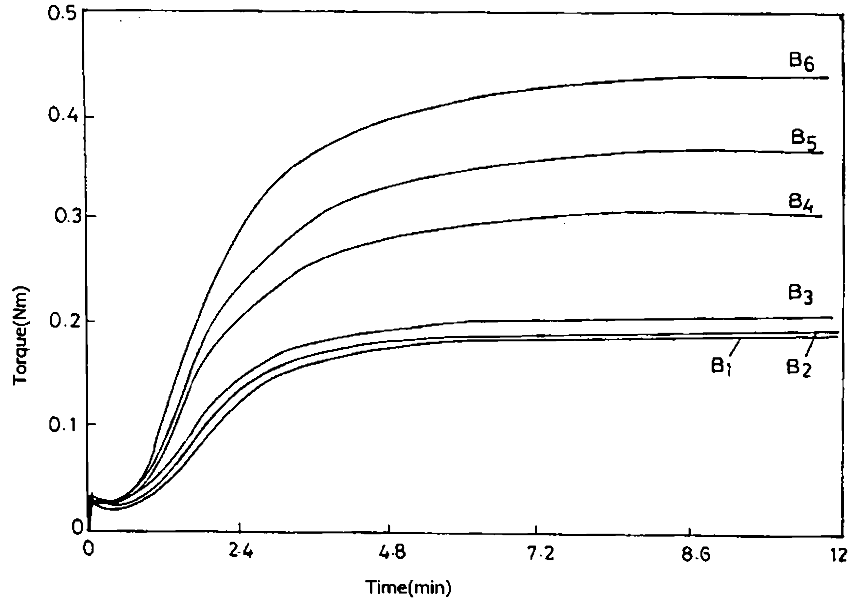


Fig. 4.2.6. Cure curves of the compounds given in table 4.2.6. at 125°C

Table 4.2.9 gives the crosslink density and tensile properties of the NR gum vulcanizates (compounds A to E given in table 4.2.3) moulded at different temperatures. Figures 4.2.7 to 4.2.10 shows the crosslink density and tensile properties of the black filled vulcanizates (compounds F to H given in table 4.2.4) moulded at different temperatures. The results show that the total crosslink density increases as the temperature of curing decreases. This may be due to the better stability of the accelerator at lower temperatures. The higher values of tensile properties at lower temperatures is in agreement with their higher crosslink density values. Other mechanical properties such as abrasion resistance, compression set, flex resistance and heat build up of NR gum vulcanizates moulded at different temperatures are given in table 4.2.10 and the corresponding values of the black filled vulcanizates are given in figures 4.2.11 to 4.2.15. As expected, all the mechanical properties increases as the temperature of curing is decreased from 150°C to 60°C. At any particular temperature, the mechanical properties of the black filled vulcanizates are found to be high compared to that of the corresponding gum vulcanizate. This is due to the reinforcement of NR by carbon black. Again, it is seen that zinc xanthate /ZDC accelerator combination has got a positive synergistic effect on the mechanical properties of the NR vulcanizates compared to zinc xanthate vulcanizates and ZDC vulcanizates.

Table 4.2.9. Mechanical properties and crosslink densities of the NR gum vulcanizates at different temperatures

Mix	Temp. (°C)	Crosslink density (g/mol/cm^3)	Tensile strength (N/mm^2)	Tear strength (N/mm)	Elongation at break (%)
A	150	4.87×10^{-5}	21.23	44.48	1600
	125	5.23×10^{-5}	24.12	48.18	1565
	100	6.26×10^{-5}	25.42	55.80	1405
	80	6.43×10^{-5}	26.12	59.50	1295
	60	6.68×10^{-5}	27.34	62.62	1265
B	150	5.16×10^{-5}	22.57	48.58	1510
	125	6.43×10^{-5}	25.12	51.91	1415
	100	6.83×10^{-5}	26.43	60.38	1382
	80	6.96×10^{-5}	27.10	69.72	1275
	60	7.02×10^{-5}	27.96	73.62	1255
C	150	4.92×10^{-5}	22.13	46.72	1550
	125	5.33×10^{-5}	25.01	50.06	1477
	100	6.42×10^{-5}	25.93	57.68	1395
	80	6.57×10^{-5}	26.83	66.32	1300
	60	6.86×10^{-5}	27.78	69.76	1252
D	150	1.29×10^{-5}	10.63	27.01	750
	125	2.36×10^{-5}	19.02	32.65	673
	100	3.26×10^{-5}	20.90	55.61	651
	80	4.48×10^{-5}	23.12	58.49	647
	60	5.62×10^{-5}	24.72	60.86	533
E	150	4.20×10^{-5}	20.01	35.68	862
	125	4.56×10^{-5}	21.62	40.65	751
	100	4.98×10^{-5}	22.16	50.43	702
	80	-	-	-	-
	60	-	-	-	-

Table 4.2.10. Properties of the NR gum vulcanizates at different temperatures

Mix	Temp. (°C)	Abrasion loss (cc/hr)	Compression set (%)	HeatBuild up (ΔT) °C	Flex resistance	
					Crack initiation (cycles)	Crack growth (cycles)
A	150	13.70	31.52	20	32,432	68,525
	125	5.65	29.88	15	41,782	85,335
	100	3.42	29.79	12	99,698	5,93,552
	80	2.57	26.81	11	1,09,928	6,23,498
	60	2.24	24.53	10	1,10,468	6,24,423
B	150	10.59	29.71	13	36,348	88,341
	125	5.21	28.92	11	46,373	97,420
	100	2.98	27.34	10	4,53,904	14,01,125
	80	2.35	19.42	9	4,78,926	15,78,320
	60	1.72	18.62	9	4,83,496	15,91,426
C	150	11.52	30.42	16	34,523	76,428
	125	5.27	29.36	12	45,403	92,335
	100	3.10	28.13	11	3,67,980	13,92,652
	80	2.37	23.61	10	3,83,426	14,20,246
	60	2.15	22.29	10	3,85,628	14,28,328
D	150	21.36	37.68	23	21,125	41,123
	125	18.25	33.04	18	30,456	69,987
	100	12.32	31.63	15	68,147	3,58,852
	80	7.98	28.65	13	86,987	4,16,963
	60	4.36	26.35	11	91,456	5,03,159
E	150	14.36	33.65	19	29,456	63,357
	125	10.25	31.47	16	33,852	78,147
	100	7.85	30.58	13	84,654	4,97,158
	80	-	-	-	-	-
	60	-	-	-	-	-

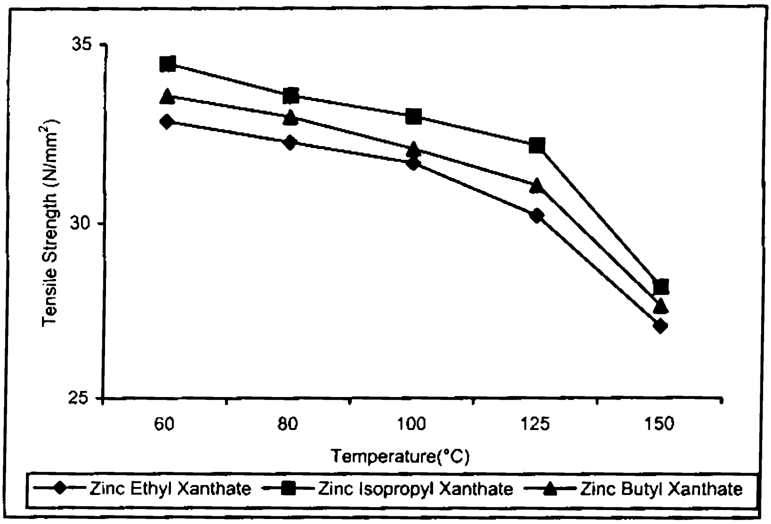


Fig.4.2.7. Tensile strength of the black filled NR vulcanizates

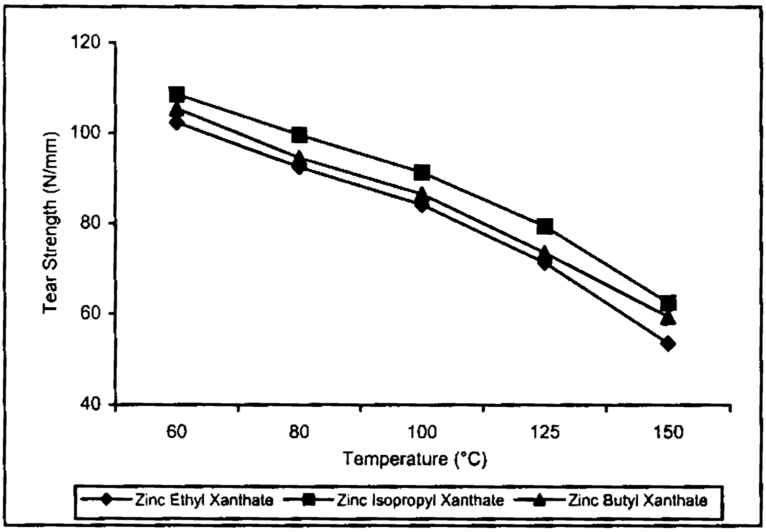


Fig.4.2.8. Tear strength of the black filled NR vulcanizates

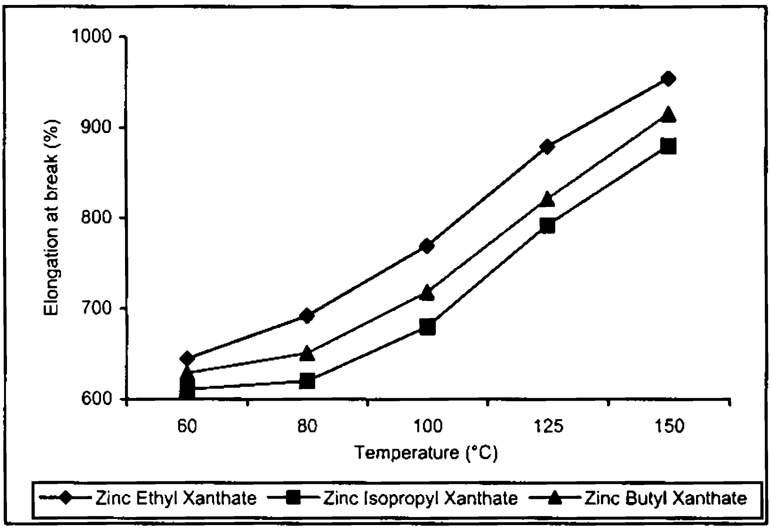


Fig.4.2.9. Elongation at break of black filled NR vulcanizates

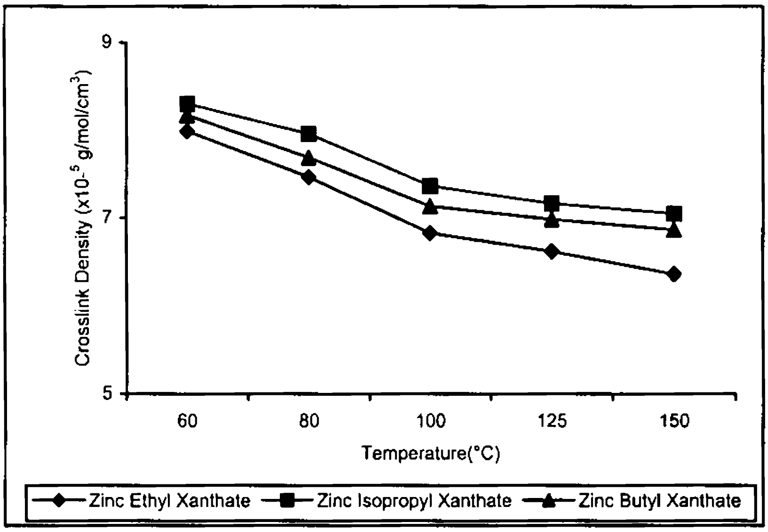


Fig. 4.2.10. Crosslink density of black filled NR vulcanizates

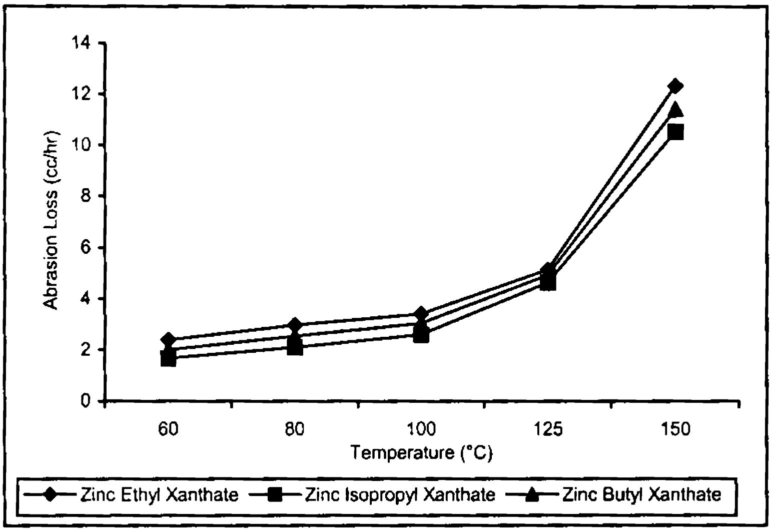


Fig.4.2.11. Abrasion resistance of black filled NR vulcanizates

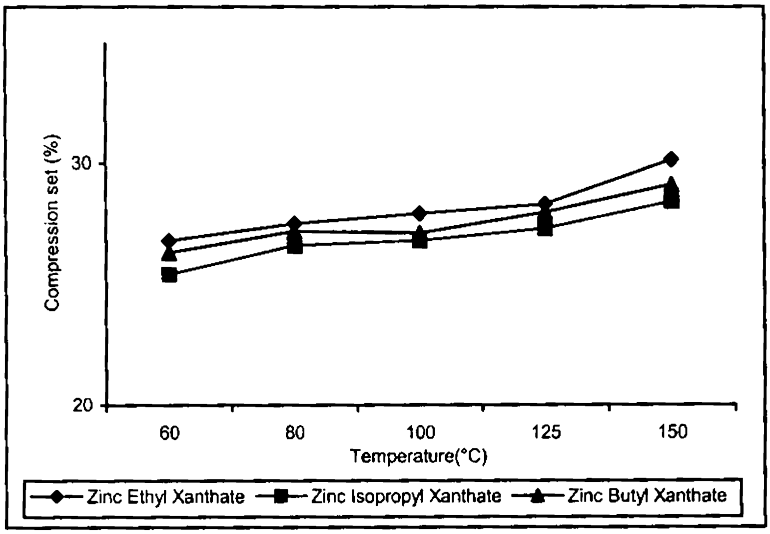


Fig.4.2.12. Compression set of black filled NR vulcanizates

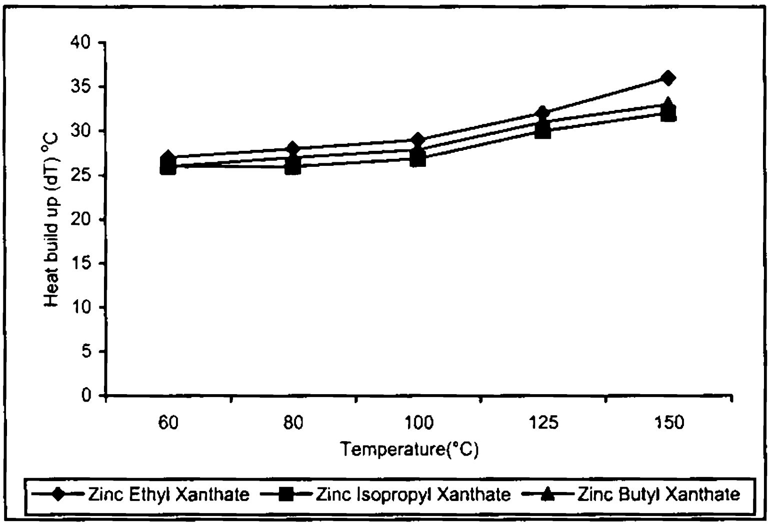


Fig.4.2.13. Heat build up of Black filled NR vulcanizates

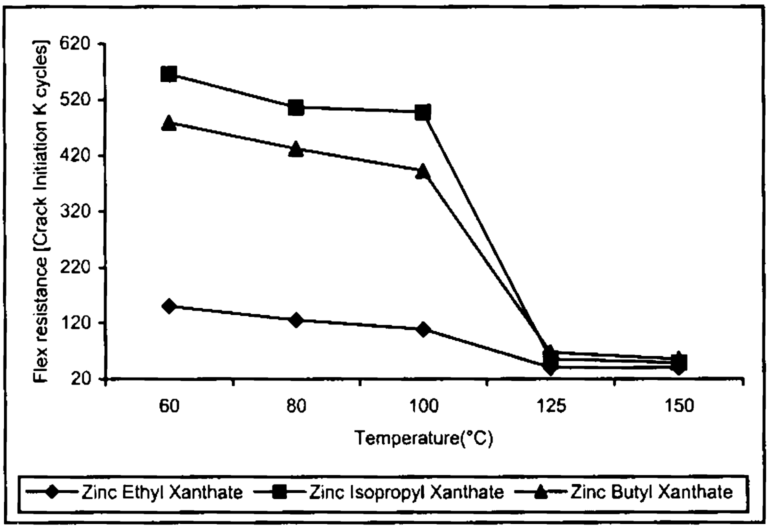


Fig. 4.2.14. Flex resistance of Black filled NR vulcanizates

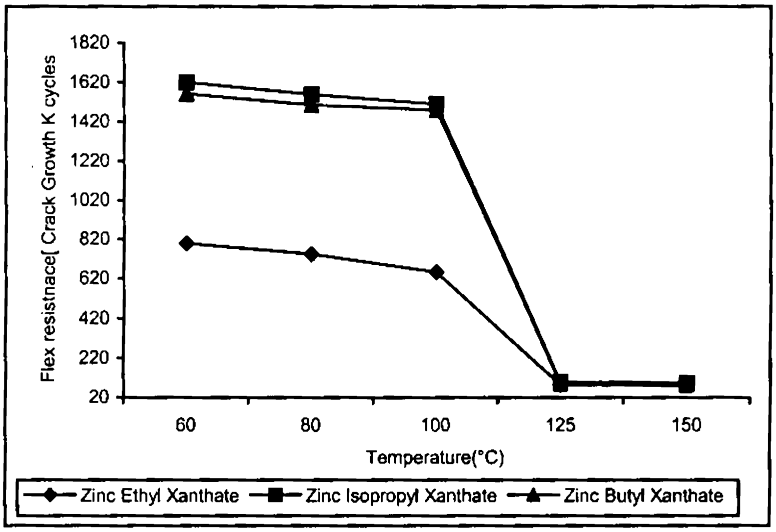


Fig.4.2.15. Flex resistance of black filled NR vulcanizates (crack growth)

4.2.3. Conclusions

1. Zinc xanthate /ZDC accelerator combination can vulcanize NR at all temperatures from 60°C to 150°C.
2. The total accelerator concentration could be reduced to 1.75 phr and the mechanical properties of the NR vulcanizates could be improved by using zinc xanthate /ZDC accelerator combination in place of xanthates alone.
3. As the temperature of vulcanization is reduced from 150°C to 60° C, the mechanical properties are found to be increased.
4. At a particular temperature, the cure time is minimum for the compound containing $Zn(bxt)_2$/ZDC.
5. The cure rate of NR is found to be decreased by the addition of carbon black.
6. The cure times of black filled NR compounds could be made equal to that of gum compounds by increasing the accelerator concentration.

Part 3

4.3. Room temperature vulcanization of NR and NR latex

4.3.1.Experimental

Gum and black filled NR compounds were prepared on a (6x12 inch) laboratory mixing mill as per the formulations given in table 4.3.1 and 4.3.2. The optimum cure times of the compounds were determined at 30°C from the tensile strength values by trial and error method and are reported in table 4.3.4. The compounds were moulded in an electrically heated hydraulic press at room temperature at a pressure of 200kg/cm^2. The chemical crosslink density was estimated by swelling the samples in toluene as described in detail in chapter 2. The crosslink density values of the vulcanizates are given in table 4.3.4. Dumb bell shaped tensile test pieces were punched out of the compression moulded sheets along the mill grain direction. Angular test specimens were used to measure the tear resistance according to ASTM D 624.86. The tensile properties of the vulcanizates were evaluated on a Zwick universal testing machine using a cross head speed of 500 mm/minute according to ASTM D 2240 and are reported in table 4.3.4

NR latex is compounded as per the formulations given in table 4.3.3. The compound was given maturation for16 hours and the sheets were prepared by casting. The time for prevulcanisation of latex was determined from the tensile strength values of the sheets prepared from the latex compound measured at a time interval of 1 hour for three days. It is also confirmed by chloroform test. The tensile properties measured after the completion of curing are reported in table 4.3.5. Properties like mechanical stability time (MST), pH, KOH number and VFA of the prevulcanised latex were measured at different time intervals like one month, two months and three months after prevulcanization and the values are reported in table 4.3.6. These values are compared with those of the commercially available Revertex prevulcanized latex.

Table 4.3.1. Formulation of mixes

Mix	**A**	**B**	**C**	**D**	**E**	**F**
Natural Rubber	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
ZDC	-	-	-	0.75	0.75	0.75
$Zn(ext)_2$	2.5	-	-	1.0	-	-
$Zn(ipxt)_2$	-	2.5	-	-	1.0	-
Zn(bxt)	-	-	2.5	-	-	1.0
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

Table 4.3.2. Formulation of mixes

Mix	A_1	B_1	C_1	D_1	E_1	F_1
Natural Rubber	100	100	100	100	100	100
Zinc Oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
HAF, N 330	25	25	25	40	40	40
Aromatic oil	3	3	3	5	5	5
HS	0.5	0.5	0.5	0.5	0.5	0.5
Vulcanox 4020	0.5	0.5	0.5	0.5	0.5	0.5
ZDC	-	-	-	0.75	0.75	0.75
$Zn\ (ext)_2$	2.5	-	-	1.0	-	-
$Zn\ (ipxt)_2$	-	2.5	-	-	1.0	-
$Zn\ (bxt)_2$	-	-	2.5	-	-	1.0
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

Table 4.3.3. Formulation of NR latex mix

Latex Mix	A
NR latex	167
10% KOH	1.0
10% Potassium oleate	0.5
50% ZnO	1.0
50% ZDC	1.5
50% $Zn(bxt)_2$	1.5
50% Sulphur	2.5

4.3.2. Results and discussion

Table 4.3.4. gives the cure times and tensile properties of gum and black filled NR compounds containing zinc xanthates and zinc xathate / ZDC combinations at room temperature. Using zinc xanthate alone requires an accelerator concentration of 2.5phr. When zinc xathate/ZDC combination is used, the total accelerator concentration could be reduced to 1.75phr, eventhough there is a slight increase in cure time. The tensile properties of NR vulcanizates were improved when zinc xanthate / ZDC accelerator combination is used than using zinc xanthate alone.

Table 4.3.5.shows the time for prevulcanisation of NR latex at room temperature and the tensile properties of the prevulcanized latex sheets. The prevulcanization of NR latex takes 54 hours for completion at room temperature. The high tensile properties obtained for the room temperature prevulcanized latex compared to the commercially available prevulcanised latex are due to the non-application of temperature on latex. Table 4.3.6. gives properties of the prevulcanised latex such as MST, pH, KOH number and VFA measured at different time intervals. pH, KOH number and VFA of the room temperature prevulcanized latex is comparable with that of the commercially available prevulcanized latex ; the MST values are found to be higher for the room temperature prevulcanized latex.

Table 4.3.4. Cure time and tensile properties of the vulcanizates at room temperature

Mix	Cure time (hrs)	Tensile strength (N/mm^2)	Tear strength (N/mm)	Elongation at break (%)	Crosslink density ($g/mol/cm^3$)
A	42	21.00	55.21	651	3.18×10^{-5}
B	42	23.10	58.90	661	5.45×10^{-5}
C	42	21.32	57.10	598	4.43×10^{-5}
D	60	24.16	52.65	621	5.62×10^{-5}
E	48	28.06	62.15	561	6.92×10^{-5}
F	36	26.97	58.99	578	6.85×10^{-5}
A_1	42	24.43	59.01	625	2.96×10^{-5}
B_1	42	25.80	65.90	548	4.96×10^{-5}
C_1	42	24.10	61.26	562	4.23×10^{-5}
D_1	78	29.86	29.86	611	6.15×10^{-5}
E_1	72	33.02	33.02	526	6.95×10^{-5}
F_1	58	32.60	32.60	539	6.93×10^{-5}

Table 4.3.5. Cure time and tensile properties of the prevulcanised latex.

Mix	Cure time	Tensile strength	Tear strength	Crosslink denstity
A	54 hours	28.85 N/mm^2	67.50N/mm	$2.6206 \times 10^{-5} g/mol/cm^3$

Table 4.3.6. Properties of the prevulcanised latex

Properties	Revertex PVL	Xanthate PVL After		
		1 month	2 months	3 months
pH	9.87	11.650	11.68	11.66
KOH number	0.45	0.5060	0.5116	0.5132
VFA	0.035	0.0415	0.0417	0.0419
MST	480	890	880	850

4.3.3. Conclusions

1) Zinc xanthates and zinc xanthate / ZDC combinations can vulcanize NR at room temperature.
2) When zinc xanthate alone is used, the accelerator concentration required is 2.5phr; when zinc xanthate / ZDC accelerator combination is used, the total accelerator concentration could be reduced to 1.75phr along with an improvement in mechanical properties
3) Zinc xanthate / ZDC combination can prevulcanise NR latex at room temperature.
4) Tensile properties and properties like MST, VFA, pH and KOH number of the room temperature prevulcanised latex are found to be better than that of the commercially available prevulcanised latex.

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Chapter 5

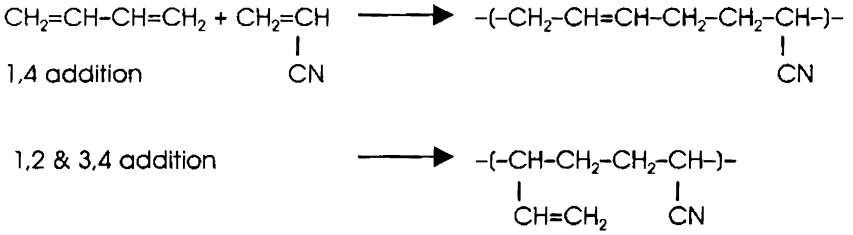
USE OF ZINC XANTHATE ACCELERATORS IN COMBINATION WITH DITHIOCARBAMATE FOR THE CURING OF NBR AT DIFFERENT TEMPERATURES

Introduction

Natural and synthetic rubbers differ in the rate of curing and vulcanizate properties. Compared to NR, synthetic rubbers are vulcanized with higher concentration of accelerators with a corresponding reduction in sulphur. Synthetic rubbers like SBR, BR, NBR etc. do not undergo stress induced crystallisation and hence the green strength and tensile properties of the gum vulcanizates of these rubbers are inferior to those of NR.

Nitrile rubber (NBR) is a copolymer of butadiene and acrylonitrile and is considered as a 'special purpose synthetic rubber'[1]. It has excellent oil resistance but is subject to degradation at very high temperatures[2-3]. It is widely used in products like oil seals, water pump seals, blow out preventors, fuel lines, hoses, fuel pump diaphragms etc. because of its high oil, solvent and fuel resistance and gas impermeability[4]. The acrylonitrile (ACN) content in NBR usually varies from 20 – 50 % by weight and accordingly NBR is classified into three types – low ACN content NBR with less than 25%, medium with 25-35% and high with 35-50%. Major properties of the elastomer depend on the ACN content. The service temperature in presence of oxygen is estimated to be 130°C[5].

The basic reaction in NBR production is as shown below. There are three possible additions, viz. 1,2 ; 1,4 and 3,4. The first and the third give identical products.



1,4 addition

$$CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}\underset{\displaystyle CN}{\underset{|}{CH}} \longrightarrow -(-CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CN}{\underset{|}{CH}}-)-$$

1,2 & 3,4 addition

$$\longrightarrow -(-\underset{\displaystyle CH{=}CH_2}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}\underset{\displaystyle CN}{\underset{|}{CH}}-)-$$

Analysis of a 28% ACN rubber is found to contain 89.5% 1,4 units and 10.5% 1,2[6]. Apart from the type of addition, the stereochemistry also is to be considered. It is seen that a higher percentage of trans 1,4 addition occurs at the expense of 1,2 when polymerisation is done by cold process (7°C). This results in a more linear structure, with improved processibility and compound viscosity.

The properties of NBR vulcanizates depends mainly on the ACN content. Usually, in a rubber the properties like oil resistance and low temperature flexibility are mutually incompatible. As the ACN content increases, the oil resistance increases. For example, a 20% ACN, NBR shows a volume swell of 59% whereas in a 50% ACN rubber, it is only 7%[7]. Further, a 50% ACN rubber shows a low temperature brittleness of 3°F, whereas a 20% ACN rubber shows it to be $^-69$°F. Other properties affected by monomer ratio are processibility, cure rate, heat resistance and resistance to permanent set. With increased ACN content, processibility is easier, cure rate is higher and heat resistance is better. But resistance to permanent set is decreased; higher viscosity, low die swell etc can also be expected. Mooney viscosity of NBR ordinarily ranges from 30 to 80.

Basically nitrile rubbers are compounded like natural rubber. NBR shows no self-reinforcing effect, as there is no crystallinity. So the unfilled vulcanizates have very low tensile strength[8]. When used in combination with reinforcing fillers, vulcanizates with excellent mechanical properties are obtained[9]. The dynamic properties, which are important for applications like tires, are altered significantly by the addition of carbon black[10]. In black filled compounds, reinforcement is proportional to the fineness of the black. Precipitated silica is the most reinforcing among the non-black fillers, but when used in higher quantities, it gives stocks that are hard and boardy.There have been a number of studies on the reinforcement mechanism of fillers in rubber[11-14]. Studies on filled systems have also been reviewed by Kraus[15] and Voet[16]. It is generally agreed that strong links exist between rubber chains and reinforcing filler particles[17-18].

Plasticizers are used in almost all nitrile compounds to aid processing, to improve low temperature flexibility and to reduce hardness. Plasticizer level generally varies from 5-50phr. Processing will be difficult below 5 phr level and above 50 phr, plasticiser may bleed out and physical properties may deteriorate unacceptably. Generally, three types of plasticizers are used – organic esters to get the best low temperature flexibility, coal tar resins to maintain tensile properties and to improve the building tack, and polymeric esters to obtain high temperature aging.

Vulcanization of nitrile rubber is usually accomplished with sulphur, accelerator and zinc oxide – fatty acid activator. In special cases peroxides may also be used. The higher ACN content rubbers cure faster than lower content ones. The amount of sulphur to be used is based on butadiene content and is generally lower than that used for natural rubber and ranges from 0.7 to 2.3 phr. The solubility of sulphur is considerably less than in NR and affect its uniform dispersion. For this reason, sulphur is added early in the mix.

In this chapter, the effect of zinc xanthate / ZDC accelerator combination on the curing and mechanical properties of black filled, gum and silica filled NBR compounds at different temperatures are discussed.

Part 1

5.1 Black filled NBR vulcanizates containing zinc xanthate/ZDC

5.1.1. Experimental

Materials used

NBR (Acrylonitrile content - 33%, mooney viscosity (ML(1+4) at 100°C - 40.9) was supplied by Apar polymers Pvt. Ltd., Gujarat. Compounding ingredients, ie, zinc oxide, stearic acid, ZDC, dioctyl phthalate (DOP), carbon black(HAF N 330), vulcanox 4020, HS, silica and sulphur were commercial grade. Denatured spirit, isopropyl alcohol, n-butyl alcohol, potassium hydroxide, carbon disulphide, diethylene glycol (DEG), styrenated phenol (SP) and methyl ethyl ketone (MEK) used for swelling studies were of reagent grade. Zinc sulphate used for precipitation was commercial grade.

Zinc salts of ethyl, isopropyl and butyl xanthates were prepared in the laboratory as per the procedure described earlier. Black filled NBR compounds were prepared using [Zn(ext)$_2$]/ZDC, [Zn(ipxt)$_2$]/ZDC and [Zn(bxt)$_2$]/ZDC accelerator systems. A reference NBR compound containing TMTD/MBTS was also prepared.

Compounding

In order to optimize the amount of accelerator for vulcanization in NBR compounds, the concentration of Zn(ipxt)$_2$ was changed from 0 to 2 phr as shown in table 5.1.1 and the concentration of ZDC was changed from 1 to 1.75 phr as shown in table 5.1.2. The cure characteristics of the mixes were determined using a Goettfert elastograph model 67.85 as per ASTM D 1646(1981) at 150°C. The minimum torque, maximum torque, scorch time, optimum cure time and the cure rate of the above mixes were reported in table 5.1.3.

NBR was compounded on a (6×12") laboratory-mixing mill according to the formulations given in table 5.1.4. The optimum cure times of the compounds were determined and are reported in table 5.1.5. NBR compounds were moulded in an electrically heated laboratory hydraulic press at various temperatures from 60°C-150°C upto their optimum cure times at a pressure of 200 kg/cm^2. Dumb bell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick universal testing machine using a cross head speed 500 mm/ minute according to ASTM D 2240 and are graphically represented in fig. 5.1.1 to 5.1.3. Crosslink density of the samples were determined by equilibrium swelling methods using MEK as the solvent. The degree of crosslinking was calculated using the Florey Rehner equation[19] and are shown in fig 5.1.4. Abrasion resistance was tested using DIN abrader according to DIN 53516 and are given in fig.5.1.5. The flex resistance of the samples was determined by using a Wallace De Mattia flexing machine as per ASTM D 340-57 T and are given in fig. 5.1.6. Compression set of samples (6.25 mm thick and 18 mm diameter) was determined by compressing to constant deflection (25%) and were kept for 22 hours in an air oven at 70°C(ASTM D 395-61, method B) and are given in fig. 5.1.7. The heat build up was measured using the Goodrich flexometer conforming to ASTM D 623.78 (method A) and the values are given in fig. 5.1.8.

Table 5.1.1. Formulation of mixes

Mix	A_1	A_2	A_3	A_4	A_5	A_6
NBR	100	100	100	100	100	100
ZnO	4	4	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
$Zn(ipxt)_2$	0	1.0	1.25	1.5	1.75	2.0
ZDC	3	1.5	1.5	1.5	1.5	1.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5

Table 5.1.2 Formulation of mixes

Mix	B_1	B_2	B_3	B_4
NBR	100	100	100	100
ZnO	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5
$Zn(ipxt)_2$	1.75	1.75	1.75	1.75
ZDC	1.0	1.25	1.50	1.75
Sulphur	1.50	1.50	1.50	1.50

Table 5.1.3 Cure Characteristics of the mixes given in table 5.1.1 and table 5.1.2

Mix	Min torque (Nm)	Max torque (Nm)	Scorch time (min)	Optimum cure time (min)	Cure rate (Nm/min)
A_1	0.024	0.285	1.40	2.82	0.14
A_2	0.027	0.264	1.11	2.41	0.16
A_3	0.034	0.272	1.02	2.20	0.19
A_4	0.039	0.279	0.84	2.12	0.21
A_5	0.040	0.291	0.75	1.99	0.24
A_6	0.041	0.290	0.74	1.99	0.23
B_1	0.035	0.258	0.83	2.16	0.22
B_2	0.039	0.315	0.81	1.91	0.27
B_3	0.040	0.291	0.75	1.99	0.24
B_4	0.039	0.290	0.73	2.02	0.24

Table 5.1.4. Formulation of mixes

Mix	A	B	C	D
NBR	100	100	100	100
ZnO	4.0	4.0	4.0	4.0
Stearic Acid	1.5	1.5	1.5	1.5
HAF	40	40	40	40
DOP	6.0	6.0	6.0	6.0
Vulcanox 4020	1.0	1.0	1.0	1.0
HS	0.5	0.5	0.5	0.5
MBTS	1.5	–	–	–
TMTD	0.5	–	–	–
ZDC	–	1.25	1.25	1.25
$Zn(ext)_2$	–	1.75	–	–
$Zn(ipxt)_2$	–	–	1.75	–
$Zn(bxt)_2$	–	–	–	1.75
Sulphur	1.5	1.5	1.5	1.5

5.1.2. Results and discussions

Table 5.1.5 shows the cure times of the mixes given in table 5.1.4 at different temperatures. It is seen that at 150°C and 125°C, the curing of NBR compound containing MBTS/TMTD is slow compared to the compound containing ZDC/xanthate. Below 125°C, MBTS/TMTD combination cannot cure NBR.

ZDC and zinc alkyl xanthates are ultrafast accelerators and both ensure low temperature vulcanization. Xanthates are found to be much more effective accelerators compared to dithiocarbamates because of the presence of electronegative oxygen atom. The cure characteristics given in table 5.1.3 show that the maximum torque and cure rate are maximum and the optimum cure time is minimum for the compound containing 1.25 phr ZDC and 1.75 phr zanthate. This compound has enough scorch time and may not cause processing problems. So 1.25 phr ZDC and 1.75 phr xanthate are taken as the optimum dosage for NBR compounds.

Table 51.5 shows that the optimum cure times of the NBR compounds containing $Zn(ext)_2/ZDC$, $Zn(ipxt)_2/ZDC$, $Zn(bxt)_2/ZDC$ increase as the temperature of curing is changed from 150°C to 60°C. Again, it is clear that, at a particular temperature the cure times of the NBR compounds containing the xanthate accelerators decrease in the following order.

$Zn\,(ext)_2/ZDC \rightarrow Zn(ipxt)_2/ZDC \rightarrow Zn(bxt)_2/ZDC$.

Figs. 5.1.1- 5.1.3 show the tensile properties of the mixes B, C, and D given in table 5.1.4. At all temperatures, the NBR compounds show considerable tensile properties. But, when the temperature of curing is changed from 150°C to 60°C, tensile strength and tear strength increases and elongation at break decreases. This is because of the lesser degradation of rubber at lower temperatures. Fig. 5.1.4 shows the crosslink density of the mixes B, C and D. Crosslink density increases as the temperature of curing is changed from 150°C to 60°C. This may be due to the higher stability of the accelerator at lower temperatures. Fig. 5.1.5, fig. 5.1.6, fig.5.1.7 and fig. 5.1.8 show the abrasion loss, flex resistance, compression set and heat build up respectively. At all temperatures, NBR compounds show considerable mechanical properties. But when the temperature of curing is changed from 150°C to 60°C, all the mechanical properties are found to increase. This is due to the higher crosslinking at lower temperatures.

Table 5.1.5 Cure times of the mixes given in table 5.1.4(in minutes)

Temp (°C)	A	B	C	D
150	3.1	2.5	1.91	1.78
125	9.8	6.7	5.7	4.9
100	No curing	17.1	15.6	14.1
80	No curing	45.1	40.2	36.56
60	No curing	72.6	69.38	67.58

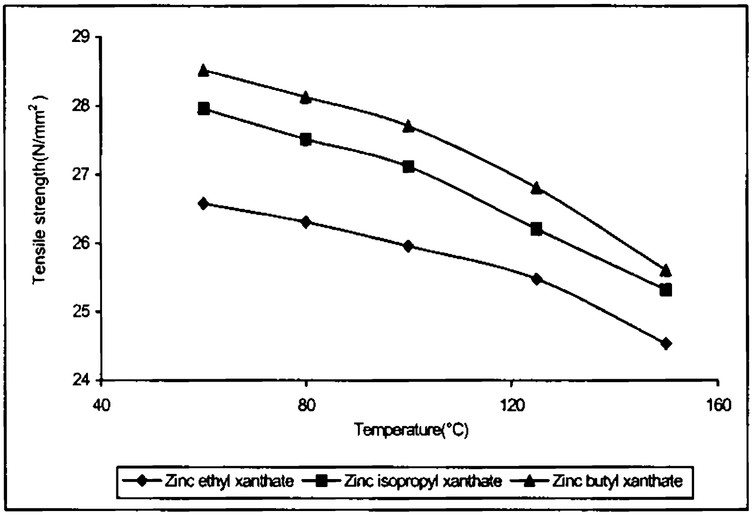


Fig.5.1.1. Tensile strength of the black filled NBR vulcanizates

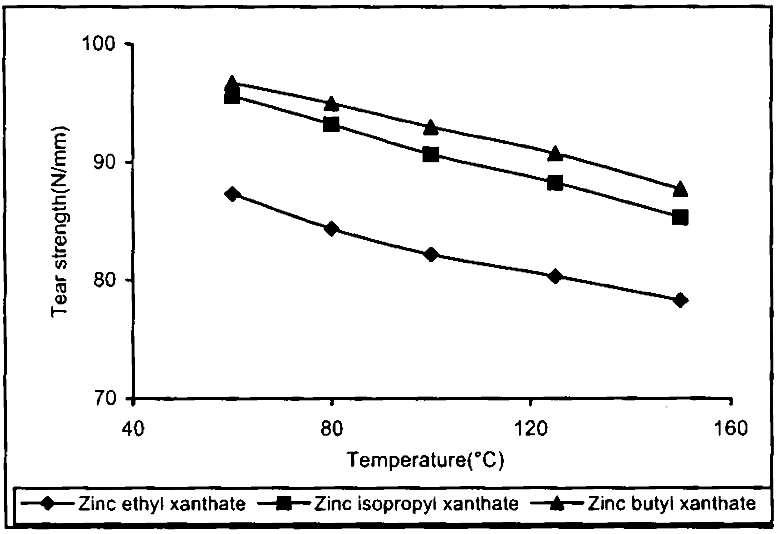


Fig.5.1.2. Tear strength of the black filled NBR vulcanizates

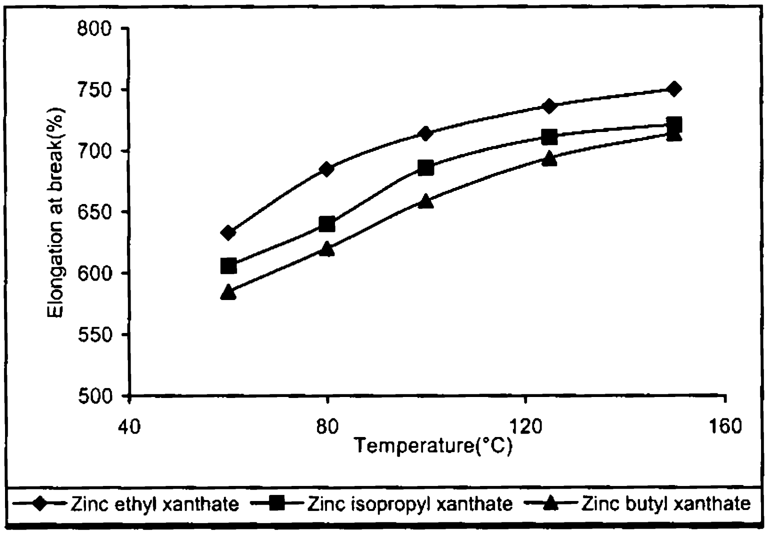


Fig. 5.1.3. Elongation at break of the black filled NBR vulcanizates

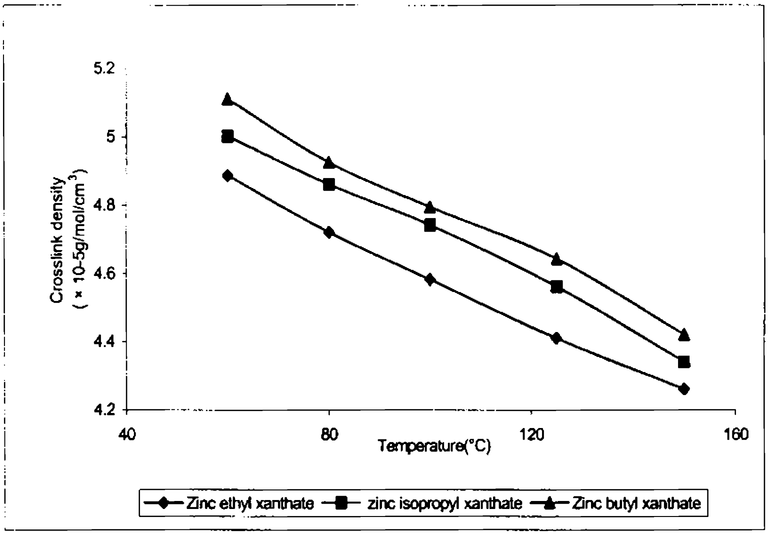


Fig. 5.1.4. Crosslink density of the black filled NBR vulcanizates.

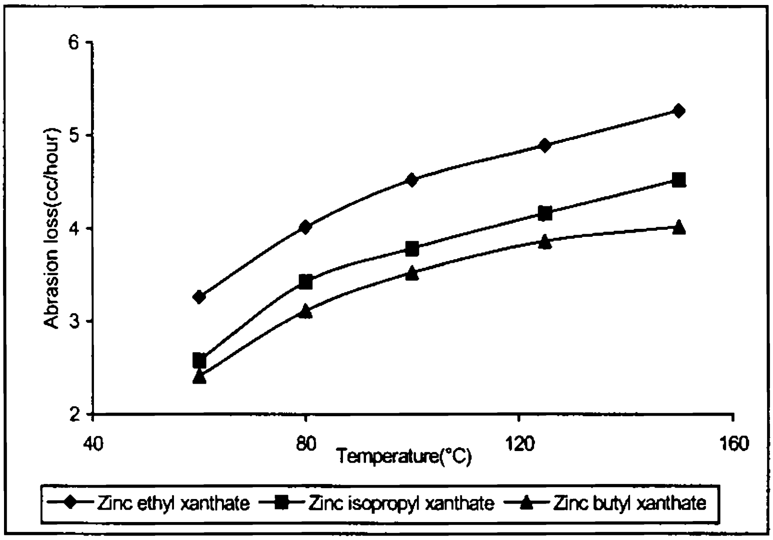


Fig.5.1.5. Abrasion loss of the black filled NBR vulcanizates

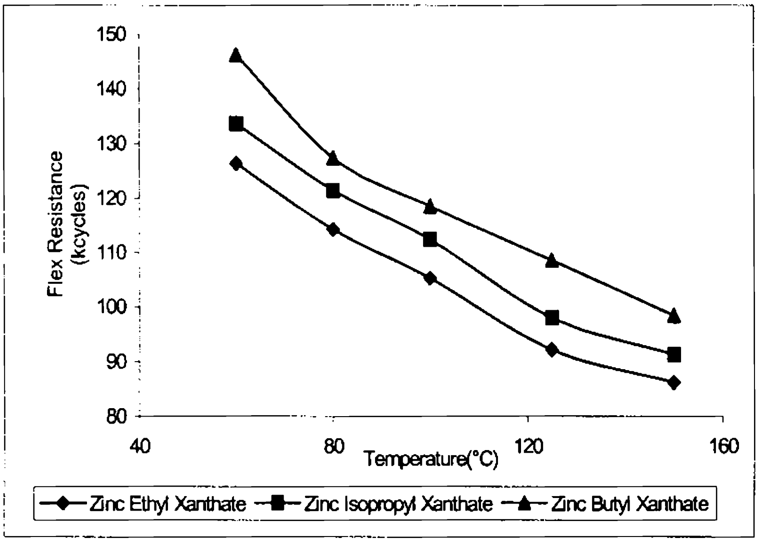


Fig.5.1.6. Flex resistance of the black filled NBR vulcanizates

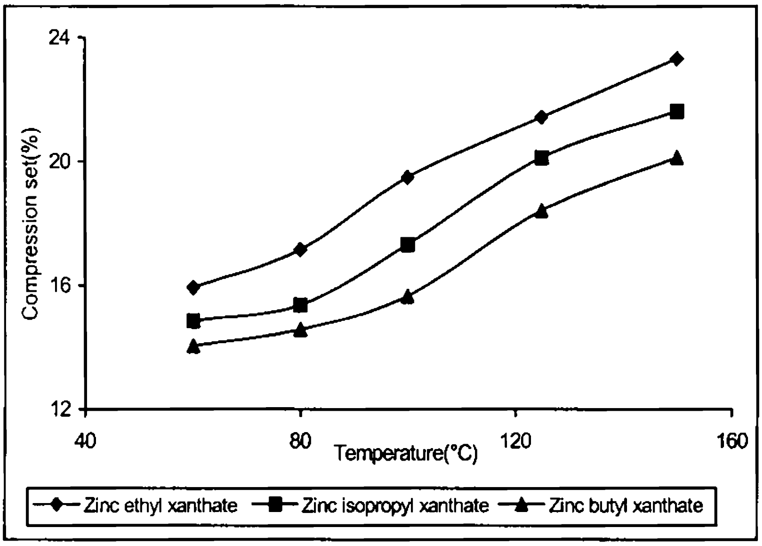


Fig. 5.1.7. Compression set of the black filled NBR vulcanizates

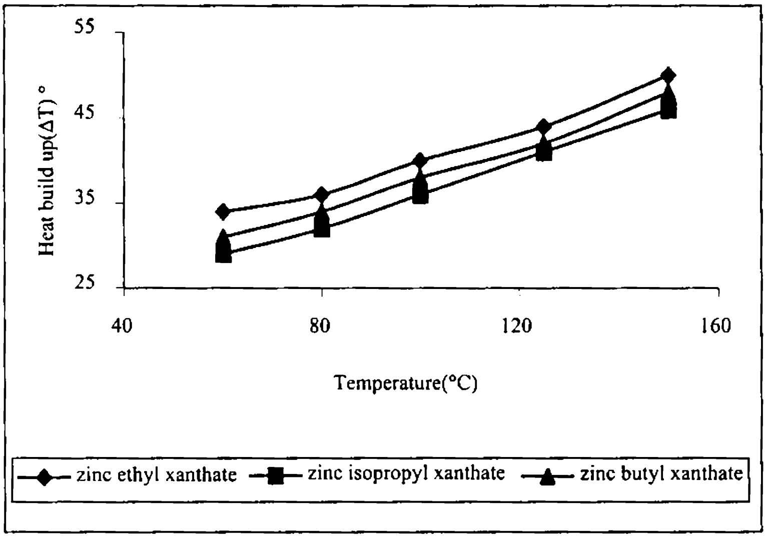


Fig.5.1.8. Heat build up of the black filled NBR vulcanizates

5.1.3. Conclusions

1. Zinc salts of xanthate/ZDC combination can be used to vulcanize carbon black filled NBR compounds at temperatures varying from 60°C - 150°C.
2. NBR compounds with MBTS/TMTD combination cures slower compared to zinc salt of xanthate/ZDC combination at 150°C and 125°C and below 125°C, MBTS/TMTD combination cannot cure NBR compounds.
3. As the temperature of vulcanization decreases from 150°C to 60°C, all the mechanical properties of the NBR vulcanizate are increased.
4. At a particular temperature, the cure time is minimum and mechanical properties are maximum for the compound containing $Zn(bxt)_2$/ZDC compared to the other two xanthates.

Part 2

5.2. NBR gum vulcanizates containing zinc xanthate/ZDC

5.2.1. Experimental

NBR gum compounds were prepared using ($Zn(ext)_2$)/ZDC, ($Zn(ipxt)_2$)/ZDC and ($Zn(bxt)_2$)/ZDC accelerator systems on a (6×12") laboratory-mixing mill according to the formulations given in table 5.2.1. The optimum cure times of the compounds were determined using a Goettfert elastograph model 67.85 as per ASTM D 1646(1981) and are reported in table 5.2.2. NBR compounds were moulded in an electrically heated laboratory hydraulic press at various temperatures from 60°C – 150°C upto their optimum cure times at a pressure of 200 kg/cm^2. Dumb bell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick universal testing machine using a cross head speed 500 mm/ minute according to ASTM D 2240 and are reported in table 5.2.2.

Table 5.2.1. Formulation of mixes

Mix	A	B	C
NBR	100	100	100
ZnO	4.0	4.0	4.0
Stearic acid	1.5	1.5	1.5
ZDC	1.25	1.25	1.25
$Zn(ext)_2$	1.75	-	-
$Zn(ipxt)_2$	-	1.75	-
$Zn(bxt)_2$	-	-	1.75
Sulphur	1.5	1.5	1.5

Crosslink density of the samples were determined by equilibrium swelling method in MEK solvent. The degree of crosslinking was calculated using the Florey Rehner equation[19] and are given in table 5.2.2. Abrasion resistance was tested using DIN abrader according to DIN 53516 and are given in table 5.2.3. The flex resistance of the samples was determined by using Wallace De Mattia flexing machine as per ASTM D 340-57 T and are given in table 5.2.3. Compression set of 6.25 mm thick and 18 mm diameter samples were determined by compressing to constant deflection (25%) and were kept for 22 hours in an air oven at 70°C(ASTM D 395-61, method B) and are given in table5.2.3. The heat build up was measured using the Goodrich flexometer conforming to ASTM D 623.78 (method A) and the values are given in table 5.2.3.

5.2.2. Results and discussion

Table 5.2.2. Tensile properties of NBR gun vulcanizates

Mix	Temperature (°C)	Cure time (min.)	Crosslink Density (g/mol/cm^3)	Tensile strength (N/mm^2)	Tear strength (N/mm)	Elongation at break (%)
A	150	1.31	2.96×10^{-5}	2.29	13.67	824
	125	4.20	3.09×10^{-5}	2.41	14.92	821
	100	12.32	3.65×10^{-5}	2.42	16.07	806
	80	33.96	3.96×10^{-5}	2.92	16.54	791
	60	62.54	4.03×10^{-5}	2.96	16.93	780
B	150	1.12	3.46×10^{-5}	2.25	15.06	826
	125	3.94	3.89×10^{-5}	2.64	15.44	812
	100	10.61	4.25×10^{-5}	2.80	16.01	790
	80	31.07	4.65×10^{-5}	3.21	16.29	772
	60	59.38	4.93×10^{-5}	3.28	17.32	761
C	150	0.98	3.26×10^{-5}	2.13	14.96	832
	125	3.16	3.59×10^{-5}	2.68	15.54	826
	100	10.36	4.01×10^{-5}	2.79	15.96	800
	80	29.65	4.36×10^{-5}	3.20	16.32	789
	60	56.04	4.97×10^{-5}	3.25	17.16	775

Table 5.2.2. shows the cure times of the mixes given in table 5.2.1 at different temperatures from 60°C to 150°C. It is seen that curing of NBR gum compounds is fast compared to the corresponding black filled compounds at all temperatures.

As expected, the cure time decreased as the temperature of curing was increased from 60°C to 150°C. The crosslink density values increased as the temperature of curing decreased. The increase in tensile properties with decrease in temperature are in agreement with the crosslink density values. But, since there is no self reinforcement in NBR, the tensile properties of the gum vulcanizates are very low. The other mechanical properties of the gum vulcanizates given in table 5.2.3 also prove the non-self reinforcing nature of NBR.

Table 5.2.3. Mechanical properties of NBR gum vulcanizates

Mix	Temp.(°C)	Abrasion loss (cc/hr)	Compression set (%)	Heat build up (ΔT) °C	Flex resistance (k cycles)
A	150	11.63	29.32	33	48.2
	125	9.42	26.45	31	51.6
	100	8.16	25.97	29	62.7
	80	7.29	22.78	27	81.3
	60	6.16	21.01	24	95.1
B	150	9.42	25.10	28	67.0
	125	8.26	23.81	27	77.4
	100	6.98	22.32	25	93.9
	80	5.86	20.75	22	108.8
	60	5.21	17.23	20	125.2
C	150	10.49	27.49	30	55.9
	125	9.10	24.50	29	64.7
	100	8.03	23.67	28	81.2
	80	6.25	22.42	24	96.2
	60	2.81	19.62	21	111.5

5.2.3. Conclusion

1. Zinc xanthate /ZDC accelerator combination can vulcanize NBR gum compounds at all temperatures ranging from 60°C to 150°C.

Part 3

5.3. Silica filled NBR vulcanizates containing zinc xanthate/ZDC

5.3.1. Experimental

Silica filled NBR compounds were prepared using $(Zn(ext)_2)$/ZDC, $(Zn(ipxt)_2)$/ZDC and $(Zn(bxt)_2)$/ZDC accelerator systems on a (6×12") laboratory-mixing mill according to the formulations given in table 5.3.1. The optimum cure times of the compounds were determined using a Goettfert elastograph model 67.85 as per ASTM D 1646(1981) and are reported in table 5.3.2. NBR compounds were moulded in an electrically heated laboratory hydraulic press at various temperatures from 60°C - 150°C upto their optimum cure times at a pressure of 200 kg/cm^2. Dumb bell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick universal testing machine using a cross head speed 500 mm/ minute according to ASTM D 2240 and are reported in table5.3.2.

Crosslink density of the samples were determined by equilibrium swelling method using MEK as the solvent. The degree of crosslinking was calculated using the Florey Rehner equation[19] and are given in table5.3.2. Abrasion resistance was tested using DIN abrader according to DIN 53516 and are given in table 5.3.3. The flex resistance of the samples was determined by using Wallace De Mattia flexing machine as per ASTM D 340-57 T and are given in table 5.3.3. Compression set of 6.25 mm thick and 18 mm diameter samples were determined by compressing to constant deflection (25%) and were kept for 22 hours in an air oven at 70°C(ASTM D 395-61, method B) and are given in table5.3.3. The heat build up was measured using the Goodrich flexometer conforming to ASTM D 623.78 (method A) and the values are given in table 5.3.3.

Table 5.3.1. Formulation of mixes

Mix	A	B	C
NBR	100	100	100
ZnO	4.0	4.0	4.0
Stearic acid	1.5	1.5	1.5
Silica	40	40	40
DOP	5.0	5.0	5.0
DEG	2.0	2.0	2.0
SP	1.5	1.5	1.5
ZDC	1.25	1.25	1.25
$Zn(ext)_2$	1.75	-	-
$Zn(ipxt)_2$	-	1.75	-
$Zn(bxt)_2$	-	-	1.75
Sulphur	1.5	1.5	1.5

5.3.2. Results and discussions

Table 5.3.2 shows the cure time and tensile properties of the mixes A, B and C given in table 5.3.1. The optimum cure time values show that curing of silica filled NBR compounds is faster compared to the carbon black filled compounds. It is reported that the rate of vulcanization slows down as a result of the adsorption of organic accelerators on the surface of carbon black particles[20]. The functional groups of carbon blacks which enter into side reactions with accelerator may reduce the accelerator concentration to a point where its residual amount is no longer sufficient to ensure a fast vulcanization[21].

The tensile properties given in table 5.3.2 show that as the temperature of vulcanization decreases, the properties improve which are in good agreement with the increased crosslink densities at lower temperatures. The mechanical properties given in table 5.3.3. show that the properties are better at lower temperatures. This may be a consequence of the higher crosslink densities, lower degradation of rubber and higher stability of the accelerator at low temperatures. The mechanical properties of the black filled vulcanizates are found to be better at higher temperatures compared to those of the silica filled vulcanizates. But at lower temperatures, silica filled vulcanizates have superior mechanical properties.

Table 5.3.2. Tensile properties of the silica filled NBR vulcanizates.

Mix	Temperature (°C)	Cure time (min.)	Crosslink Density (g/mol/cm^3)	Tensile strength (N/mm^2)	Tear strength (N/mm)	Elongation at break (%)
A	150	1.31	3.98×10^{-5}	21.51	68.35	760
	125	4.20	4.12×10^{-5}	22.80	72.47	744
	100	12.32	4.86×10^{-5}	23.79	81.06	713
	80	33.96	4.98×10^{-5}	24.08	88.59	661
	60	62.54	5.16×10^{-5}	25.01	90.34	610
B	150	1.12	4.22×10^{-5}	22.16	77.34	749
	125	3.94	4.50×10^{-5}	22.94	81.97	711
	100	10.61	4.98×10^{-5}	23.57	88.01	654
	80	31.07	5.09×10^{-5}	25.65	95.97	612
	60	59.38	5.42×10^{-5}	26.93	98.78	576
C	150	0.98	4.32×10^{-5}	22.89	79.15	732
	125	3.16	4.91×10^{-5}	23.06	83.90	698
	100	10.36	5.20×10^{-5}	24.73	88.71	619
	80	29.65	5.42×10^{-5}	26.97	96.36	590
	60	56.04	5.65×10^{-5}	27.35	100.51	552

5.3.3. Conclusions

1. Zinc xanthate /ZDC accelerator combination can vulcanize silica filled NBR compounds at all temperatures from 60°C to 150°C.
2. Curing of silica filled NBR compounds are faster than the corresponding black filled compounds.
3. As the temperature of vulcanization decreases, the mechanical properties of the silica filled NBR vulcanizates progressively get improved. The silica filled

vulcanizates have superior mechanical properties compared to those of the black filled vulcanizates at lower temperatures.

Table 5.3.3. Mechanical properties of silica filled NBR

Mix	**Temp.(°C)**	**Abrasion loss (cc/hr)**	**Compression set (%)**	**Heat build up (ΔT) °C**	**Flex resistance (k cycles)**
A	150	6.35	25.32	61	80.34
	125	5.01	22.41	53	87.56
	100	4.51	19.24	49	107.43
	80	3.85	16.89	44	120.59
	60	3.01	14.82	39	131.02
B	150	5.07	22.15	55	89.93
	125	4.56	19.05	50	97.42
	100	3.69	16.14	44	115.10
	80	3.10	14.07	41	128.43
	60	2.42	13.23	35	136.35
C	150	4.81	21.24	52	101.90
	125	4.17	17.36	46	107.76
	100	3.55	15.19	41	120.87
	80	3.01	12.80	37	134.43
	60	2.28	12.13	33	153.50

Part 4

5.4. Room temperature vulcanization of nitrile rubber

5.4.1. Experimental

Gum, black filled and silica filled NBR compounds were prepared using (Zn(ext)$_2$)/ZDC, (Zn(ipxt)$_2$)/ZDC and (Zn(bxt)$_2$)/ZDC accelerator systems. The compounds were prepared on a (6×12") laboratory-mixing mill according to the formulations given in table 5.4.1.

Table 5.4.1 Formulation of mixes

Mix	a	b	c	d	e	f	g	h	I
NBR	100	100	100	100	100	100	100	100	100
ZnO	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
S.Acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
HAF	-	-	-	40	40	40	-	-	-
DOP	-	-	-	6.0	6.0	6.0	5.0	5.0	5.0
4020	-	-	-	1.0	1.0	1.0	-	-	-
HS	-	-	-	0.5	0.5	0.5	-	-	-
Silica	-	-	-	-	-	-	40	40	40
DEG	-	-	-	-	-	-	2.0	2.0	2.0
SP	-	-	-	-	-	-	1.5	1.5	1.5
ZDC	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
Zn(ext)$_2$	1.75	-	-	1.75	-	-	1.75	-	-
Zn(ipxt)$_2$	-	1.75	-	-	1-75	-	-	1.75	-
Zn(bxt)$_2$	-	-	1.75	-	-	1.75	-	-	1.75
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

The optimum cure times of the compounds were determined by trial and error method and are reported in table 5.4.2. NBR compounds were moulded in an electrically heated laboratory hydraulic press at room temperature up to their optimum cure times at a pressure of 200 kg/cm^2. Dumb bell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick universal testing machine using a cross head speed 500 mm/ minute according to ASTM D 2240 and are reported in table 5.4.2. Crosslink density of the samples were determined by equilibrium swelling method using MEK as the solvent. The degree of crosslinking was calculated using the Florey Rehner equation[19] and are given in table5.4.2.

5.4.2. Results and discussion

Table 5.4.2. gives the cure times of gum, black filled and silica filled NBR compounds and tensile properties of the vulcanizates at room temperature. Zinc xanthate /ZDC accelerator combination can vulcanize gum, black filled and silica filled NBR compounds at room temperature. When compared to NR, room temperature curing of NBR compounds is slow. Among the different NBR compounds, vulcanization of black filled compounds is slow compared to that of gum and silica filled compounds. The tensile properties are in the order, silica filled vulcanizates > black filled vulcanizates > gum vulcanizates.

Table 5.4.2. Tensile properties of NBR compounds vulcanized at room temperature

Mix	Cure time (hours)	Crosslink density (g/mol/cm^3)	Tensile strength (N/mm^2)	Tear strength (N/mm)	Elongation at break (%)
a	70	3.10×10^{-5}	2.91	12.47	726
b	52	3.54×10^{-5}	3.06	14.87	701
c	42	3.86×10^{-5}	3.25	15.39	689
d	84	4.10×10^{-5}	22.96	75.63	650
e	78	4.58×10^{-5}	25.06	85.54	626
f	62	4.76×10^{-5}	26.70	89.39	614
g	72	4.20×10^{-5}	24.82	81.64	641
h	55	4.59×10^{-5}	26.91	88.45	625
i	46	4.80×10^{-5}	28.32	92.16	609

5.4.3. Conclusions

1. Zinc xanthate /ZDC accelerator combination can vulcanize gum, black filled and silica filled NBR compounds at room temperature.
2. Room temperature curing of black filled NBR compounds is slow compared to the gum and silica filled compounds.

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Chapter 6

USE OF ZINC XANTHATE/ ZDC ACCELERATOR COMBINATION FOR THE VULCANIZATION OF NR/BR BLENDS AT DIFFERENT TEMPERATURES.

Introduction

Synthetic rubbers are classified into general purpose rubbers and special purpose rubbers. Polybutadiene (BR) comes under general purpose rubbers which are used in the manufacture of tyres and general mechanical products. Polybutadiene is having very high abrasion resistance and it is related to its ability to undergo rapid deformation which in turn is a function of the segment flexibility. This increases with an increase in the difference between Tg and the test temperature. Since BR has very low Tg, its abrasion resistance is high. It has got very good resilience also. However, one type of rubber may not possess all the physical properties desired in a finished product. Much attention is currently being devoted to the simplest route for combining the outstanding properties of different existing polymers; ie, the formation of polymer blends[1-5]. For example, (1) In tread compounds the high abrasion resistance under certain conditions conferred by the use of polybutadiene is desirable but the poor road holding and rib tearing properties are not, hence blends of BR with natural rubber (NR) and styrenebutadiene rubber (SBR) are usually employed. (2) The resistance of polychloroprene (CR) to ozone is outstandingly good but its price is high and accordingly blending of CR with cheaper rubber is normally practiced for applications in white sidewalls. Ethylene-propylene-diene-rubber (EPDM) is added to elastomer formulations for improved oil acceptance and ozone resistance, acrylonitrile-butadiene rubber (NBR) for improved oil resistance, polychloroprene (CR) for improved flame resistance, polybutadiene (BR) for improved low temperature flexibility, butyl rubber (IIR) for improved gas impermeability etc[6].

When blends are prepared with dissimilar polymers having large differences in polarity and unsaturation (such as EPDM and NBR), the physical properties of the cured blend will be inferior. In polymer blends with similar polarity and similar unsaturation the cured blends frequently show additive properties, the so-called 'covulcanized' state is realized. A typical example of covulcanization would be in blends of SBR and BR[7].

Compatibility is the fundamental property, deciding the practical utility of a polymer blend[8-10]. If the two elastomers in a blend are incompatible, it will exist in the form of two separate phases and the cured blend will show inferior properties[11]. The properties of miscible blends will follow relationships that are functions of composition and to some extend, the degree of interaction between the blend components[12-13].

The mechanical properties of non-stress crystallizing rubbers can be greatly improved by the incorporation of carbon black. When filler is added to a binary elastomer blend, it goes to the less viscous polymer and when the viscosity becomes equal to that of the highly viscous polymer, it would be taken up by both the polymers.[14] So the low viscosity polymer gets highly loaded. Hess[15] demonstrated that carbon black normally locates preferentially in the BR component of a 50/50 NR/BR preblend and that this distribution results in optimum vulcanizate performance. The incorporation of carbon black into 50/50 elastomer preblends indicated that black affinity decreased in the order of BR, SBR, CR, NBR, NR, EPDM and IIR[15]. The factors that dominate the partitioning of carbon black are the degree of saturation of the polymers, their viscosities and their polarities and the method of mixing[16].

In NR/BR blends, BR shows improved tread wear and grove cracking resistance without reduction in resilience[17]. Sarbach and co-workers reported a 20% higher tread wear index for 50/50 NR/BR over straight NR[18-19]. Brown and co-workers[20] showed similar results and also reported that a finer carbon black (N 220) was needed to maximize the BR tread wear advantage. In addition to improved tread wear resistance, lower running temperature and improved cold weather performance for BR compounds were also reported. Evstratov[21] and co-workers evaluated the tread wear performance of NR/BR and SBR/BR blends under different road conditions. Under test conditions with considerable breaking and turning, the wear advantage of treads containing BR was found to increase.

From the foregoing discussion it is clear that the most important advantage of adding BR to NR is the improved abrasion resistance. However, the improvement in elasticity and abrasion resistance is at the expense of the tensile strength and modulus of NR. On the other hand, addition of NR to BR improves the poor processing properties of BR. The sulphur and accelerator requirements of BR are intermediate between those of natural rubber and those of styrene butadiene rubbers. As compared with natural rubber, rather less sulphur and more accelerator are required.[22] It is based on this rule of thumb that now formulations are designed for NR/BR blends. Some studies are reported on the effect of different formulations on the vulcanizate properties of NR/BR blends. It has been pointed out that if sulphur content of 50/50 NR/BR blends is decreased, accelerator content must be increased to maintain modulus but although scorch, aging resistance and compression set are improved, strength as well as resistance to tearing, flex cracking and cut growth are reduced[23]. However, no systematic study has been undertaken to determine the influence of different formulations on the network structure of NR/BR vulcanizates and how the network structure affects the mechanical properties of vulcanizates.

6.1 Black filled NR/BR blends containing $Zn(bxt)_2$/ZDC

6.1.1. Experimental

Materials used

NR (ISNR-5, Mooney Viscosity ML (1+4) 100°C value of 82, was supplied by the Rubber Research Institute of India, Kottayam. BR (97 % 1,4(cis); Mooney viscosity ML (1+4) at 100°C, 48.0). Compounding ingredients, ie, zinc oxide, stearic acid, ZDC, carbon black (HAF N 330), aromatic oil, vulcanox 4020, HS and sulfur were commercial grade. n-butyl alcohol, potassium hydroxide, carbon disulphide and toluene used for swelling studies were of reagent grade. Zinc sulphate used for precipitation was commercial grade. $Zn(bxt)_2$ was prepared in the laboratory as per the procedure described earlier.

Black filled NR, BR, and NR/BR blend compounds were prepared on a mixing mill. In order to optimize the amount of accelerator for vulcanization, the concentration of ZDC was changed from 0.75 to 1.5 phr as shown in table 6.1.1 and the concentration of $Zn(bxt)_2$ was changed from 0.75 to 1.5 phr as shown in table 6.1.2.The cure characteristics of the mixes were determined using a Goettfert elastograph model 67.85 as per ASTM D 1646(1981) at 150°C. The minimum torque, maximum torque, scorch time, optimum cure time, and the cure rate of the above mixes were reported in table 6.1.3.

NR, BR and NR/BR blend were compounded on a (6×12") laboratory mixing mill according to the formulations given in table 6.1.4. As compared with NR, BR requires less sulfur and more accelerators. So when the amount of BR in the blend is changed, the concentration of accelerators and the concentration of sulfur are slightly changed as shown in table 6.1.4. The cure curves of the mixes A,B and D (given in table 4) at 150°C are shown in fig.6.1.1. The optimum cure times of the compounds A to E (given in table 6.1.4) were determined at various temperatures from 60°C to 150°C and are reported in table 6.1.5. These compounds were moulded in an electrically heated laboratory hydraulic press at various temperatures upto their optimum cure times at a pressure of 200 Kg/cm^2. Dumb bell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. Crosslink density of the samples were determined by equilibrium swelling methods using toluene as the solvent. The degree of crosslinking was calculated using the Florey Rehner equation[24] and are shown in fig 6.1.2. The tensile properties of the vulcanizates were evaluated on a Zwick universal testing machine using a cross head speed 500 mm/minute according to ASTM D 2240 and are graphically represented in fig. 6.1.3 to 6.1.5. Compression set was determined by compressing to constant deflection (25%) as per ASTM D 395-61, method B and are given in fig.6.1.6. Abrasion resistance was tested using DIN abrader according to DIN 53516 and are given in fig.6.1.7.

Table 6.1.1 Formulation of Mixes

Mix	A_1	A_2	A_3	A_4
NR	70	70	70	70
BR	30	30	30	30
ZnO	5	5	5	5
Stearic Acid	2	2	2	2
HAF, N 330	50	50	50	50
Aromatic oil	7.0	7.0	7.0	7.0
Vulcanox HS	0.5	0.5	0.5	0.5
40-20	0.5	0.5	0.5	0.5
ZDC	0.75	1.0	1.25	1.50
$Zn(bxt)_2$	1.0	1.0	1.0	1.0
Sulfur	2.2	2.2	2.2	2.2

Table 6.1.2. Formulation of Mixes

Mix	B_1	B_2	B_3	B_4
NR	70	70	70	70
BR	30	30	30	30
ZnO	5	5	5	5
Stearic Acid	2	2	2	2
HAF, N 330	50	50	50	50
Aromatic oil	7.0	7.0	7.0	7.0
Vulcanox HS	0.5	0.5	0.5	0.5
4020	0.5	0.5	0.5	0.5
ZDC	1.0	1.0	1.0	1.0
$Zn(bxt)_2$	0.75	1.0	1.25	1.5
Sulfur	2.2	2.2	2.2	2.2

Table 6.1.3. Cure Characteristics of the mixes given in table 6.1.1 and table 6.1.2. at 150°C

Mix	Min.Torque (N/m)	Max.Torque (N/m)	Scorch Time (min)	Optimum Cure time (min)	Cure Rate (Nm/min)
A_1	0.0410	0.421	0.752	2.08	0.510
A_2	0.0454	0.488	0.662	1.86	0.567
A_3	0.0424	0.415	0.620	1.99	0.495
A_4	0.0439	0.451	0.560	2.10	0.493
B_1	0.0396	0.389	0.671	2.14	0.389
B_2	0.0453	0.488	0.662	1.86	0.567
B_3	0.0465	0.481	0.516	1.92	0.565
B_4	0.0466	0.479	0.462	1.93	0.523

Table 6.1.4. Formulation of mixes

Mix	A	B	C	D	E
NR	100	-	80	70	60
BR	-	100	20	30	40
ZnO	5	5	5	5	5
Stearic Acid	2	2	2	2	2
HAF	50	50	50	50	50
Aromatic oil	7.0	7.0	7.0	7.0	7.0
Vulcanox HS	0.5	0.5	0.5	0.5	0.5
4020	0.5	0.5	0.5	0.5	0.5
ZDC	0.75	1.0	0.9	1.0	1.1
$Zn(bxt)_2$	1.0	1.5	0.9	1.0	1.1
Sulfur	2.5	2.0	2.3	2.2	2.1

6.1.2. Results and discussion

Table 6.1.3 gives the cure characteristics of the mixes given in table 6.1.1 and table 6.1.2. It shows that compound B_2 and B_3 have the same optimum cure times. But the maximum torque and cure rate are high for the compound B_2. This compound is having enough scorch safety also. So 1.0 phr ZDC and 1.0 phr $Zn(bxt)_2$ are taken as the optimum dosage for the 70/30 NR/BR blend.

Fig.6.1.1 shows the cure curves of the mixes A, B, and D at 150°C. It is seen that the 100% NR based compound (compound A), cures faster than all the other compounds and the scorch time is found to be very low. But in 100 % BR based compound (compound B), the curing is very slow as expected. Since the double bond in NR is more active due to the presence of $-CH_3$ group, the curatives will be more soluble in NR, which leads to a high cure rate for NR (compared to BR). The blend compound (compound C) gives enough scorch safety and at the same time, the cure time is very close to that of NR. This shows that blending of BR with NR improves scorch safety without much change in the cure time.

Table 6.1.5 shows the optimum cure times of the compounds given in table 4 at different temperatures. Compound A undergoes curing at all temperatures from 150°C - 60°C with gradual increase in cure time. Compound B doesn't cure below 100°C. Compound C undergoes curing upto 60°C and the cure times are closer to that of pure NR compounds. With compound D, curing takes place only upto 80°C. At 60°C, curing is incomplete even after 2 hours. Compound E doesn't cure below 100°C. So it is clear that low temperature curing become difficult as the amount of BR in the blend increases and It is impossible with 100 % BR compounds.

Fig. 6.1.2 shows the total crosslink density of the compounds A to E. Compared to NR vulcanizates, crosslink density of BR vulcanizates is very low. Among the blends, 80/20 NR/BR blend shows a crosslink density comparable to pure NR vulcanizates. 60/40 blend shows low crosslink density, closer to that of pure BR vulcanizates.

Fig. 6.1.3 to 6.1.5 show the tensile properties of the mixes given in table 6.1.4. The results show that the tensile strength and tear strength increases and elongation at break decreases as the temperature of curing is changed from 150°C to 60°C. This may be due to the lesser degradation of rubber at lower temperatures and also due to the higher stability of the accelerator at lower temperatures. At a particular temperature, the tensile properties are maximum for NR compounds, minimum for BR compounds and in between for the blends. But the tensile properties of the blends are more closer to the NR compounds than that of BR compounds. The elongation at break is also close to the arithmetic average. Among the three blends, the tensile properties are maximum for the 70/30 blend.

Fig. 6.1.6 shows the compression set of the mixes A to E at different temperatures. Compression set values of the BR compounds are high compared to that of NR compounds. The values for the blends are intermediate between that of NR and BR.

Fig.6.1.7 shows the abrasion resistance of the vulcanizates given in table 6.1.4. The abrasion resistance is high for the BR compounds at high temperatures than that of NR compounds. Upto 100°C, the abrasion resistance values of the 70/30 and 60/40 blends are more closer to that of the 100 % BR based compounds. The 80/20 blend shows abrasion resistance values closer to that of NR compounds. Below 100°C, the abrasion resistance values of all the blends are closer to that of

NR vulcanizates and a high value is shown by the 70/30 blend. So addition of BR to NR improves the abrasion resistance at all temperatures.

The 80NR/20BR blend shows more or less the properties of NR alone; obviously due to the low concentration of BR. When the amount of BR in the blend increases to 30 phr, the properties settle at an intermediate value between those of BR and NR. This may be due to the good compatibility of the two rubbers resulting in an almost single phase behavior [25-26]. When the amount of BR in the blend is 40 phr, the properties are closer to BR.

Table 6.1.5. Optimum cure times in minutes

Temp.(°C)	A	B	C	D	E
150	1.26	4.0	1.41	1.86	3.86
125	6.11	13.0	6.36	7.1	11.96
100	21.24	41.0	22.02	23.16	38.64
80	53.62	-	55.42	56.98	-
60	78.31	-	80.16	-	-

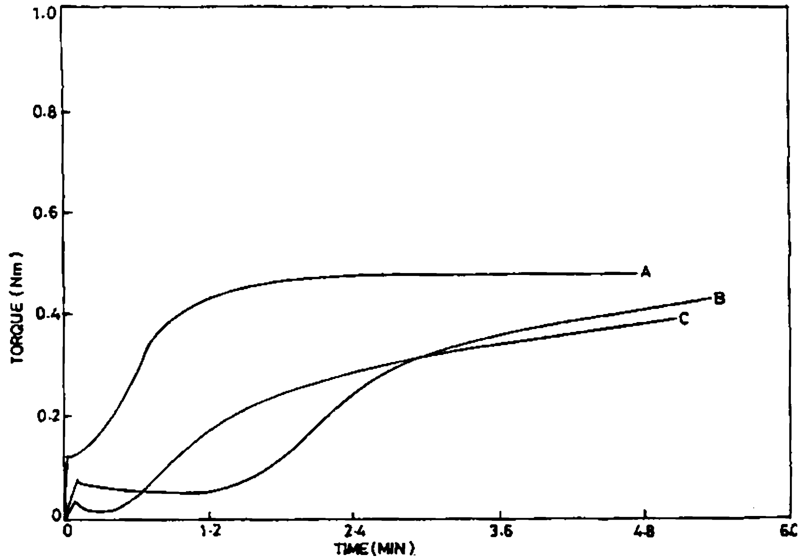

Fig. 6.1.1 : Cure curves of the compounds A, B and D at 150°C

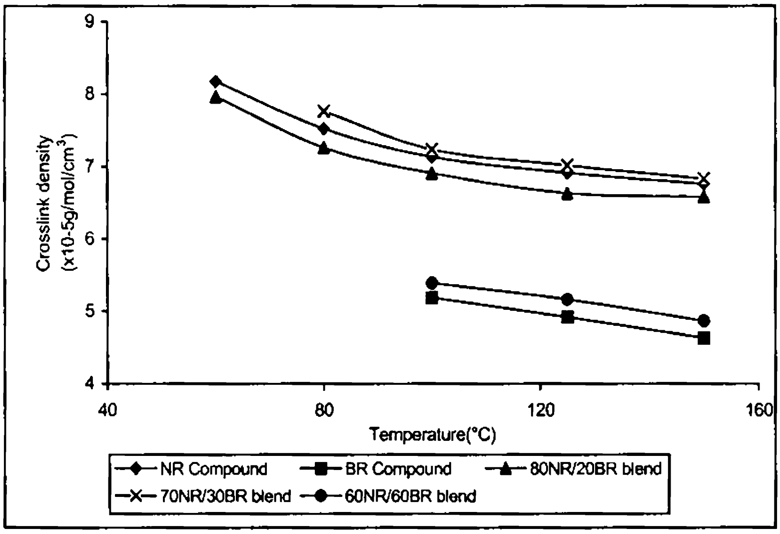

Fig. 6.1.2. Variation of crosslink density with temperature

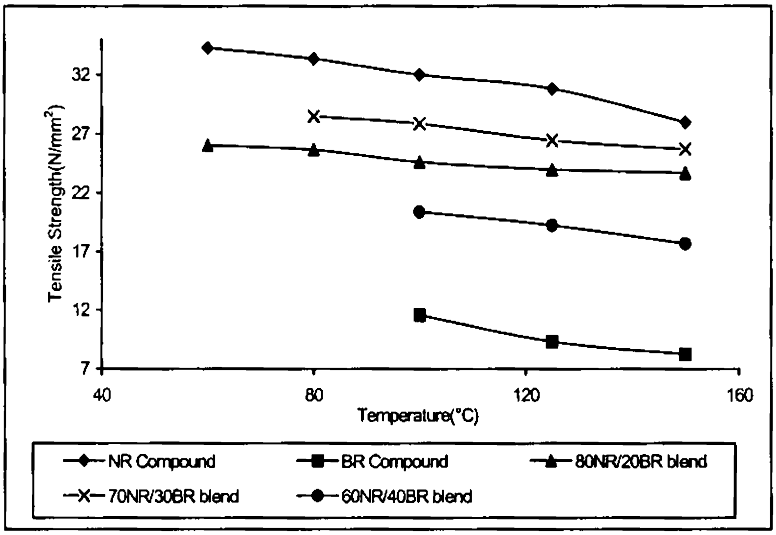

Fig. 6.1.3. Variation of tensile strength with temperature

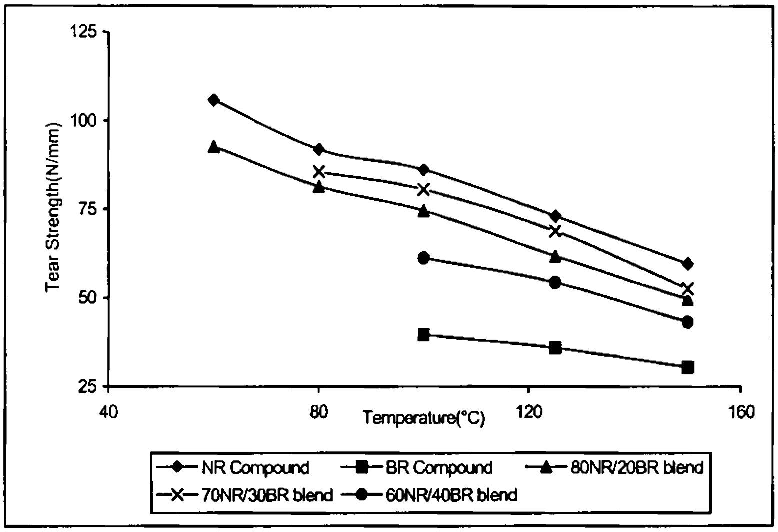

Fig.6.1.4. Variation of tear strength with temperature

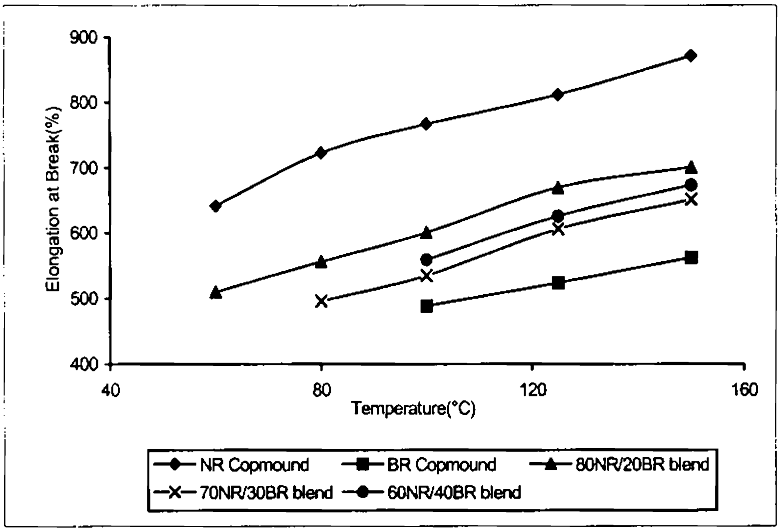

Fig.6.1.5. Variation of elongation at break with temperature

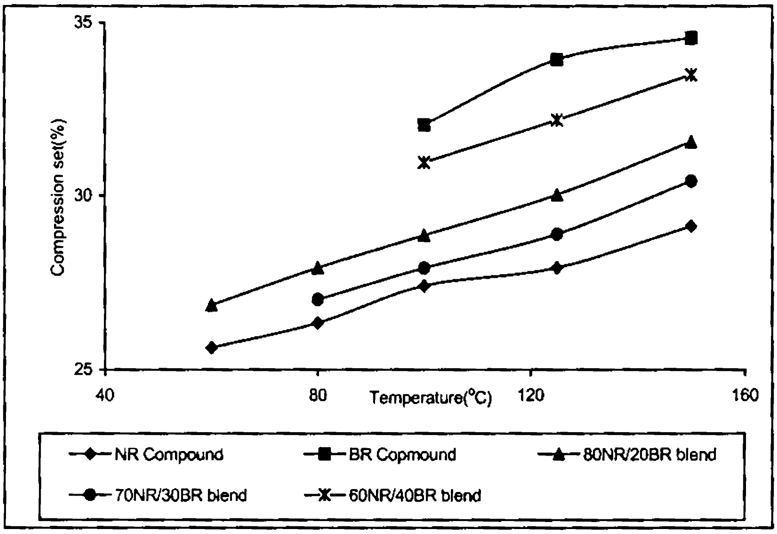

Fig. 6.1.6 Variation of compression set with temperature

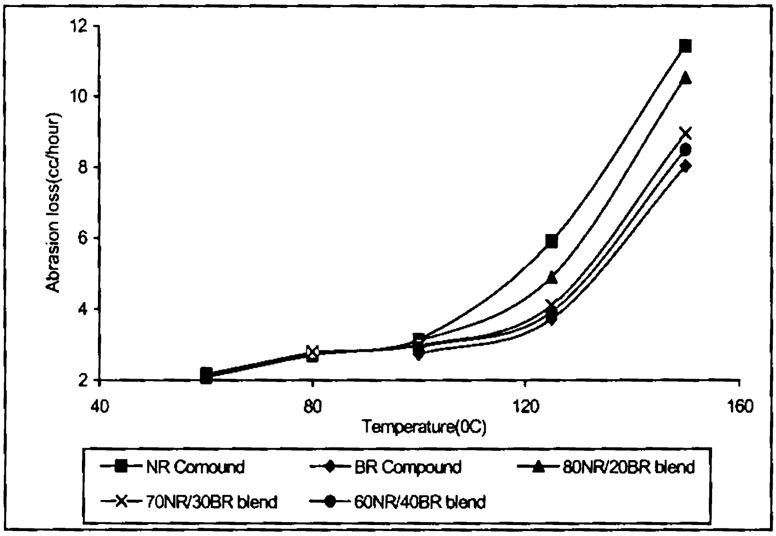

Fig.6.1.7 Variation of abrasion loss with temperature

6.1.3. Conclusions

1. Zn $(bxt)_2$/ ZDC accelerator combination can vulcanize NR at all temperatures from 150°C to 60°C; but it cannot vulcanize BR compound below 100°C. Among the NR/BR blends, 80/20 blend undergoes curing at all temperatures from 150°C to 60°C, 70/30 blend cures only upto 80°C and 60/40 blend cures only upto 100°C.
2. Addition of BR to NR increases the scorch time.
3. The tensile properties of the pure BR compounds are poor compared to the NR compounds.
4. The mechanical properties of the 80NR/20BR blends are more closer to that of NR vulcanizates, that of 60/40 blends are more closer to the BR vulcanizates while the 70/30 blends shows an intermediate property.
5. The 70/30 NR/BR blend and 60/40 NR/BR blend show better abrasion resistance than the NR vulcanizates when cured at higher temperatures.

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Chapter 7

SUMMARY AND CONCLUSIONS

The primary objective of the study was to develop a novel accelerator system for vulcanization of rubber compounds at temperatures lower than those employed conventionally. Lowering the vulcanization temperature may have a great influence in improving the quality of the rubber product, since rubber undergoes degradation at higher temperatures. Theoretically, xanthates are known to act as low temperature curing accelerators.

In rubber technology, the use of mixed accelerator systems for vulcanization has received considerable attention since such systems usually exhibit synergism. Binary accelerator systems are increasingly used now-a-days as they provide efficient vulcanization and impart improved physical properties for the finished product. A major part of the study is on the use of novel binary accelerator system, which is capable of providing efficient vulcanization at temperatures lower than those employed conventionally.

Chapter 1 gives an introduction about vulcanization and the mechanism of vulcanization. The various ingredients added during rubber compounding and their functions in the compound are discussed in detail. A brief history of the development of various accelerators and their classification is also given. The advantage of binary accelerator system over single accelerator system is mentioned. The difference between accelerated and unaccelerated vulcanization is briefly discussed. The CV, EV and SEV systems of vulcanization and their effect on the vulcanizate properties are outlined. The advantages of low temperature vulcanization is included in the survey. The principal objectives of the present study are also listed.

Chapter 2 gives the specifications of all the materials used in the study and summarises the different experimental techniques used. The rubber compounds were prepared on a two roll mixing mill as per ASTM D 3182-89. The cure characteristics of the compounds were studied on a Goettfert elastograph model 67.85. These compounds were compression moulded in an electrically heated hydraulic press. The tensile properties of the vulcanizates were studied using a universal testing machine. The ageing resistance was studied as per ASTM 573-88. The abrassion resistance of the vulcanizates were studied using a DIN abrader as per DIN standard. The compression set of the samples were determined as per ASTM D 395. The chemical crosslink density was determined by equilibrium swelling methods. The heat build up of the vulcanizates was studied using Goodrich flexometer. The flex resistance was studied using Wallace De mattia flexing machine.

For latex compounding, the aqueous dispersions of the ingredients were made by grinding action in a ball mill.

In the present work, xanthate accelerators were prepared and characterised and these xanthates alone and in combination with ZDC were tried in the vulcanization of NR, NBR and NR/BR blends and the mechanical properties of the vulcanizates were studied.

The zinc salts of methyl, ethyl, isopropyl, butyl and ethylene glycol xanthates were prepared in the laboratory and these xanthates were characterised using IR, NMR and TGA techniques. The IR spectra gave information about the C = S and C – S bonds in all the xanthates. The ^1H NMR spectra gave information about the various alkyl groups present in the xanthates. TGA curves showed that the xanthates finally decompose to ZnO and also gave information about the thermal stability of the xanthates.

NR compounds were prepared using these xanthates and the cure characteristics were studied. The cure times of the compounds gradually decreased as the size of the alkyl group in the xanthate increases. But the cure time of the compound containing ethylene glycol xanthate was high compared to the other compounds due to the presence of one free alcoholic group in $Zn(egxt)_2$.

Gum and black filled NR compounds containing zinc xanthate alone and zinc xanthate/ZDC combination were prepared. The optimum dosage of xanthates when used alone was found to be 2.5 phr. The cure times of these compounds were determined at different temperatures and the mechanical properties of the vulcanizates were studied. $Zn(ext)_2$, $Zn(ipxt)_2$ and $Zn(bxt)_2$ can vulcanize NR at all temperatures from room temperature to 150°C. As the temperature of vulcanization decreased, cure time increased. At a particular temperature, cure time was minimum for the compound containing $Zn(bxt)_2$. All the mechanical properties of the NR vulcanizates improved as the temperature of vulcanization was decreased. At any temperature, curing of black filled compounds was slow compared to the gum compounds ; but the mechanical properties were better for the black filled vulcanizates. The mechanical properties of the NR vulcanizates moulded at 150°C was very low due to the decomposition of xanthates.

When zinc xanthate/ZDC combination was used in NR, the total accelerator concentration could be reduced to 1.75 phr even though there was a slight increase in cure time compared to the compounds containing zinc xanthate alone. In this case also, the mechanical properties of NR vulcanizates improved as the temperature of vulcanization was reduced. Curing was slow in black filled NR compounds compared to the gum compounds. But by gradually increasing the accelerator concentration, the cure times of black filled compounds could be made equal to those of gum compounds.

Zinc xanthate/ZDC combination could prevulcanize NR latex at room temperature. Tensile properties and properties like MST, VFA, pH and KOH number of the room temperature prevulcanized latex were found to be better than those of the commercially available prevulcanized latex.

Gum, silica filled and black filled NBR compounds containing zinc xanthate/ZDC accelerator combination were prepared. The cure times of these compounds were determined at different temperatures and were moulded at these temperatures. The mechanical properties of the vulcanizates moulded at different temperatures were studied.

Zinc xanthate/ZDC accelerator combination was found to vulcanize gum, black filled and silica filled NBR compounds at all temperatures from room temperature to 150°C. The cure times of these compounds were compared with those of NBR compounds containing MBTS/TMTD. NBR compounds using MBTS/TMTD combination were cured slower compared to zinc salt of xanthate/ZDC combination at 150°C and 125°C and below 125°C, MBTS/TMTD combination couldnot cure NBR compounds. As the temperature of vulcanization decreased from 150°C to 60°C, all the mechanical properties of the NBR vulcanizate improved. Curing of silica filled NBR compounds were faster compared to the curing of the corresponding black filled compounds. The silica filled vulcanizates displayed superior mechanical properties compared to those of the black filled vulcanizates. The mechanical properties of NBR gum compounds containing zinc xanthate/ZDC were found to be inferior to black filled vulcanizates.

Black filled NR, BR and NR/BR blend compounds containing $Zn(bxt)_2$/ZDC were prepared. The optimum accelerator concentration was determined to be 2 phr. 80NR/20BR, 70NR/30BR and 60NR/40BR blends were prepared and the cure times of these compounds were determined at different temperatures. Below 100°C, $Zn(bxt)_2$/ZDC accelerator combination couldnot vulcanize BR. 80NR/20BR blend gets cured in the temperature range 150°C – 60°C while 70NR/30BR blend cured only above 80°C and 60NR/40BR blend only above 100°C. Addition of BR to NR increased the scorch time of the compound. The tensile properties of the pure

BR compounds were poor compared to the NR compounds. The mechanical properties of the 80NR/20BR blends are comparable to those of NR vulcanizates, while those of 60/40 blends are comparable to the BR vulcanizates and the 70/30 blends show an intermediate property.

List Of Abbreviations

Polymers

NR	Natural Rubber
NBR	Acrylonitrile Butadiene Rubber
BR	Polybutadiene Rubber (PB)
CR	Chloroprene Rubber
SBR	Styrene Butadiene Rubber

Additives

ZnO	Zinc Oxide
HAF	High Abrasion Furnace
MBTS	Mercapto Benzthiazole Disulphide
ZDC	Zinc Diethyl Dithiocarbamate
TMTD	Tetramethyl Thiuram Disulphide
DOP	Dioctyl Phthalate
S	Sulphur
SP	Styrenated Phenol
$Zn(mxt)_2$	Zinc Methyl Xanthate
$Zn(ext)_2$	Zinc Ethyl Xanthate
$Zn(ipxt)_2$	Zinc Isopropyl Xanthate
$Zn(bxt)_2$	Zinc Butyl Xanthate
$Zn(egxt)_2$	Zinc Ethylene Glycol Xanthate
MEK	Methyl Ethyl Ketone

Other abbreviations

ISNR	Indian Standard Natural Rubber
ASTM	American Society for Testing and Materials
ACN	Acrylonitrile

phr	Parts per hundred rubber
Nm	Newton meter
mm	Millimeter
min	Minutes
IR	Infrared
NMR	Nuclear Magnetic Resonance
TGA	Thermogravimetric Analysis
ML(1+4) 100°C :	Mooney viscosity determined using large rotor after a dwell time of one minute and the value noted at the 4th minutes at 100°C
V_r	Volume fraction of rubber
V_s	Molar volume of the solvent
T_{90}	Optimum cure time
T_{10}	Scorch time
UTM	Universal Testing Machine

List Of Publications From The Work

1. Shiny Palaty, Rani Joseph; ***Xanthate accelerators for low temperature curing of natural rubber,*** Journal of applied polymer science, **78,** 1769 (2000)
2. Shiny Palaty, Rani Joseph; ***A novel accelerator combination for the low temperature curing of NR,*** Paper presented at the 13th Kerala Science Congress (2001).
3. S. Palaty, R. Joseph; ***Studies on xanthate - zinc diethyl dithiocarbamate accelerator combination in natural rubber,*** Plastics Rubber and Composites, **30** 270 (2001).
4. Shiny Palaty, Rani Joseph ; ***Low temperature curing of NBR for property improvement,*** Journal of Elastomers and Plastics (communicated)
5. Shiny Palaty, Rani Joseph; ***Synergism of xanthate/dithiocarbamate accelerator combination in carbon black filled NR compounds*** (communicated).
6. Shiny Palaty, Rani Joseph; ***Studies on xanthate/ dithiocarbamate accelerator combination in NR/BR blends*** (communicated).
7. Shiny Palaty, Rani Joseph; ***Low temperature curing of black filled NR for property improvement.*** Paper presented at the 14th Kerala Science Congress (2002).
8. Shiny Palaty, Rani Joseph; ***Studies on xanthates/dithiocarbamate accelerator combination in silica filled NBR compounds*** (communicated).