STUDIES ON THE USE OF DRYING OILS AS INGREDIENT IN THE VULCANIZATION OF ELASTOMERS

A THESIS SUBMITTED BY

V NANDANAN

IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
OF
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY
COCHIN UNIVERSITY OF SCIENCE AND TEHCHNOLOGY
COCHIN - 682022

JUNE 2000

CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by Mr. V. Nandanan under our supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology. No part of the work reported in this thesis has been presented for any other degree from any other institution.

Kochi. 682 022

26 June 2000

Dr. Rani Joseph,
(Co guide)
Professor, Department of Polymer
Science and Rubber Technology, Cochin
University of science and Technology

Dr. D. Jospeh Francis
(Supervising Teacher)
Emeritus Scientist (CSIR)
Former Head of the Department of
Polymer Science and Rubber Technology
and Dean, Faculty of Technology, Cochin
University of Science and Technology

DECLARATION

I hereby declare that the thesis entitled " Studies on the use of drying oils as ingredient in the vulcanization of elastomers" is the original work carried out by me under the supervision of Dr. D.Joseph Francis, former Head of the Department of Polymer Science and Rubber Technology and Dr. Rani Joseph, Professor, Deaprtment of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682022, and no part of this thesis has been presented for any other degree from any other institution.

Kochi 682 022 V. NANDANAN

26 June 2000.

ACKNOWLEDGEMENT

I wish to place on record my deep sense of gratitude to Dr. D. Joseph Francis, Emeritus Scientist (CSIR), Former Head of the Department of Polymer Science and Rubber Technology and Former Dean , Faculty of Technology, Cochin University of Science & Technology and Dr. Rani Joseph, Professor , Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology for their valuable guidance throughout the course of this work.

Prof. Dr. K.E.George, Head of the Department of Polymer Science and Rubber Technology was the inspiring force throughout the course of the work. His valuable suggestions and help made the smooth completion of the work. His skill in editing publications helped the easy publication of part of the work. I am much indebted to him.

Prof. Dr. A.P. Kuriakose, Dean. Faculty of Technology and Former Head of the Department was always keen in the progress of the work. He was always helpful in his capacity as the Head of the Department and has presented part of the work in the IRI Conference. I am greatly thankful to him.

I acknowledge the valuable suggestions and help extended by other faculty members of the department, the non teaching staff and my colleagues. I also thank Mr. C.I Soman for the neat preparation of the figures.

V.NANDANAN

LIST OF ABBREVIATIONS

Polymers

NR	Natural rubber
SBR	Styrene-butadiene rubber
NBR	Acrylonitrile-butadiene rubber
CR	Chloroprene rubber
PB	Polybutadiene (BR)
EPDM	Ethylene propylene ter polymer rubber
PVC	Polyvinyl chloride
EVA	Ethylvinyl acetate
IIR	Isobutylene -isoprene rubber

Additives

ZnO	Zinc Oxide
MBTS	Mercapto benzthyazyl disulfide
TMTD	Tetramethyl thiuram disulfide
DNPT	N,N –Dinitroso pentamethylene tetramine
MOR	2-Morpholino thio benzothiazole
HAF	High abrasion furnace carbon black
HSR	High styrene resin
CI	Coumarone indene
DOP	Dioctyl phthalate
DOS	Dioctyl sebacate
DAE	Distillate aromatic extract
SP	Styrenated phenol
AO	Aromatic oil
LO	Linseed oil
SBO	Soyabean ouil
CO	Castor oil
RSO	Rubber seed oil
PO	Punnal oil

ELO	Epoxidised linseed oil
ESO	Epoxidised soyabean oil

Other abbreviations

ISNR	Indian stanadrd natural rubber
ASTM	American society for testing and materials
ACN	Acrylonitrile
VGC	Viscosity gravity constant
rpm	Revolutions per minute
phr	Parts per hundred rubber
Nm	Newton meter
V_r	Volume fraction of rubber

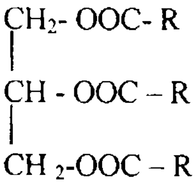
CONTENTS

INTRODUCTION

1.1 OILS AND FATS

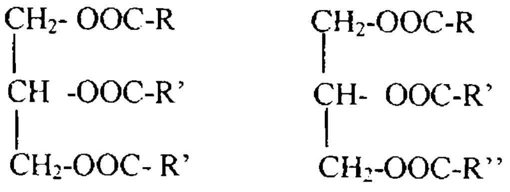
Oils and fats are the major component of a class of organic compounds called lipids. Other components of this class are phospholipids, sulpholipids, cyanolipids, sphingolipoids etc. The source of oils and fats are plants and animals. Usually the product obtained form plants is called oils and that from animals is called fats. The difference between fats and oils is in their physical state; the product in the liquid state at ordinary temperature is called oils and that which is solid or semisolid is called fats. Thus oils belonging to the lipids means oils from plants and not of petroleum origin.

Vegetable oils are further classified into fixed oils and essential oils. The oils referred to in **'oils and fats'** are fixed oils and not essential oils. Essential oils are a mixture of different low molecular weight volatile organic compounds like alcohols, aldehydes, ketones etc; Fixed oils and fats are esters of long chain fatty acids with glycerol. In oils and fats all the three hydroxyl groups of glycerol are esterified with fatty acids and hence they are called triglycerides. In one glyceride molecule the three fatty acids present may be the same or different. If the three fatty acids present in a glyceride are the same, then that glyceride is called a simple triglyceride. If two or more different acids are present in one glyceride it is called mixed triglyceride. Again in an oil or fat the acids present, in one simple triglyceride molecule may not be the same, as that in another one, and that present in a mixed triglyceride may not be the same as that present in another molecule. So **chemically oils and fats are mixtures of mixed triglycerides**. The structures of simple triglyceride and mixed triglycerides are as shown below.



$$\begin{array}{l} CH_2-OOC-R \\ | \\ CH-OOC-R \\ | \\ CH_2-OOC-R \end{array}$$

Simple triglyceride



$$\begin{array}{l} CH_2-OOC-R \\ | \\ CH-OOC-R' \\ | \\ CH_2-OOC-R' \end{array} \qquad \begin{array}{l} CH_2-OOC-R \\ | \\ CH-OOC-R' \\ | \\ CH_2-OOC-R'' \end{array}$$

Mixed triglyceride

The fatty acids present in oils and fats are generally acids with even number of carbon atoms. This is because of the particular structure and name of common biosynthetic mechanism by which the acid grows by the addition of two-carbon atoms at a time. The acids from six carbon atoms onwards are generally called fatty acids, because no lower acid is usually seen in fats and oils. The fatty acids are given under.

Saturated fatty acids

No.	Name	Molecular formulae	structure
1	Caproic Acid	$C_6H_{12}O_2$	$CH_3-(CH_2)_4-COOH$
2	Caprilic Acid	$C_8H_{16}O_2$	$CH_3-(CH_2)_6-COOH$
3	Capric Acid	$C_{10}H_{20}O_2$	$CH_3-(CH_2)_8-COOH$
4	Lauric Acid	$C_{12}H_{24}O_2$	$CH_3-(CH_2)_{10}-COOH$
5	Myristic Acid	$C_{14}H_{28}O_2$	$CH_3-(CH_2)_{12}-COOH$
6	Palmitic Acid	$C_{16}H_{32}O_2$	$CH_3-(CH_2)_{14}.COOH$
7	Stearic Acid	$C_{18}H_{36}O_2$	$CH_3-(CH_2)_{16}-COOH$
8	Arachidic Acid	$C_{20}H_{40}O_2$	$CH_3-(CH_2)_{18}-COOH$
9	Behenic Acid	$C_{22}H_{44}O_2$	$CH_3-(CH_2)_{20}-COOH$

Unsaturated fatty acids

No.	Name	Molecular formulae	Structure
1	Oleic Acid	$C_{18}H_{34}O_2$	CH_3-$(CH_2)_7$-CH=CH-$(CH_2)_7$-COOH
2	Linoleic Acid	$C_{18}H_{32}O_2$	$CH_3(CH_2)_4CH$=CH-CH_2- CH=CH$(CH_2)_7$COOH
3	Linolenic Acid	$C_{18}H_{30}O_2$	CH_3CH_2CH=$CHCH_2CH$=$CHCH_2CH$=CH $(CH_2)_7$-COOH
4	Palmitoleic Acid	$C_{16}H_{30}O_2$	$CH_3(CH_2)_5$-CH=CH-$(CH_2)_7$-COOH

The major components of almost all fats and oils are the C_{18} saturated and unsaturated acids, the exception being coconut oil and palm kernel oil where the fatty acid present is lauric acid with a good quantity of myristic and palmitic acid. Considerable amount of still lower fatty acids are also seen in this oil. The nature of the fatty acid composition of an oil or fat is obtained from the two important specifications; the saponification and the iodine values. Saponification value (SV) is the number of milligrams of KOH required to saponify one gram of oil or fat. It gives a measure of the length of fatty acid chain in the oil or fat. An oil or fat with higher content of low molecular weight fatty acids will have a higher value for SV and vice versa.

Similarly the amount of unsaturated fatty acid present in the oil or fat is given by the iodine value (IV). It is the number of grams of iodine that can be added to 100 grams of oil or fat. When the oil or fat is treated with Iodine monochloride (ICl) solution, iodine is added to the double bonds in the fatty acids. The amount of iodine added can be volumetrically estimated.

1.2 Edible and non edible oils

Fats and oils are the most nutritious food materials. The calorific value of fats and oils is 13-14 k. cal/gm, whereas carbohydrates, the most common food material has got a value of 4.5 k.cal/gm While most fats are edible, some of the vegetable oils are non-edible, due to peculiar reasons.

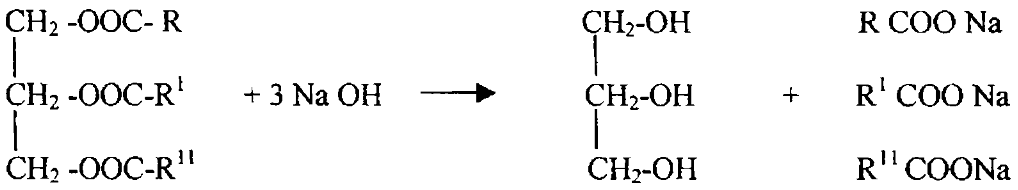
Oils like cottonseed oil, rubber seed oil, calophyllum oil, kusum oil etc are non edible due to the presence of small amounts of toxic components like cyanolipids or cyanoglucoside or small amount of coumarines. Oils like castor oil, hydnocarpus oil etc are non-edible due to the presence of large percentage of fatty acids with special functional groups. Castor oil contains a major percentage of ricinoleic acid (12-hydroxy oleic acid), and hydnocarpus oils contains a cyclopentenyl fatty acid, hydnocarpic acid. Both fatty acids cause stomach disorder and hence are non edible. Though linseed oil contains no toxic components it is not used for edible purpose due to the presence of large amount of linoleic and linolenic acids, which are considered to be the precursor of cholesterol.

1.3 Industrial uses of oils and fats

1.3 .1 Soaps and detergents

The major use of non-edible oils is in the manufacture of soaps and detergents. Sodium salt of fatty acid is called soap. When oils and fats are boiled with aqueous alkali, hydrolysis occurs to produce soap and glycerol. Since soap is produced during the reaction, this process is called saponification.

A general saponification reaction is as shown below.



$$\begin{array}{lccccc} CH_2\text{-}OOC\text{-}R & & & CH_2\text{-}OH & & R\,COO\,Na \\ | & & & | & & \\ CH_2\text{-}OOC\text{-}R^{1} & + 3\,Na\,OH & \longrightarrow & CH_2\text{-}OH & + & R^{1}\,COO\,Na \\ | & & & | & & \\ CH_2\text{-}OOC\text{-}R^{11} & & & CH_2\text{-}OH & & R^{11}\,COONa \end{array}$$

Glycerol Soap

In industrial process for the manufacture of soap, the oil is boiled with aqueous solution of calculated amount of alkali. Common salt is added to the aqueous solution of soap formed, when soap precipitates. The precipitated soap is removed from the boiler dried and made in the desired shape. For laundry soap, any oil or fat is used and the alkali used is sodium hydroxide. In toilet soaps, precaution is taken to avoid the presence of excess alkali. The crude soap is mixed with coloring materials and perfumes and then packed.

In soft soaps, like baby soaps and shaving soaps, the alkali used is KOH. Potassium salt of fatty acid is softer and forms lather readily. The softness of soaps again depends on the size of the fatty acid. Lower fatty acids give softer soaps than higher ones and hence generally coconut oil or palm kernel oil is used in manufacture of soft soaps.

Synthetic detergents are more effective than soaps in removing the dirt and oils from fabric. They usually contain a non-polar aliphatic portion at one end of the molecule and a polar water-soluble portion at the other end of the molecule. Alkyl sodium sulphonate is a typical example of a detergent. The fatty alcohols derived from fats and oils are usually sulphonated to get alkyl suphonates.

1.3.2 Paints and varnishes

Drying, semi drying and non drying oils.

Some oils when coated to surfaces exposed to atmosphere sets to a thin film forming a dry protective coating. This property is used in the industrial production of oil based coating materials like paints and varnishes. The drying of oils is through polymerization and cross linking, and this behavior is related to the unsaturation in the oil.

The amount of unsaturation in an oil is represented by its iodine value. Hence, oils are conventionally classified, based on their iodine values in to three groups, drying, semidrying and non-drying. The generally accepted demarcations are respectively >140, 140-125 and <125. These numbers are more or less arbitrarily assigned. When oil contains conjugated double bonds, the iodine value determined is usually low due to incomplete halogen absorption. Such a classification can only be used for a rough guidance.

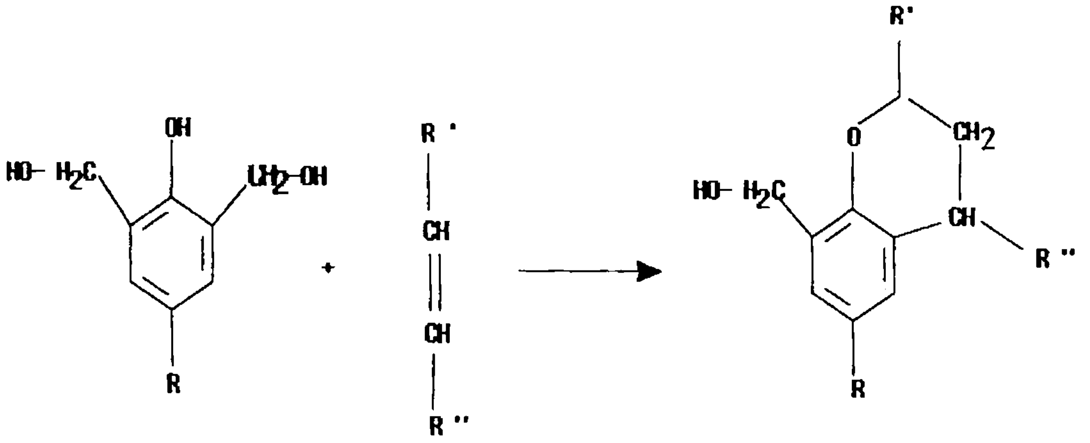
Historically, drying oils have been the major film former of coating, including prints, varnishes and inks. The early renaissance was probably the real beginning of paints as we know them today. The Von Eyk brothers (1388-1441) are said to be the first to use linseed oil as a binder (1) whereas in China tung oil has been used for centuries as coating for wood objects including, boat, house and furnitrue.

The form in which drying oils are used in coating application has gone through an evolutionary change over time. The simplest and most premature way is to use them directly as the film former of the coatings. It was discovered that drying oils may be made more useful by altering their natural state. By ageing in vats, by heating or by blowing air through, the viscosity and drying characteristics of the drying oils may be changed enough to improve its gneral properties for coating application. In the case of fast drying oils with conjugated double bond, such as tung oil and dehydrated castor oil, heat treatment is necessary to gas proof them, so that the oils do not dry to form undesirable wrinkled films.

The oils are not often used in its original form of triglycerides for coating application. It has become a common practice to hydrolyse them first and the free fatty acids are then used to synthesize coating resins with certain advantages. Through trials; it was found that some mixtures of different oils could be used with greater advantage and that natural gums could be added. Thus oleoresinous varnishes were born.

1.3.3 Oleoresinous varnishes

Oleoresinous varnishes were an advancement to coating system for improved performances. These are basically oils that have been hardened or modified by treatment with one or more suitable resins, natural or synthetic. The oils and resins are combined usually by heating together at temperatures of 250^0C or above until a homogenous mixture is formed. In most cases it is simply a case of dissolving the resin or resins in the oil. In some cases chemical reaction may have taken place between the resins and the oil, such as that between the methylol group of a "heat reactive" phenolic resin and the double bond of a drying oil in forming a chroman ring structure as shown below (2).



The major improvements obtained by incorporating resins into drying oils are faster drying, greater film hardness, higher gloss, better water and chemical resistance and greater durability. The degree of property change depends on the type and the amount of the resin incorporated in the oil. Varnish makers express the oil to resin ratio in terms of oil length, which is defined as the number of gallons of oil used for 100 lbs. of the resin in the varnish. Varnishes are categorized according to their oil length as short (5-15 gal), medium (16-30 gal) and long oil (30+ gal) varnishes. The demarcations are somewhat arbitrary and not universally agreed.

1.3.4 Oleochemicals

Oleochemicals by their name may be defined as chemicals from oil. These could be natural fats and oils or of petroleum origin. To have a clear distinction, oleochemicals derived from natural oils are termed natural oleochemicals, whereas those derived from petroleum oils are termed synthetic Oleochemicals, (3).

The natural Oleochemicals are obtained form natural oils with the least change in structure of the carbon chain fraction. In contrast synthetic oleochemicals are built from ethylene to the desired carbon chain fraction or from oxidation of petroleum waxes. Natural fats and oils formed by splitting or trans esterification such as, fatty acids methyl esters and glycerine are termed basic oleochemicals. Fatty alcohols and fatty amines may also be counted basic oleochemicals because of their importance in the manufacture of derivative. Further processing of the basic oleochemicals by different routes such as esterification, ethoxylation, sulphation and amidation, produces other oleochemicals products, which are termed oleochemicals derivatives. The different oleochemicals and the process by which they are manufactured are summarized in Fig.2. Oils and fats also find considerable use in leather processing textile processing, topical pharmaceuticals and in cosmetics.

1.4. Mechanism of film drying in oil based coatings

1.4.1. Non conjugated system

Wiele and Jones (4) suggested that the methylene group between two double bonds, i.e., CH_2 group allylic to two C=C group are much more reactive than those allylic to only one C=C group and are mostly responsible for the drying of conjugated oil. Thus the average number of such groups fn in an oil molecule serves as a better indicator of the drying characteristics of the oil. An oil with an fn value greater than 2.2 is a drying oil, those with fn value somewhat less than 2.2 are semidrying and there is no sharp deviding composition between semidrying and non drying oils .

The chemical mechanism of drying has been established as an oxidative radical chain reaction process which has been summarized as follows (5)

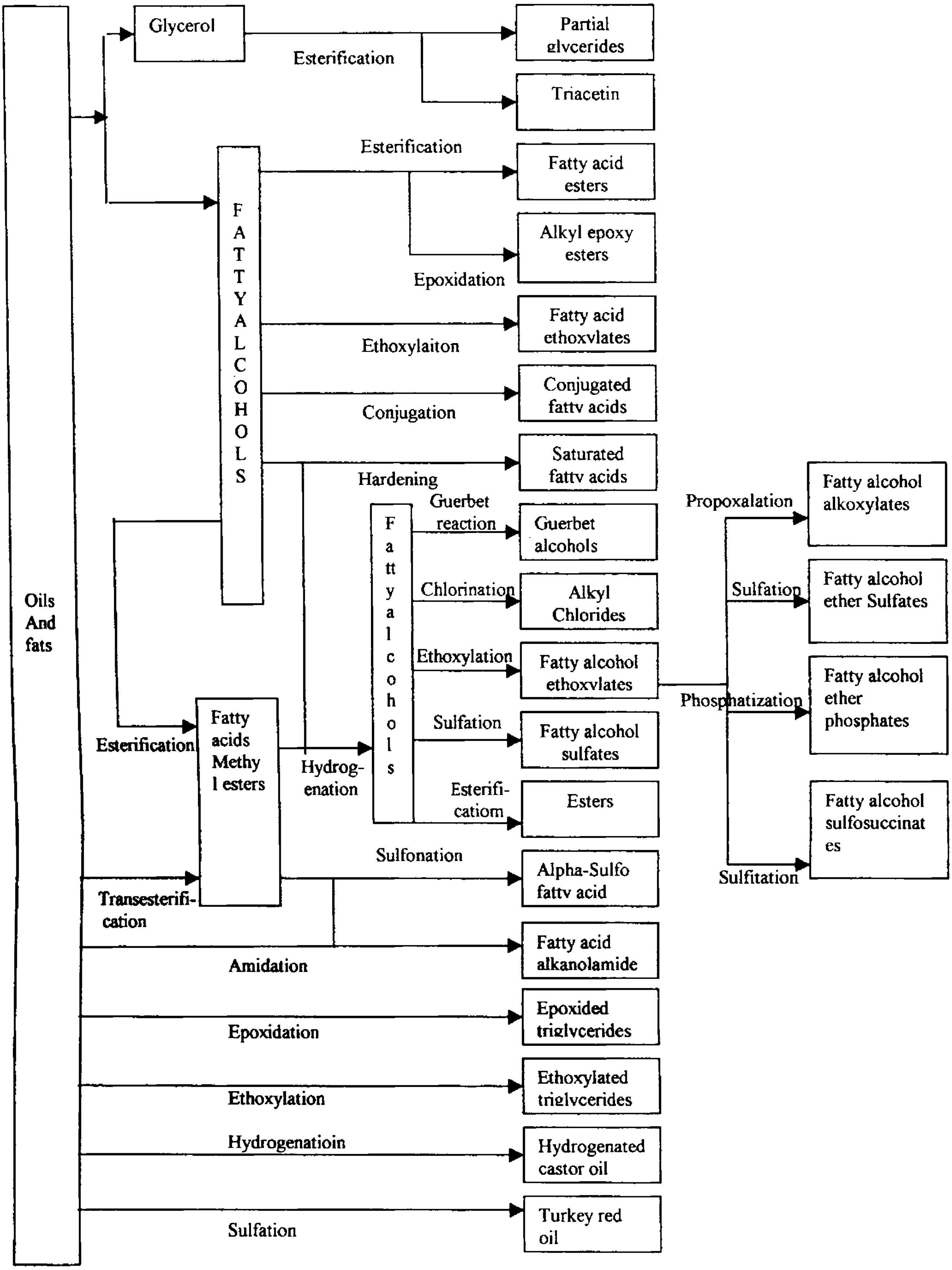
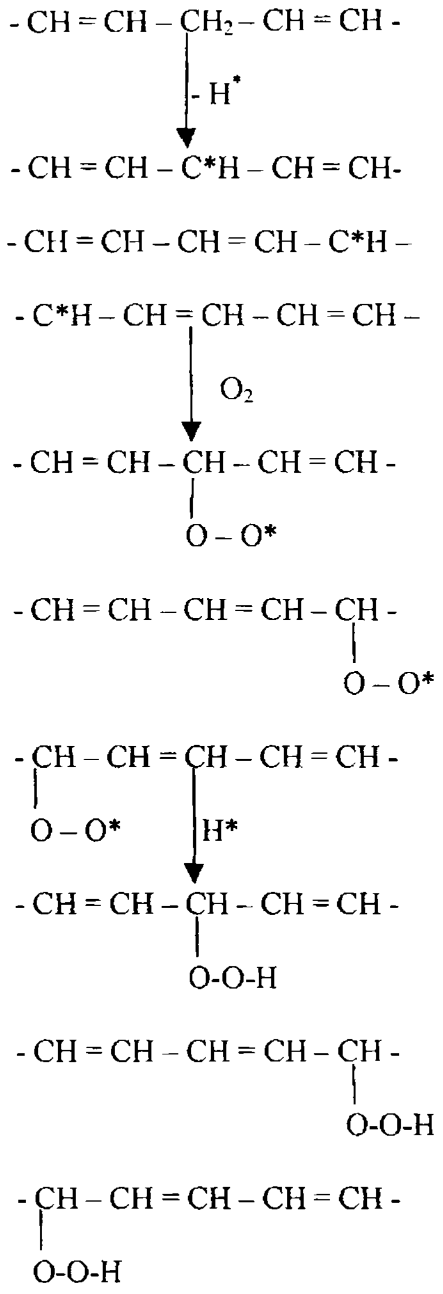


Fig.2 . Oleochemicals and the method of their manufacture



Abstraction of hydrogen

Resonance hybrid free radicals

Three possible hydroperoxides

Addition of hydrogen abstracted

from another linoleate molecule.

Three possible hydroperoxides,

two of which are conjugated.

The initial step is believed to be the dehydrogenation from the alpha-methylene group to form a radical. Since such a hydrogen extraction would acquire a considerable amount of energy, a number of investigations proposed that the hydrogen is removed through reaction with a free radical. Thus a radical $A^{\cdot}$ abstracts hydrogen from a molecule of linoleate, RH, to form the radical R*.

$$RH+A^{\cdot} \longrightarrow R^{*}+AH$$

Since the radical is allylic to the double bonds on either side of it, resonance hybrid free radicals are formed resulting in shifting the double bonds to a conjugated position. This is then followed by

$$R^{*} + O_2 \longrightarrow ROO^{*}$$

and

$$ROO^{*} + RH \longrightarrow ROOH + R^{*}$$

The net reaction is hydroperoxide formation

$$RH + O_2 \longrightarrow ROOH$$

During the oxidation of hydroperoxides the natural cis, cis unsaturation of linoleate is converted to cis, trans and trans, trans isomers. Privett and coworkers (7) concluded that at least 90%of linoleate hydroperoxides preparations are conjugated. It is also seen that when the oxidation is conducted at 0^0C the hydroperoxides are predominantly trans isomers, but room temperature oxidation produces a large amount of trans unsaturation (8,9).

The autoxidation of linoleate described above shows the characteristic features of a chain reaction involving free radicals. Materials that decompose to form free radicals catalyse the reaction even when present in small amounts to produce high yields of hydroperoxides. Initiation of the reaction by light can produce quantum yields much greater than unity; and easily oxidized substance that consumes free radicals but does not by itself undergo significant autoxidation, can markedly inhibit the chain reactions

Chemically the air drying of a non conjugated oil such as linseed oils characterized by the absorption of 12-16% by weight of oxygen. The reactivity of drying oils is based on the mesomeric stabilization of the radical intermediate. The unpaired electron is delocalized over several carbon atoms, and less energy is required to eliminate the proton as illustrated below.

Triglyceride	Mesomers	Activation Energy (KJ/mol)	Relative rate of oxidation
Stearate	Saturated	415	0
Oleate	2	335	1
Linoleate	5	289	120
Linolenate	11	168	330

1.4.2 Drying of a conjugated system

Tung oil, whose dominant feature is the conjugated cis, trans, trans, 9,11,13 octa deca trienoic acid (alpha-oleostearic acid), dries to a coherent film with absorption of only 5% by weight of oxygen. Privett (10) suggested oxidation through 1,2 or 1,4 addition to the diene system to yield non cyclic peroxide Faulkner (11) identified 1,6 peroxides in addition and suggested that the autoxidation does not proceed via hydroperoxide group but rather via cyclic peroxide. It has also been found that the triene content decreased and the diene content increased in proportion to the absorption of oxygen (12,13). The main reaction is believed to consist of a direct attack by oxygen on the C=C bonds to form cyclic peroxide and triens. The peroxides then react with allylic methylene groups or thermally dissociate to give radicals, initiating a radical chain reaction forming polymers via C- or C-O-C bond (14).

1.5 Vegetable oils and oil derivatives in the field of Polymers

Almost every available polymeric materials has been or can be used as a material for surface coatings, films, sheeting small articles, or even for massive engineering structures. Yet preparation of any useful articles from any polymeric materials is virtually impossible without auxiliary materials or additives. For coating applications these may be solvents, thinners, stabilizers, oxidation inhibitors, oxidation promoters, defoamers, leveling agents, fungicides, pigments and plasticisers. In a rubber they may be vulcanizing agents, oxidants, antiozonants, reinforcing fillers, non-reinforcing fillers, extender oils, and plasticizers. In a thick article they may be stabilizers, UV-absorbers, pigments and dyes, reinforcing fibers, particulate fillers, lubricants, flow aids, impact modifiers, odour masks special fragrances and plasticizers. Since the product study includes the use of vegetable oils mainly as a plasticiser, a brief discussion about plasticizers is necessary.

1.5.1 Plasticizers

It is impossible to draw a distinct line between process aids, plasticisers and softeners. The ASTM regulation for softeners is "a compounding materials used in small proportion to soften a vulcanizate or facilitate processing or incorporation of filler". Plasticizer is "a compounding material used to enhance the deformability of a polymeric compound. It may also be noted that in some cases oil loading exceeding half the weight of rubber is made and still the function of the oil is as a softener. Again in some cases a plasticizer added for greater flexibility at low temprature, has also a softening action. The availability of a large number of these ingredients, made their assessment difficult, though an exhaustive study (15) was made.

Theory of plasticization

As with so many facets of compounding, it is not known exactly how softeners and plasticizers achieve their result, some have a solvent-like effect on rubber. There are some general rules that indicate the strength of the solvent action on polymers. Aromatic solvents are more effective solvents of aromatic polymers than aliphatic and aliphatic solvents are more effective with aliphatic polymers than aromatic. Such fluid effects on polymers are reviewed by Files (16).

Apart from solvation theory, several other theories have been proposed. Stephens (17) in an overview, recognized three of them as prominent. These are the lubricity theory, the gel theory and the free volume theory.

In lubricity theory the polymer may be visualised as a non-woven fabric. The individual fibres are like the polymer chains. Although randomly oriented, they are so entwined that moving them is difficult. When a plasticizer is introduced between the chains, they become physically separated and can slide past one another more easily. The whole mass becomes more deformable.

The gel theory says that the polymer is stiff due to the three dimensional structure or gel like network, active sites along the chain serving as hooks between chins. The added plasticiser masks these points of alteration and there is a swelling of the gel; so deforming is made easier.

According to free-volume theory the purpose of the plasticizer is to lower the glass transition temperature Tg of the polymer. When Tg is decreased, free volume is increased which is considered to be a function of temperature and structure.

Classification of plasticizers

Classification of plasticizers is mainly done on the basis of its origin, and more than 99% of these agents fall in the following classes.

1. Petroleum
2. Pine tar and pine products
3. Synthetic resins
4. Esters
5. Natural fats and oils

1. Petroleum-based plasticizers

Undoubtedly petroleum oils are the most widely used plasticizers and softeners in compounding. This is because these oils are versatile, effective, tightly controlled for quality, economical in price and being liquids they are easy to use.

Basically rubber processing oils are higher boiling fractions obtained from refining of petroleum. They cannot be classified by their chemical composition directly. Some idea of their composition can be obtained by correlation with the physical properties of pure high molecular weight compounds. Oils are made up largely of ring structure. The oils with unsaturated ring structure is called aromatic, that with saturated ring structure is called naphthenic, and those with fewer naphthenic and larger number of saturated side chains is called paraffinic oil. The aromaticity of oil is obtained from its viscosity gravity constant (VGC) and it is obtained from the following equation

$$\mathrm{VGC} = \frac{10G - 1.0752 \log (V-38)}{10 - \log (V-38)}$$

Where G is the specific gravity at 60 F and V is the Saybolt Viscosity at 100 ^{0} F. The oils with VGC > 0.95 is termed aromatic, 0.85 – 0.95 is naphthenic and < 0.85 is paraffinic.

Aromatic oils are usually dark in color and so are rarely used in white stocks. Highly naphthenic oils have excellent color and heat stability. Paraffinic oil shows excellent resistance to discoloration by UV light and have good low temperature flexibility. However, they have poor compatibility with nitrile, neoprene and SBR rubbers. Selection of oil for a particular rubber is made after considering different factors involved, and such an assessment is made in table I-2.

Table I-1 Petroleum oil selection chart for rubbers

Rubber	Oil used		
	Aromatic	Naphthenic	Paraffinic
Natural Rubber	Fair	Fair	Excellent
SBR	Excellent	Good	Fair
Butyl	Poor	Good	Excellent
Polybutadiene	Excellent	Good	Fair
Neoprene	Excellent	Good	Fair
Nitrile	Excellent	Good	Poor
EPDM	Good	Good	Excellent

Recently there has been concern about the medical acceptability of some rubber process oils. The International Agency for Research on Cancer classifies untreated naphthenic oils as carcinogenic . All these oils are generally called distillate aromatic extracts (DAE) and several studies have indicated that DAEs are potential carcinogens. The health and environmental concerns over the use of DAEs in tire compounds were highlighted in KEMI report published in 1944. The European Union Dangerous Substance Directive Classified DAEs as carcinogenic due to high levels of polycyclic aromatics present and requires them to be labeled with a skull and cross bones, plus the phrase R45 'May cause Cancer' (18,19.) and by the beginning of 1990's industries were in search of a proper alternative to DAEs, the major concern being the availability of appropriate oils in the necessary quantities to meet the industry demands.

2. Pine tar

Pine tar, a residue from the distillation of pine gum is an efficient softener especially for natural rubber. It is rarely used at levels higher than 5 phr. Besides its softening action it helps in the dispersion of carbon black, has age resistance qualities, and enhances building tack. Because of its dark colour, pine tar cannot be used for white or light coloured goods.

Terpenes usually β-pinene can be polymerized to give resins that have special niches in compounding. These resins can vary form viscous liquid to hard, brittle materials. They are thermoplastic and very tacky when soft. Terpene resins are compatible with NR,SBR IIR, CR, petroleum hydrocarbons, vegetable oils, and waxes. Because they are non toxic, non phytotoxic, and non sensitizing to the skin, they can be used in compounds that come in contact with food products. Terpene resins are often used as a base for chewing gum.

3. Synthetic Resins

The other resins used in rubber are coumarone indene resin (CI resin) and petroleum hydrocarbon resin. The CI resin is produced form heavy, solvent naphtha obtained from the distillation of coal tar. Heavy solvent naphtha is rich in coumarone and indene. These unsaturates are polymerized by sulphuric acid or BF_3. The catalyst can be removed by alkaline wash or lime after polymerization. The resin can be obtained by steam distilling off the unreacted naphtha. CI resins are largely polymers of indene and have relatively low molecular weights, light in colour and have good colour stability.

Unlike processing oils neither CI resin nor other resins are used primarily to soften the mix, rather they act as plasticizers, help in the dispersion of pigments, and hold stress-strain properties at high levels. It is important that mixing temperature be high, to melt the resin if the higher grades are used.

Because CI resin production is limited by the availability of feed stocks, petroleum hydrocarbon resins are replacing them in most areas. The unsaturated monomer from the cracked petroleum fractions are polymerized using BF_3 as catalyst. Hydrocarbon resins are pale yellow to dark brown and range from liquid to hard brittle solids. Based on the feed stock, hydrocarbon resins are of two types. An aliphatic olefin resin, dark in color formed form C-5 fractions and aromatic resin from C-4 feed stock with no C-5 material. Hydrocarbon resins are used in a wide variety of rubber products.

Functionally modified aromatic resins or aromatic modified aliphatic resins can be used as tackifiers and reinforcing resins. Aliphatic types are mainly used as tackifiers.

The phenolic resins are a group of synthetic resins with special properties. They are made from phenol, formaldehyde, cresols and higher aldehydes. The range of possible product is increased, including olefins, which can react with phenol. In general the resins are compatible with NR, SBR, CR, NBR and BR rubbers.

4. Esters

Esters are condensation products of acids with alcohols. Esters are rarely used except for specific purposes as they are relatively high priced. They are used in highly polar rubbers like neoprene and nitrile to impart low temperature flexibility. There are a wide variety of ester plasticizers with varying properties The characteristics to be noticed when selecting a plasticizer include, compatibility with the polymer, effectiveness in improving the properties like low temperature flexibility, cure rate, resistance to ozone etc.

5. Natural fats and oils

These are materials, which are occasionally used in rubber compounding. It is mentioned that oils like linseed ,rape seed, and sunflower oils are used in neoprene rubbers for low temperature flexibility, tear resistance and antiozonant activity (20). Vulcanized vegetable oils (Factice) are considered to be substitute for rubber itself. Unsaturated animal or vegetable oils can be vulcanized with sulphur or sulphur monochloride (S_2Cl_2) to give a rubbery product called factice. The vulcanizate with sulfur is dark and is called brown factice. If S_2Cl_2 is used the product is light colored and is called white factice.

The vulcanized oils are not thermoplastic. They flow under pressure, and they can absorb large amount of liquid rubber plasticizers. Their fluidity under pressure does help in dispersing other ingredients in the mix, serving as a dry plasticizer. Factice is used with synthetic rubbers to make soft rubber products.

Other than factice, oils are subjected to other modifications like, epoxidation, ethoxylation, dehydration etc to get products, which are reported to be used in plastics and rubber as ingredients. The production of oleochemicals is already mentioned in this chapter. Some of those products are also tried in plastics and rubbers. Though majority of the reports are about the use of oils, and their derivatives in plastics, several examples are there for their use in the field of rubbers. As the present study is about the use of vegetable oils as ingredients in rubber compounding a detailed survey of their use in this field is necessary.

Linseed oil

Linseed oil is the widely used one among drying oils, especially in the field of paints, varnishes and other coatings. A general modification usually done to unsaturated oils is epoxidation. There are so many reports about the use of epoxidised linseed oil and raw linseed oil for various functions in plastics and rubbers.

Epoxidised linseed oil (ELO) is a generally accepted plasticizer for PVC. A 1-5% loading in PVC imparts good heat stability. (21). It is also used in pressure sensitive PVC adhesive tapes (22). As in the case of plastics it can impart heat stability, low temperature flexibility etc to elastomers also. Aokin et.al. (23) patented the use of ELO in SBR for heat stability. Reaction product of ELO with alpha or beta naphthylamine can be used in NR as a plasticizer and antioxidant. It decreases the viscosity, does not bloom and disperses well in NR (24) Dynamically cross linked thermoplastic Nitrile rubber blends with good processbility and physical properties are prepared by the addition of about 2 phr ELO (25). Boccaccio reported (26) its use as plasticizer in several plastics and rubbers. It is also reported to be used as vulcanizing agent in carboxylated nitrile rubber - ionomer blends (27). Aniline and phenyl hydrazine modified ELO is used as multipurpose ingredients in NR and NBR. They act as plasticizer, accelerator and antioxidant. There are a few example, where derivatives other than epoxide are also used as plasticiser; eg. linseed oil methyl ester diacetal (29). Acetoxy methyl derivative of linseed oil as plasticizer in PVC can give equal or superior properties compared to conventional diester plasticisers (30).

Linseed oil as such is used as plasticizer in a few elastomers. A 10-15 phr loading of linseed oil in vulcanizates of neoprene rubbers, showed a heat resistance of >500 hr at 120^{0}C and >50 hr at 150^{0}C (31). Soybean oil and rape oil also showed this property. Heat and ozone resistance of chloroprene rubber compounds with modified linseed oil (3-3.5 phr) is also reported (32) Vulcanizate properties of neoprene and 1:1 blend of cis 1,4 polyisoprene with 1,4 cis butadiene with linseed and other oils were evaluated by Velchewa et.al. (33). Plant oils were found to have a better plasticizing effect than mineral oil or DOS and also impart better low temperature flexibility.

Soyabean oil

It is one of the most widely used edible oils and comes under the category of semidrying oils. Soybean oil like linseed oil is also subjected to various modifications like epoxidation, blowing etc, and the products advantageously used in plastics and rubbers. A survey of the literature about its use in polymers, shows that this oil and its derivatives are advantageous ingredients in polymer processing. Though there are only a few examples of its use in elastomers they are seen widely used in plastics.

Vegetable oils and their derivatives are generally better plasticizers for vinyl chloride polymers. Epoxidized soybean oil can also impart, low temperature flexibility and heat resistance, to these class of polymers. Along with the above mentioned properties light resistance also is imparted to vinyl chloride polymers by epoxidized soybean oil (34). Plasticizers of high stability and compatibility are prepared by epoxidizing acetylated monoglyceryl acetates of soybean oil, cottonseed oil etc(35). It is also reported that asphalt saturates and stearin bitumen in weather proofing of fibrous coatings on electrical conductors can be substituted with ester gums plasticized with ESO (36). The storage stability of EPDM (37) and the heat stability of its vulcanizates (38) are reported to be increased by incorporating ESO. A 2% ESO in chlorinated rubber films can increase its heat stability, where as DOP has little effect (39). Lockshaw et.al. patented a process for preparing hard, strong and abrasion resistant vulcanizates from carboxylated nitrile rubber with ESO as plasticizer (40). It is also reproted to impart good mouldability and release properties to acrylonitirle-styrene polymer (41).

Soybean oil as such is used as a plasticizer in rubber solutions, which are to be dipped and cured with S_2Cl_2 and forms a factice in situ. The ultimate elongation of the vulcanizate is increased and the latter rendered more supple. The effect being more pronounced than that brought about by the addition of factices because of the more intimate mixture., but there is a tendency for the vulcanizate to age poorly (42). A 2-20 phr soybean oil in EPDM rubber products, imparts low Tg, low melt viscosity, and improved processability (43).

Hammond Thimothy et. al. (44) and Hamilton et.al (45) patented in use of LO as plasticizer in biodegradable plastics, especially in poly hydroxy alkanoates and Ando Sahio in using it as plasticizer in heat laminated adhesion prevention sheets prepared from thermoplastic resins like PVC, EVA etc (46). A method for the preparation of reclaimed rubber using SBO is developed by Oshilide Kakimoto (47). Reclaimed rubber is prepared by the usual method i.e. by mixing the oil with the vulcanizate. The mixture is then vulcanized with 'S' under various conditions.

Castor oil

It is one of the few vegetable oils with functional acids. More than 60% of fatty acid present in this oil is recinoleic acid (12-hydroxy oleic acid). The presence of this acid makes castor oil inedible. The high viscosity, compared to other common vegetable oil is also due to this. Though non-edible, it is used as a laxative in the field of medicine.

Castor oil like linseed and soybean oil, is subjected to various modifications like, epoxidation, blowing, acetylations etc, along with dehydration to give dehydrated castor oil (DCO). All these derivatives and the raw oil is seen to be used in plastics and rubbers, more widely than the oils mentioned earlier. It is seen that acetylated castor oil imparts better tensile strength and modulus to EVA copolymer films (40). Epoxidised acetylated castor oil as plasticiser, gives advantageous thermal stability for PVC (49). The same authors have patented for the preparation of a plasticizing resin for PVC from the same derivative (50) and it's use as plasticiser in diene rubber (51). If dehydrated castor oil is substituted for DBP in nitrile rubber, plasticizing effect is increased, maintaining physicochemical properties and ageing resistance at an equal level (52).

Glycerides including castor oil when used in small amounts, gave polymeric products with improved toughness and ductility, from a blend containing 1-15% diene rubber with a copolymer of vinylidine aromatic hydrocarbon and an unsaturated nitrile rubber (53). Surinder Singh and coworkers reported the advantages of castor oil based plasticiser, in PVC over DOP (54). Castor oil was used as plasticiser, in hardening epoxy compositions to give products with increased extensibility on elongation, and pliability in bending (55) and it is seen that, castor oil plasticised SBR vulcanizate is useful as mould for cementatious materials, since the oil continuously leaches to the surface preventing the mould from adhering to the moldings (56).

Though no detailed study about the use of castor oil in individual rubbers has been made, a few reports are there, about its effect on some properties. It is reported to impart stability to butyl rubber vulcanizates (57) and to decrease the rigidity of porous polyamide films (58). Polyvinyl butyral resin with good workability and stability is prepared by incorporating about 45 phr castor oil (59) and polyvinyl acetal coating with good releasability by using 50 parts (60). A normal concentration, is used in intumiscent pulley or mastic composition (61) and in diene rubbers for valves for game ball (62). Less than 1% castor oil slightly increases the tensile strength of cellulose derivatives, but higher concentrations decreases the tensile strength (63). The shore A hardness of photopolymerisable urethane rubber for the manufacture of elastic printing plates, was seen to decrease from 90 to 40 by the use of castor oil as plasticizer. Plasticised urethane resists swelling in ethyl alcohol (64)

Castor oil as plasticizer is seen to affect the stereochemistry of polymer formed, and also the crystallanity of polymers. Isotactic polypropylene formed in the presence of castor oil as plasticizer has more perfect structure and decreased tendency for recrystallisation compared to unplasticized one (65). The supramol structure of natural rubber, induced by the introduction of petroleum plasticizer and machine oil (solubility parameters 1.74 and 1.75 respectively) were same. Degradation and disappearance of spherulites followed by secondary crystallization occurs, whereas castor oil (s.p. 1.85) cones as a film on the interface between crystal and amorphous domains (66).

Rubber seed oil

Rubber seed oil is a non edible semidrying oil generally used for soap manufacture. But this oil is also subjected to modification, like epoxidation, sulphation etc and the products tried in industrial application. The characterization of rubber seed oil is made by Eka (67) There are only very few literature references for its use in polymers. Epoxidised rubber seed oil (ERSO) rubber seed oil (RSO) and its soap were tried as plasticiser in PVC (68). The soaps were found to be more effective in suppressing the initial degradation of PVC. Sulphated rubber seed oil was used in fat liquoring and as a plasticizer in the finishing process for leather (69) and it was found to give comparable results with other fat liquors. A series of acylated alkyds (70) and three series of hydroxy functional acylated alkyds (71) were prepared from refined rubber seed oil. Rubber seed oil is also tried as a fuel in diesel engine (72). The oil as such and its blend with diesel performed like diesel fuels in short term tests. The special fuel consumption is higher for rubber seed oil than diesel due to its low calorific value, but the thermal efficiency is higher than that of diesel. Emission of CO and C was higher for rubber seed oil.

Calophyllum inophyllum oil (Punnal oil)

It is the seed oil of calophyllum inophyllum, a tree generally seen in tropical countries. It is a non edible oil, and also comes under the category of non drying oils.

This oil is seen to contain a large variety of other components than triglcyerides. Glycolipids and phospho lipids are the major components in this category. Detailed analysis by Hemavathy et.al (73) showed that the oil consists only 60.1% refined lipids. Total lipids consisted of 92% neutral lipid 6.4% glycolipids and 1.6% phospholipids. Out of the neutral lipids 82.3% is triglyceride and 7.4% free fatty acids.

At least four glycolipids were identified which are

1. Acyl mongalactosyl diglycerides
2. Monogalactosyl mono acyl glycol
3. Monoglactosyl diacyl glycerol
4. Acylated sterol glucoside

The first two are major components. The phospholipids identified are

1. Phospatydyl ethanol amine
2. Phosphatydyl choline
3. Phosphatidic acid
4. Phosphalydyl serine
5. Lyso phospatydyl choline

The first two are the major components and the remaining are present in very small amounts. Besides the compounds mentioned above, some oxygen containing, polycyclic compounds like coumarine and its derivative (74) ponnalide (75) calophynnic acid (76) Crepenefinic acid and dihydro crepenafenic acid (77) etc were shown to be present in this oil. The calophyllum oil is generally used for the manufacture of soaps. So far it has not been used in the field of polymers.

1.6 Scope of the present work

The role of auxiliary materials or additive in the preparation of products from polymeric materials cannot be overemphasised. In an elastomer, the important classes of additives are vulcanizing agents of different types, reinforcing fillers, processing aids, plasticizers, activators, accelerators, antioxidants etc. The common practice is to use individual components for each function mentioned above, except in cases where the same substance acts as processing oil and palsticizer, and that too because of the undefined demarcation between the two.

The function of the processing oil in rubber compounding is to impart better processibility during the addition of fillers. They usually improve the processability by acting as lubricants between the rubber molecules. Even though they are rubber soluble at low concentrations, they may exude and the tackiness of the compounds will be reduced. The physical and chemical properties usually affect the efficiency of the processing oil, which again depends on the type of rubber used. High boiling point, low vapor pressure, and good chemical stability are necessary for processing oils especially when the processing and application temperatures are high. The gel point of the oil affects the elastic properties of the vulcanizates at low temperatures and the viscosity affects the hardness.

Aromatic, paraffinic and naphthenic oils are the most widely used processing oils. The use of these oils in rubbers is selective mainly due to the compatibility and also due to the staining nature of aromatic oil. As these oil are of petroleum origin they are not renewable. Further many of them are toxic. Due to these reasons, the polymer industry is on the look out for new materials, which can substitute these oils and can minimize the above mentioned problems.

Though there are several instances of vegetable oils being used as processing aids or plasticisers, which are reviewed in this chapter, a systematic and detailed study of their use in elastomers , with the object of standardising their use, has not yet been made. The present investigation has been undertaken to fill this gap to make a systematic study of the use of a few typical vegetable oils, belonging to various classes like drying, semidrying and nondrying, as processing aids or plasticizers in elastomers.

The oils proposed to be tried are linseed from the class of drying oils soybean, castor and rubber seed from the semidrying and calophyllum inophyllum oil form the non drying classes. The selection has been made such that the effect of unsaturation of oil on the compounding characteristics and vulcanizate properties of the elastomer can be understood.

Vegetable oils are generally non toxic, have high boiling point and are stable at the processing and application temperature of many commercially important elastomers. Further they have generally lower viscosity, than aromatic or naphthenic oils except castor oil. . Their Viscosity Gravity Constant is given in Table I.2 and the values are comparable with that of naphthenic or paraffinic oils

Table I.2 VGC of vegetable oils

No	Oil	V.G.C
1	Linseed oil	0.8756
2	Soybean oil	0.8755
3	Castor oil	0.8589
4	Rubber seed	0.8816
5	Calophyllum inophyllum	0.8744

Natural and synthetic rubbers differ in vulcanization characteristic and vulcanizate properties. Compared to NR, synthetic rubbers are vulcanized with a higher concentration of accelerators with a corresponding reduction in sulfur. Synthetic rubbers do not stress crystallize as much as NR and hence the green strength and tensile properties of the gum vulcanizates of NR are better, than those of synthetic rubbers. Another factor which guides the selection of ingredients for elastomers for specific purposes is the polarity of the rubbers. In view of the above mentioned reasons and also considering the abundance in the use , it is proposed to try natural rubber (NR) (non polar), styrene butadiene rubber (SBR) (synthetic, slightly polar) and nitrile rubber (NBR) (synthetic, polar) in this investigation.

Rubber compounding also involves the use of activators. They are substances, which increase the efficiency of accelerators. The most popular activator system is zinc oxide and stearic acid where stearic acid acts as a co-activator and about 1-3 phr stearic acid is usually used in rubbers. Rubber grade stearic acid is usually a mixture of fatty acids, containing about 60% stearic acid, 21% palmitic acid and9% myristic acid. In general small amounts of fatty acids are necessary as vulcanization activators. If larger amounts are used, they act as plasticizers, affecting the tackiness. and the rate of vulcanization.

Raw vegetable oils generally contain free fatty acids at concentrations as low as 1% to as high as 45% in some cases. It is also proposed to investigate whether these fatty acids present in oils can act as co-activators in rubber vulcanization. The effect of these oils on the processing characteristics, cure characteristics and vulcanizate properties etc of the different mixes are also proposed to be evaluated.

Sulphur vulcanized rubbers are usually susceptible to attack by oxygen. This oxidation may be initiated by various external factors each giving rise to different form of degradation. The unsaturation in diene rubbers makes it possible to cure them with sulfur, but at the same time imparts sensitivity towards oxygen, ozone and other reactive substances. At higher temperatures, these effects are more pronounced. Since unreacted double bond occurs in the vulcanizates the possibility of such reaction exists even after vulcanization. These degradation processes can be retarded by the addition of chemicals, commonly called age resistors (anti oxidants, antiozonants etc) and are used in amounts of 1-3 phr. The nature of the antioxidants determines the extent of protection. Amines and phenols are the most common antioxidants used.

Most of the vegetable oils contain phenolic compounds like tocopherols, sterols, sesamols, coumarines etc. and phosphotides with free hydroxyl group. Linseed oil and soybean oil contain tocopherols and phosphatides. Soybean oil contains methionine and N-acetyl methionine, both having antioxidant properties (78) synergestic with tocopherols. The optimum concentration of tocopherol for antioxidant activity within the oil is reported to be α 50-70 mg, γ and δ 30-40 mg. The activities are in the ratio 100:187:273 (79). Anti oxidants like butylated hydroxy anisol (BHA), butylated hydroxy toluene (BHT) and nor dihydroguaianetic acids, were also detected in soybean oil (80). Rubber seed oil is found to contain α,γ and δ tocotrienols at 30. 165 and 4 mg/gm respectively (81). Calopyllum inophyllum oil is reported to contain sterols like, campesterol, stigmasterol, and β-sitosterol (82).Generally, the antioxidants protect the elastomers form degradation, by preferentially undergoing oxidation themselves. In the present study it is also proposed to evaluate the antioxidant activities of the oils mentioned above and to use them in the vulcanization of NR, SBR and NBR.

The principal objectives of the present study are

1. To study the effect of using vegetable oils like linseed oil, soyabean oil, castor oil, rubber seed oil and calophyllum oil on the cure characteristics and vulcanizate properties of the following rubbers.
    a. Nitrile rubber (NBR)
    b. Styrene - butadiene rubber (SBR)
    c. Natural rubber (NR)
2. To standardise the conditions for their use and evaluate their activity as plasticizer, activator and antioxidant.
3. To study the effect of vegetable oils on the properties of some typical rubber products like tyre tread, micro cellular soles, and sponge.

CHAPTER II

EXPERIMENTAL TECHNIQUES

The materials used and the experimental procedures adopted in the present investigations are given in this chapter.

2.1 Materials used

Natural Rubber (NR)

ISNR –5 used in this study was supplied by the Rubber Research Institute of India, Kottayam. It had the following specifications.

Dirt content by mass	0.05
Volatile matter, % by mass	1.00
Nitrogen, % by mass	0.70
Ash, % by mass	0.60
Initial plasticity, P_o	30.00
Plasticity retention Index (PRI)	60.00

Stryrene –butadiene rubber (SBR)

Synaprene- 1502 having the following specifications was supplied by Synthetics and Chemicals Ltd., Bareilly, U.P., India.

Volatile matter, % by mass	0.75
Total ash, % by mass	0.50
Bound styrene content, % by mass	25.00

Butadiene- acrylonitrile rubber (NBR)

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

Nitrile content (by weight)	34
Mooney Viscosity (ML 1+4) at 100^{0}C	42

Polybutadiene (BR or PB)

Polybutadiene used in this study is Cisamer-1220, supplied by Indian Petrochemicals Corporation Ltd.,Vadodara.

Mooney Viscosity{ ML (1+4) at 100^0 C	45

High styrene resin (HSR)

The HSR used in this study is Synaprene 1958 grade supplied by Synthetics and Chemicals Ltd, Bareilly.

Styrene content (% by mass)	49

Compounding Ingredients

i.Zinc oxide

Zinc oxide was supplied by M/S .Meta Zinc Ltd., Bombay. It had the specifications given below.

Specific gravity (g/ cm^3)	5.5
Zinc oxide content	98%
Acidity	0.4%
Loss on heating (2 hrs at 100^{0}C)	0.5%

ii.Stearic acid

Stearic acid used in the study was supplied by Godrej Soaps (Pvt.) Ltd., Bombay, had the following specifications:

Melting point	65^0 C
Acid number	200
Iodine number	9.05
Specific gravity (g/cm^3)	0.8
Ash	0.1%

iii. Mercaptobenzthiazyl disulphides (MBTS)

Mercaptobenthiazyl disulphide was supplied by Bayer Chemicals, Bombay. It had the following specifications.

Sprecific gravity (g/cm^3)	1.34
Melting point	165^0 C

iv. Tetramethyl thiuram disulphide (TMTD)

TMTD was supplied by Polyolefins Industries Ltd., Bombay. Its specifications are:

Melting point	138^0C
Specific gravity (g/cm^3)	1.4
Ash	0.5%
Moisture	1.0%

v. Vulcafor F

Supplied by Bayer India Ltd., Mumbai. It had the following specifications.

Composition	An activated thiazole
Appearance	Cream coloured powder
Specific Gravity at 25^0 C	1.46

2-morpholino thio benzo thiazole (MOR)

MOR used in this study is supplied by National Organic Chemical Industries Ltd., Thane, Mumbai.

vi. Sulphur

Sulphur was supplied by Standard Chemical Company, Madras. It had the following specifications:

Specific gravity (g/cm^3)	2.05
Acidity	0.01%
Ash	0.10%
Solubility in CS_2	98%

vii. Fillers

High abrasion furnace black (HAF N-330) used in these experiments was supplied by M/S Philips Carbon, Bombay and had the following specification.

Appearance	Black granules
DBP absorption	102±5 cc/ 100 g
Pour density	23.5 lbs/ft^3
Iodine number	82
Loss on heating/hr (max) at 125^{0}C	2.5 %

viii. Crumb

NR/HSR micro crumb used is ground microcellular sole scrap having 200 mesh size, supplied by M/s. Paragon Rubbers , Kottayam.

ix. Process oils

Aromatic oil was supplied by Hindustan Organic Chemicals. It had the following specifications:

Aniline point (^{0}C)	43
Ash content	0.01%
Viscosity gravity constant	0.96
Specific gravity (g/cm^3)	0.98

Naphthenic oil having the following specifications was supplied by M/S. Hindustan Petroleum Ltd., Bombay.

Colour	Light
Pour point (^{0} C)	-20
Aniline point (^{0} C)	-78
Viscosity gravity constant	0.87
Aromaticity as %	20

Paraffinic oil having the following specifications was supplied by M/S. Hindustan Petroleum Ltd., Bombay

Colour	Light coloured oil
Viscosity gravity constant (VGC)	0.8 – 0.85
Aniline point (^{0} C)	96

Dioctyl phthalate (DOP) used is commercial grade supplied by Rubo-synth Impex Pvt.Ltd, Mumbai and had the following specifications.

Specific Gravity	0.986
Viscosity (cps)	60

Vegetable oils

Linseed oil used is refined linseed oil marketed by Camlin Ink India Ltd. Rubber seed oil and Calophyllum Inophyllum oil (Punnal oil) were obtained by expulsion from their locally collected dried seeds. Castor oil and Soyabean oil were commercial grade obtained from local market.

They have the following specifications.

Oil	Colour	Sp.Gr.	Saponification value (S.V.)	Iodine value (I.V)	Saybolt viscosity
Linseed	Pale yellow	0.935	188-196	170-185	128.2
Soyabean	Colourless	0.9175	189-195	120-141	165
Castor	Colourless	0.926	188-202	146-166	1297
Rubber seed	Pale brown	0.9234	185-190	135-145	182
Punnal	Pale yellow	0.916	186-190	91-94	155

x. Antioxidants

Vulcanox 4020 used is (N – (1,3-dimethyl-butyl)- N^1- phenyl-p-phenylene diamine, supplied by Bayer India Ltd. Mumbai.

Vulcanox HS used is acetone-anilines supplied by Bayer India Ltd.

2.2 Study of the processability of the compounds using Brabender Plasticorder

Brabender plasticorder has been widely used for measuring processability of polymer. This torque rheometer is essentially a device for measuring the torque generated due to the resistance of a material to mastication or flow under pre selected conditions of shear and temperature. The heart of the torque rheometer is a jacketed mixing camber whose volume is approximately 40 cc for the model used (PL 3S). Mixing and shearing of the material in the mixing chamber is done by horizontal rotors with protrusions. The resistance put up by the test material against rotating rotors in the mixing chamber is indicated with the help of a dynamometer balance. The dynamometer is attached to a mechanical measuring system which records the torque. A D.C thyrister controlled drive is used for speed control of the rotors (0 to 150 rpm). The temperature can be varied up to 300^0C. Stock temperature thermocouple with a recorder is used for temperature measurements. Different types of rotors can be employed depending upon the nature of the polymer used. The rotors can be easily mounted using the simple fastening and coupling system. The materials are charged into the mixing chamber after setting the test conditions and the final torque shown by the mixture after homogenization is measured. The experiment is repeated by varying the rpm and also at different temperatures. The flow curves of the compounds are obtained by plotting (torque/rpm) which represents viscosity against rpm representing shear rate.

2.3 Mixing and homogenization of rubber compounds

Mixing and homogenization of elastomers and compounding was done on a laboratory size (15x33 cm) two roll mill at a fraction ratio of 1:1.25. The elastomer was given one pass through the nip of (o.002x100)". Then it was given two passes through the nip (0.002x55)" and allowed to band at the nip of (0.002x55)". The temperature of the rolls was maintained at 60 ± 5^0 C during the mastication. After the nerve had disappeared, the compounding ingredients were added as per sequence given in ASTM D 3182 (1982). Before the addition of accelerators and sulphur the batch was thoroughly cooled. After completion of the mixing, the compound was homogenized by passing six times endwise through a tight nip and finally sheeted out at nip gap of 3 mm. Mixing time and temeperature were controlled during the process.

2.4 Determination of cure characteristics of the compounds

The cure characteristic of the mixes were determined using a Gottfert Elastograph model 67.85. It is a microprocessor controlled rotorless curemeter with a quick temperature control mechanism and well defined homogeneous temperature distribution in the test chamber. In this instrument , the specimen(circular shape) is kept in the lower half of the cavity which is oscillated through a small deformation angle ($\pm0.2^0$). The frequency is 50 oscillations per minute. The torque is measured on the lower oscillating die half. The important cure parameters obtained from the elastograph are:

1. Minimum torque: Torque obtained after homogenizing at the test temperature and before the onset of cure.

2. Maximum torque: This is maximum torque recorded after the curing of the mix is completed.
3. Scorch time: This is the time taken for 10% vulcanization.
4. Optimum Cure time: This is the time taken for obtaining 90% of the maximum torque.
5. Cure rate: Cure rate is determined from the following equation.

$$\text{Cure rate(Nm/min)} = \frac{L_{max} - L_{min}}{t_{90} - t_{10}} \qquad 2.1$$

Where, L_{max} and L_{min} are the maximum and minimum torque and t_{90} and t_{10} are the times corresponding to the optimum cure time and scorch time respectively.

2.5 Moulding of test specimens

The test specimens for determining the physical properties were prepared in standard moulds by compression molding on a single day light, electrically heated press having 18"x 18" platens at a pressure of 200 Kg/ cm^2 on the mould. The rubber compounds were vulcanized up to their respective optimum cure time at 150^{0}c.Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cool and dark place for 24 hours and were used for subsequent physical tests. For samples having thickness more than 6 mm (compression set, abrasion resistance etc.) additional curing time based on the sample thickness was given to obtain satisfactory moldings.

2.6 Physical tests on vulcanizates

a. Tensile stress-strain properties

Tensile properties of the vulcanizates were determined as per ASTM D 412 (1980) using dumb-bell specimens on a Zwick Universal Testing Machine (model 1445). All tests were carried out at 28 ± 2^0C. Samples were punched out from compression molded sheets using a dumb-bell die (C-type). The thickness of the narrow portion was measured by bench thickness gauge. The sample was held tight by the two grips on the UTM , the upper grip of which was fixed. The rate of separation of the power actuated lower grip was fixed at 500 mm/min. the tensile strength, elongation at break and modulus were printed out after each measurement by the microprocessor.

b. Tear resistance

This test was carried out as per ASTM D 624 (1981) using unnicked, 90^0 angle test pieces. The samples were cut from the compression molded sheets parallel to the mill grain direction. The test was carried out on the Zwick Universal Testing machine. The speed of extension was 500 mm/min and the test temperature 28 ± 2^0C.

c. Compression set

The samples (6.25 mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hours in an air oven at 70^0c. After the heating period, the samples were taken out, cooled at room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows:

$$\text{Compression set } (\%) = (t_o - t_1)/(t_o - t_s) \qquad 2.2$$

Where t_o and t_1 are the initial and final thickness of the specimen respectively and t_s the thickness of the spacer bar used. The procedure used was ASTM D 395 (1982 method B).

d. Abrasion resistance

The abrasion resistance of the samples were determined using a DIN abrader (DIN 53516). Samples having a diameter of 6±0.2 mm and a thickness of 6 mm was kept on a rotating sample holder and 10 N load was applied. Initially a pre-run was given for the sample and its weight taken. The weight after the final run was also noted. The difference in weight is the abrasion loss. It is expressed as the volume of the test piece abraded by its travel through 42 m on a standard abrasive surface. The abrasion loss was calculated as follows:

$$V = \Delta M / \rho \qquad 2.3$$

Where ΔM = mass loss, ρ = density of the sample and V = abrasion loss.

e. Rebound resilience

Rebound resilience is measured using a vertical rebound resilience tester as per ASTM D 2632-88. A plunger weighing 28±0.5 g is dropped from a height of 40 cm to the sample of thickness 12.5 mm and the rebound height is measured

Ageing studies were carried out according to ASTM D 573-88. Dumb-bell samples were kept in an air oven at 100^{0}C for 48 hours. Physical properties like tensile strength, elongation at break, modulus etc were measured after ageing. Knowing the values of this test before ageing, the retention of these properties were calculated for assessing the effect of ageing .

f. Determination of chemical crosslinks of the vulcanizates

The crosslink density of the vulcanizates were determined by equilibrium swelling method and using Florey-Rehner equation. Samples of approximately 0.3 g were cut and kept to swell in solvents for 24 hours . The outer portion of the swollen samples were then dried using a filter paper and weighed. It was then placed inside the oven at 60°C for 24 hours to remove the solvent . The de swollen weight was determined. The volume fraction of rubber in the de swollen network was then calculated by the method reported by Fllis and Welding (88) using the following equation.

$$V_r = \frac{(D - FT)\,\rho_r^{-1}}{(D - FT)\,\rho_r^{-1} + A_0\,\rho_s^{-1}} \qquad 2.4$$

Where T = weight of the test specimen; D = de swollen weight; F = weight fraction of the insoluble component; A_0 = weight of the absorbed solvent corrected for the swelling increment; ρ_r = density of the test specimen; ρ_s = density of the solvent.

In the case of vulcanizates containing filler the value V_r obtained as above were converted into V_r^0 by the equation.

$$V_r^0 = V_r\,(0.56\,e^{-Z} + 0.44) \qquad 2.5$$

Where V_r is the volume fraction of the rubber without the filler, Z is the weight of the filler divided by total weight of all ingredients, and V_r^0 is the volume fraction of rubber with filler. This value was then substituted in the Florey-Rehner equation.

g. Determinatioin of concentration of different types of crosslinks

The concentration of poly sulfidic crosslinks (-Sx-) was estimated from the determination of chemical crosslink densities of the vulcanizate before and after treatment with thiolamine. Treatment of the vulcanizate with propane –2- thiol (0.4 M) and piperidine(0.4 M) in tolune at room temperature for two hours cleaves the polysulfidic crosslink in the network. The experimental method used is as described by Campbell (89,90).

h. Heat build up

The heat build up of the vulcanizates were determined using a Goodrich flexometer, conforming to ASTM D 623 – 67 Method A. The temperature rise (^{0}F) at the end of 20 minutes was taken as heat build up.

i. 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.

j. Blooming

Blooming is determined by visual method.

k. Compression Deflection

The compression deflection of sponge is measured as per ASTM D 1056.

CHAPTER. III

STUDIES ON THE EFFECT OF VEGETABLE OILS ON THE CURE CHARACTERISTICS AND VULCANIZATE PROPERTIES OF NITRILE RUBBER (NBR)

Nitrile rubber is a copolymer of butadiene and acrylonitrile. NBR has good resistance to a wide variety of oils and solvents and hence is widely used in products like oil seals, pipe protectors, blow out preventors, etc. NBR shows no self reinforcing effect, as there is no crystallinity. The service temperature in presence of oxygen is estimated to be 130^{0}C (83).

Basically nitrile rubbers are compounded much like natural rubber. Since it does not crystallise, reinforcing fillers are necessary to obtain reasonable tensile , tear and abrasion levels. In black compounds reinforcement is proportional to the fineness of the black. Non black fillers give best heat resistance and also can be used with compound that might be in contact with the food products. Fine precipitated silica is the most reinforcing among the non black fillers.

Plasticizers are used in almost all nitrile compounds first to aid processing and then to improve low temperature flexibility resilience and flexing, or to reduce hardness. Plasticizer level will ordinarily vary from 5-50 phr. Processing can be difficult below 5 phr. level, and over 50 phr the material may bleed out and physical properties may deteriorate unacceptably. Three types of plasticizers are generally used. Organic esters to get the best in low temperature flexibility, coal tar resins like CI resin to maintain tensile properties and to improve building tack, and polymeric esters to obtain high temperature ageing.

Nitrile rubber requires age resistors in addition to those they already have in order to give long service. Where staining is not a problem, amine type antioxidants may be used. If staining is objectionable then phosphites or hindered phenol antioxidants will serve better.

Vulcanization of nitrile rubber is usually accomplished with sulfur, accelerator and zinc oxide and fatty acid as activator. In special cases peroxide may also be used. NBR cures relatively fast. The higher ACN content rubbers curing faster than lower content ones. The amount of sulfur 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 sulfur is considerably less than in NR and affect it's uniform dispersion, For this reason sulfur is added early in the mix.

Because of the relatively fast rate of cure , NBR is usually compounded with only one accelerator, often of the sulfenamide class. If accelerator of the thiazole type are used, a second activating accelerator like tetramethyl thiuram mono sulfide (TMTM) or tetramethyl thiuram di sulfide (TMTD) might be used. Activating this vulcanizing system would be 5 phr zinc oxide and 1–2 parts stearic acid.

It is already mentioned in this chapter that esters or polymeric esters are used as plasticizers in nitrile rubber. Vegetable oils are esters and have a higher molecular weight compared to the conventional synthetic esters. More over they contain free fatty acids which can function as a coactivator. Almost all vegetable oils contain phenolic compounds like tocopherols, which are potential antioxidants and can protect the elastomers from oxidation. So vegetable oils can be a potential multipurpose ingredient especially in nitrile rubbers. In the present study vegetable oils especially drying oils were used as multipurpose ingredient in nitrile rubber. Though calophyllum inophyllum oil is not a drying oil, it is also used in this study due to the presence of various non-fatty materials in it, and also due to it's low cost.

3.1 Linseed oil as a multipurpose additive in NBR

Linseed oil is a typical drying oil widely used in paints and varnishes. The major fatty acids present in the oil are oleic 16%, linoleic 14.2%, linolenic 60%. The oil is also found to contain small amounts of tocopherols and phosphatides, which are having antioxidant properties. In the present study linseed oil is used as a multipurpose additive in nitrile rubber.

Experimental

Nitrile rubber conforming to the specifications given in chapter.II was compounded on a two roll mixing mill (6" x 12") as per ASTM-D 15- 627 according to the formulation given in table.3.1.1. In formulations where linseed oil is present it is used as a substitute for DOP and stearic acid.. The results reported were the average of at least five specimens.

Results and discussion

Fig 3.1.1 shows the flow curve of the compounds obtained from the Brabender Plasticorder as (torque/rpm) representing viscosity and rpm representing shear rate, at different temperatures. All the compounds are highly pseudoplastic. The flow behaviour of the compounds containing 5 phr linseed oil closely resembles that of the compound containing 6 phr DOP. It may be concluded that the processability of the compounds in which linseed oil replaces stearic acid and DOP is not adversely affected. In fact, viscosity is marginally lower showing the higher plasticizing action of linseed oil. The difficulty in processing without plasticizer is clearly shown by the curve.

Fig.3.1.2 shows the cure curves of the compounds. The curing behaviour of the compound containing 5 phr linseed oil and the compound containing 6 phr DOP are very similar, as in the case of their flow curves. The compound without plasticizer show the highest torque similar to it's flow behaviour. The curing becomes progressively faster with increase in the amount of the linseed oil. The cure time is decreased by 15% when DOP is substituted with the same loading of linseed oil. It may be noted that the increase in cure rate does not affect the scorch safety (Table 3.1.2).The main reason for the increase in cure rate may be due to the activation of the polymer molecule by the plasticizer, by reducing their intermolecular attraction. It may also be due to the higher activity of unsaturated fatty acids compared to stearic acid.

Fig. 3.1.3 shows the variation of tensile strength with DOP and linseed oil concentrations. It is interesting to compare the plasticizing nature of DOP and linseed oil. The tensile strength of the vulcanizates with linseed oil shows an increase up to a concentration of 4phr and then starts decreasing slowly, whereas vulcanizates with DOP shows a gradual decrease with increase in DOP concentration. But vulcanizates with linseed oil always show a higher tensile strength than that with the same loading of DOP.This shows that there is some phenomena other than mere plasticization, and it is likely that the linseed oil gets covulcanized with the elastomer. The variation in tensile strength can also be related to the cross-link density and additionally to the better filler incorporation. But as the concentration of linseed oil increases, the oil may undergo self vulcanization to form factice which reduces the strength of the vulcanizate The decrease in crosslink density (Fig. 3.1.5) may be due to the additional use of sulphur for factice formation.The vulcanizate without plasticizer also have a higher tensile strength compared to the control mix with DOP and this is possibly due to the higher crosslink density and also due to the absence of plasticizer effect on tensile strength.

Table.3.1.4. shows the percentage of polysulphidic crosslinks of elastomers with various types of plasticizers and also without any plasticizer. It is seen that plasticizers affect the concentration of different types of crosslinks in all the three elastomers used in this study. Vulcanizates without plasticizer shows a higher percentage of polysulphidic crosslink. The effect of vegetable oils in reducing its concentration is comparable with that of the conventional plasticizers Though there is variation in crosslink density with change in plasticizer, the percentage composition of different types of crosslinks is not affected.

Fig . 3.1.5 shows the variation of modulus with linseed oil concentration which is directly proportional to the variation of cross link density as expected while the elongation at break is inversely proportional to the variation of cross link density (Fig.3.1.7) The variation of tear resistance is similar to tensile strength and can be explained on similar lines (Fig.3.1.4).

The air resistance and oil resistance of the vulcanizate containing DOP and linseed oil do not show much variation. But the absence of plasticizer make the vulcanizate less resistant to air oxidation while oil resistance is improved. The samples were aged in engine oil at 70^{0}C for 72 hrs and in air at 100^{0}C for 48 hrs. The properties of the aged samples were compared with that of the fresh sample (Table 3.1.2).

Leachability is considerably reduced by substituting DOP with linseed oil. The percentage loss in weight of the aged samples were compared with that of the control mix in Table 3.1.3. Generally it is seen that leachability is reduced when vegetable oils are substituted for DOP. DOP remain in the original liquid state in the vulcanizate leading to improved transportation of low molecular weight ingredients to the surface and allow blooming , whereas vegetable oils undergo physical and chemical change to solid or semisolid by self vulcanization or covulcanization or even drying during the process of vulcanization which prevent movement of its own and other ingredients. Thus preventing leachability and blooming. This view is supported by the lower leachability of vulcanizate without plasticizerThe sample containing 6 phr linseed oil shows only 40% leachability of the one containing 6 phr DOP. The compression set of the vulcanizates is also lowered by incorporation of linseed oil (Table.3.1.3), or even when no plasticizer is used. This is due to the increase in crosslink density when no plasticizer is used and linseed oil is substituted for DOP.

Conclusion

The study shows that linseed oil is a very useful additive in NBR. Use of linseed oil gives appreciable increase in properties like tensile strength, tear resistance etc. in nitrile rubber vulcanizates. The viscosity of the compound is marginally lower than that of the compound with DOP. Cure rate is increased while leachability is reduced. The optimum concentration of linseed oil seems to be in the range 2 - 5 phr and this can advantageously replace about 6 phr DOP and 2 phr stearic acid in conventional NBR vulcanizates. Further the cost of the compound can also be reduced by substituting linseed oil for DOP and stearic acid. Though there is advantage in properties like tensile strength and leachability when no plasticizer is used, the difficulty in processing seems to outweigh these advantages.

FIG 3.1.1 FLOW CURVE

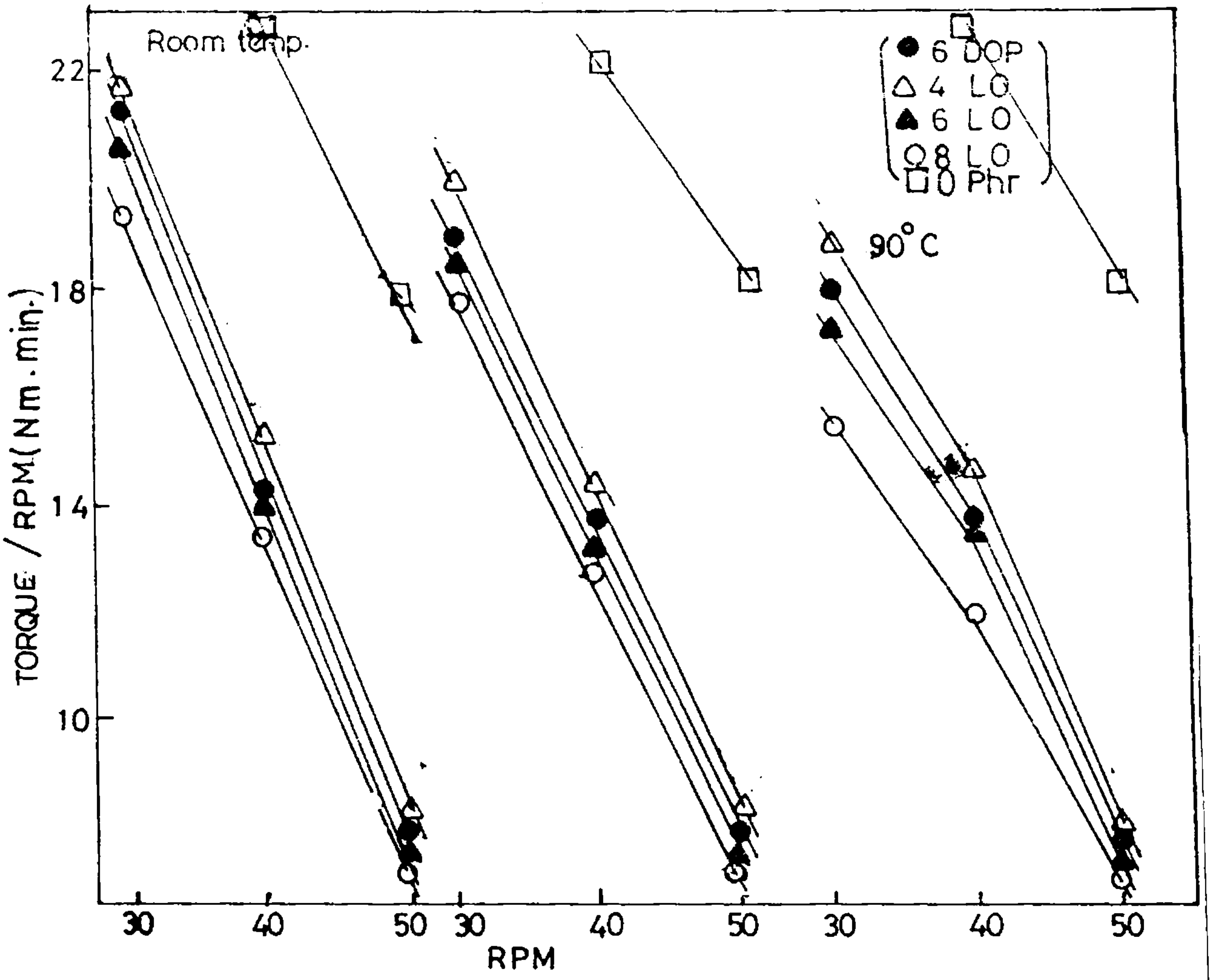


FIG 3.1.2 CURE CURVE

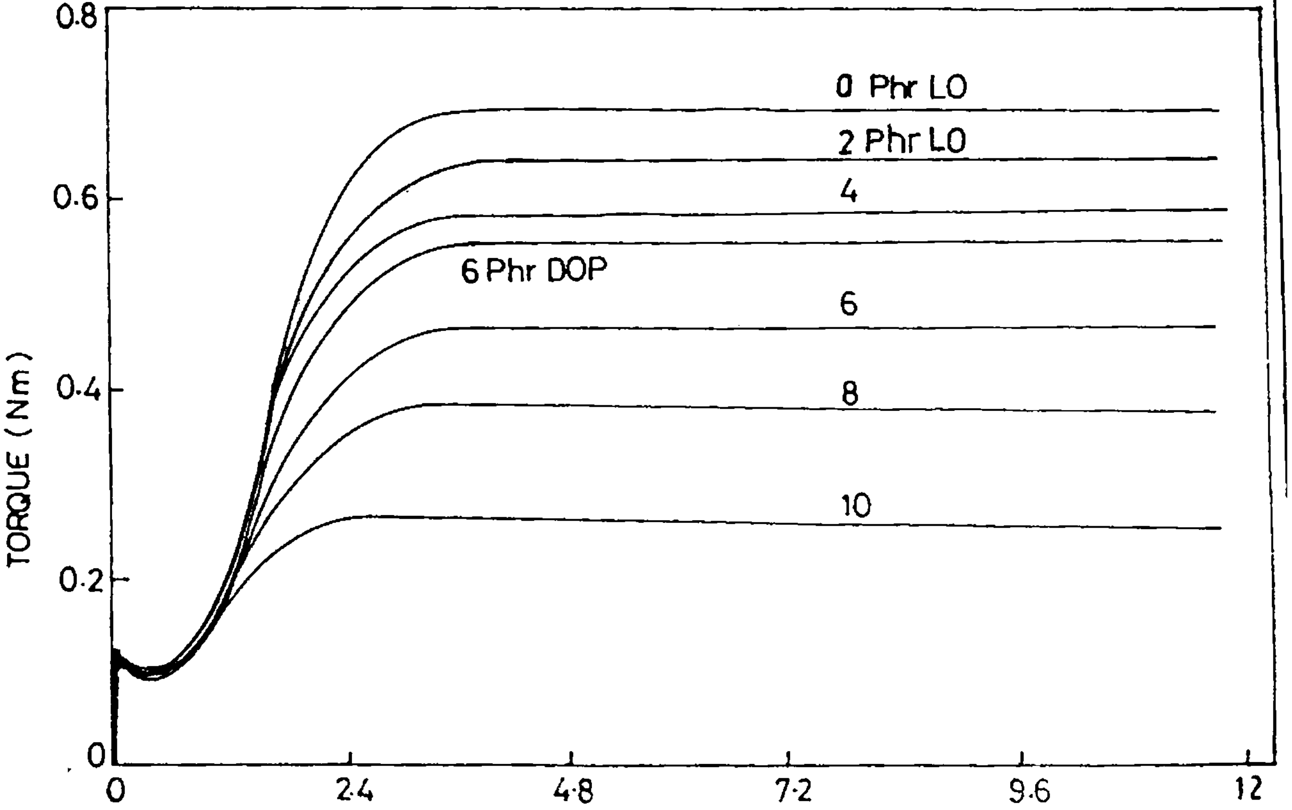


Fig.3.1.3 VARIATION OF TENSILE STRENGTH WITH DOP AND LINSEED OIL CONTENT

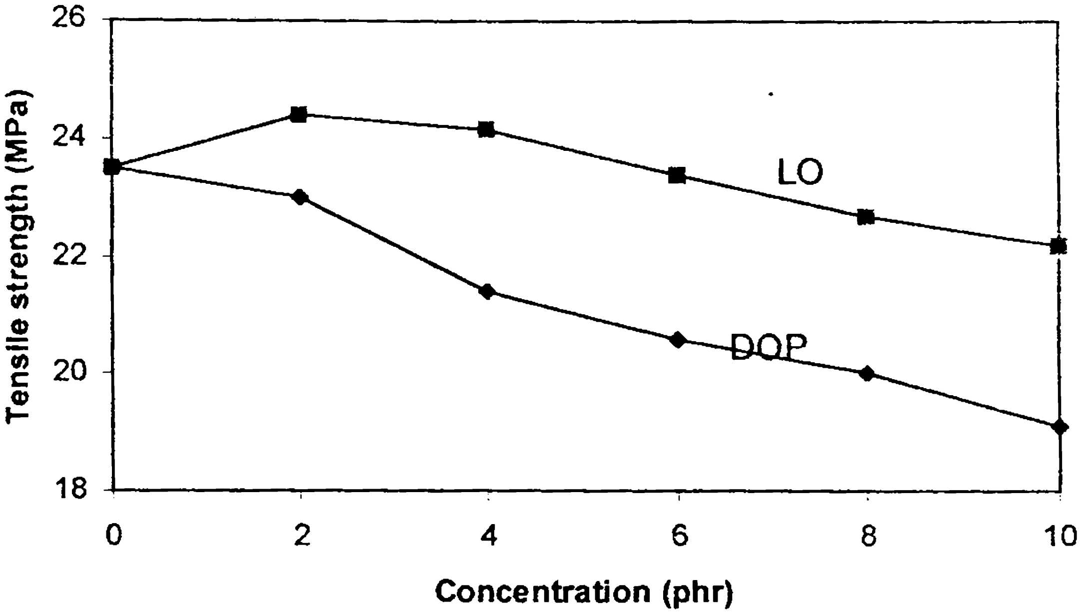


Fig.3.1.4 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT

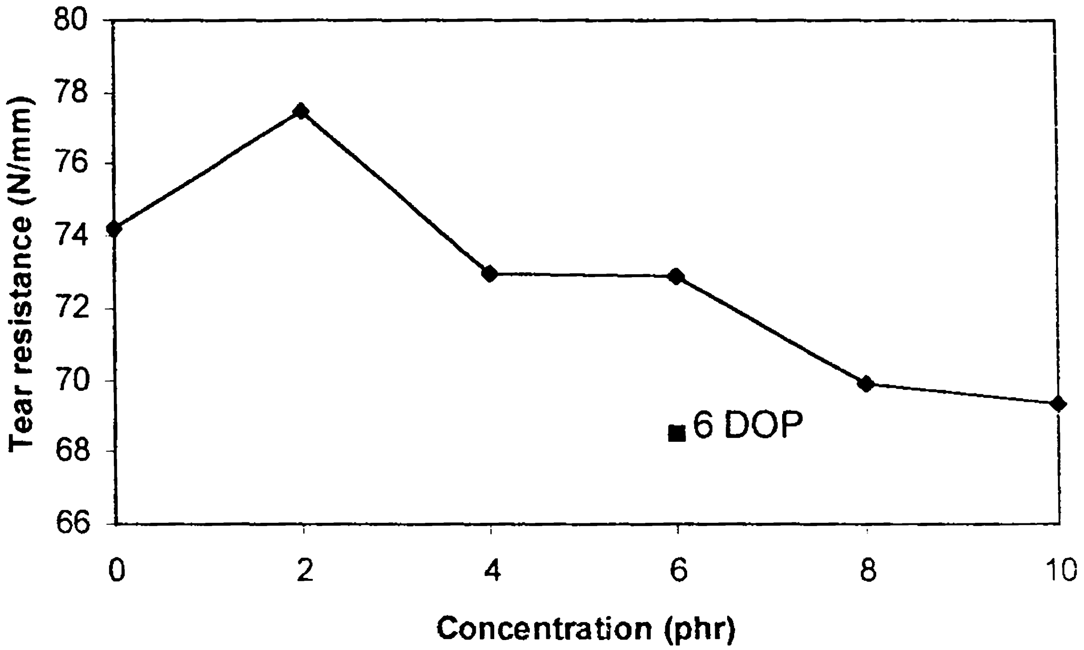
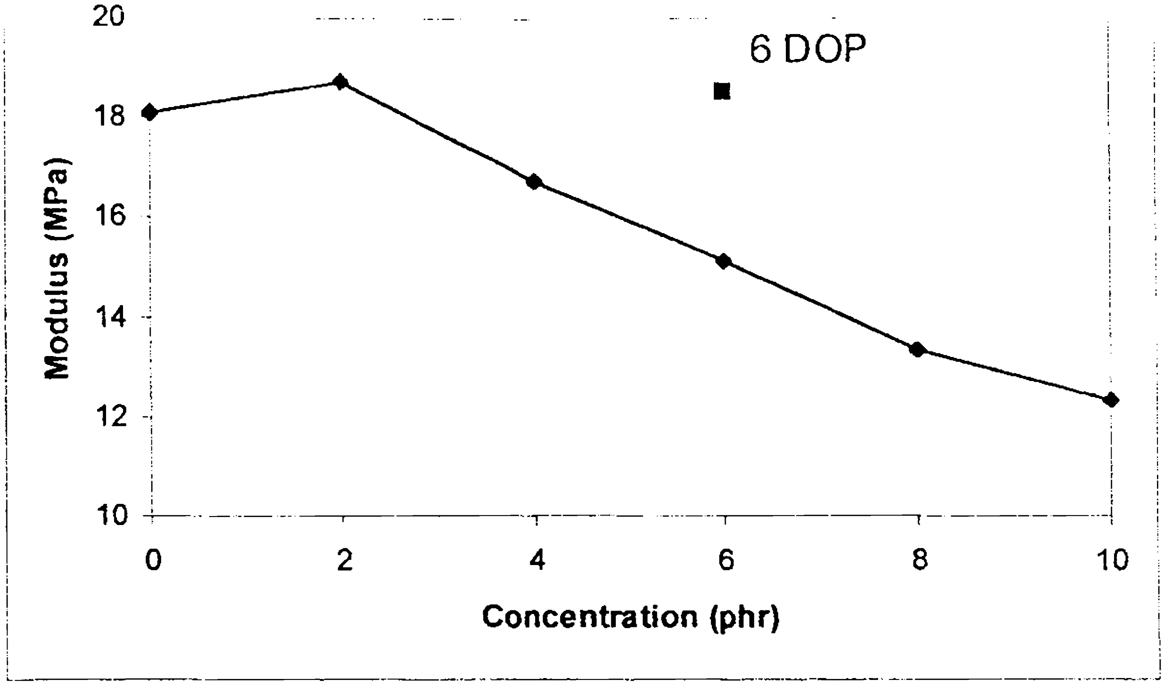


Fig.3.1.5 VARIATION OF MODULUS WITH OIL CONTENT



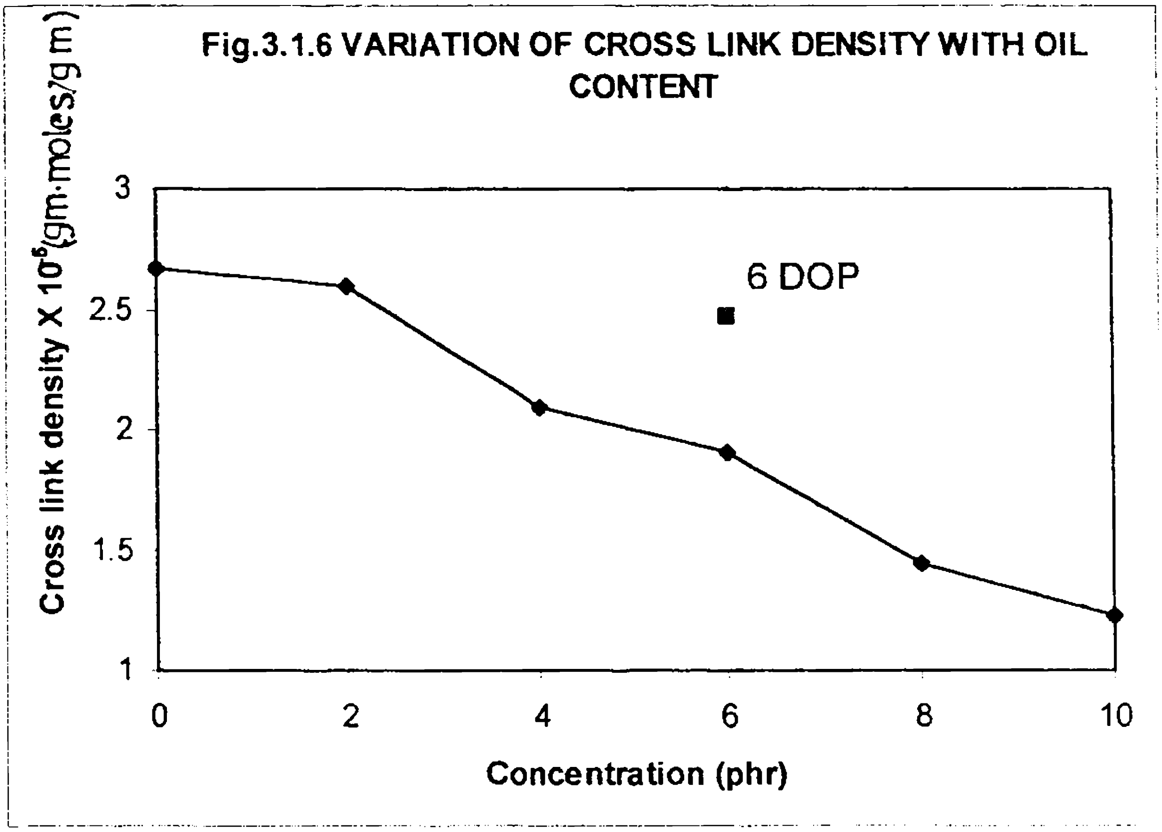


Fig.3.1.6 VARIATION OF CROSS LINK DENSITY WITH OIL CONTENT

Fig.3.1.7 VARIATION OF EB WITH OIL CONTENT

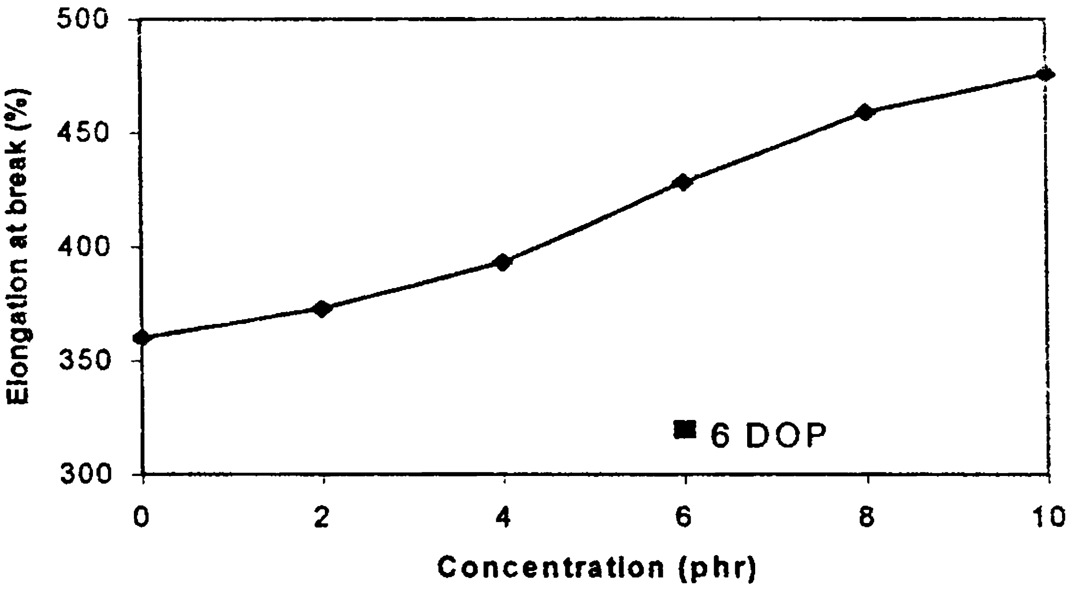


Table 3.1.1. Formulation

NBR	100 phr.
HAF	50 „
Zinc oxide	5 „
Stearic acid	2 „
MBTS	1 „
TMTD	0.2 „
Sulphur	1.5 „
Vulcanox HS	1.0 „
Vulcanox 40 20	0.5 „
DOP	6 phr

Table. 3.1.2 Cure characteristics and tensile strength of aged and unaged samples

Sample Composition	Scorch time {t_{10}) min	Cure time { t_{90} }min	Cure rate Nm/min	Tensile strength { M Pa }		
				Unaged	Air aged	Oil aged
6 DOP	1.4	2.84	0.3529	20.45	17.65	14.56
0 phr plasticizer	1.36	3.88	0.1759	23.50	17.78	17.80
2 phr linseed oil	1.28	2.80	0.3698	24.41	21.56	17.92
4 „	1.28	2.80	0.3744	24.15	20.44	16.32
6 „	1.32	2.40	0.3588	23.36	21.22	16.09
8 „	1.32	2.20	0.3076	22.68	20.70	16.94
10 „	1.28	2.00	0.2853	22.17	18. 29	15.04

Table 3.1.3 Leachability and compression set of vulcanizates

Sample Composition	Leachability (% loss in weight)	Compression set (%}
6 DOP	1.7	35.8
0 phr plasticizer	0.9	30.5
2 phr linseed oil	0.2	28.1
4 „	0.6	27.9
6 „	0.6	31.3
8 „	0.8	32.2
10 „	0.8	34.7

Table.3.1.4. Percentage of polysulphidic crosslink of vulcanizates.

Composition of vulcanizate	NBR	SBR	NR
0 phr plasticizer	58.1	41.2	73.1
6 phr DOP/Aromatic oil	38.4	22.3	65.3
6 phr LO	37.2	24.5	71.0
6 phr SBO	37.9	23.6	68.1
6 phr CO	39.8	26.2	70.2
6 phr RSO	39.1	24.7	62.5
6 phr PO	38.6	25.1	64.7

3.2. Soyabean oil as a multipurpose additive in NBR.

Soyabean oil is a semidrying edible oil. It is a pale yellow, low viscosity oil and is available in most part of the world . The fatty acid composition is 7 - 15% palmitic, 2 - 6 % stearic, 15 - 33% oleic, 43 - 45% linoleic and 5 - 11% linolenic (4). In addition to the triglycerides, the oil is found to contain small amounts of tocopherols, phosphatides, methionine, N-acetyl methionine, all having antioxidant nature. Other compounds with antioxidant nature, detected in soyabean oil are butylated hydroxy tolune(BHT) and butylated hydroxy anisole (BHA). According to Minshew (5), soyabean oil has many advantages, but also some disadvantages compared to other vegetable oils. The advantages include 1. High level of unsaturation present, 2.The oil remaining liquid over a relatively wide temperature range, 3. Can be hydrogenated selectively for blending with semi solid or liquid oils, 4.When partially hydrogenated it can be used as a pourable semisolid ,5. Phosphatides, traces of metals and soaps in soyabean oil can be removed with out much difficulty to obtain high quality products. The disadvantages are 1. Relatively large amount of phosphatides (2-3%) and high levels of linolenic acid. But all the above mentioned properties can be advantageous when the oil is used as an ingredient in elastomers. In the present study soyabean oil is used as a plasticizer and fatty acid component of the activator in nitrile rubber.

Experimental

NBR is compounded according to the formulation given in Table.3.1.1. Wherever soyabean oil is used it is used as a substitute for DOP and stearic acid. The properties of the compounds and vulcanizates with varying amounts of soyabean oil was compared with those of the control mix with DOP.

Results and Discussion

Fig 3.2.1 shows the flow behaviour of compounds with different loadings of soyabean oil, obtained from the Brabender plasticorder. The flow curve of the compound with 4 phr soyabean oil closely resembles that of the control mix with 6 phr DOP. This shows that soyabean oil is highly plasticizing in NBR giving a lower viscosity for the compounds, than DOP. Soyabean oil seems to be more plasticizing than linseed oil also. The compounds without plasticizer differ from other compounds in having very high viscosity.

Fig 3.2.2 shows the cure curves of the compounds. As in the case of their flow curves the curing behaviour of the compounds with 4 phr soyabean oil and that with 6 phr DOP are similar. The curing becomes progressively faster as the concentration of the oil increases (Table 3.2.1).Similar to the case of linseed oil this may also be due to the activation of rubber molecules by the plasticizer and also due to higher activity of unsaturated fatty acids compared to stearic acid.

Fig 3.2.3 shows the variation of tensile strength with soyabean oil and DOP concentrations.The behaviour of soyabean oil is similar to linseed oil discussed in the previous section. The oil shows a substantial increase in tensile strength up to a concentration of about 4 phr and then starts decreasing. But vulcanizates with soyabean oil always show a higher value for tensile strength than that with the same loading of DOP. This may be due the covulcanization of the oil with the elastomer and better filler incorporation. The gradual decrease in the value of tensile strength with increase in concentration of the oil above 4 phr level is due to the factice formation. This view is supported by the variation in crosslink density (Fig.3.2.4) The tensile strength of vulcanizates increases directly with crosslink density up to a certain maximum value beyond which it is independent of crosslink density.

The modulus (Fig.3.2.5) and tear resistance (Fig.3.2.7) are directly proportional to crosslink density and their variations are due to the variation in crosslink density. The elongation at break is as expected and is inversely proportional to the crosslink density (Fig. 3.2.6).

The ageing resistance and oil resistance are determined by measuring the retention in tensile strength after ageing the sample in air at 100^{0}C for 48 hrs and in oil at 70^{0}C for 72 hrs. respectively. Table 3.2.1 gives the tensile strength of aged and unaged samples. Though an improvement is shown for oil resistance, not much variation is seen in air resistance. The vulcanizate without plasticizer is seen to be less resistant to air oxidation. The compression set of vulcanizates with soyabean oil and that without plasticizer are lower compared to that of the control mix. (Table, 3.2.2). The variation is also as expected and is inversely proportional to the cross link density.

Leachability is highly reduced for vulcanizates with soybean oil. Table 3.2.2 gives the percentage loss in weight of vulcanizates with different loading of oil. The zero leachability up to 4 phr level shows that this is the optimum level of soyabean oil which gives the best incorporation of ingredients in to the rubber matrix. The vulcanizate without plasticizer also have a lower leachability. These variations are similar to that with linseed oil and can be explained on a similar line.Vulcanizates were also tested for blooming and showed very little blooming compared to the control mix.

Conclusion

Use of soyabean oil, in nitrile rubber gives better processability to the compounds, along with reduced cure time. For oil, which is compatible with the rubber, cure time is seen to be inversely proportional to the oil loading. Soybean oil gives appreciable increase in tensile strength modulus and tear resistance along with decreased compression set, leachability and blooming. 4 phr soybean oil is the preferred concentration which can substitute 6 phr DOP and 2 phr staeric acid in nitrile rubber vulcanizate for any use.

FIG 3.2.1 FLOW CURVE

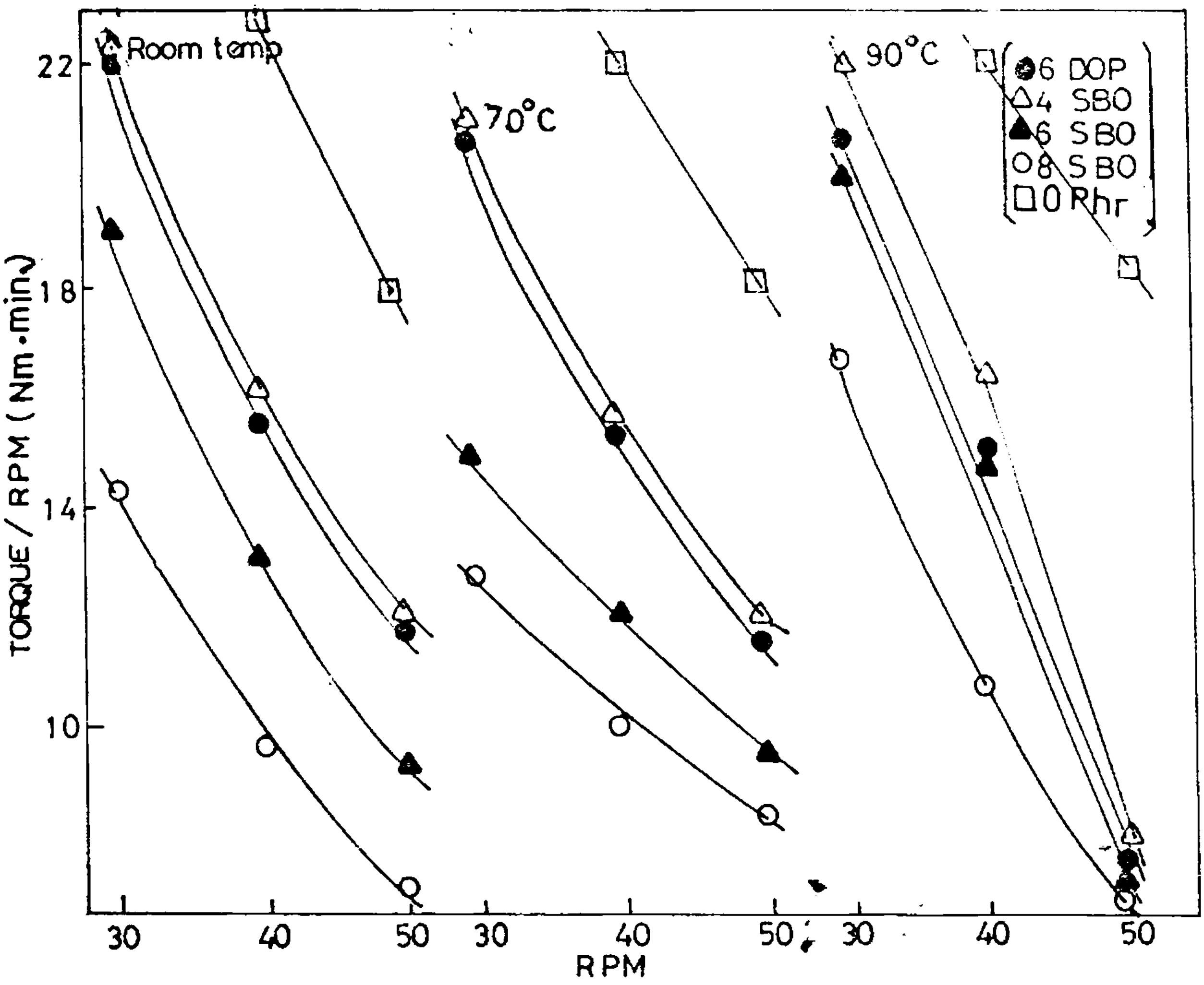


FIG 3.2.2 CURE CURVE

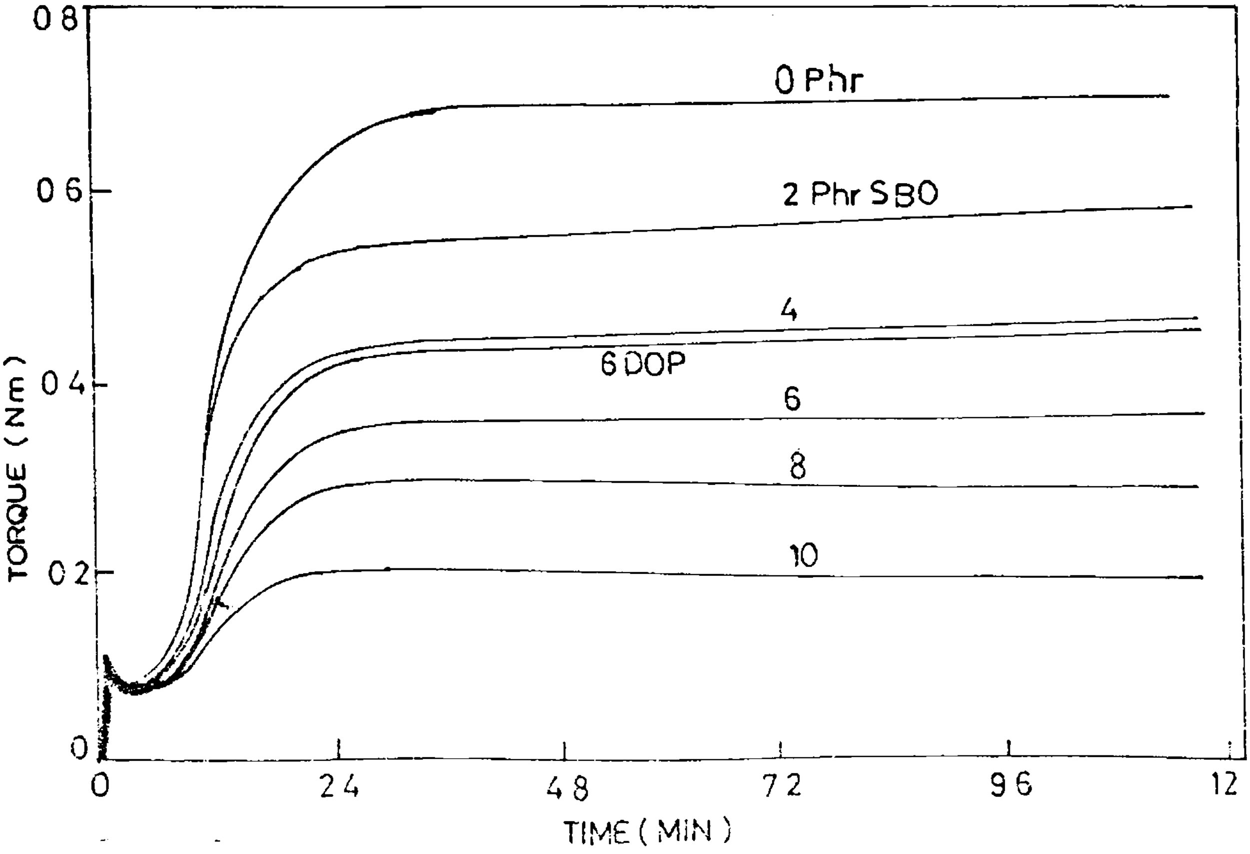


FIG. 3.2.3 VARIATION OF TENSILE STRENGTH WITH DOP AND SOYABEAN OIL CONTENT

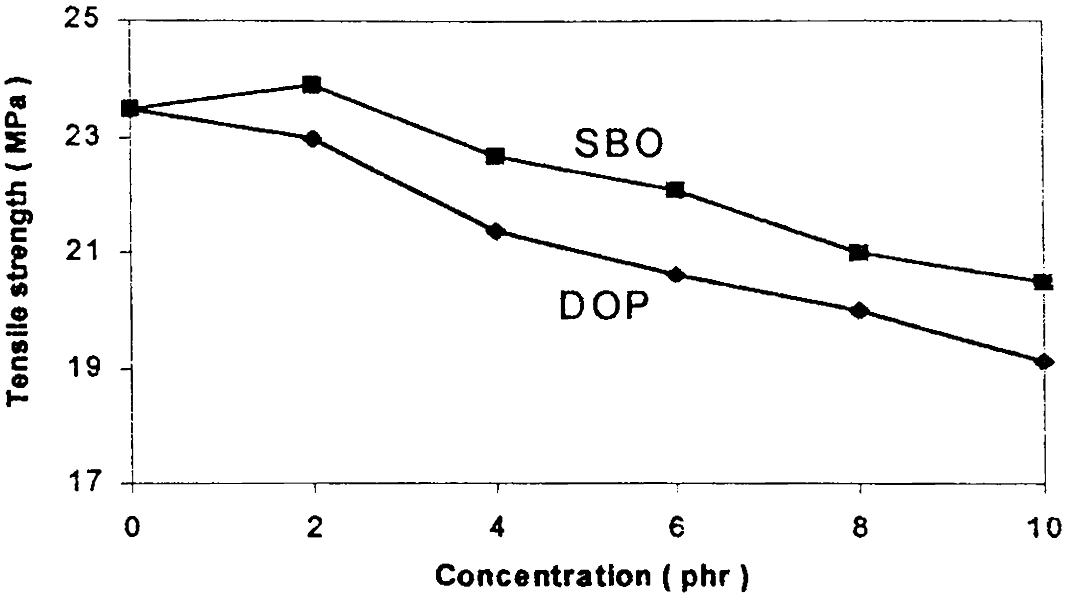


FIG.3.2.4 VARIATION OF CROSSLINK DENSITY WITH OIL CONTENT

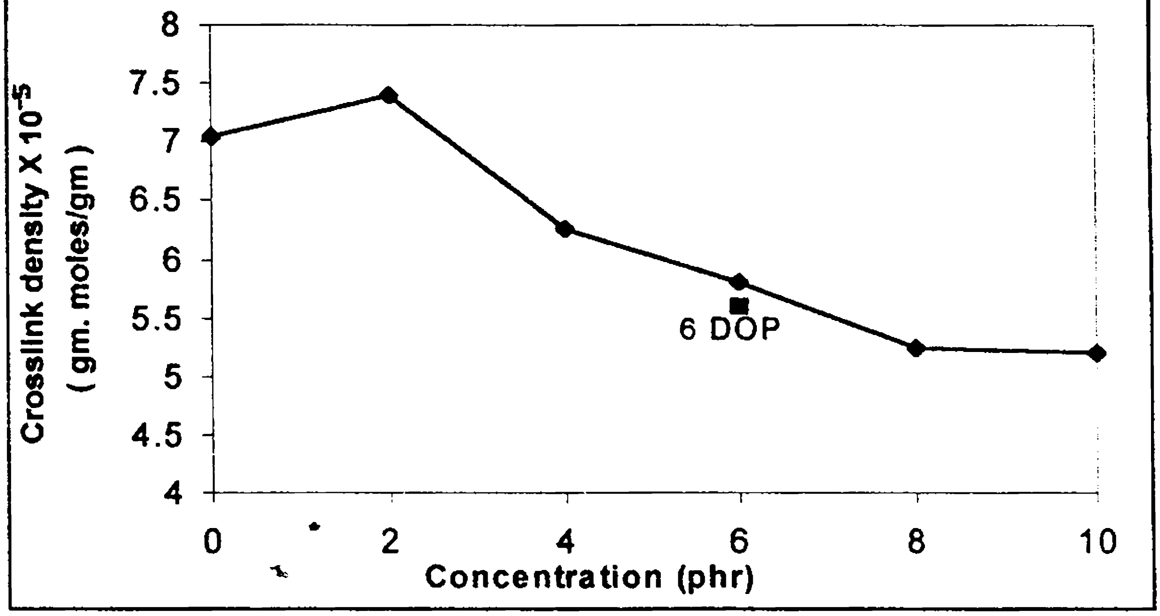


Fig.3.2.5 VARIATION OF MODULUS WITH OIL CONTENT

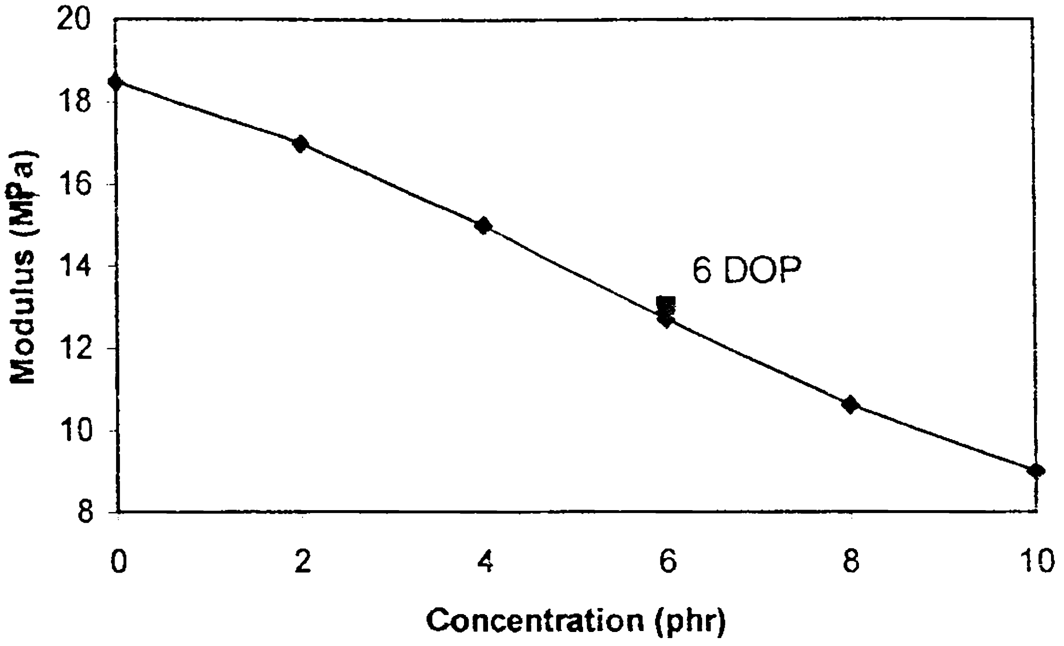
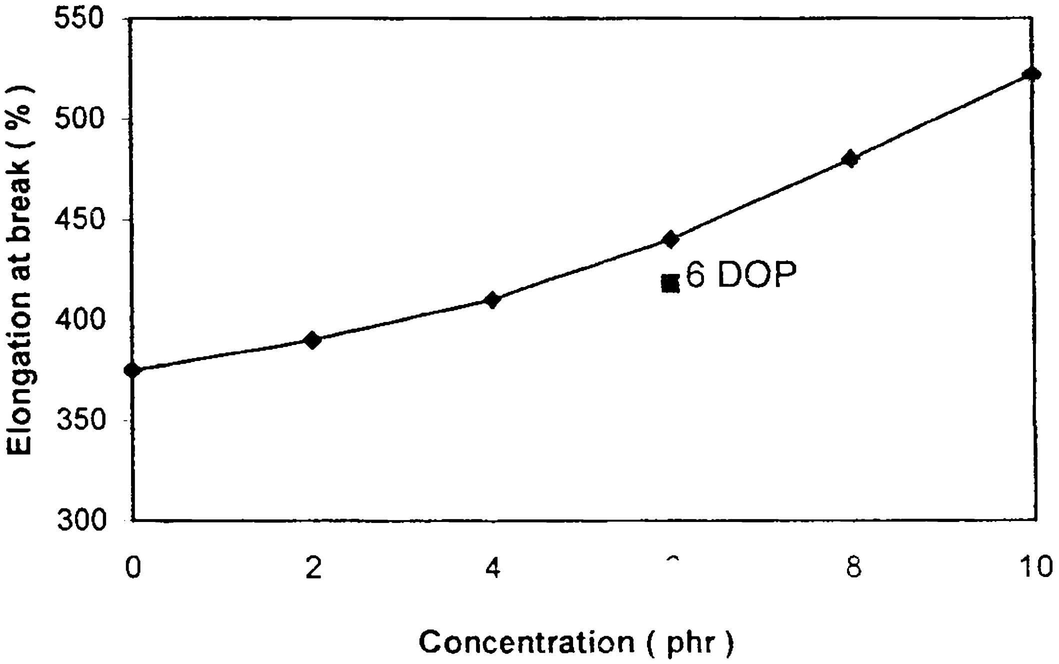


Fig. 3.2.6 VARTIATION OF EB WITH OIL CONTENT



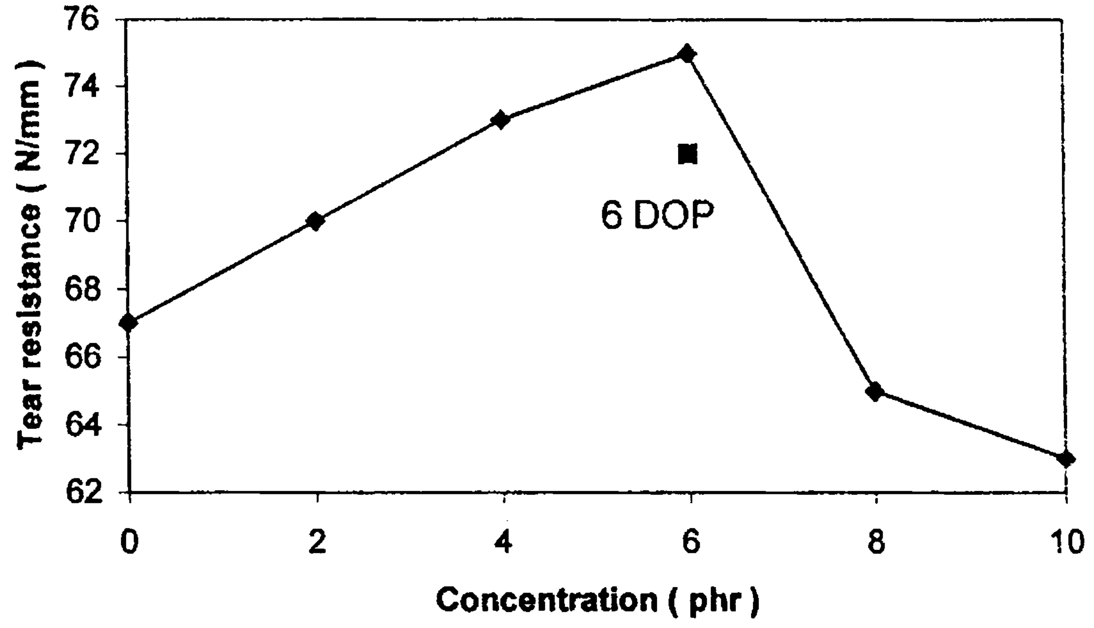


Fig. 3.2.7 VARIATION TEAR RESISTANCE WITH OIL CONTENT

Table 3.2.1 Cure characteristics of the compounds and ageing resistance of vulcanizates

Sample Composition	Scorch time (t_{10})min.	Cure time (t_{90}) min.	Cure rate Nm/min.	Tensile strength (M Pa)		
				Fresh	Air aged	Oil aged
6 DOP	1.4	2.84	0.3203	20.45	17.65	14.56
0 phr plasticizer	1.36	3.88	0.1757	23.5	17.78	17.8
2 phr soyabean oil	1.36	3.04	0.3569	23.96	19.27	19.71
4 „	1.4	2.84	0.3356	22.97	19.00	19.69
6 „	1.4	2.69	0.3237	22.18	17.98	18.27
8 „	1.4	2.36	0.2421	21.15	17.48	17.2
10 „	1.4	2.32	0.2064	20.8	16.36	16.78

Table. 3.2.2 Leachability and compression set of vulcanizates

Sample composition	Leachability (Percentage loss in wt)	Compression set (%)
6DOP	1.7	35.8
0 phr plasticizer	0.9	30.5
2 phr soyabean oil	0.0	27.8
4 „	0.0	27.9
6 „	0.2	34.2
8 „	0.4	36.0
10 „	0.4	38.0

3.3. Castor oil as a multipurposadditive in NBR

Castor oil is a colourless oil with a comparatively higher viscosity. A major portion of fatty acid present is recinoleic acid (12- hydroxy octadeca 9-enoic acid), which causes the higher value for the viscosity of the oil. The fatty acid composition is palmitic 2%, stearic 2% oleic 5%, linoleic 7%, linolenic 2% and ricinoleic 82%. The oil is used as a multipurpose additive in nitrile rubber. NBR is compounded as per formulations given in table 3.1.1. Wherever castor oil is used it is used as a substitute for DOP and stearic acid. The properties of the compounds and vulcanizates were compared with that of the control mix.

Results and discussion

Fig. 3.3.1 compares the flow behavior of compounds with different loadings of castor oil, with that of the controll mix. Compounds with castor oil are having a higher viscosity compared to DOP. The poor plasticizing effect of castor oil in NBR is due to the presence of a considerable amount of ricinoleic acid (12-hydroxy octa-deca 9-enoic acid) present in the oil. Generally oil molecules occupies the space between the adjacent rubber chains and acts as a lubricant reducing the viscosity of the compound. But the hydroxyl group in ricinoleic acid form hydrogen bond with the CN groups of adjacent rubber molecules and reduces the mobility of the molecules causing a higher viscosity for the compound. The compound without plasticizer shows a higher viscosity than that with castor oil and DOP.

The cure curves of this compound (Fig.3.3.2) shows that 10 phr castor oil is necessary for the compound to show a cure behavior similar to the compound with 6 phr DOP. It is to be noted that, while linseed oil and soybeans showed a decrease in cure time with increased oil concentration, castor oil behaved in a different manner. This shows that ricinoleic acid is poor as an activator and the decreased cure rate is due to the higher activation energy required as there is strong interaction between the plasticizer and the elastomer through hydrogen bonding (Table 3.3.1). The compound without plasticizer shows the highest torque and the lowest cure rate.

Fig. 3.3.3 shows the variation of tensile strength with DOP and castor oil concentrations. Though tensile strength linearly decreases with DOP concentration castor oil shows a substantial difference. As in the case of linseed and soybean oil the tensile strength of vulcanizates with castor oil show an increase up to 4 phr level and then starts decreasing. But the decrease in tensile strength with increase in castor oil content seems to be nominal. This may be due to the poor plasticizing ability of castor oil. It may be noted that tensile strength of vulcanizate with 10 phr castor oil is considerably higher than that with 6 phr, or even an equal loading of DOP. It may also be noted that the tensile strength of vulcanizates with castor oil is higher than that with the same loading of linseed oil or soyabean oil. This may be due to the plasticizer-elastomer hydrogen bond which adds to the strength due to crosslinking. The variation of cross link density with oil loading (Fig 3.3.4) supports the variation in tensile strength.

Fig.3.3.5 shows the variation of modulus with oil concentration. Modulus is seen to vary directly with crosslink density, whereas elongation at break is inversely proportional to the crosslink density as expected (Fig 3.3.6). The variation of tear resistance is similar to tensile strength and can be explained in a similar way (Fig 3.3.7). Unlike linseed oil and soybean oil, castor oil imparts better air ageing resistance and oil ageing resistance to the vulcanizates. The vulcanizates with different loadings of oil were aged in air at 100^0 C for 48 hours and in engine oil at 70^0 C for 72 hours. The retention in tensile properties of the aged samples were compared with that of the control mix. (Table 3.3.1). The higher ageing resistance of vulcanizates with castor oil may also be due to the presence of ricinoleic acid which is susceptible to easy oxidation. The vulcanizate without plasticizer shows poor ageing resistance compared to that with castor oil or DOP.

Compression set is seen to be inversely proportional to the cross link density. Compounds with below 4 phr level of oil shows lower compression set and the set gradually increases with oil concentrations (Table 3.3.2). This gradual increase in set may be due to the gradual decrease in crosslink density. Leachability reduced to a considerable extent by incorporating castor oil, for DOP. The percentage loses in weight of the vulcanizates with different loadings of castor oil is compared with those of the control mix (Table 3.3.2). The sample containing 6 phr castor oil has only less than 30% of the leachability of the control mix.. Sulphur blooming is also considerably reduced by the use of castor oil in place of DOP. This reduced leachability and blooming can be explained on a similar way to oils discussed earlier. But vulcanizates with higher loading of castor oil, generally shows sweating.

Conclusion

Use of castor oil gives appreciable increase in tensile strength, tear resistance etc in nitrile rubber vulcanizates, along with improved ageing resistance, and reduced leachability. The viscosity of the compounds with castor oil is higher than that with DOP, and the cure rate is slightly lower. A 5-6 phr castor is an optimum concentration which can give appreciable increase in vulcanizate properties if lower processability can be ignored. Further the cost of the compound can also be reduced.

FIG.3.3.1 FLOW CURVE

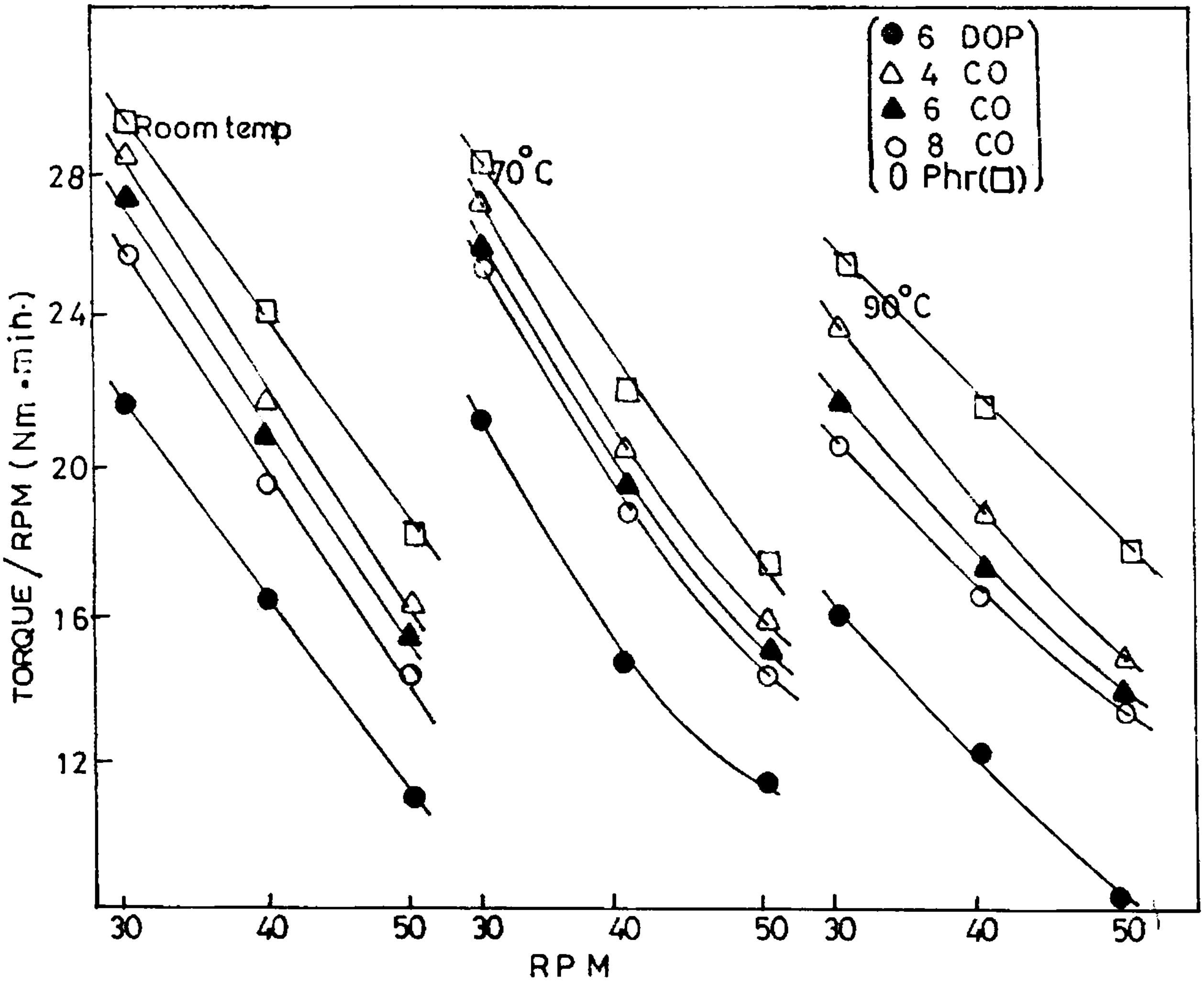


FIG 3.3.2 CURE CURVE

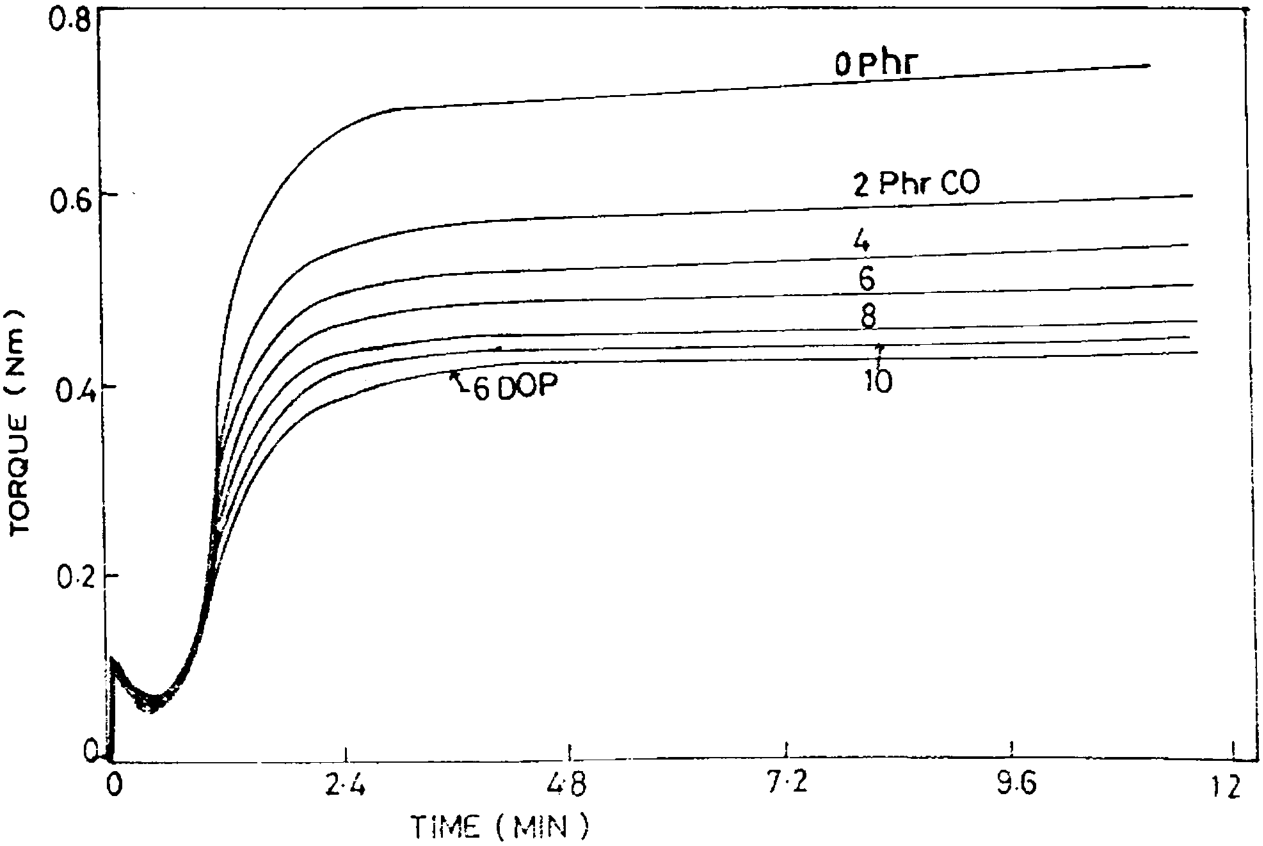


Fig.3.3.3 VARIATION OF TENSILE STRENGTH WITH CASTOR OIL CONTENT

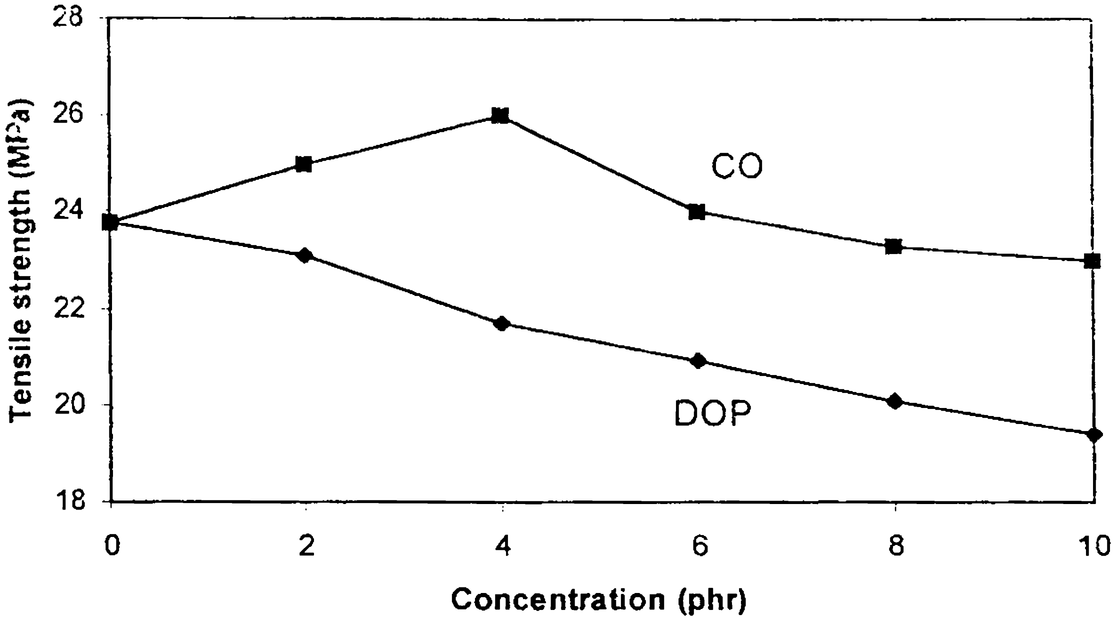


Fig.3.3.4 VARIATION OF CROSSLINK DENSITY WITH OIL CONTENT

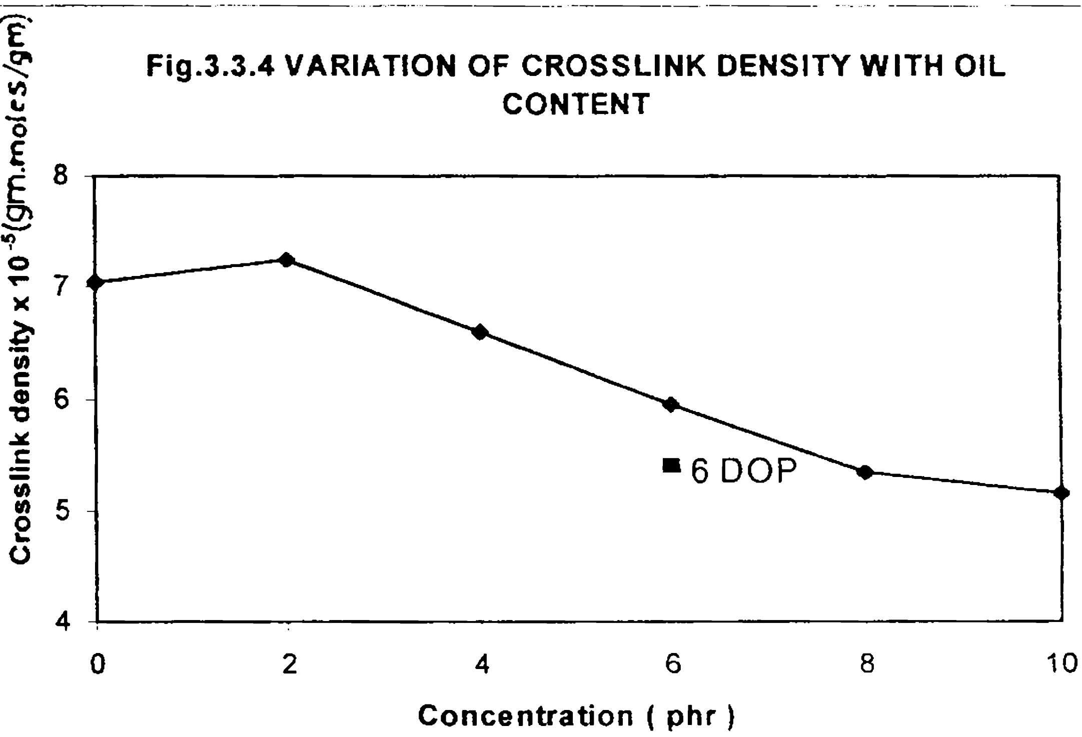


Fig.3.3.5 VARIATION OF MODULUS WITH OIL CONTENT

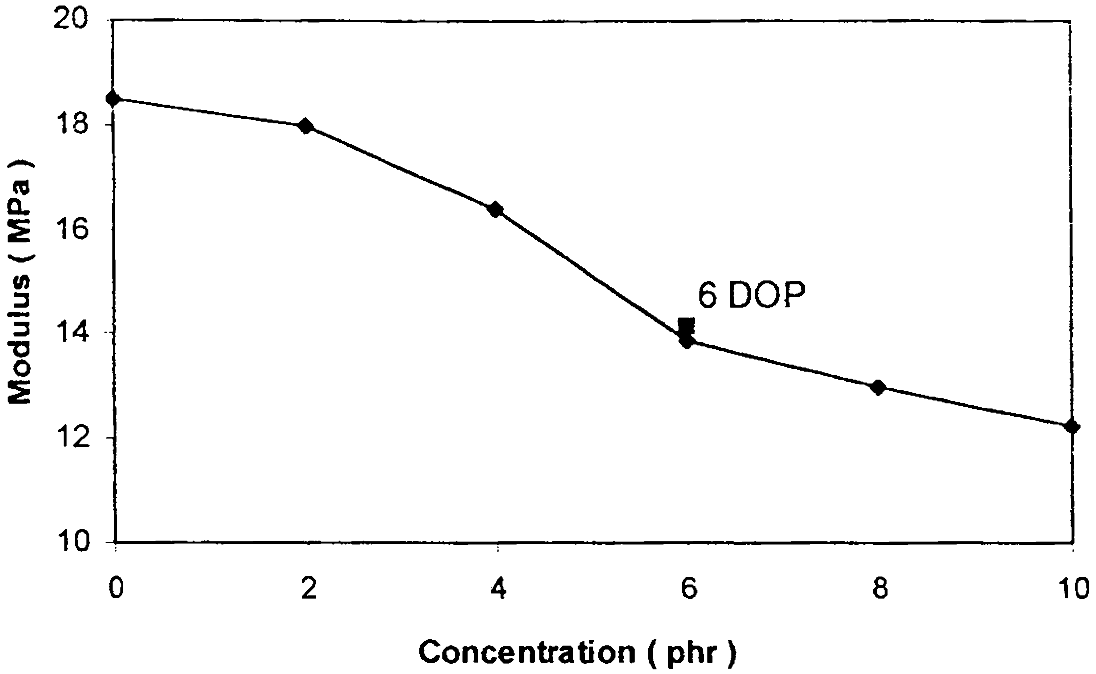
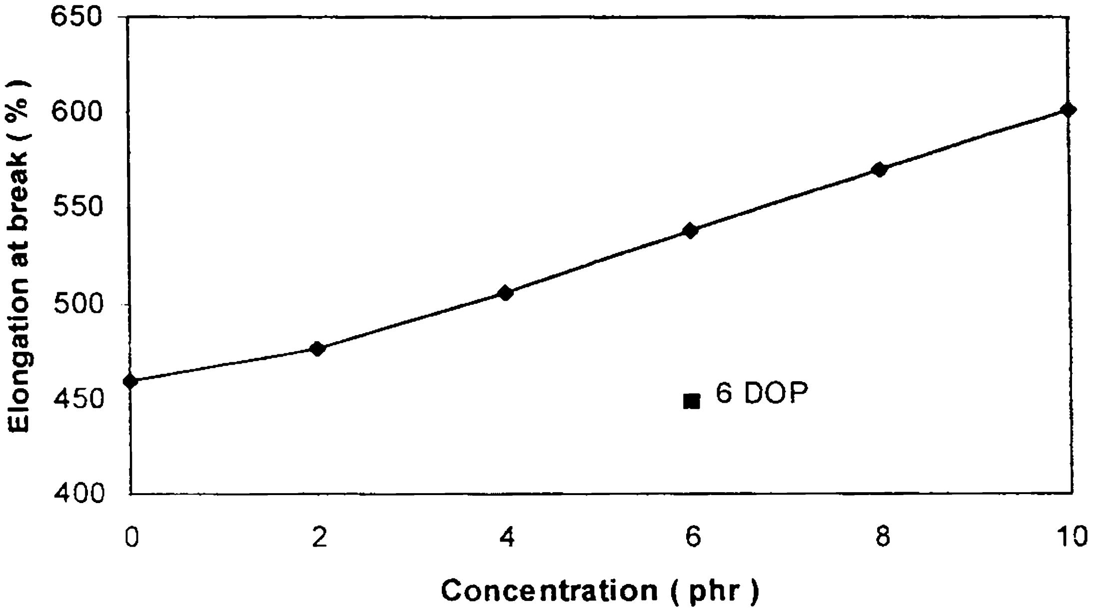


Fig.3.3.6 VARIATION OF EB WITH OIL CONTENT



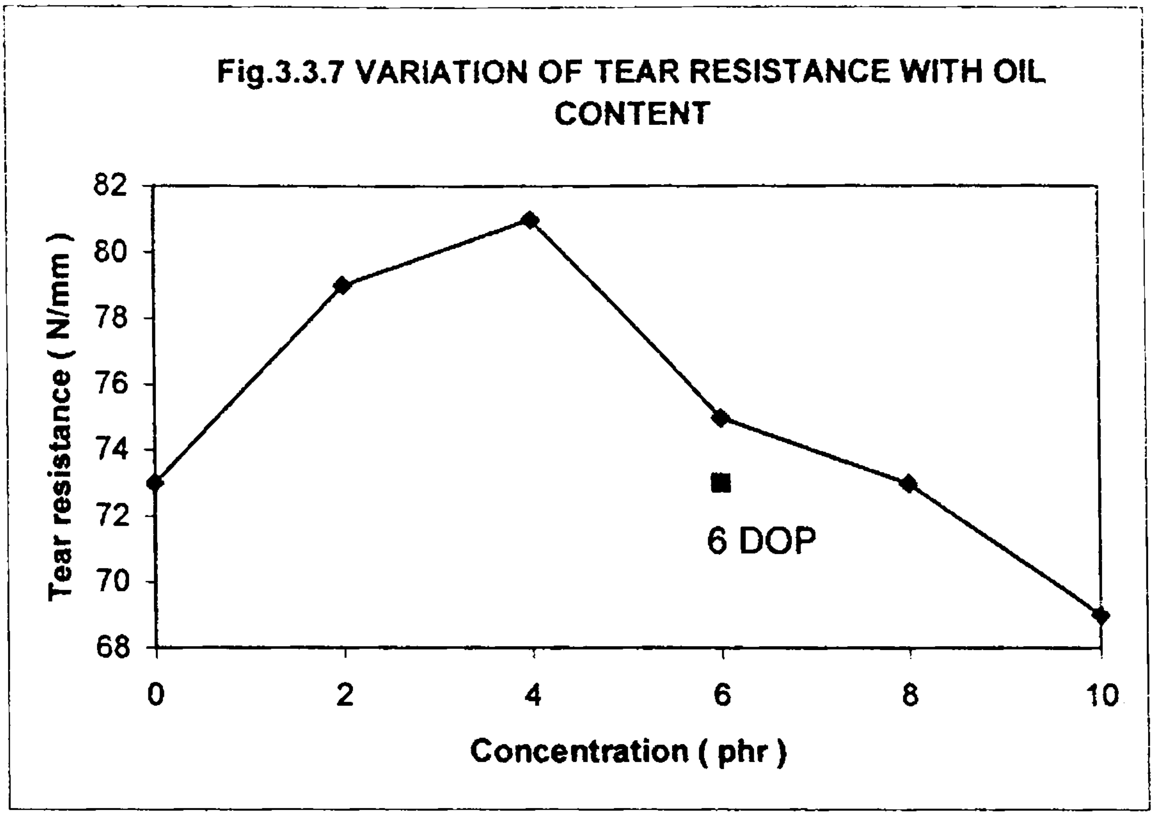


Fig.3.3.7 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT

Table 3.3.1 Cure chracteristics and tensile strength of aged and unaged samples

Sample composition	Scorch time (t_{10})	Cure time (t_{90})	Cure rate Nm/min.	Tensile strength (M.Pa)		
				Fresh	Air aged	Oil aged
6 DOP	1.42	2.84	0.2894	20.9	17.65	14.56
0 phr plasticizer	1.36	3.88	0.1757	23.5	17.78	17.8
2 phr castor oil	1.32	3.0	0.3793	26.3	21.97	24.15
4 „	1.4	3.16	0.3137	26.18	21.48	23.09
6 „	1.36	3.24	0.2810	24.87	21.25	23.22
8 „	1.4	3.36	0.2672	24.30	21.00	23.90
10 „	1.4	3.36	0.2371	23.14	20.65	23.00

Table. 3.3.2 Leachability and compression set of vulcanizates

Sample composition	Leachability (% loss in weight)	Compression set (%)
6 DOP	1.685	35.75
0 phr plasticizer	0.92	30.5
2 phr castor oil	0.0	34.0
4 „	0.0	37.6
6 „	0.46	43.2
8 „	0.73	40.0
10 „	1.2	42.44

3.4. Rubber seed oil as a multipurpose additive in NBR.

Rubber seed oil is semidrying non edible oil obtained from the seeds of rubber tree (Haevea Braziliensis). The fatty acid composition is palmitic 8%, stearic 10%, oleic 20%, linoleic 38%, and linolenic 21%. Out of this about 15% is present as hexabromide derivative. Crude rubber seed oil has a high content of nonsaponifiable matter which are slightly hypercholesteronic and slightly toxic (6). The oil is also found to contain small amount of different types of tocopherols.In the present study rubber seed oil is used as a multipurpose additive in nitrile rubber. NBR is compounded as per formulation given in table 3.1.1. Wherever rubber seed oil is used it is used as a substitute for DOP and stearic acid The processibility, cure characteristics and vulcanizate properties were compared with those of the control mix.

Results and discussion

Fig. 3.4.1 shows the flow behavior of compounds without plasticizer, with rubber seed oil and DOP, obtained from the Brabender plasticorder.The flow behavior of compounds with 6 phr rubber seed oil and that with 6 phr DOP are seen to be very close showing a comparable plasticizing action by the oil with that of DOP. The cure characteristics of these compounds are also similar as can be seen on the cure curves (Fig. 3.4.2) .But rubber seed oil increases the cure rate and as the concentration of the oil increases, there is a gradual decrease in cure time (Table 3.4.1). This behaviour is similar to that shown by linseed and soyabean oil and is explained on a similar line. The compound without plasticizer shows a higher viscosity, higher torque and cure time, showing the difficulty in processing.

Fig. 3.4.3 shows the variation of tensile strength of the vulcanizates with varying amounts of rubber seed oil and DOP. The behavior of rubber seed oil seems to be similar to that of the oils already discussed and can be explained similarly. The variation of modulus (Fig .3.4.4.),crosslink density (Fig. 3.4.5) tear resistance (Fig. 3.4.6) and elongation at break (Fig. 3.4.7) are also similar to these oils.

The ageing resistance in air and oil show marginal improvement especially at higher concentrations of the oil (Table . 3.4.1). This is due to the increase in amount of natural anti oxidants present in the oil along with the increase in oil content. Leachability of the vulcanizate shows tremendous decrease, when DOP is substituted with rubber seed oil. Table 3.4.2. shows the percentage loss in mass of vulcanizates with different loadings of oil. The vulcanizates with 6 phr rubber seed oil has only 10% or even less loss in weight compared to that with 6 phr DOP. This lower leachability is explained on similar way to oils discussed earlier.The compression set of vulcanizates with rubber seed oil increases linearly with increase in oil content (Table 3.4.2). This increase in set may be due to the decrease in crosslink density with increase in oil content. Even at low concentrations of the oil set value is equal or even higher than that of the control mix. The vulcanizate without plasticizer shows a lower compression set and leachability than the controll mix with DOP, but slightly higher leachability ,compared to that with rubber seed oil.

Conclusion

Rubber seed oil is a good additive for nitrile rubber. It gives a comparable processability and cure characteristics with DOP. The properties like tensile strength, modulus , tear resistance etc. are increased, along with improvement in ageing resiatance. Leachability and blooming are also reduced, though there is a disadvantage with compression set. A 4 - 6 phr rubber seed oil seems to be the optimum concentration which can substitute 6 phr DOP and 2 phr stearic acid in nitrile rubber vulcanizates.

FIG 3.4.1 FLOW CURVE

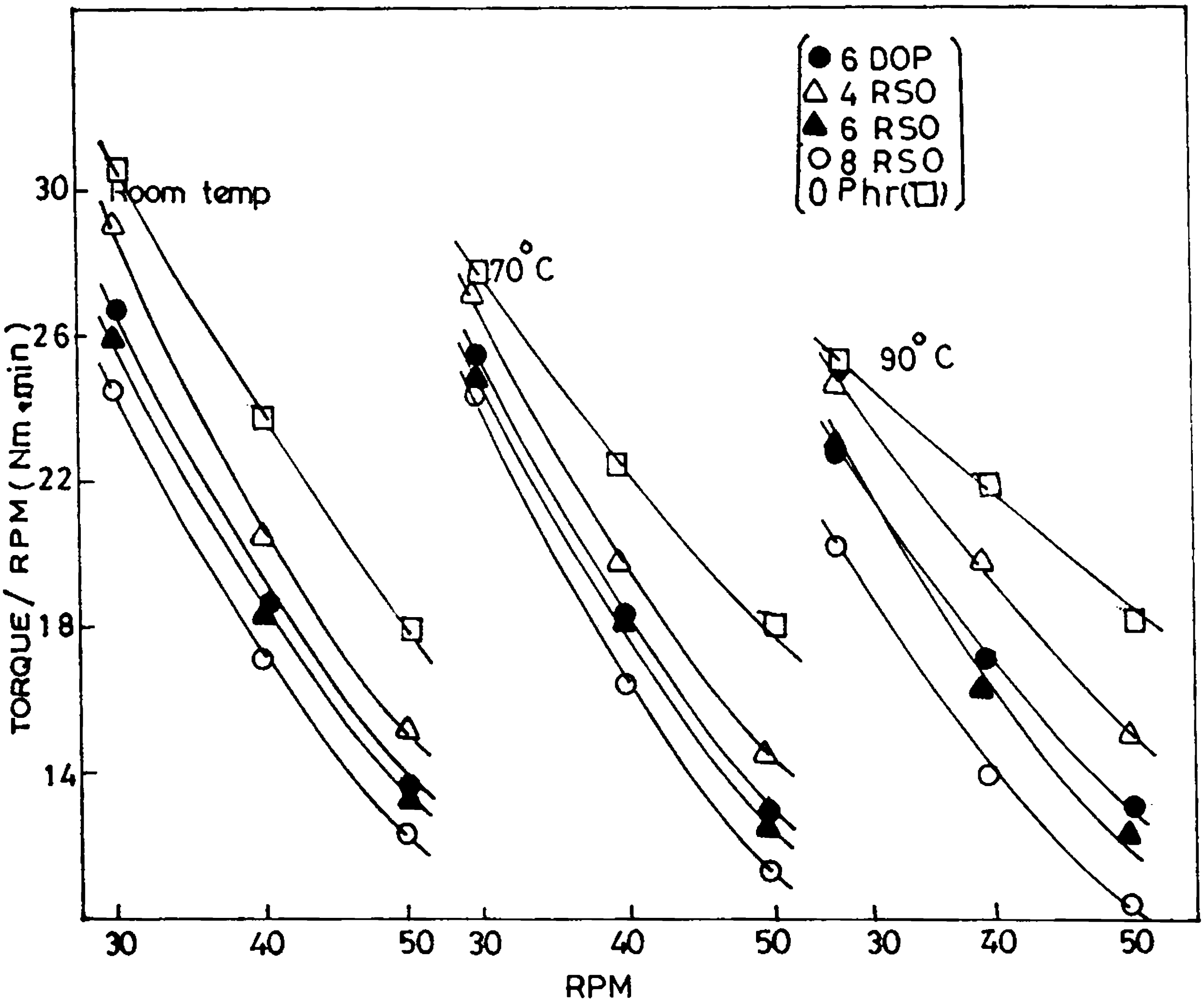


FIG 3.4.2 CURE CURVE

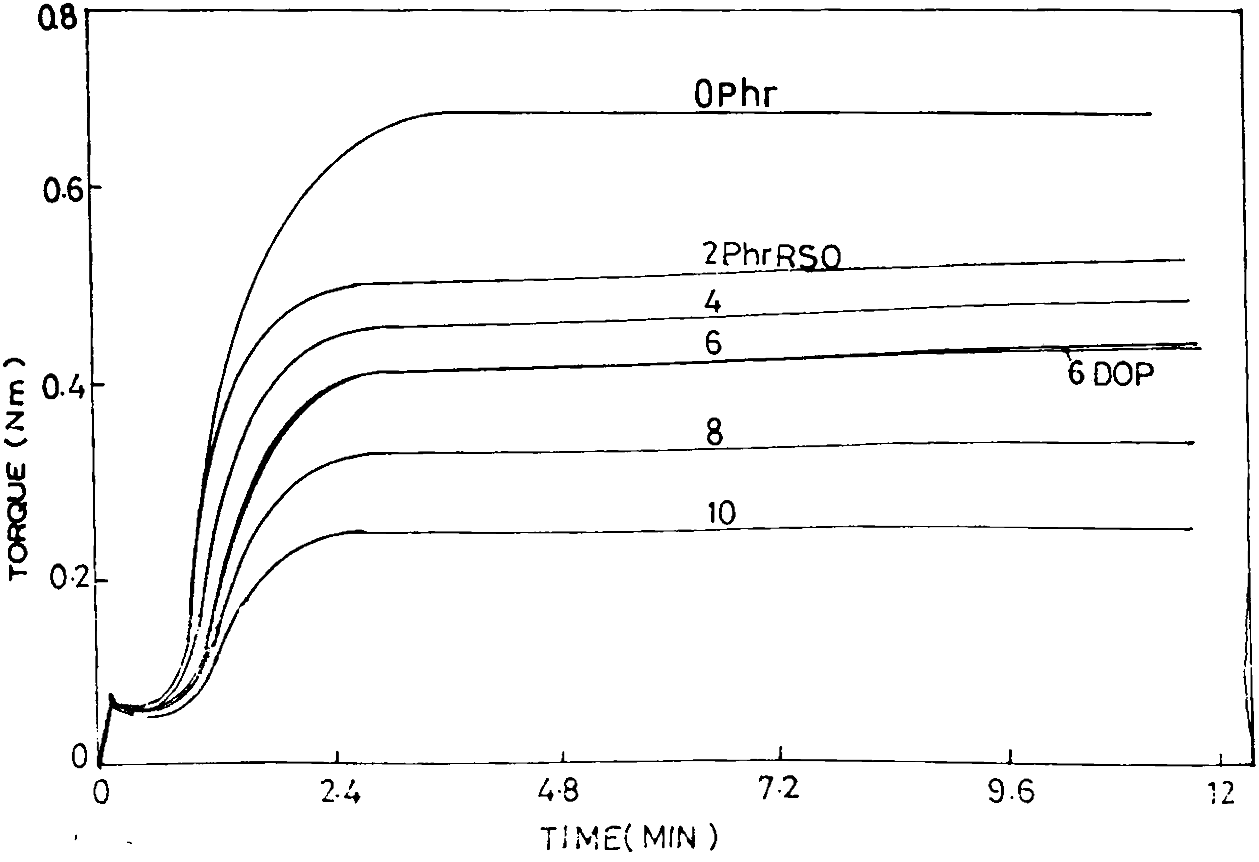


Fig.3.4.3 VARIATION OF TENSILE STRENGTH WITH DOP AND RUBBER SEED OIL

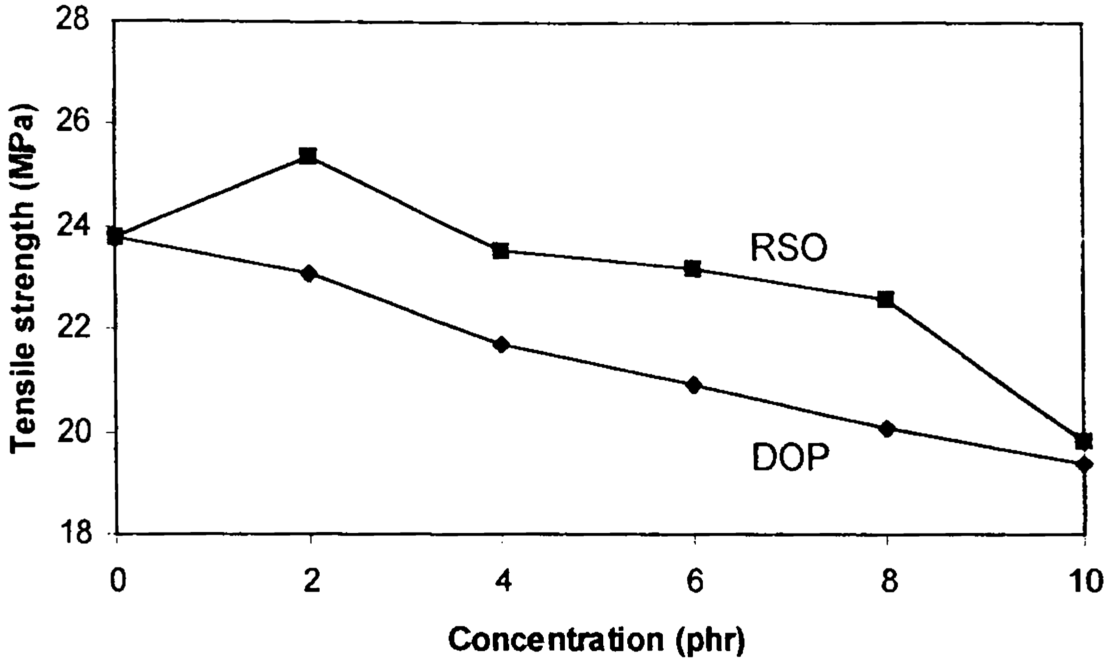


Fig.3.4.4 VARIATION OF MODULUS WITH OIL CONTENT

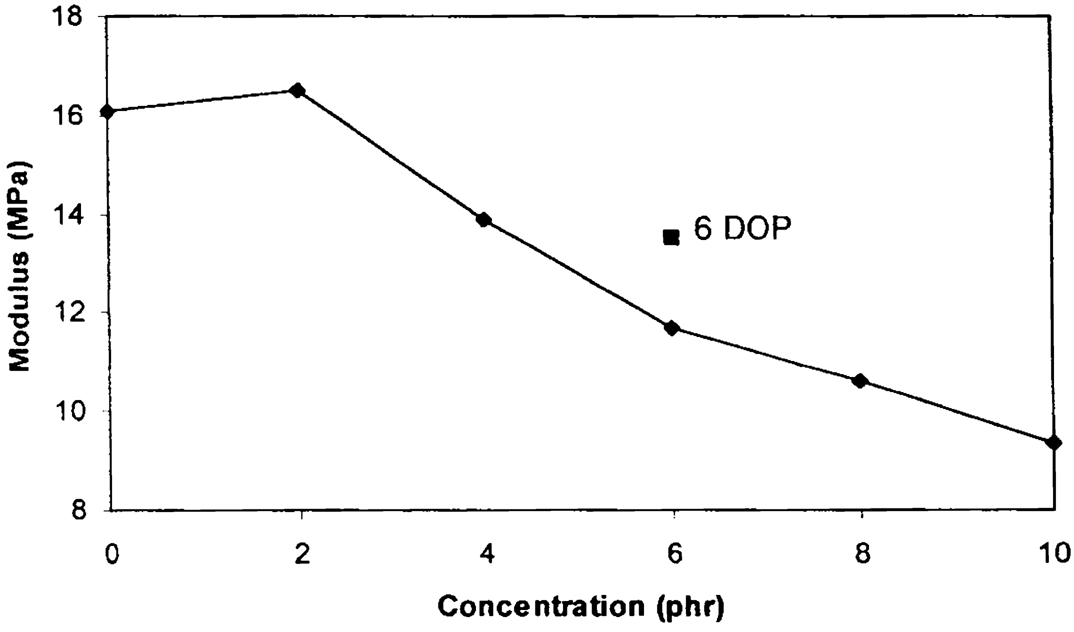


Fig.3.4.5 VARIATION OF CROSS LINK DENSITY WITH OIL CONTENT

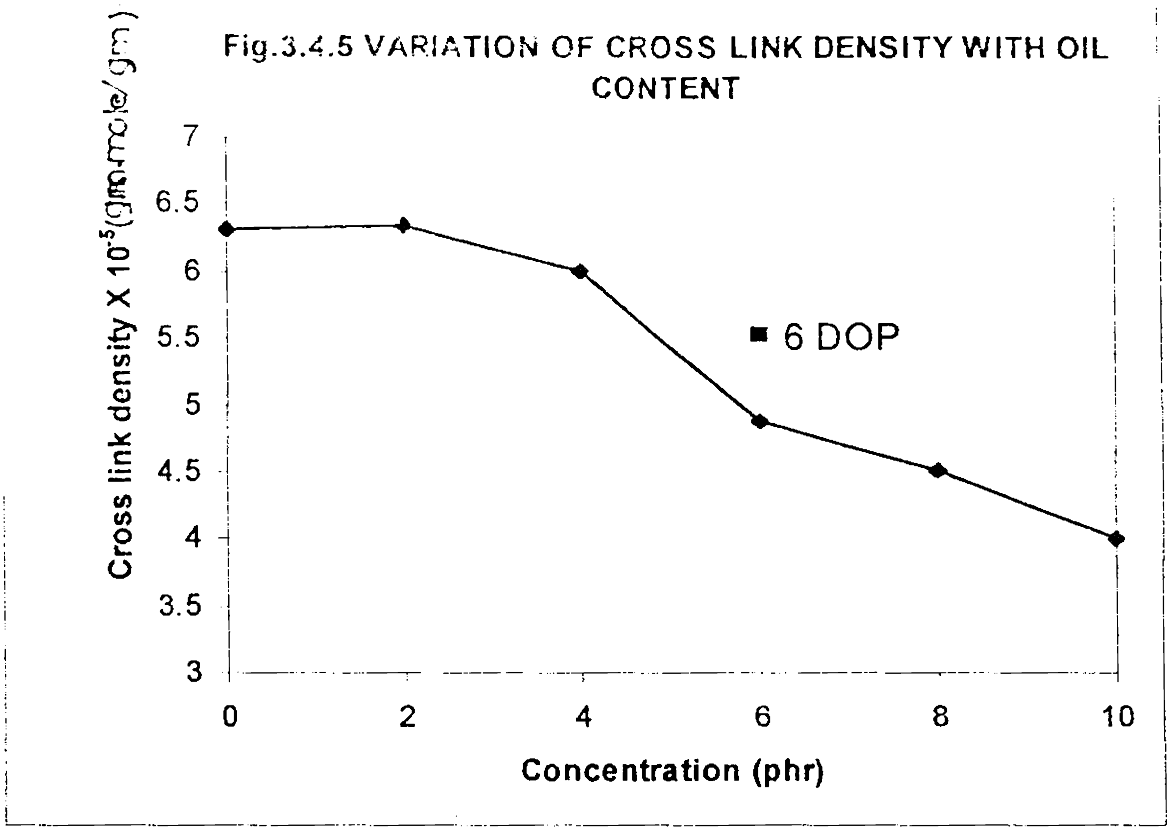


Fig3.4.6 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT

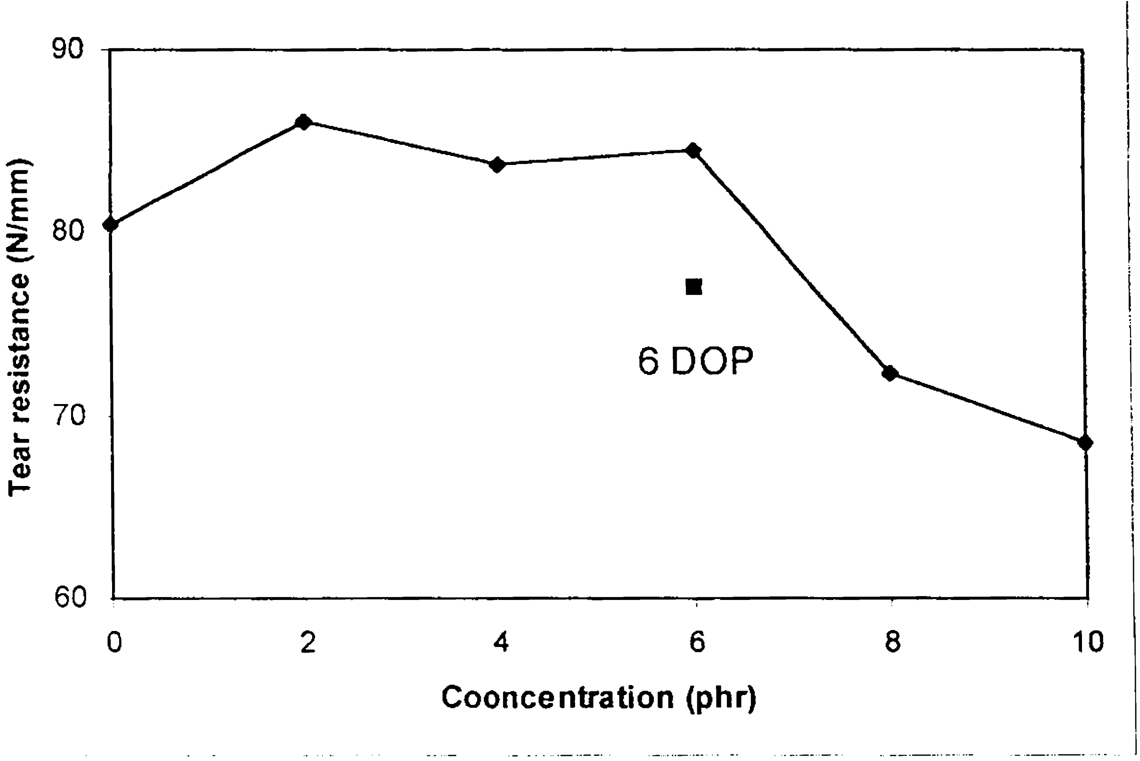


Fig.3.4.7 VARIATION OF EB WITH OIL CONTENT

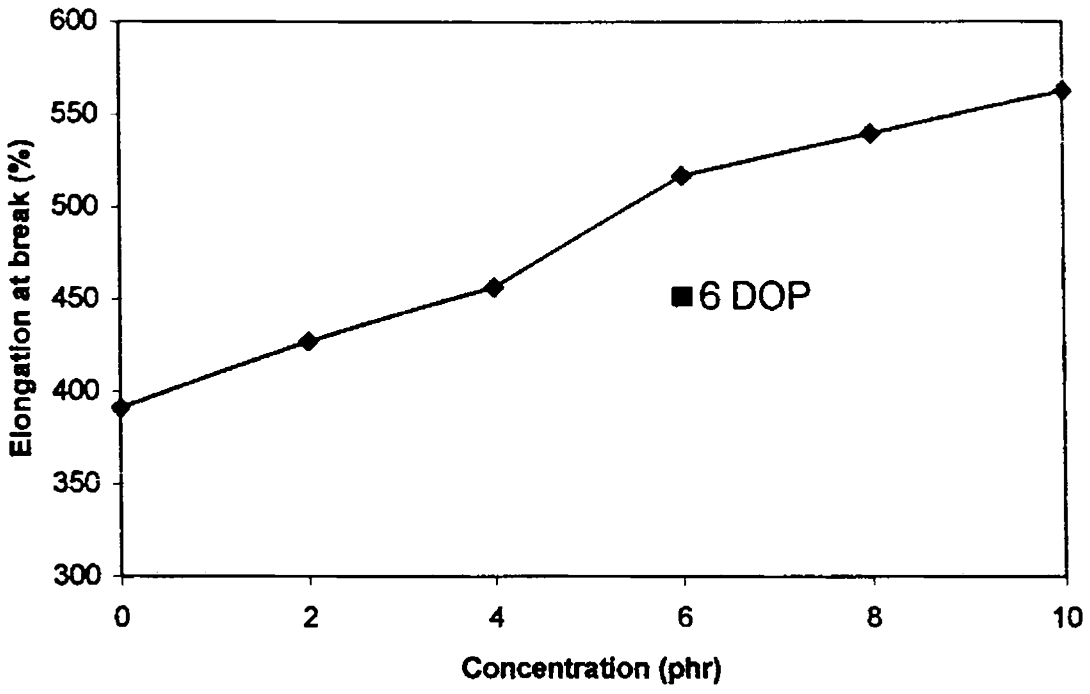


Table. 3.4.1 Cure characteristics and tensile strength of aged and unaged samples

Sample composition	Scorch time (t_{10})	Cure time (t_{90})	Cure rate Nm/min.	Tensile strength (MPa)		
				Fresh	Air aged	Oil aged
6 DOP	1.32	2.88	0.2419	22.18	18.4	19.95
0 phr plasticizer	1.36	3.88	0.1757	23.5	17.78	17.80
2 phr rubber seed oil	1.24	2.48	0.3603	25.20	19.83	22.20
4 „	1.28	2.60	0.3085	23.55	19.8	21.85
6 „	1.36	2.60	0.2787	23.20	19.48	20.20
8 „	1.32	2.36	0.2497	22.59	19.45	20.10
10 „	1.36	2.32	0.1932	19.84	16.50	18.20

Table. 3.4.2 Leachability and compression set of vulcanizates

Sample composition	Leachability (% loss in weight)	Compression set (%)
6 DOP	1.4	53.3
0 phr plasticizer	0.9	30.5
2 rubber seed oil	0.0	52.4
4 ,,	0.0	56.8
6 ,,	0.1	62.3
8 ,,	0.1	66.9
10 ,,	0.1	68.5

3.5. Punnal oil (Calophyllum inophyllum oil) as a multipurpose additive in NBR.

It is the seed oil of the punnal tree (calophyllum inophyllum) a tree generally found in tropical countries. The oil is non edible due to a higher percentage of non saponifiable matter. It is a nondrying oil and the major fatty acid present are, palmitic ,palmitoleic, stearic, oleic and linoleic. Small amounts of other fatty acids like calophynnic acid, crepenefinic acid and dihydro crepenefinic acid are also detected. Punnal oil generally contain only 92% triglycerides and in the remaining 6.4% is glycolipids and 1.6% is phospholipids. The detailed concentration of these components are given in chapter 1.In addition to these the oil is also found to contain oxygenated polycyclic compounds like coumarin and its derivatives and also sterols like campesterol, stigmasterol and beta-sitosterol in small quantities. The oil is tried as a multipurpose additive in nitrile rubber. NBR is compounded according to formulation given in Table 3.1.1. Wherever punnal oil is used it is used as a substitute for DOP and stearic acid. The properties of the compounds and the vulcanizates were compared with that of the control mix with DOP.

Reults and discussion

Fig. 3.5.1 shows the flow behavior of compounds obtained from the Brabender. Punnal oil seems to be more plasticizing than DOP. It is seen that about 5 phr oil is enough to give viscosity to the compound that is shown by 6 phr DOP. The compound without plasticizer shows a higher vicosity showing the difficulty in processing without plasticizer. The cure behaviour also is seen to be similar to the flow behavior (Fig. 3.5.2.). But cure time is reduced without affecting the scorch safety (Table.3.5.1). The reduction in cure time is due to the activation of the elastomer molecules by the plasticizer. Compound without plasticizer shows the highest torque and cure time compared to compounds with DOP or punnal oil.

The variation of tensile strength is in accordance with the general trend shown by oils already discussed (Fig 3.5.3). The variation of modulus (Fig 3.5.4) is in tune with the variation in crosslink density (Fig 3.5.5). The variation in tear resistance is also similar to the variation in tensile strength and modulus (Fig . 3.5.6), and the elongation at break directly varies with the oil concentration (Fig 3.5.7). All this variations are similar to that shown by linseed , soyabean and rubber seed oil and can be explained on a similar manner.

The ageing resistance both in air and oil is seen to be slightly lowered as can be seen from the tensile strength of the aged and unaged samples of mixes with oil and DOP (Table 3.5.1.). This behaviour is not shown by oils discussed earlier which are either drying or semidrying. So it may be due to the very low concentration of unsaturated fatty acid which are more susceptible to oxidation and to an extent can protect the elastomer from oxidation. The compression set of vulcanizates is lower than that of the control ,mix. But it shows a gradual increase with the increase in oil content (Table 3.5.2) and this may be due to the gradual decrease in crosslink density. Though vulcanizate without plasticizer shows a lower compression set, the ageing resistance is found to be poor.

Leachability is considerably reduced by incorporating punnal oil for DOP. The vulcanizates with 6 phr oil has got a percentage loss in weight, only one fourth of that with an equal loading of DOP (Table 3.5.2) Blooming is also reduced by substituting DOP with punnal oil. This reduced leachability and blooming can be explained on a similar way to oils discussed earlier. The vulcanizate without plasticizer shows a lower value for its leachability than that with DOP, but higher than that with punnal oil.

Conclusion

Calophyllum inophyllum oil is a good substitute for DOP in nitrile rubber . The oil gives advantages in processability, cure time along with improved physical properties like tensile strength, modulus, tear resistance and compression set. Leachability and blooming are also reduced though a slight lowering in ageing resistance is noticed. The optimum concentration of punnal oil is found to be 3 - 5 phr which can advantageously substitute 6 phr DOP and 2 phr stearic acid in nitrile rubber compounds.

FIG 3.5.1 FLOW CURVE

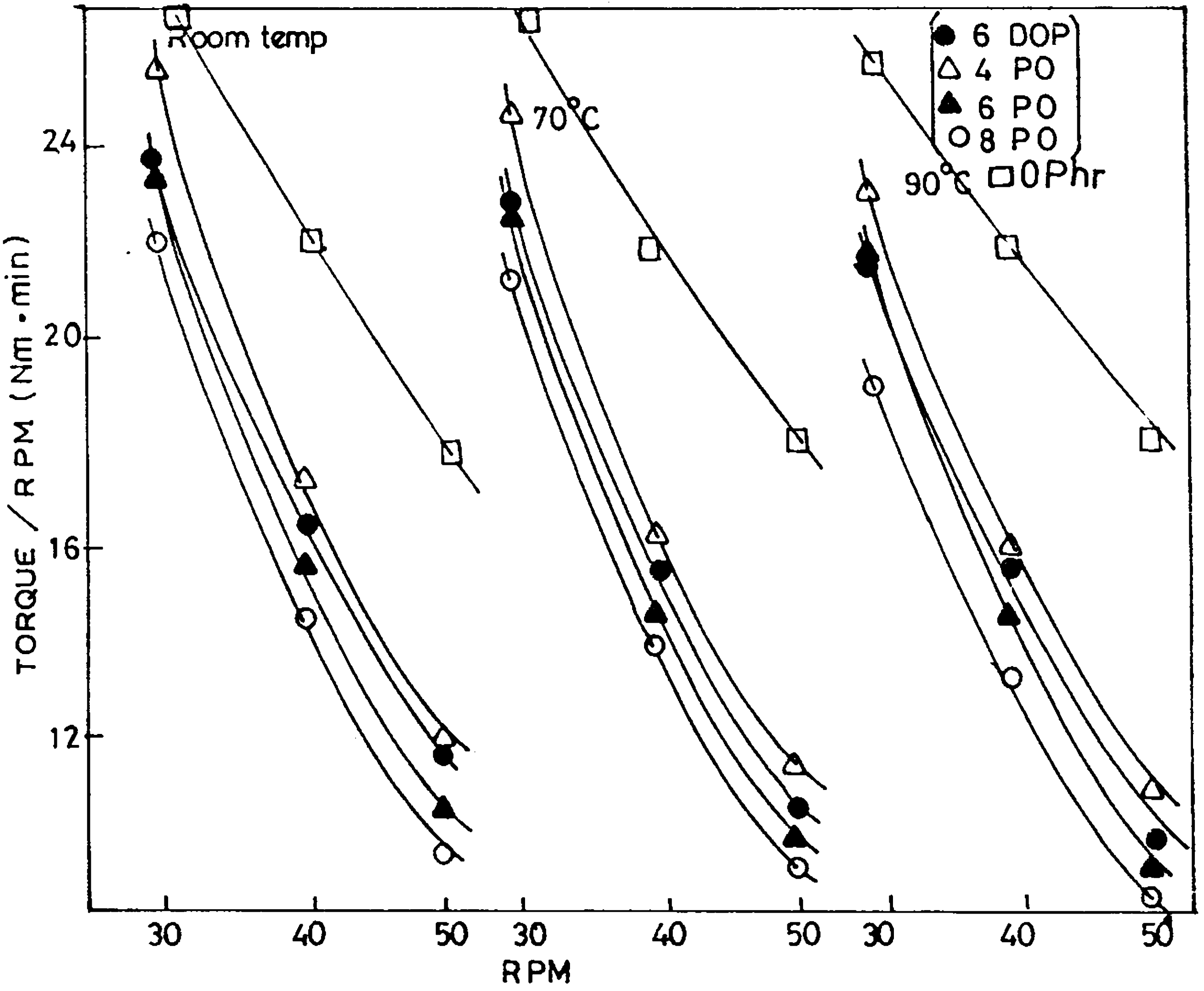
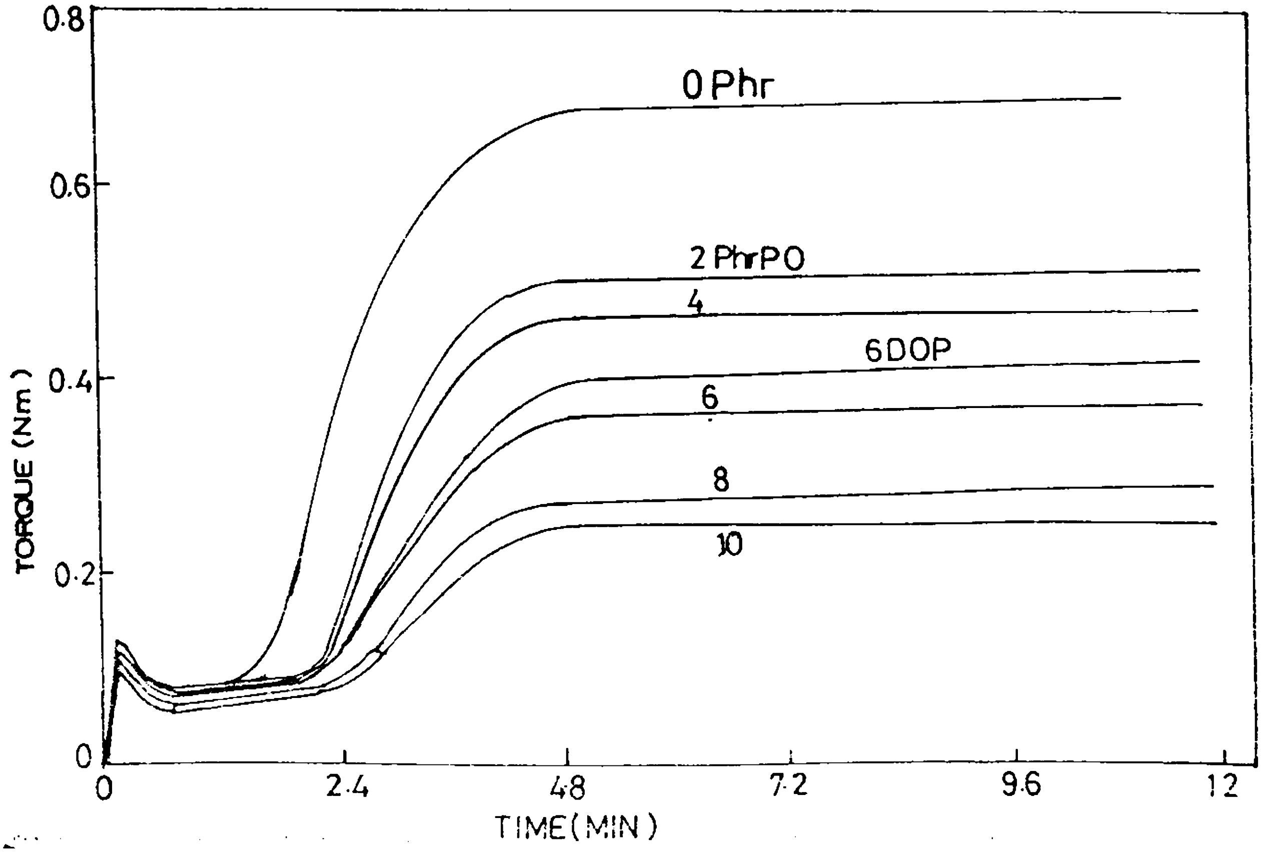


FIG.3.5.2 CURE CURVE



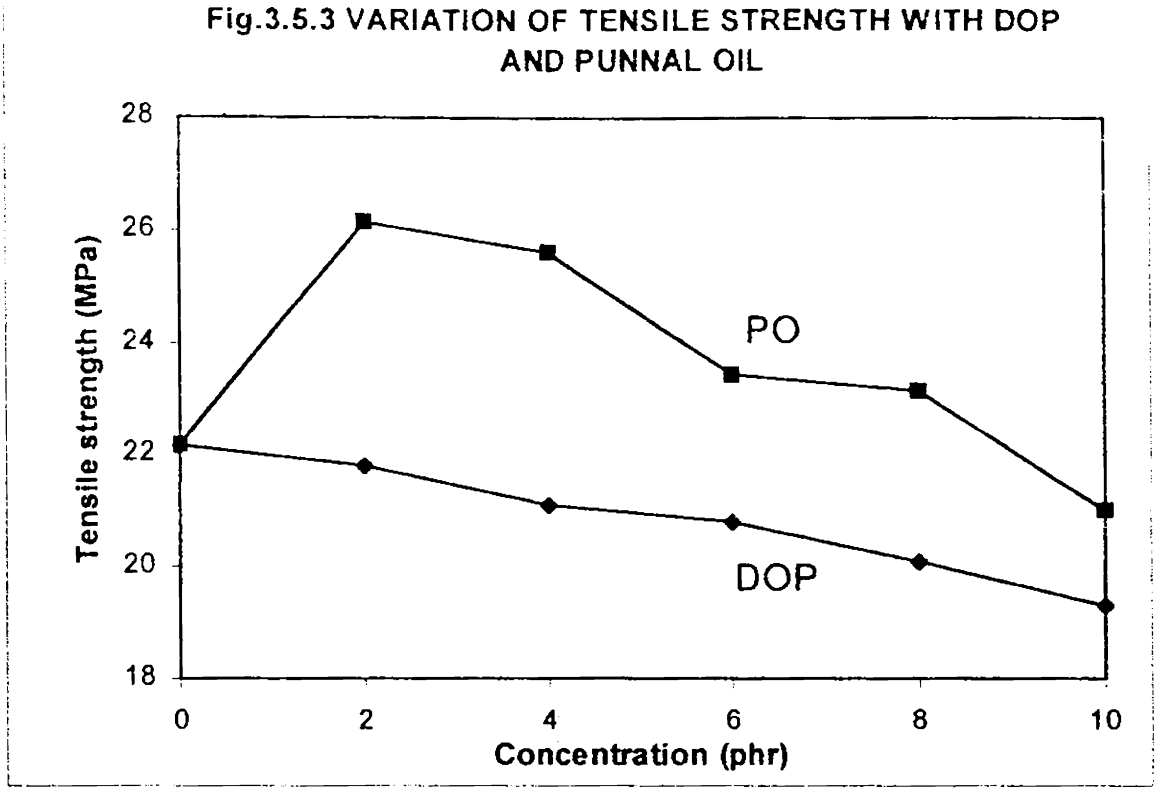


Fig.3.5.3 VARIATION OF TENSILE STRENGTH WITH DOP AND PUNNAL OIL
Tensile strength (MPa)
28
26
24
22
20
18
PO
DOP
0
2
4
6
8
10
Concentration (phr)

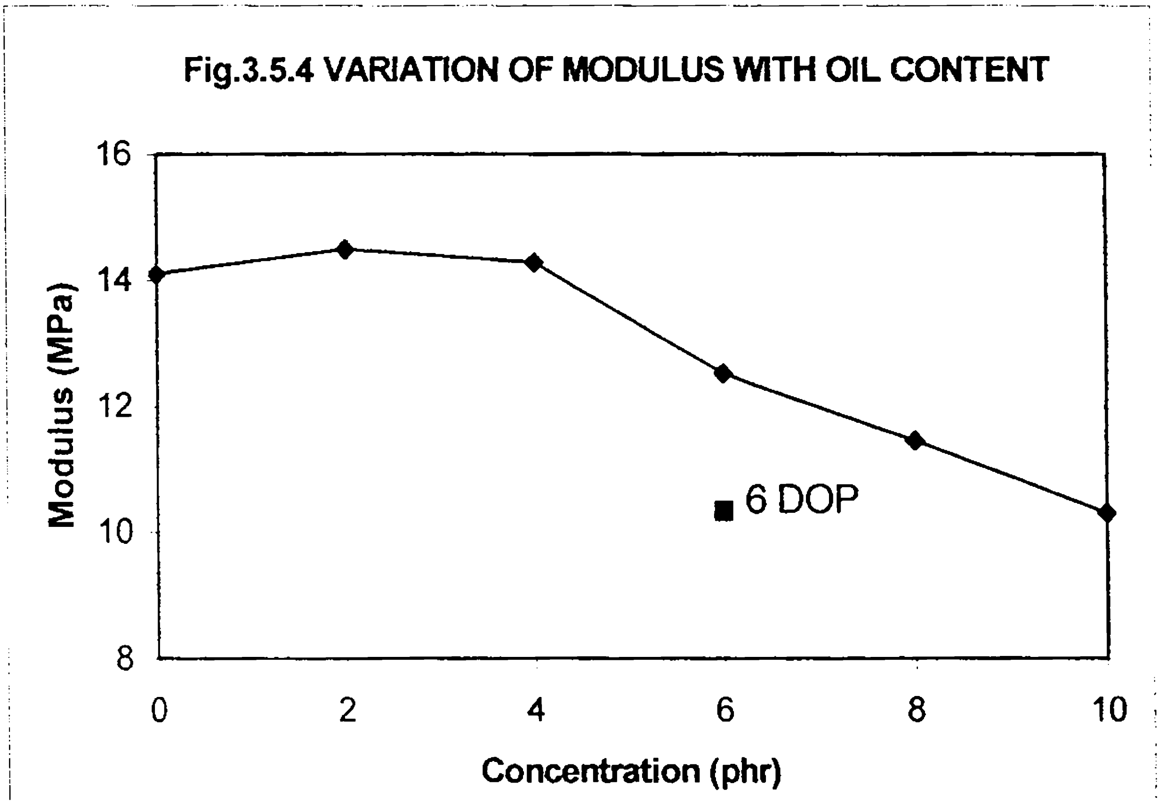


Fig.3.5.4 VARIATION OF MODULUS WITH OIL CONTENT
Modulus (MPa)
16
14
12
10
8
■ 6 DOP
0
2
4
6
8
10
Concentration (phr)

Fig.3.5.5 VARIATION OF CROSS LINK DENSITY WITH OIL CONTENT

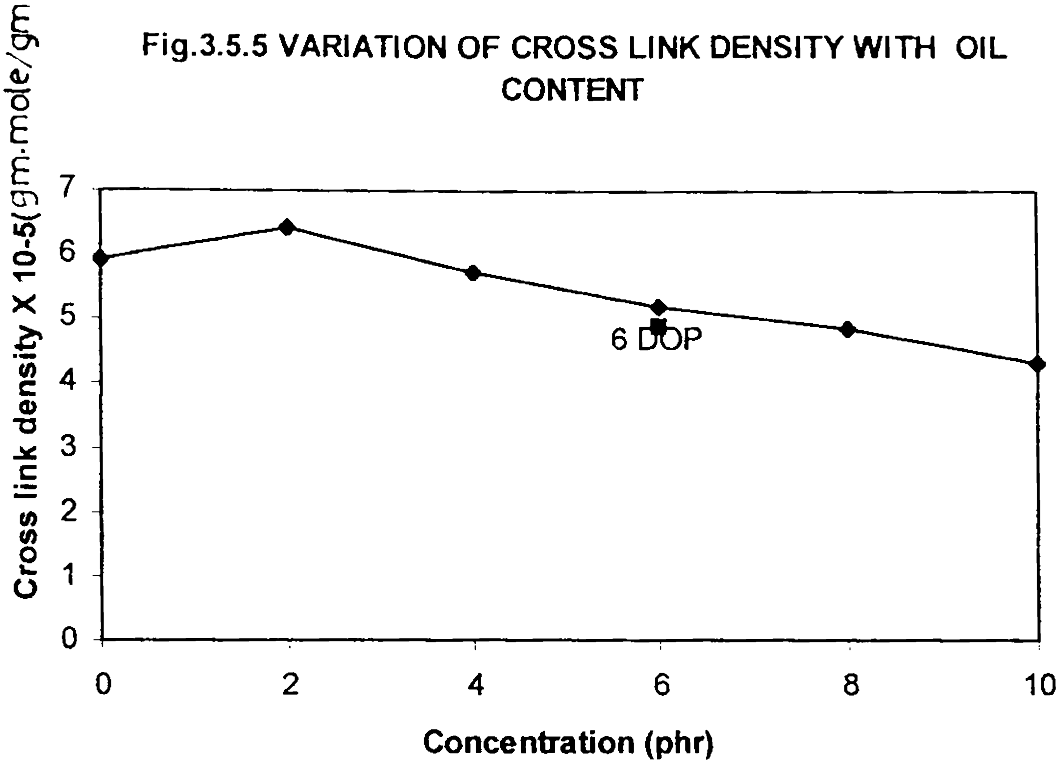
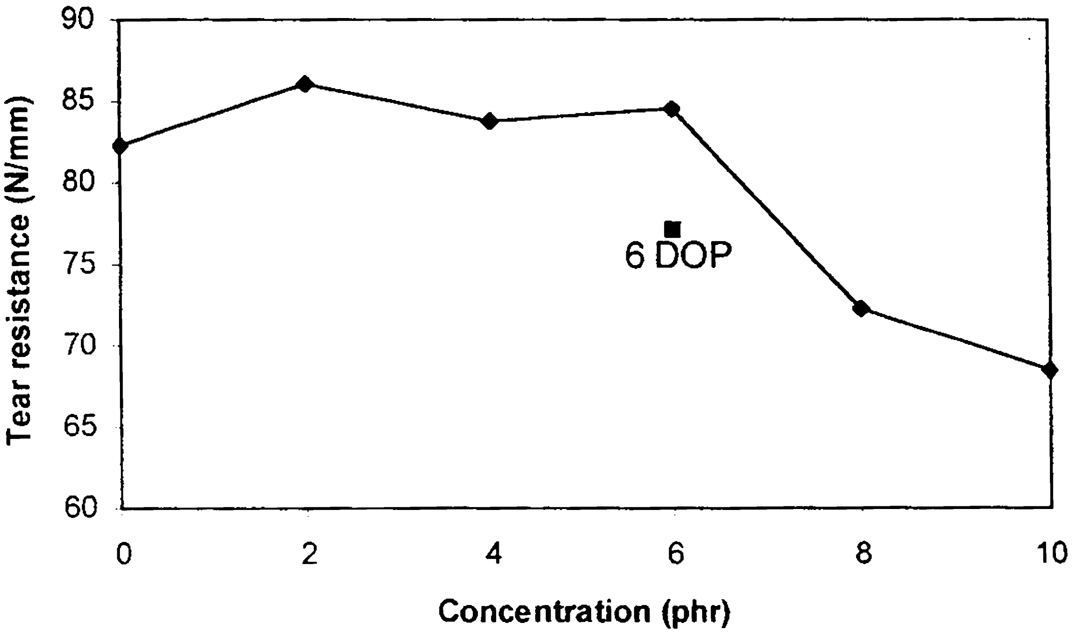


Fig.3.5.6 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT



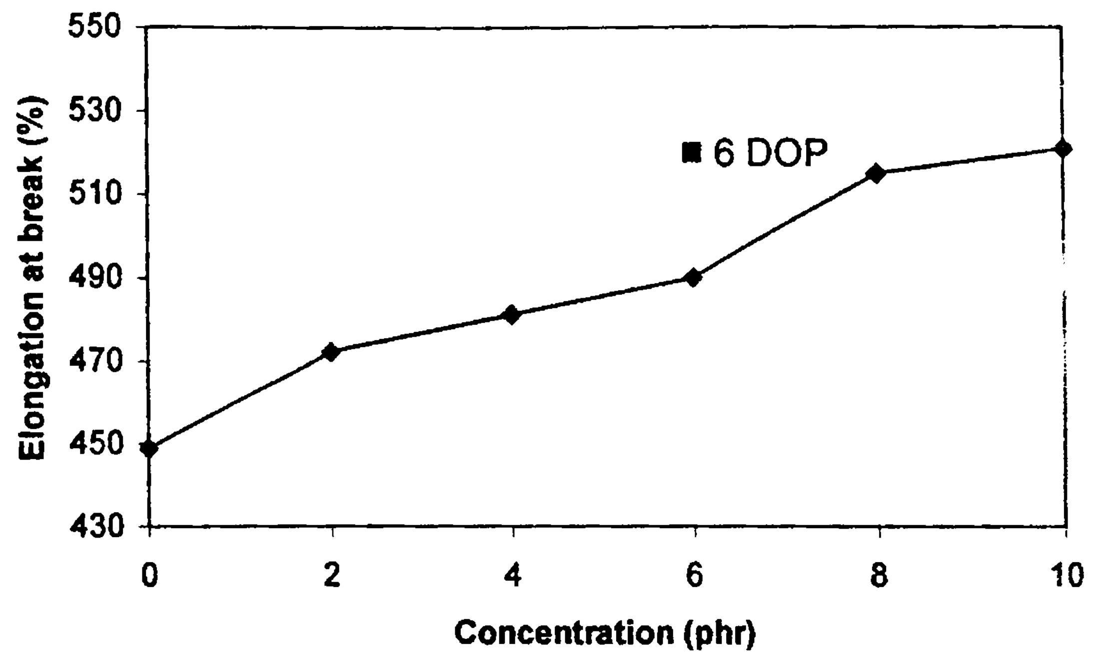


Fig.3.5.7 VARIAITON OF EB WITH OIL CONTENT

Table. 3.5.1 Cure characteristics and tensile strength of aged and unaged samples

Sample composition	Scorch time (t_{10})	Cure time (t_{90})	Cure rate Nm/min.	Tensile strength (MPa)		
				Fresh	Air aged	Oil aged
6 DOP	1.42	2.72	0.2858	20.08	16.10	18.85
0 phr plasticizer	1.36	3.88	0.1757	23.50	17.78	17.80
2 phr punnal oil	1.38	2.54	0.3939	26.16	20.08	21.07
4 „	1.40	2.46	0.3863	25.60	18.75	21.72
6 „	1.44	2.56	0.2655	23.46	18.26	21.24
8 „	1.50	2.42	0.2298	23.14	18.77	20.47
10 „	1.54	2.62	0.1758	2 1.00	16.27	20.32

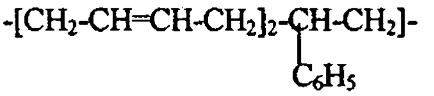
Table. 3.5.2 Leachability and compression set of vulcanizates

Sample composition	Leachability (% loss in weight)	Compression set (%)
6 DOP	2.4	53.1
0 phr plasticizer	0.9	30.2
2	0.0	43.5
4 „	0.4	46.1
6 „	0.4	50.2
8 „	0.5	55.6
10 „	0.6	57.2

CHAPTER IV

STUDIES ON THE EFFECT OF VEGETABLE OILS ON THE CURE CHARACTERISTICS AND VULCANIZATE PROPERTIES OF STYRENE BUTADIENE RUBBER (SBR)

Styrene butadiene rubber (SBR) is the most widely used among synthetic rubber. It is a copolymer of styrene and butadiene, normally containing 23.5% bound styrene. It is made both by emulsion and solution polymerization. The repeating unit in SBR is shown below.



$$-[CH_2-CH=CH-CH_2]_2-\underset{C_6H_5}{\underset{|}{C}H}-CH_2]-$$

Fig 4.1 repeating units in SBR rubber

Because of the double bond present in butadiene that portion of the molecule can be present in three forms ; cis 1,4 , trans 1,4 and vinyl 1,2. Ordinarily the proportions are about 18% cis, 65% trans and 17% vinyl. Solution SBR has about the same amount of styrene as the emulsion product, but there is a higher cis butadiene content, lower trans butadiene, and lower vinyl . The unsaturation in SBR is less than that in natural rubber and the double bonds are less reactive compared to those in NR. Hence SBR rubbers are slower curing than natural rubber and either more accelerator or a more active accelerator system is required (84).

The molecular irregularity and large pendent group in SBR prevent crystallisation on stretching. This results in lower green strength and gum tensile strength. To overcome this behaviour of SBR, incorporation of fine reinforcing fillers is required.

The ratio of tensile strengths of black filled to gum vulcanizate of SBR is reported to be 10 to 5 (85). An optimum filler loading is necessary for SBR vulcanizates to have wear and tear resistance (86).

As in the case of NBR and NR sulphur vulcanization of SBR involves heating it with accelerator, activator, co activator, antioxidant, filler, processing oil etc. Accelerators enable the vulcanization time to be reduced considerably. Zinc oxide, which is the usual activator in rubber vulcanization, enhances the action of accelerators. Stearic acid is added along with zinc oxide and is the usual co activator. Amine or phenolic type of antioxidants is used to reduce ageing process of the vulcanizates.

The function of the process oil is to provide better processability during the addition of fillers. Aromatic oil is the one usually used in SBR due to its better compatibility with this rubber. Though vegetable oils fall under the category of naphthenic or paraffinic oil in terms of their viscosity gravity constant (VGC) they may not be much incompatible with SBR due to its slightly polar nature. But the pendant phenyl group on the rubber chain may have some effect on the compatibility of the oil with the rubber that is to be looked into. Their free fatty acid content is already shown to be a substitute for stearic acid as co activator. The natural antioxidant present in the vegetable oils can retard the ageing process of the vulcanizates to some extent. In the present study, vegetable oils like linseed, soyabean, castor, rubber seed and punnal are tried as multipurpose additive in the styrene butadiene rubber.

4.1 Linseed oil as a multipurpose additive in SBR

SBR used in this study was Synaprene 1502. It is a non-staining cold rubber. It gives good physical properties in either black or light coloured products. It has high loading capacity and is used in the manufacture of tyres, molded and extruded products, foot wears, coated fabrics etc.

Experimental

SBR is compounded as per formulations given in Table 4.1.1. Wherever linseed oil is used, it is used as a substitute for aromatic oil and stearic acid.. The properties ofthe compounds and vulcanizates with linseed oil is compared with that of the control mix with aromatic oil and that without any plasticizer. The results reported are the average of at least five specimens.

Results and discussion

Fig. 4.1.1 shows the flow behaviour of the compounds obtained from the Brabender plasticoder as (torque/rpm) representing viscosity vs rpm representing shear rate. It is seen that compounds with linseed oil possesses a slightly higher viscosity compared to that with aromatic oil. The flow behaviour of compound with 8 phr linseed oil closely resembles that containing 6 phr aromatic oil. This poor plasticizing effect of linseed oil with SBR compared to aromatic oil may be due to the pendant aromatic rings on the rubber chain, which make SBR slightly polar resulting in a stronger interaction with the slightly polar vegetable oil. The cure behaviour of the compounds also show a similar trend. (Fig 4.12). The cure curve of the compound with 8 phr linseed oil coincides with that of the control mix containing 6 phr aromatic oil. The cure rate also is seen to be marginally decreased by incorporation of linseed oil. This shows the slight deactivation of rubber molecule by the oil. The compound without plasticizer shows very high viscosity and torque compared to compounds with aromatic oil or linseed oil, though cure rate is not much affected

Though mixes with 4 phr or less than 4 phr oil shows a lower or comparable cure time with that of the control mix, there is a gradual increase in cure time with increase in oil concentrations (Table 4.11). This type of behaviour is usually shown by oils which increases the viscosity of the compound by stronger rubber plasticizer interaction.

Fig 4.1.3 shows the variation of tensile strength with oil content. It should be noted that the behaviour of linseed oil in SBR is different from that shown in NBR. Tensile strength of vulcanizates with linseed oil showed a gradual marginal decrease, with increase in oil content and the value never exceeds that of the control mix at any concentration of the oil. This shows that the oil rarely gets covulcanized with the elastomer but predominantly form factice, reducing the strength of the vulcanizates. The difficulty in getting covulcanized may be due to the aromatic side chain on the rubber molecule which prevents the oil molecule form reaching the proximity of the rubber chain. Thus the possibility is better for self vulcanization than for covulcanization. This view is supported by the higher value of tensile strength of vulcanizate without plasticizer. The tear resistance also show a similar variation and can be explained on a similar line (Fig 4.1.4).

The variation of modulus with oil content is found to be marginal (Fig 4.1.5). This negligible variation in modulus is supported by the similar variation in crosslink density (Fig 4.1.6) The elongation at break (Fig. 4.1.7) shows a gradual marginal increase with increase in oil content and is inversely proportional to the crosslink density. This supports the view that sulphur is utilised for factice formation even at low concentration of the oil .The air resistance of vulcanizates with linseed oil is better than that of the control mix or even mix without plasticizer. This may be due to the presence of large amount of unsaturated fatty acid which is more susceptible to oxidation, and can protect the elastomer by preferential self oxidation. The tensile strength of aged and unaged samples were compared in Table.4.1.1.

The abrasion loss of the vulcanizates with linseed oil are marginally lower (Table 4.1.2) and the compression set marginally higher (Table 4.1.2) compared with that of the control mix. This is due to the softening of the vulcanizates by factice formation. The vulcanizate without plasticizer shows a comparable abrasion resistance and slightly lower compression set compared to the mix with aromatic oil. The DeMattia flex resistance (Table 4.1.2) and the resilience (Table 4.1.2) are improved while the heat build up showed little variation compared to the control mix.(Table 4.1.2). The increase in flex resistance can be easily explained on the basis of the "Free Volume Theory" of plasticizer action. The increase in free volume in a rubber matrix will reduce the friction between rubber molecules during flexing. Vegetable oil molecules (triglycerides) are comparatively bigger molecules compared to conventional plasticizer molecules. When these molecules are entrapped between the rubber molecules, more free volumes are produced and the flex resistance increases. As the quantity of oil increases more and more free volumes are produced and flex resistance increases many fold. The flex resistance of vulcanizate without plasticizer seems to be slightly higher and this may be due to the higher percentage of polysulphidic linkage in the vulcanizate (Table.3.1.4). The heat build up of the vulcanizate without plasticizer also shows a higher value.

Conclusion

The study shows that use of linseed oil marginally enhances the viscosity of SBR compounds. The cure time of the compound increases in the presence of linseed oil Though vulcanizate properties like ageing resistance , resilience and De Mattia flex resistance improve on addition of linseed oil, there is a marginal decrease in properties like tensile strength, tear resistance , and compression set. Properties like modulus elongation at break and heat build up are unaffected. It may be concluded that linseed oil cannot be considered a potential additive for SBR particularly as a replacement for aromatic oil. Though processability is very poor, formulations without plasticizer give higher value for tensile strength, modulus ,tear resistance and flex resistance along with lower compression set.

FIG 4.1.1. FLOW CURVE

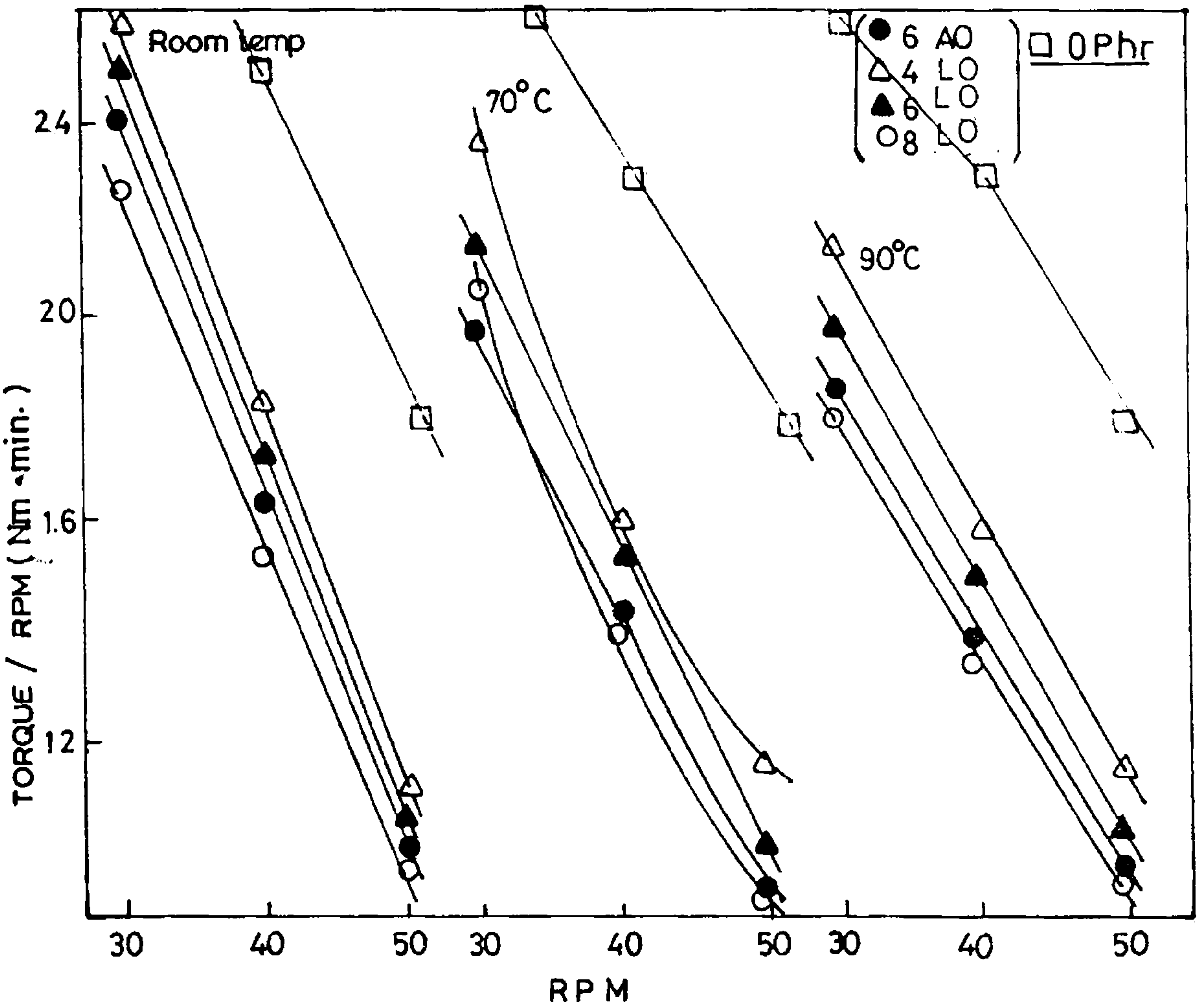


FIG 4.1.2 CURE CURVE

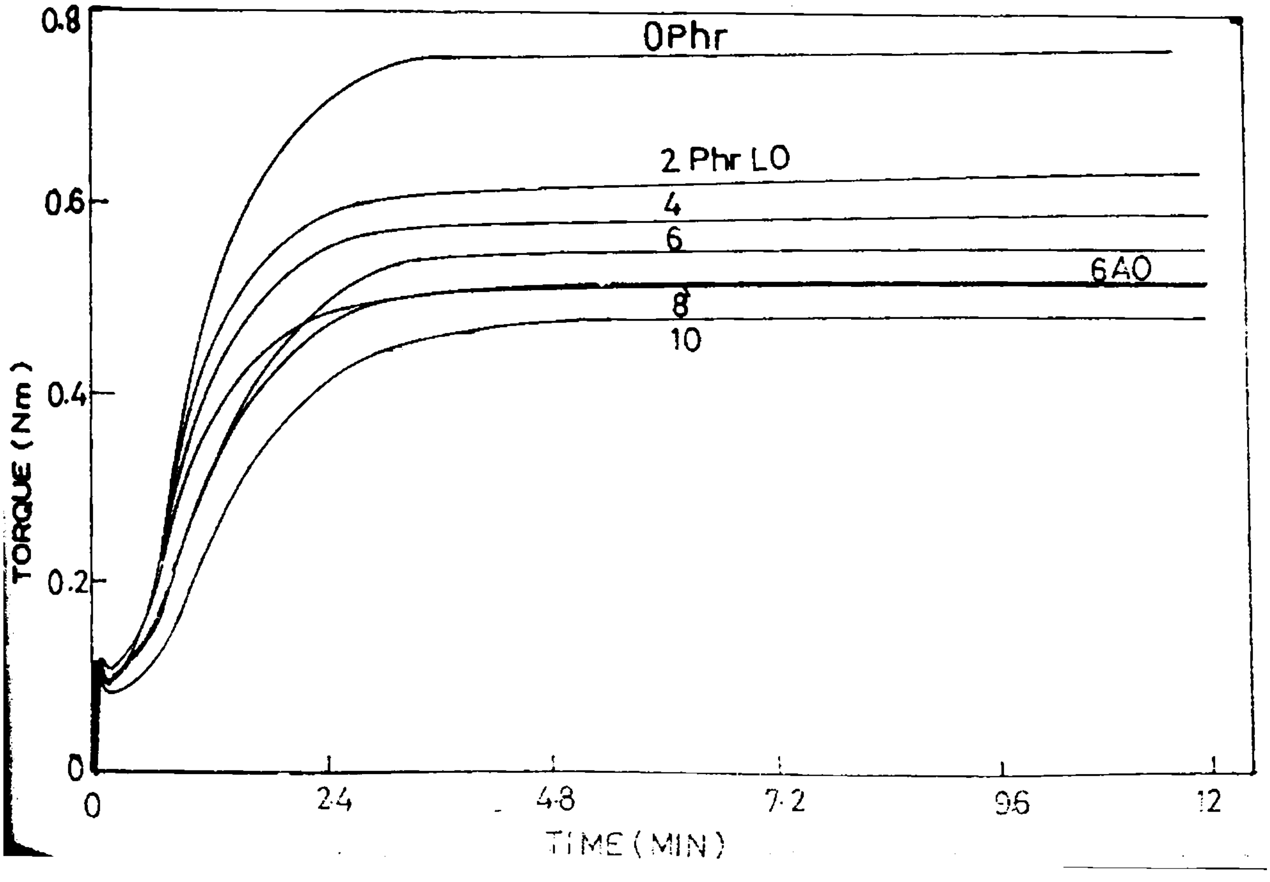


Fig.4.1.3 VARIATION OF TENSILE STRENGTH WITH AROMATIC OIL AND LINSEED OIL

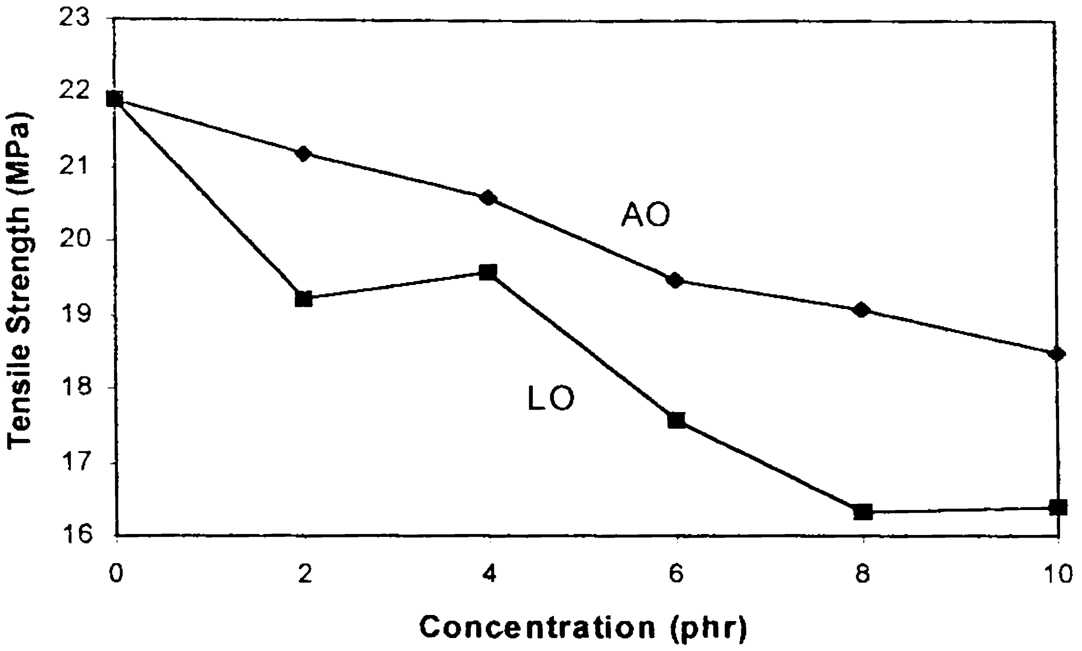


Fig.4.1.4 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT

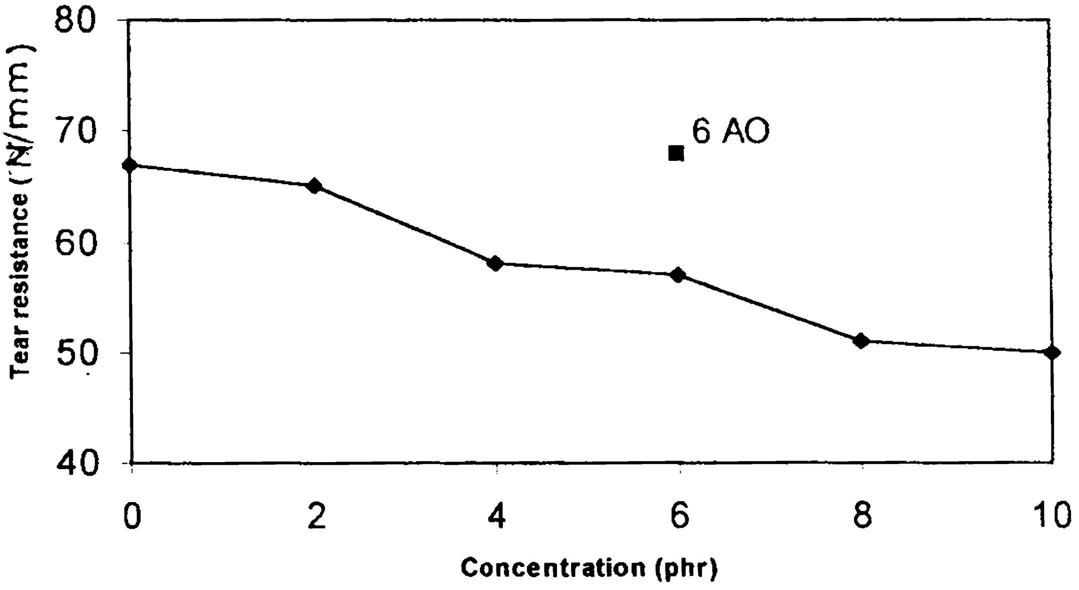


Fig.4.1.5 VARIATION OF MODULUS WITH OIL CONTENT

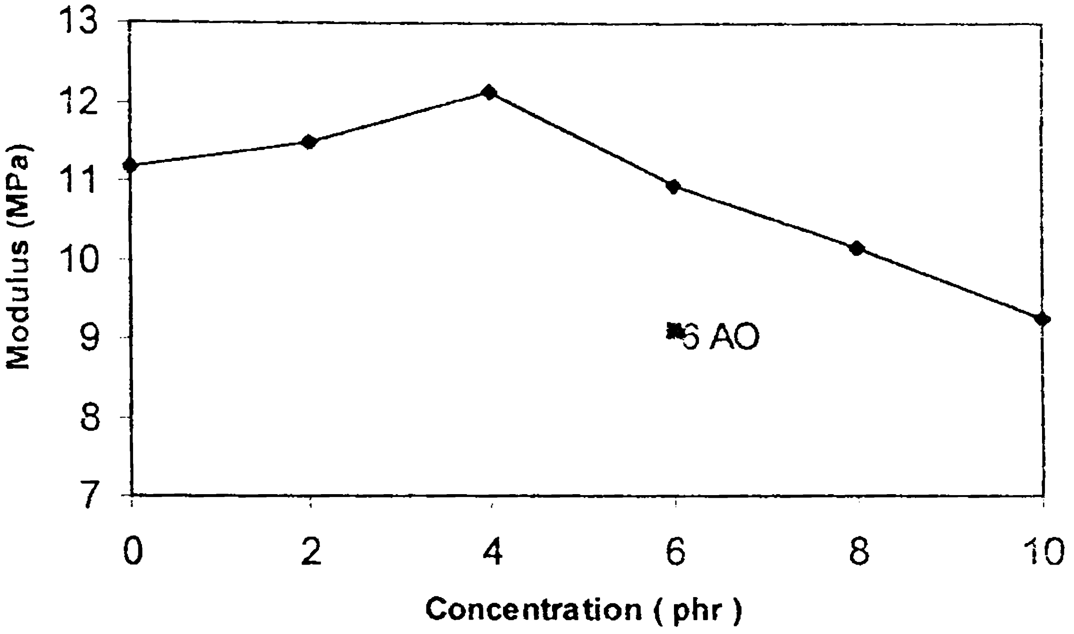
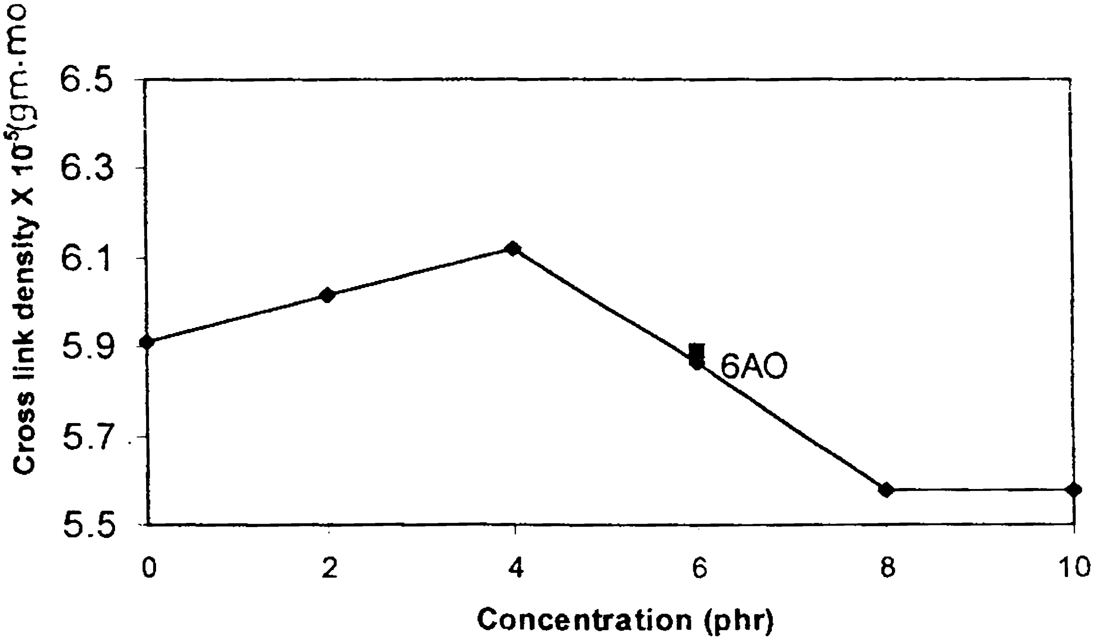


Fig.4.1.6 VARIATION OF CROSS LINK DENSITY WITH OIL CONTENT



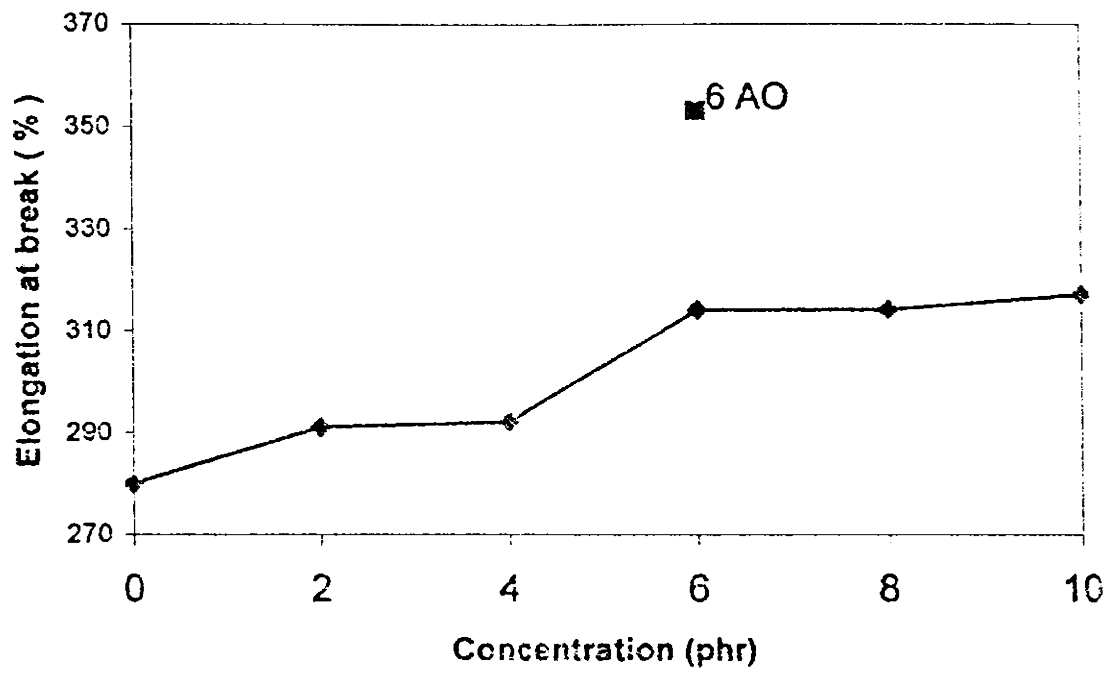


Fig. 4.1.7 VARIATION OF EB WITH OIL CONTENT

Table 4.1.1 Formulation

SBR	100 phr.
HAF	50 „
Zinc oxide	5 „
Stearic acid	2 „
MBTS	1 „
TMTD	0.2 „
Sulphur	1.5 „
Vulcanox HS	1.0 „
Vulcanox 40 20	0.5 „
Aromatic oil	6 phr

Table 4.1.2 Cure characteristics and tensile strength of aged and unaged samples

Sample composition	Scorch time (t_{10}) Min	Cure time (t_{90}) Min	Cure rate Nm/min.	Tensile strength (M.Pa)	
				Unaged	Air aged
6 phr aromatic oil	1.7	7.6	0.0826	19.50	10.50
0 phr plasticizer	2.3	8.1	0.0877	21.90	14.10
2 phr linseed oil	1.8	7.3	0.1023	19.21	14.97
4 ”	1.9	7.3	0.0944	19.57	15.54
6 ”	2.2	8.3	0.0745	17.59	15.41
8 ”	2.6	8.8	0.0574	16.32	15.14
10 ”	2.5	9.8	0.0799	16.4 0	15.32

Table.4.1.3 Abrasion resistance, compression set, De Mattia flex resistance, heat build up and resilience of vulcanizates.

Sample composition	Abrasion loss (% volume)	Compression set. (%)	Flex resistance (Cycles)	Heat build up (^{0} F)	Resilience (%)
6 phr aromatic oil	3.9	44.3	64000	92	40
0 phr plasticizer	3.8	41.2	72000	97	41
2 phr linseed oil	3.7	45.2	79000	94	40
4 ”	3.6	45.9	123000	94	42
6 ”	3.5	47.1	179000	93	42
8 ”	3.4	47.2	181000	92	43
10 ”	3.4	49.9	197000	93	43

4.2 Soyabean oil as a multipurpose additive in SBR

SBR having the specification given in chapter 2 is compounded as per formulation given in Table 4.1.1. Wherever soyabean oil is used it is used as a substitute for aromatic oil and stearic acid. Properties of compounds and vulcanizates with different loadings of oil is compared with that of the control mix with aromatic oil and that without any plasticizer.

Results and discussion

Fig. 4.2.1 shows that flow behaviour of the compounds obtained from ;the Brabender plasticorder with torque/rpm representing viscosity vs rpm representing shear rate. The effect of soyabean oil on the viscosity of the compound seems to be similar to that shown by linseed oil. The viscosity of the compound with 8 phr soyabean oil is comparable to that of the control mix with 6 phr aromatic oil. This shows that soyabean oil also is less compatible in SBR compared to aromatic oil and the lower compatibility may be due to the presence of aromatic side chain on the rubber molecule. The cure behaviour of the compounds are also similar to their flow behaviour. As can be seen from their cure curves (Fig 4.2.2) compounds with 8 phr soyabean oil gives a cure curve almost coinciding with the control mix with 6 phr aromatic oil. The compound without plasticizer shows higher viscosity and torque compared to all other mixes.

Table 4.2.1 shows the cure characteristics of the compounds. The behaviour of soyabean oil is almost similar to that shown by linseed oil. The cure time shows a marginal increase with increase in oil content, but the values are very close to that of the control mix. This shows that soyabean oil also deactivate the elastomer by interaction with it, though not as strong as linseed oil. The compound without plasticizer shows a lower cure rate.

The variation of tensile strength (Fig 4.2.3) tear resistance (Fig. 4.2.4) and modulus (Fig.4.2.5) is not significant when aromatic oil is substituted with soyabean oil. Further it may be noted that the tear resistance , tensile strength and modulus of compounds with 2 to 8 phr soyabean oil, and that of the control mix with 6 phr aromatic oil is almost the same. These results are well explained from the very little difference seen in the crosslink densities of the compounds (Fig. 4.2.7). The vulcanizate without plasticizer shows the highest value for this properties compared to that with aromatic oil or soyabean oil. The elongation at break gradually increases with oil content (Fig 4.2.6). All these observations are mutually supporting and also support the view that covulcanization of the oil with the elastomer along with self vulcanization takes place at all concentrations of oil. It is assumed that the effect of covulcanization on these properties is nullified by the effect due to self vulcanization.

It is better to compare soyabean oil and linseed oil at this instance. It is already seen that preferentially self vulcanization occurs in the case of linseed oil (Chapter 4.1). whereas both possibilities are there for soyabean oil. This difference is due to two reasons. viz. the strength of interaction of the oil with elastomer and the amount of unsaturation in the oil. Linseed oil is highly unsaturated (drying) which makes it susceptible to easy self vulcanization. Further the oil-rubber interaction is stronger in the case of linseed oil than soyabean oil, as can be seen from their cure rates. But soyabean oil being less unsaturated (semidrying) slows down the ease of self vulcanization So there is almost an equal distribution of oil between covulcanization and self vulcanization in the case of soyabean oil, whereas major portion of linseed oil get self vulcanized, leaving little oil for covulcanization.

The ageing resistance of the vulcanizates is seen to be improved by addition of soyabean oil and may be due to the presence of unsaturated fatty acid in the oil. The tensile strength of aged and unaged samples are compared in Table 4.2.1. Vulcanizate without plasticizer is comparatively poor in ageing resistance.The abrasion resistance (Table 4.2.2) and De Mattia flex resistance (Table 4.2.2) are improved, where as heat build up is slightly increased (Table 4 2.2). The increase in flex resistance is similar to that of linseed oil and can be explained on a similar line. The resilience (Table 4.2.2) and compression set of the vulcanizates showed little variation (Table 4.2.2), but blooming is considerably reduced. Vulcanizate without plasticier showed a comparable value for all these properties.

Conclusion

Substitution of aromatic oil with soyabean oil in SBR compounds improves some of the vulcanizate properties, while it adversely affects some other properties. It improves the ageing resistance flex resistance and abrasion resistance by maintaining the tensile properties, compression set, and abrasion resistance. The cure rate is not much affected, but the processability is slightly affected. It is seen that 6-8 phr soyabean oil can substitute 6 phr aromatic oil and 2 phr stearic acid in SBR vulcanizates with the benefit of avoiding aromatic oil and balancing the advantages and disadvantages shown in properties of compounds and vulcanizates.

FIG 4.2.1 FLOW CURVE

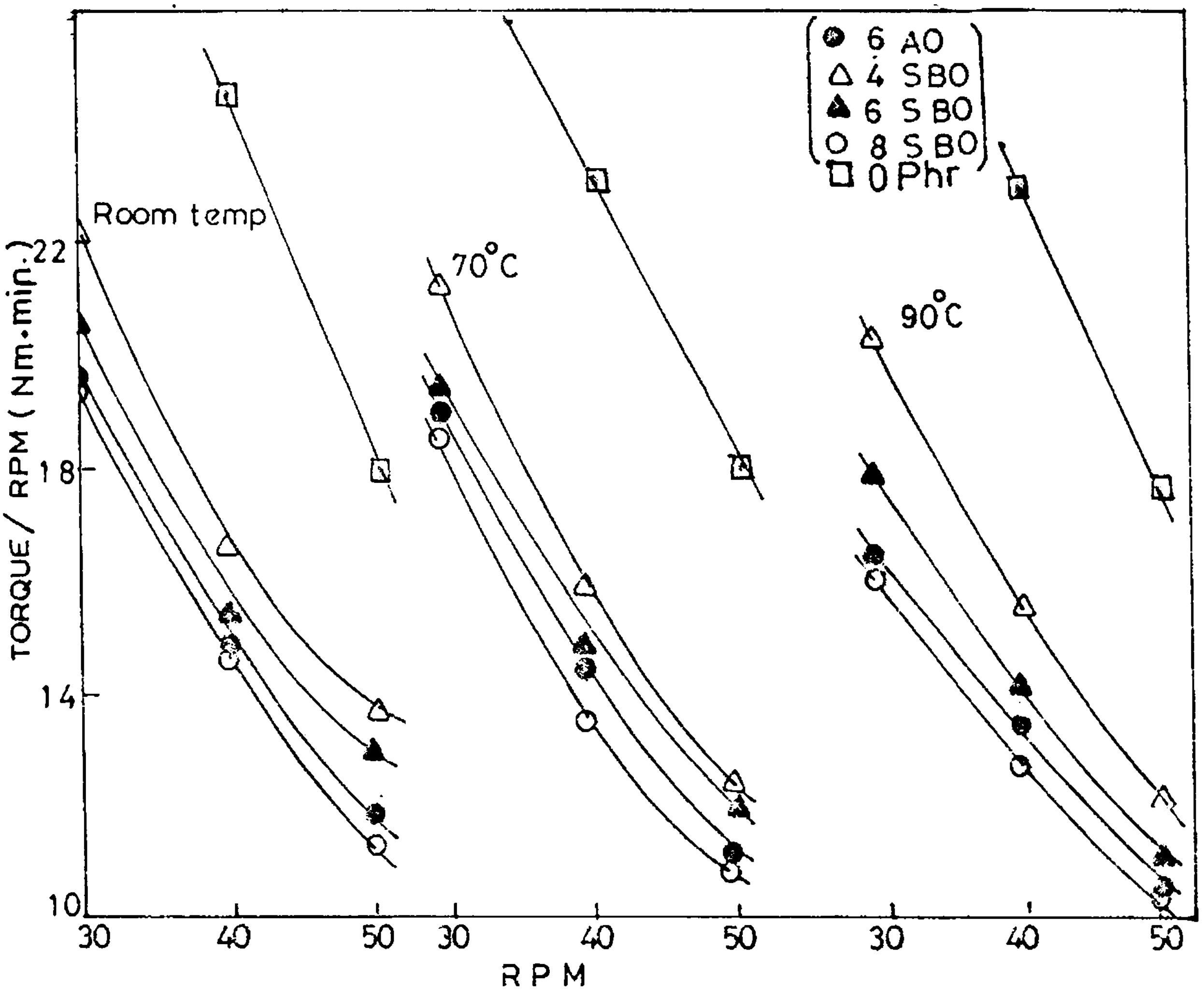


FIG 4.2.2 CURE CURVE

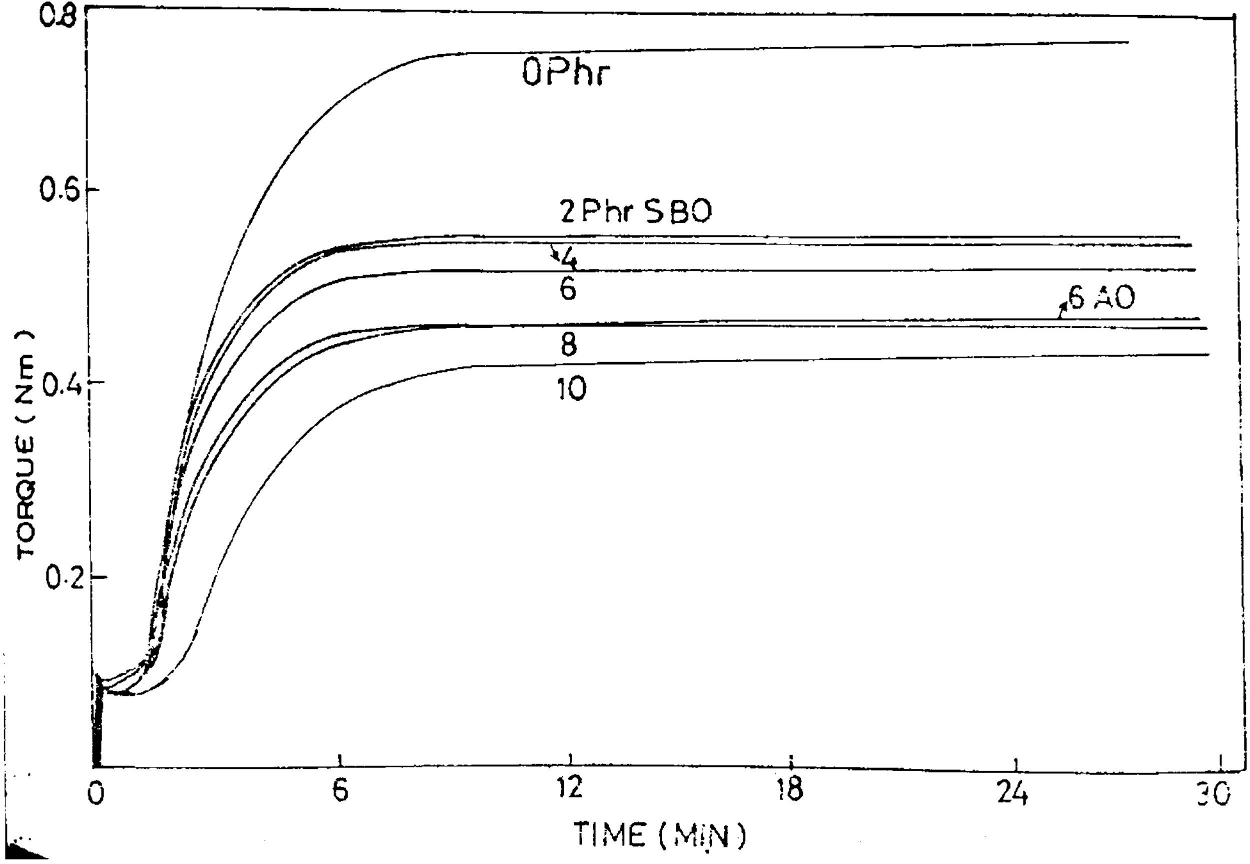


Fig. 4.2.3 VARIATION OF TENSILE STRENGTH WITH AROMATIC OIL AND SOYABEAN OIL

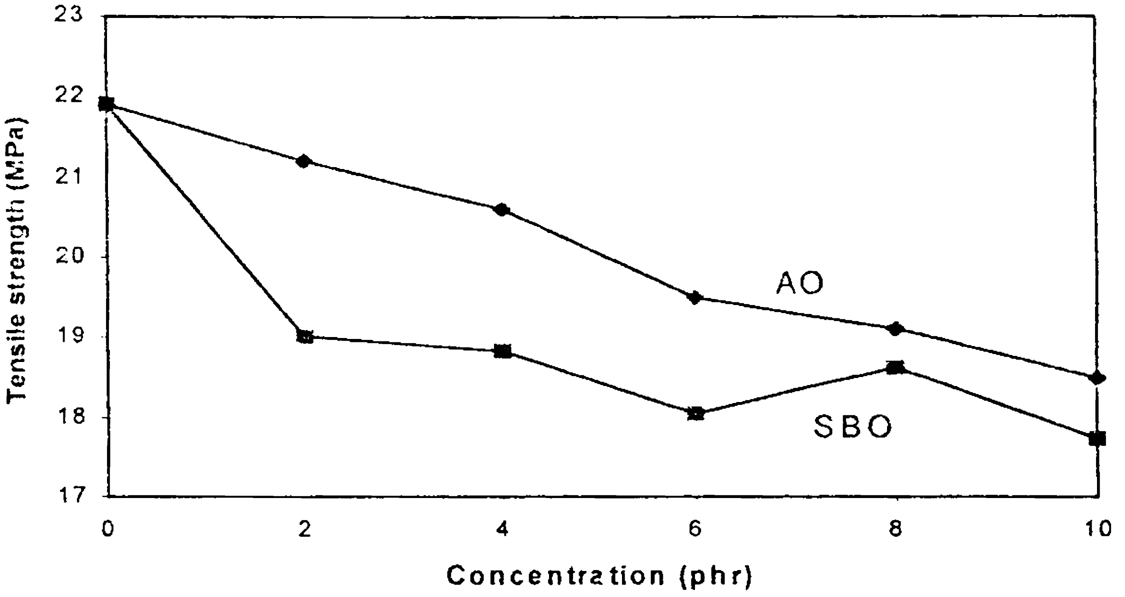


Fig. 4.2.4 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT

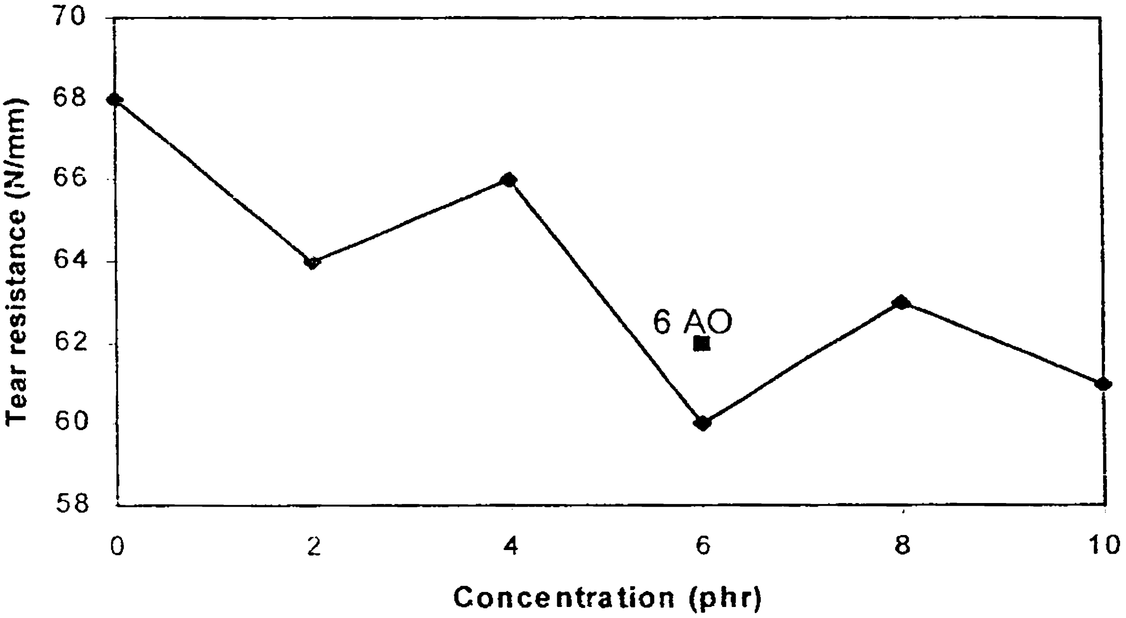


Fig 4.2.5 VARIATION OF MODULUS WITH OIL CONTENT

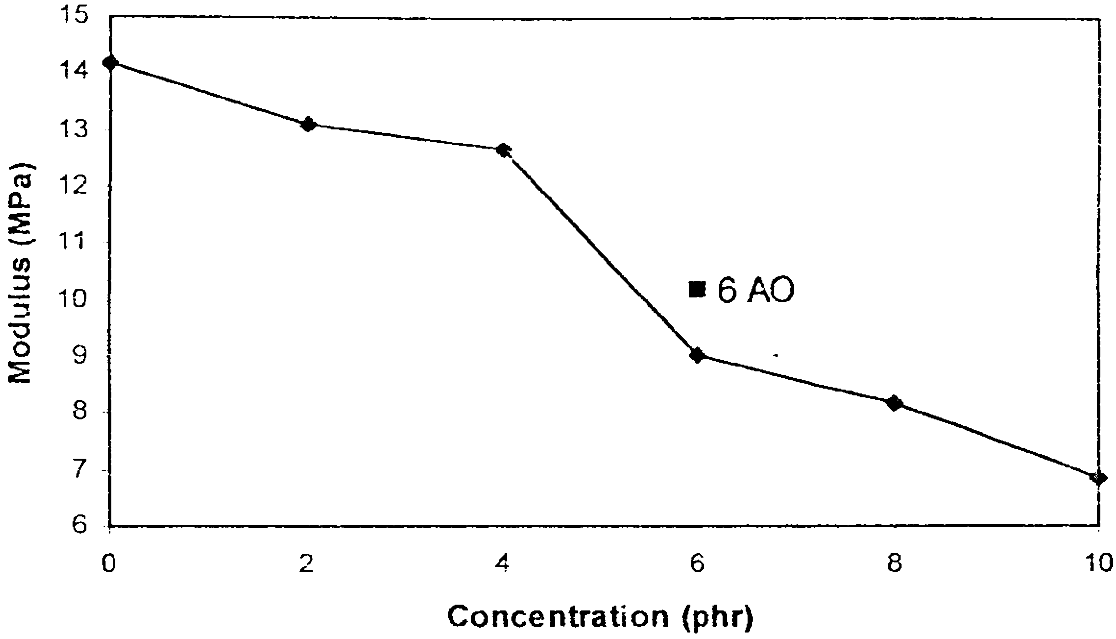


Fig.4.2.6 VARIATION OF EB WITH OIL CONTENT

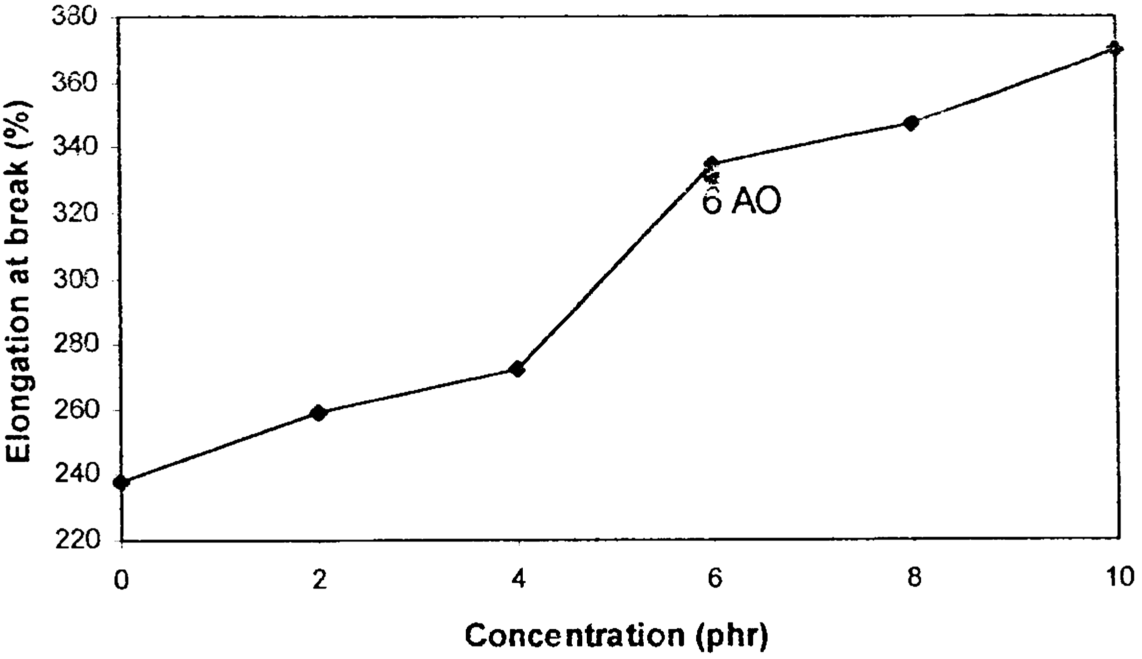


Fig. 4.2.7 VARIATION OF CROSS LINK DENSITY WITH OIL CONTENT

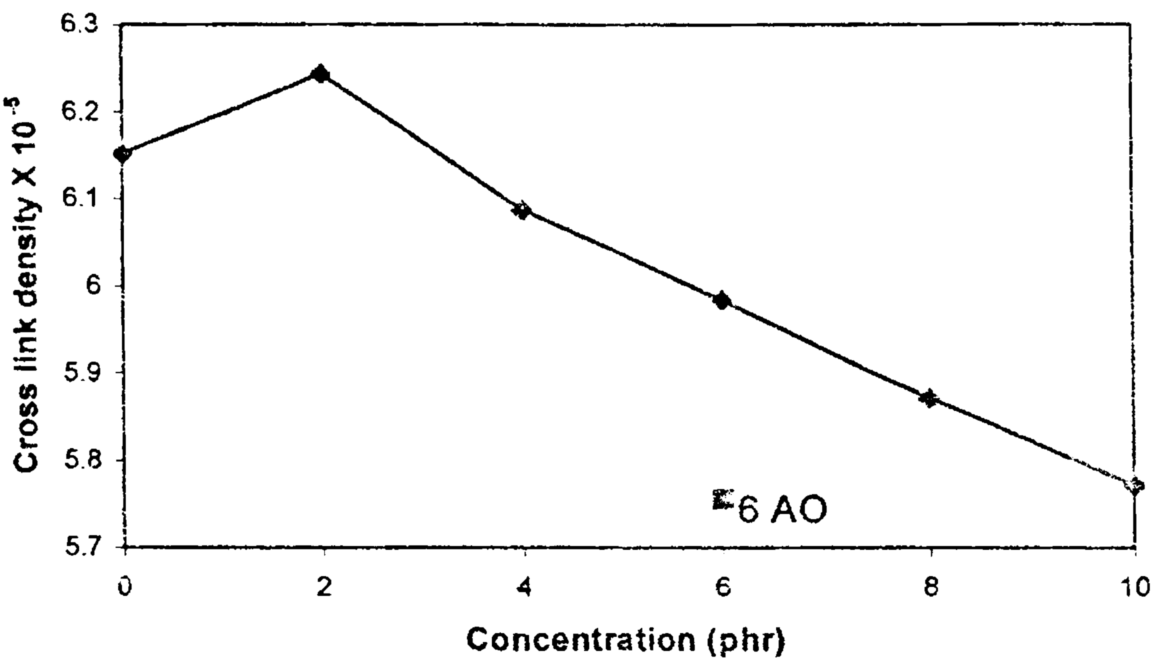


Table 4.2.1 Cure characteristics and tensile strength of aged and unaged samples

Sample composition	Scorch time (t_{10}) Min	Cure time (t_{90}) Min	Cure rate Nm/min.	Tensile strength (M.Pa)	
				Unaged	Air aged
6 phr aromatic oil	1.6	6.3	0.0798	19.50	13.51
0 phr plasticizer	2.3	8.1	0.0877	21.90	14.10
2 phr soyabean oil	2.1	5.8	0.1166	19.02	14.49
4 „	1.8	6.0	0.1448	18.82	14.84
6 „	2.0	5.9	0.1112	18.04	14.75
8 „	1.7	6.2	0.0917	18.61	14.01
10 „	2.1	6.6	0.0618	17.74	12.68

Table.4.2.2 Abrasion resistance, compression set,De Mattia flex resistance , heat build up and resilience of vulcanizates.

Sample composition	Abrasion loss (% volume)	Compression set. (%)	Flex resistance (Cycles)	Heat build up (^{0}F)	Resilience (%)
6 phr aromatic oil	4.0	43.1	71000	92	41
0 phr plasticizer	3.8	41.2	72000	97	41
2 phr soyabean oil	3.8	41.2	91000	95	39
4 „	3.7	41.7	131000	97	39
6 „	3.4	42.5	181000	96	41
8 „	3.4	43.2	201000	96	40
10 „	3.4	42.9	227000	95	39

4.3 Castor oil as a multipurpose additive in SBR

SBR is compounded as per formulation given in Table 4.1.1. Wherever castor oil is used it is used as a substitute for aromatic oil and stearic acid. The properties of the compound and the vulcanizates were compared with that of the control mix with 6 phr aromatic oil and also that without plasticizer.

Results and discussion

Fig. 4.3.1 shows the flow behaviour of compounds obtained from the Brabender. Castor oil seems to be less plasticizing than aromatic oil. The flow curve of the compound with 10 phr castor oil is very close to that of the control mix with 6 phr aromatic oil. This shows that the behaviour of castor oil towards SBR is similar to that shown by linseed and soyabean oils and can be explained on a similar way. The slightly higher viscosity of the mix compared to that with the other oils may be due to the very high viscosity of the castor itself. The cure behaviour of the compounds are also similar to their flow behaviour. The cure curve of the compound with 10 phr castor oil is very close to that of the control mix (Fig 4.3.2). The compound without plasticizer shows higher viscosity and torque compared to the compounds with aromatic oil or castor oil.

Though substitution of aromatic oil with castor oil increases the viscosity of the compounds, cure time is found to be little affected (Table 4.3.1). But as the concentration of the oil increases, there is a gradual marginal increase in cure time.This shows the deactivation of more and more elastomer molecules with the increase in oil content. The compound without plasticizer shows a slightly higher cure rate than compounds with aromatic oil or castor oil.

Fig 4.3.3 shows the variation of tensile strength with variation in aromatic oil and castor oil content. Though vulcanizates with 2-4 phr castor oil show marginally higher tensile strength than that of the control mix with 6 phr aromatic oil, the values gradually decreases with increase in oil content. But vulcanizates with castor oil always having a lower tensile strength than that with the same loading of aromatic oil. This lower value in tensile strength may be due to the lower covulcanization of the oil with the elastomer, as the pendant phenyl group on the rubber chain acts as a hindrance. So possibility is more for self vulcanization than for covulcanization. The vulcanizate without plasticizer shows a higher value for its tensile strength.

The variation in modulus (Fig. 4.3.4) and crosslink density (Fig. 4.3.5) are mutually supporting and is similar to the variation in tensile strength. The variation in tear resistance is also similar to the tensile strength and can be explained on a similar line (Fig.4.3.6). The elongation at break increases with oil content and is inversely proportional to the variation in tensile strength and modulus (Fig. 4.3.7). The vulcanizate without plasticizer shows the highest value for modulus, tear resistance and crosslink density and the lowest value for elongation at break

The ageing resistance of the vulcanizates do not show any variation. The tensile strength of the aged and unaged samples are compared with that of the control mix in Table 4.3.1. Abrasion loss of the vulcanizates are marginally lowered by substituting castor oil for aromatic oil (Table 4.3.2.),whereas De Mattia flex resistance is highly increased (Table 4.3.2). The variation in flex resistance can be explained on a similar way to oils discussed earlier. Compression set of the vulcanizates are higher than that of the control mix . (Table 4.3.2) while resilience (Table 4.3.2) and heat build (Table 4.3.2) are un affected. Though blooming is reduced, vulcanizates with higher loading of castor oil shows sweating. The vulcanizate without plasticizer shows a higher value for abrasion loss and heat build up, but shows lower compression set.

Conclusion

Substitution of aromatic oil with castor oil in SBR is not advantageous. Though improvement is seen in cure time and De Mattia flex resistance, all other properties are either un affected or adversely affected. Castor oil is not good as an additive in SBR compounds.

FIG 4.3.1 FLOW-CURVE

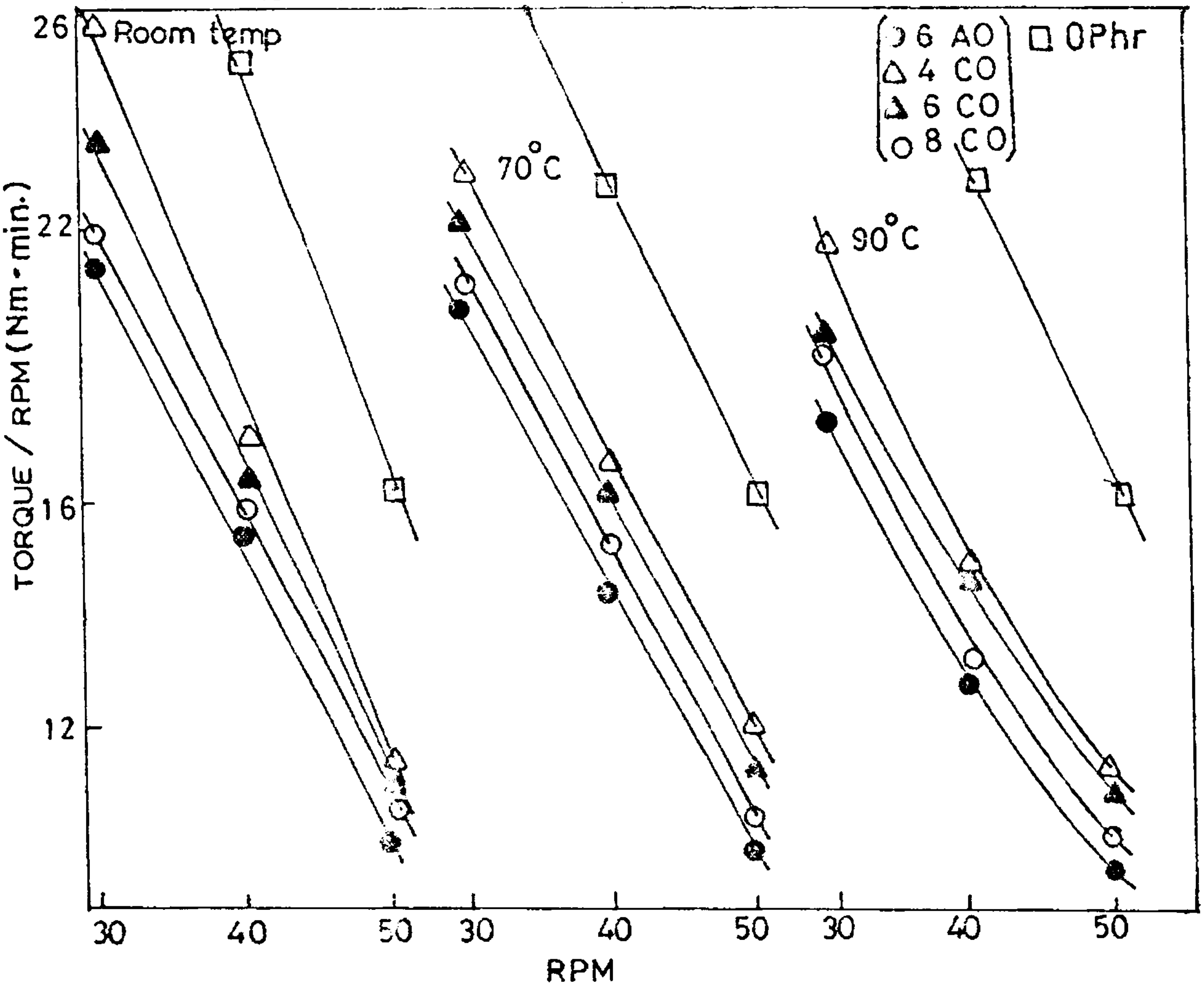


FIG4.3.2 CURE CURVE

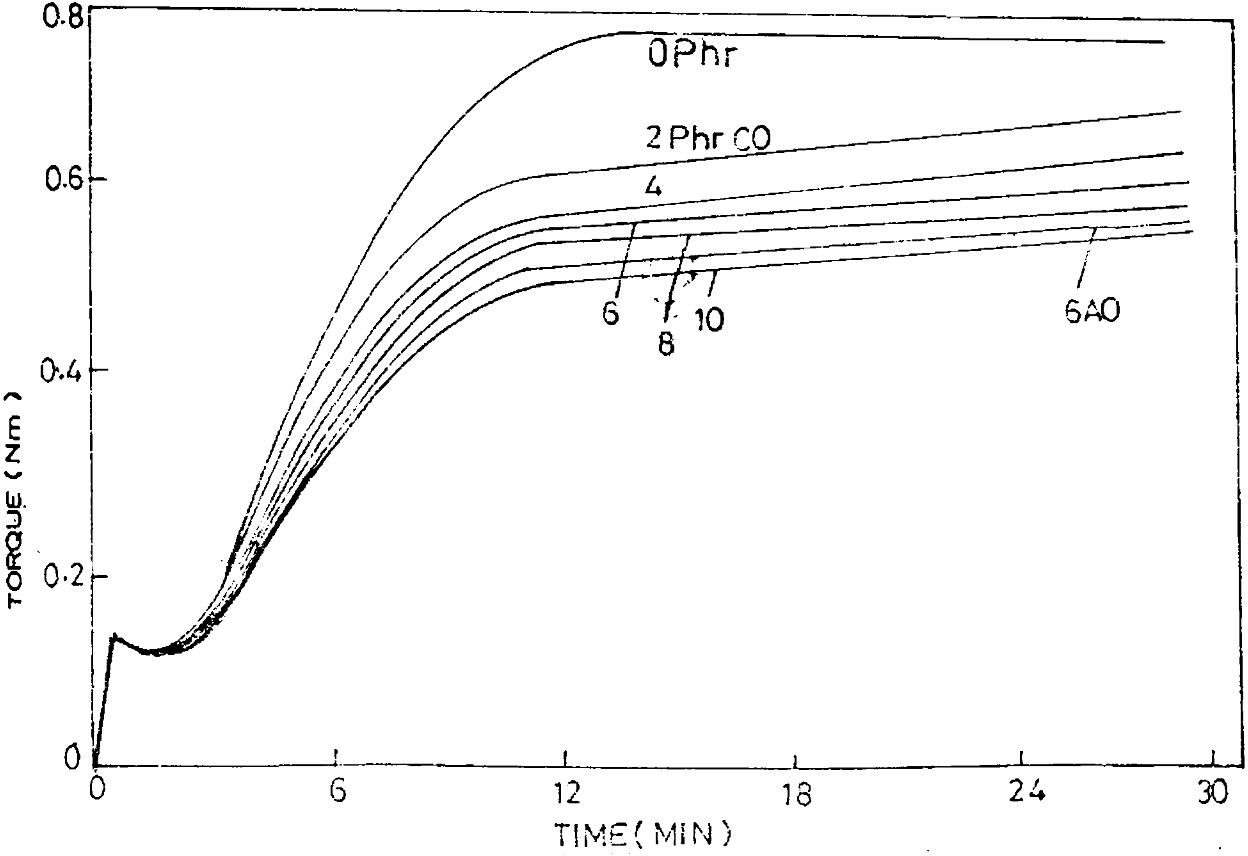


Fig.4.3.3 VARIATION OF TENSILE STRENGTH WITH AROMATIC OIL AND CASTOR OIL

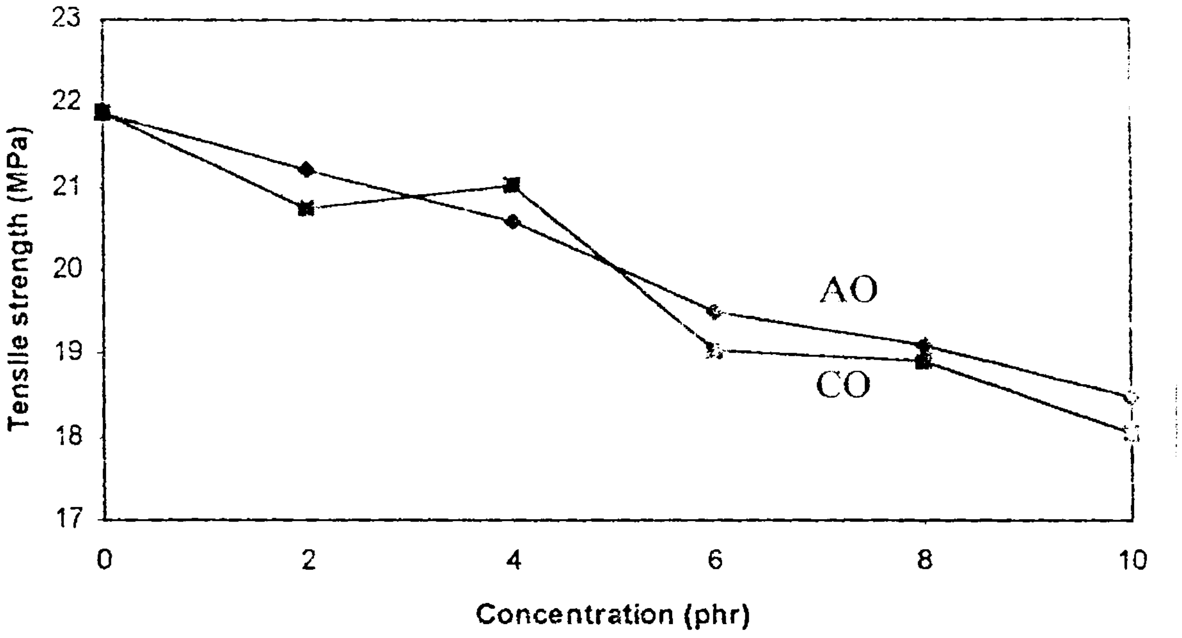
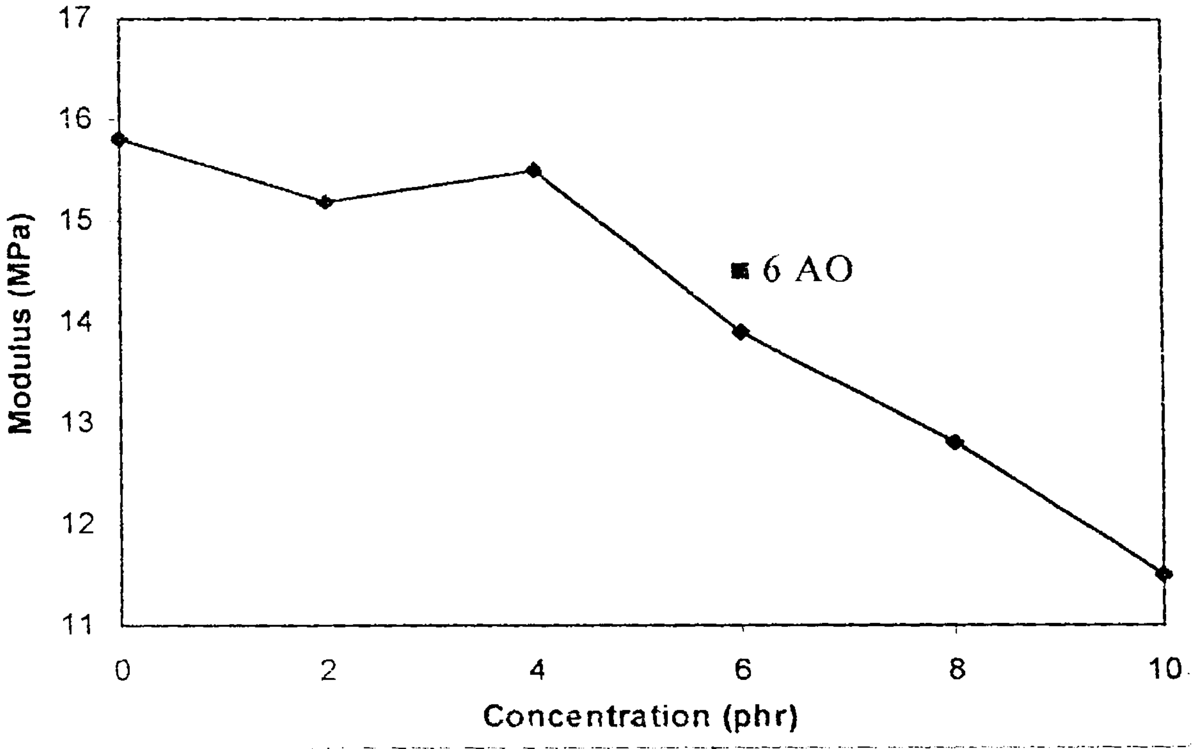


Fig 4.3.4 VARIATION OF MODULUS WITH OIL CONTENT



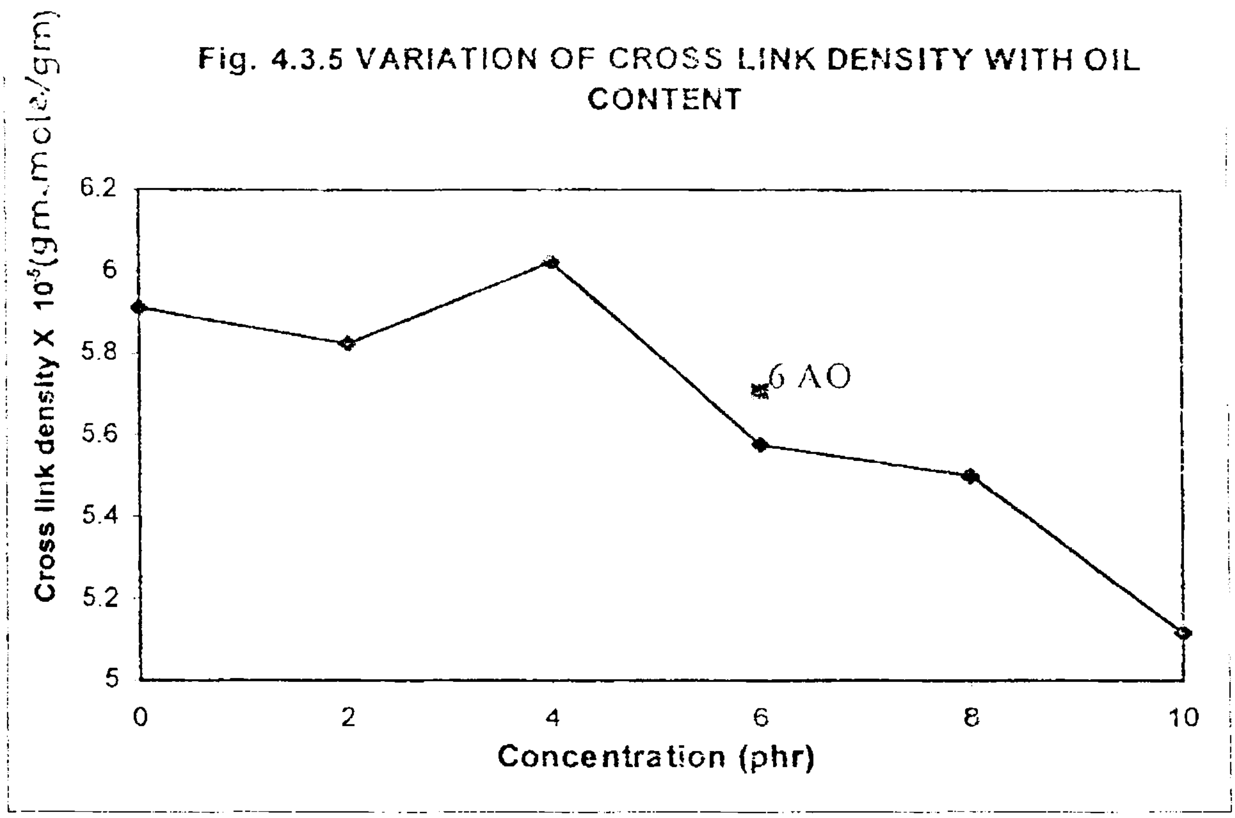


Fig. 4.3.5 VARIATION OF CROSS LINK DENSITY WITH OIL CONTENT
Cross link density X 10^5(gm.mole/gm)
6.2
6
5.8
5.6
5.4
5.2
5
0
2
4
6
8
10
Concentration (phr)
6 AO

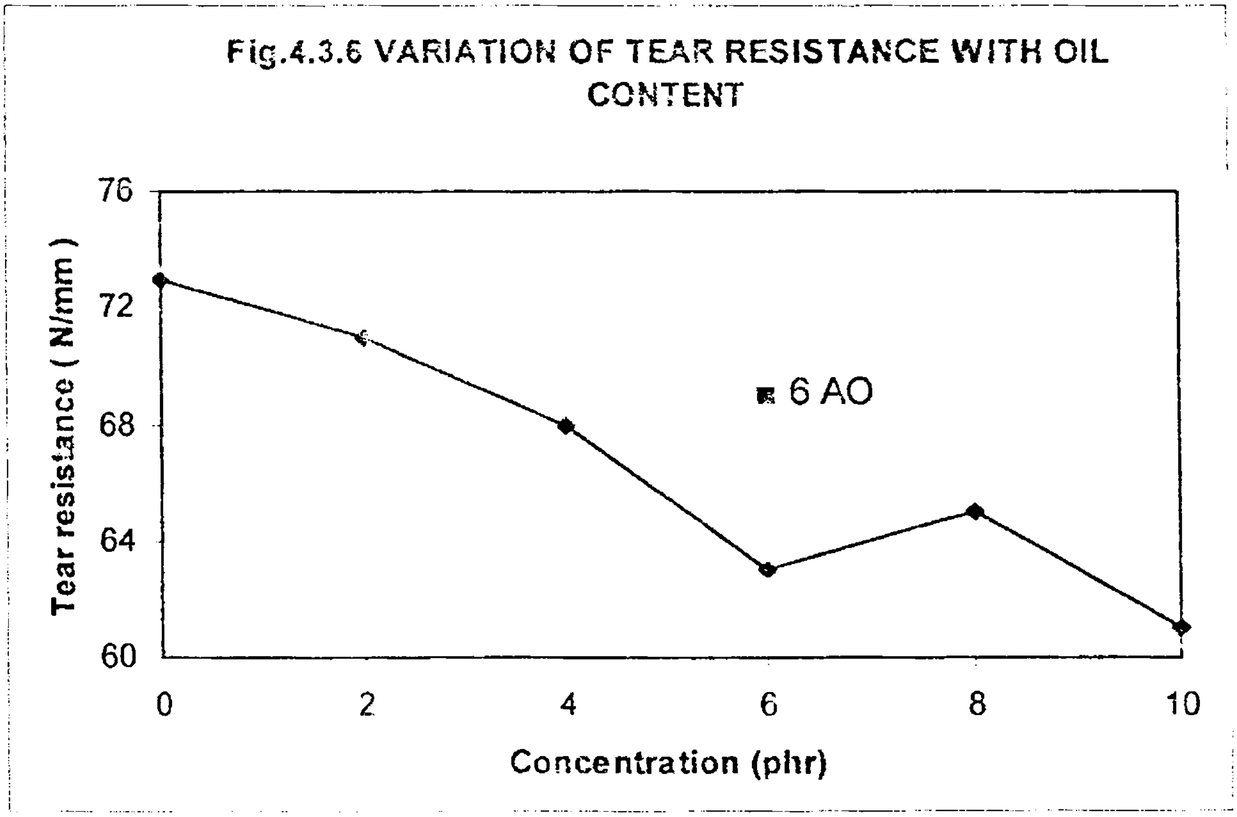


Fig.4.3.6 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT
Tear resistance (N/mm)
76
72
68
64
60
0
2
4
6
8
10
Concentration (phr)
6 AO

Fig.4.3.7 VARIATION OF EB WITH OIL CONTENT

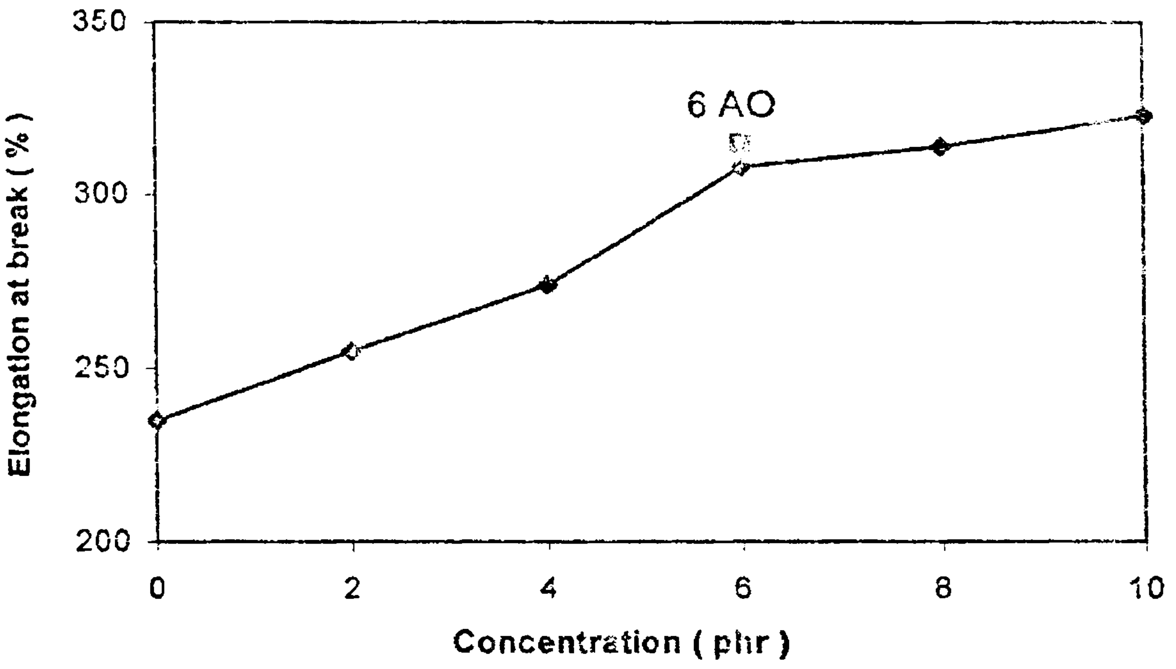


Table 4.3.1 Cure characteristics and tensile strength of aged and unaged samples

Sample composition	Scorch time (t_{10}) Min	Cure time (t_{90}) Min	Cure rate Nm/min.	Tensile strength (M.Pa)	
				Unaged	Air aged
6 phr aromatic oil	1.6	9.0	0.0565	19.50	13.01
0 phr plasticizer	2.3	8.1	0.0877	21.90	14.10
2 phr castor oil	2.1	7.5	0.0896	20.73	14.73
4 „	1.8	8.5	0.0792	21.02	13.47
6 „	2.0	9.0	0.0703	19.04	12.85
8 „	1.7	9.0	0.0688	18.91	13.30
10 „	2.1	9.4	0.0623	18.04	12.91

Table.4.3.2 Abrasion resistance, compression set,De Mattia flex resistance , heat build up and resilience of vulcanizates.

Sample composition	Abrasion loss (% volume)	Compression set. (%)	Flex resistance (Cycles)	Heat build up (^{0}F)	Resilience (%)
6 phr aromatic oil	1.8	42.5	94000	93	37
0 phr plasticizer	4.1	41.2	72000	97	41
2 phr castor oil	1,5	42.9	115000	94	39
4 „	1.7	46.2	195000	93	39
6 „	1.6	45.9	207000	94	38
8 „	1.6	49.2	222000	94	37
10 „	1.6	51.4	265000	94	38

4.4 Rubber seed oil as a multipurpose additive in SBR

SBR conforming to specifications given in chapter 2 is compounded as per formulation given in Table 4.1.1. Wherever rubber seed oil is used it is used as a substitute for aromatic oil and stearic acid. The properties of the compounds and vulcanizates with different loadings of oil are compared with that of the control mix with aromatic oil.

Results and discussion

Fig. 4.4.1 shows the flow behaviour of compounds with different loadings of rubber seed oil, obtained from the Brabender plasticorder as (torque/rpm) representing viscosity vs rpm representing shear rate. All the compounds are pseudoplastic. The flow curve of compound with 6 phr rubber seed oil is close to that of the control mix with 6 phr aromatic oil. This shows that rubber seed oil is comparatively more plasticizing in SBR, than the oils discussed earlier. This may be due to the presence of the hexabromide fatty acid (15.5% of the total fatty acids) in the oil. It may be concluded that the processability of SBR is not affected by substituting aromatic oil with rubber seed oil. Fig 4.4.2 shows the cure curves of the compounds with different loadings of rubber seed oil. As in the case of their flow curve, the cure curve of the compound with 6 phr rubber seed oil is close to that with 6 phr aromatic oil. The compound without plasticizer shows a higher viscosity and torque, compared to that with rubber seed oil or aromatic oil.

Table 4.4.1 compares the cure time and scorch time of compounds with different loadings of rubber seed oil with that of the control mix. It is to be noted that cure rate is not affected by substituting rubber seed oil for aromatic oil, and also on varying the concentration of the oil. This shows that the behaviour of rubber seed oil towards SBR is intermediate to the two general behaviours shown by vegetable oils. One in which the oil reduces the viscosity and cure time with increase in oil content (eg. linseed and soyabean in NBR) and the other in which the oil behaves in an opposite manner (eg. castor oil in NBR). This may be due to the presence of hexabromide fatty acids present in the oil. The compound without plasticizer shows a lower cure time compared to all other mixes.

Fig 4.4.3 shows the variation in tensile strength with concentration of rubber seed oil. When vulcanizates with conventional plasticisers show a gradual decrease in tensile strength with increase in plasticizer content, rubber seed oil show a different behaviour.

The tensile strength of vulcanizates increases up to concentrations of 4 phr and then start decreasing. The compounds with rubber seed oil possesses higher strength than those with the same loading of aromatic oil. It should be noted that the behaviour of rubber seed oil is different from that shown by other oils used earlier. When linseed oil and castor oil marginally lowered and soyabean oil did not affect the tensile strength, rubber seed oil shows a substantial increase. The increased tensile strength may be due to the increased covulcanization of the oil with the elastomer that may be influenced by the considerable amount of hexabromide fatty acid present in the oil. The variation in tensile strength can also be related to the variation in crosslink density and better filler incorporation. The decrease in cross link density with increase in oil concentration may be due to the factice formation (Fig 4.4.4). The vulcanizate without plasticizer shows a comparable tensile strength with that of the controll mix.

Fig 4.4.5 shows the variation of modulus with rubber seed oil content. As expected, modulus varies directly with crosslink density and inversely with elongation at break (Fig 4.4.6). But the difference in modulus of the mixes with equal loadings of rubber seed oil and aromatic oil is seen to be marginal.

The variation in tear resistance is similar to that of tensile strength and modulus and can be explained on similar lines. (Fig 4.4.7). The anti oxidant nature of rubber seed oil seems to have little effect on SBR . The tensile properties of the aged and unaged samples are given in Table 4.4.1. The compression set of vulcanizates with rubber seed oil is lower than that of the control mix, and the set varies inversely proportional to the oil content (Table 4.4.2). This decrease in compression set may be due to the higher covulcanization of the oil than factice formation.

Other major properties that may be of interest in the case of SBR are their abrasion resistance, De Mattia flex resistance, heat build up, and resilience. Abrasion loss is not considerably affected by rubber seed oil (Table 4.4.2). Flex resistance is highly improved when aromatic oil is replaced with rubber seed oil (Table 4.4.2). This increase in flex can be explained on a similar way to oils discussed earlier. The vulcanizate without plasticizer also shows a higher flex resistance compared to the controll mix and this is possibly due to the higher percentage of polysulphidic linkage in it (Table. 3.1.4.). Heat build up is slightly increased as can be seen from (Table 4.4.2). The rebound resilience of the vulcanizates is found to improve when aromatic oil is substituted by rubber seed oil (Table 4.4.2), along with reduction in blooming.

Conclusion

Rubber seed oil is an advantageous substitute for aromatic oil in styrene butadiene rubbers. It gives appreciable increase in properties like tensile strength, tear resistance, DeMattia flex resistance and rebound resilience to SBR vulcanizates. The compression set of vulcanizates are reduced, while cure rate and ageing resistance are increased. The optimum concentration of rubber seed oil is found to be 5-6 phr which can advantageously substitute 6 phr aromatic oil and 2 phr stearic acid in SBR vulcanizates.

FIG 4.4.1 FLOW CURVE

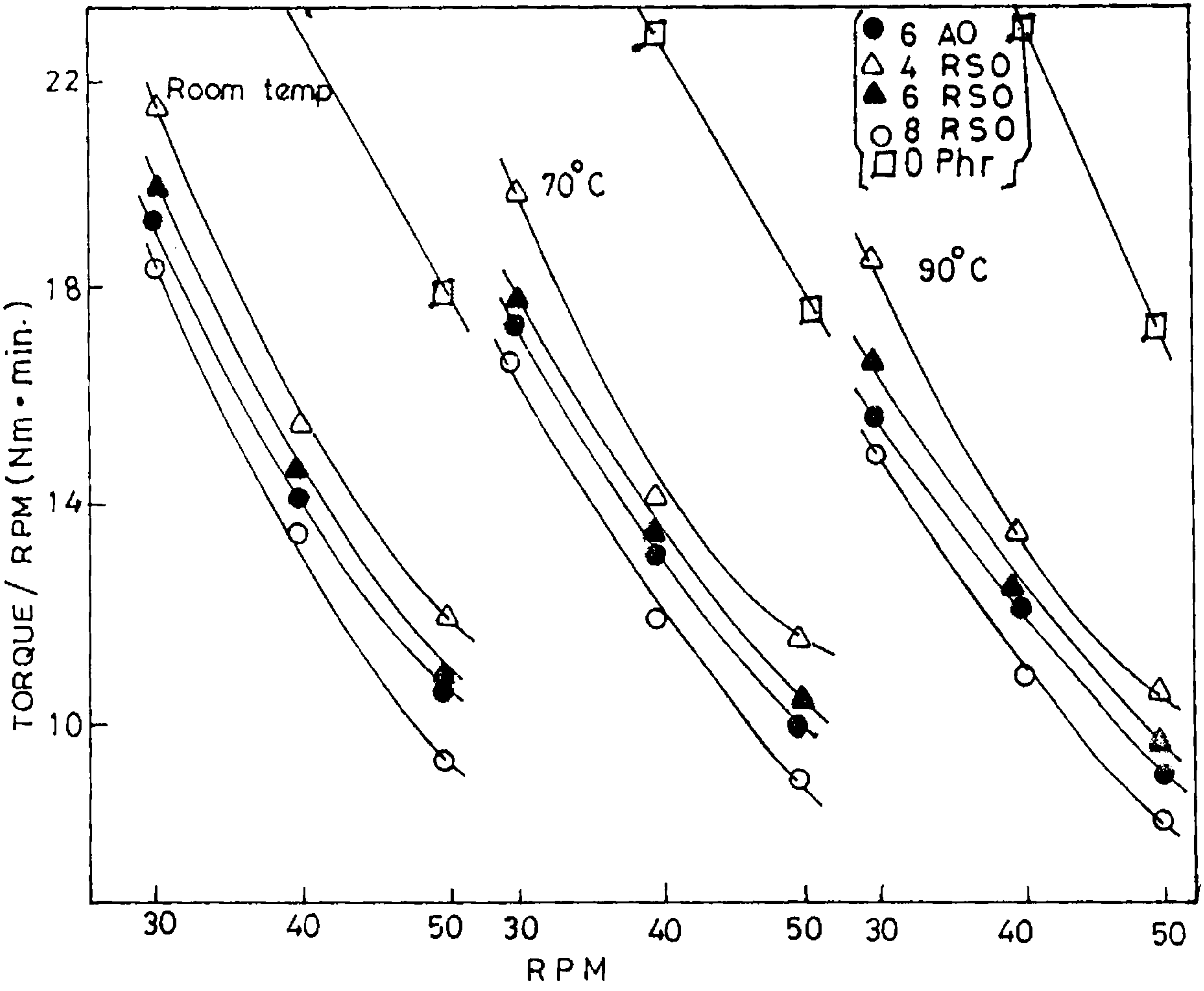


FIG 4.4.2 CURE CURVE

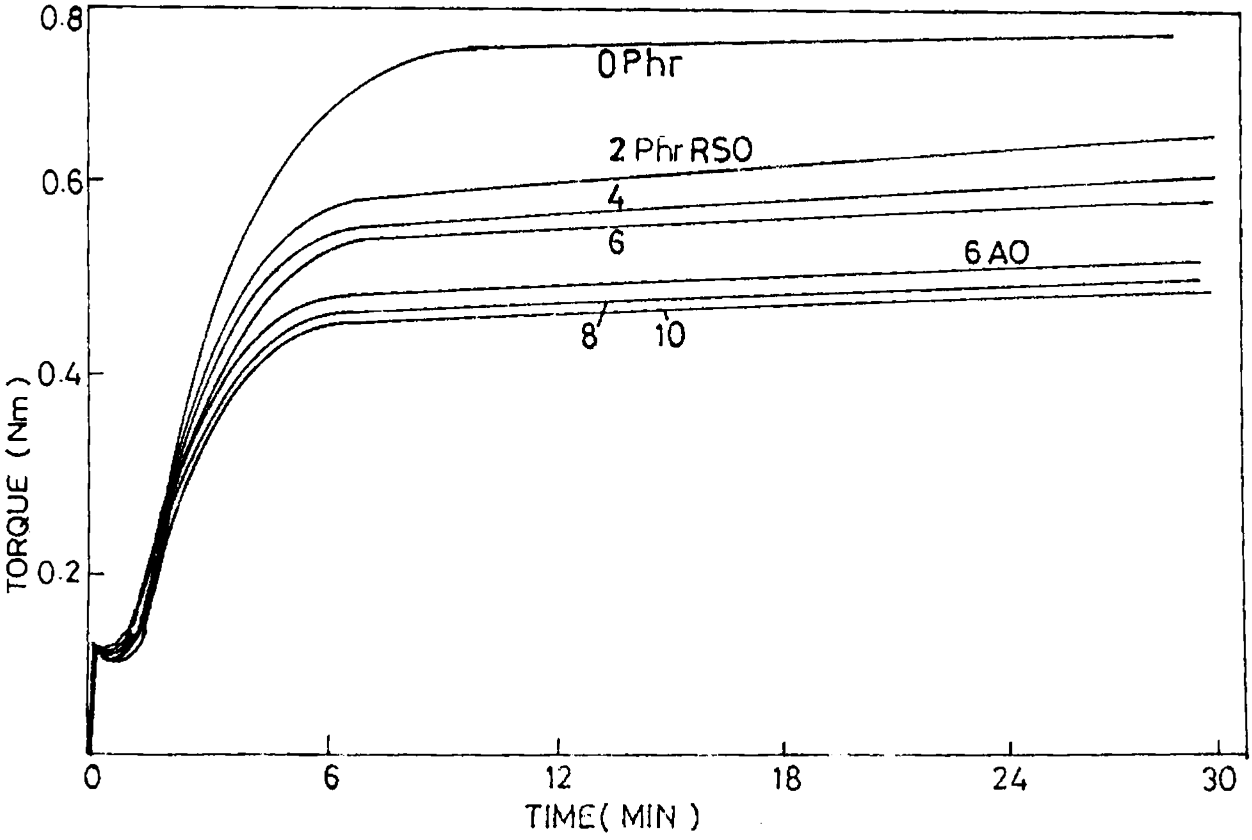


Fig.4.4.3 VARIATION OF TENSILE STRENGTH WITH DOP AND RUBBER SEED OIL

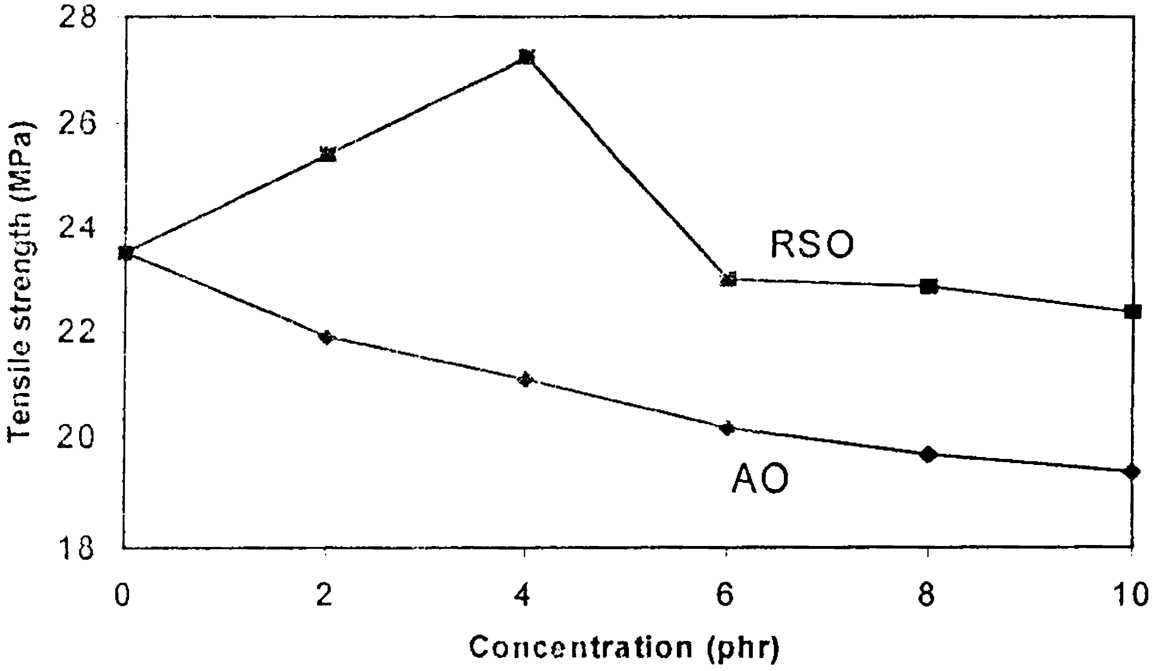


Fig.4.4.4 VARIATION OF CROSS LINK DENSITY WITH OIL CONTENT

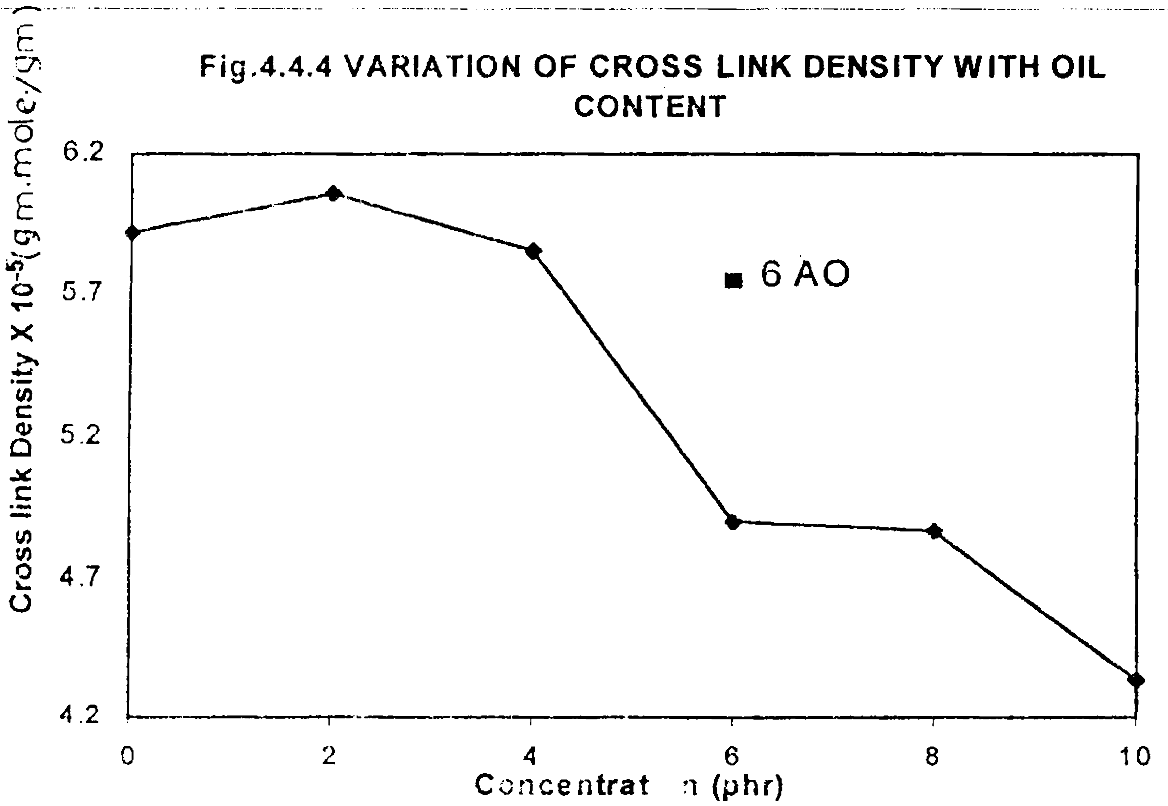


Fig.4.4.5 VARIATION OF MODULUS WITH OIL CONTENT

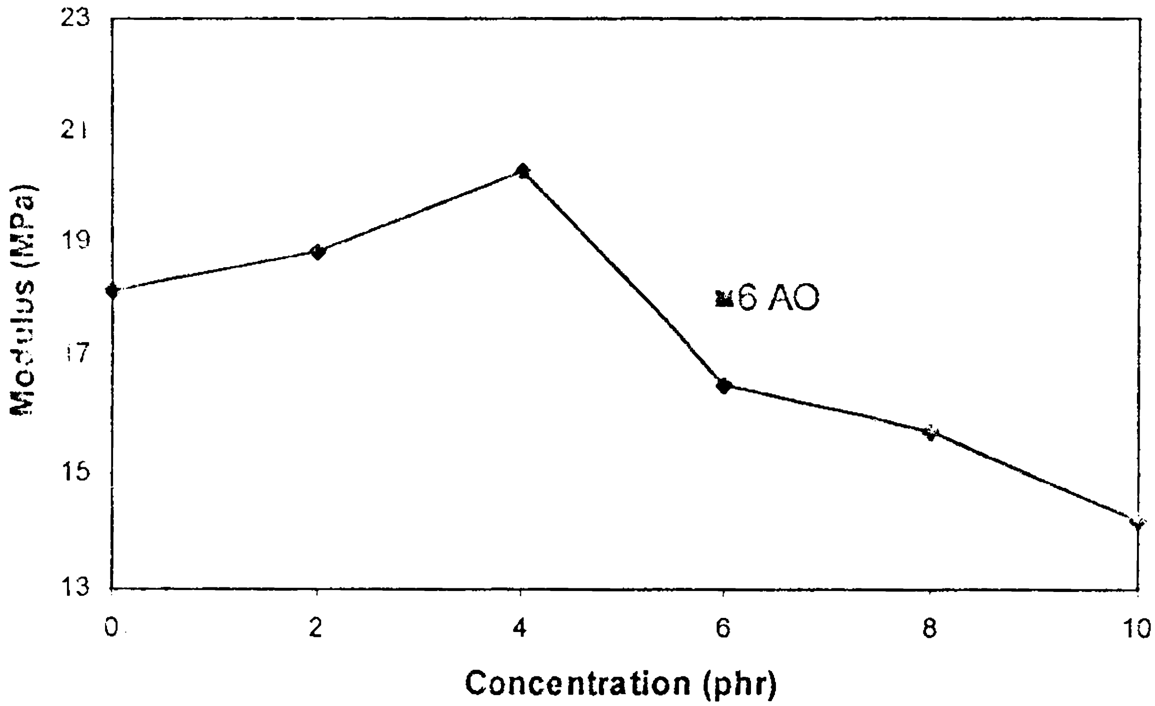


Fig. 4.4.6 VARIATION OF EB WITH OIL CONTENT

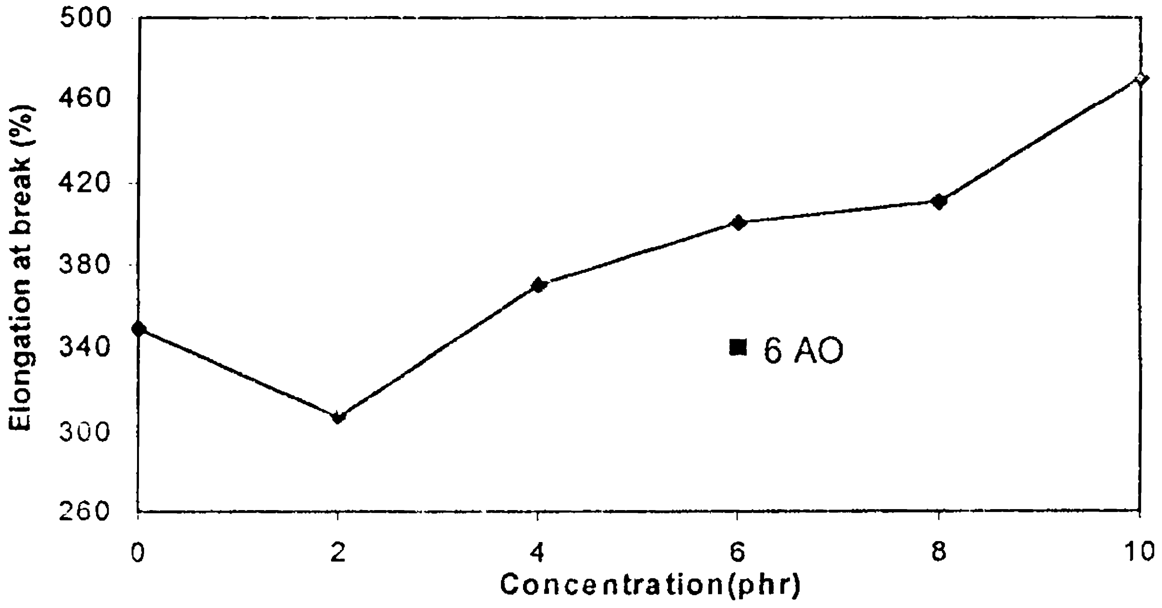


Fig.4.4.7 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT

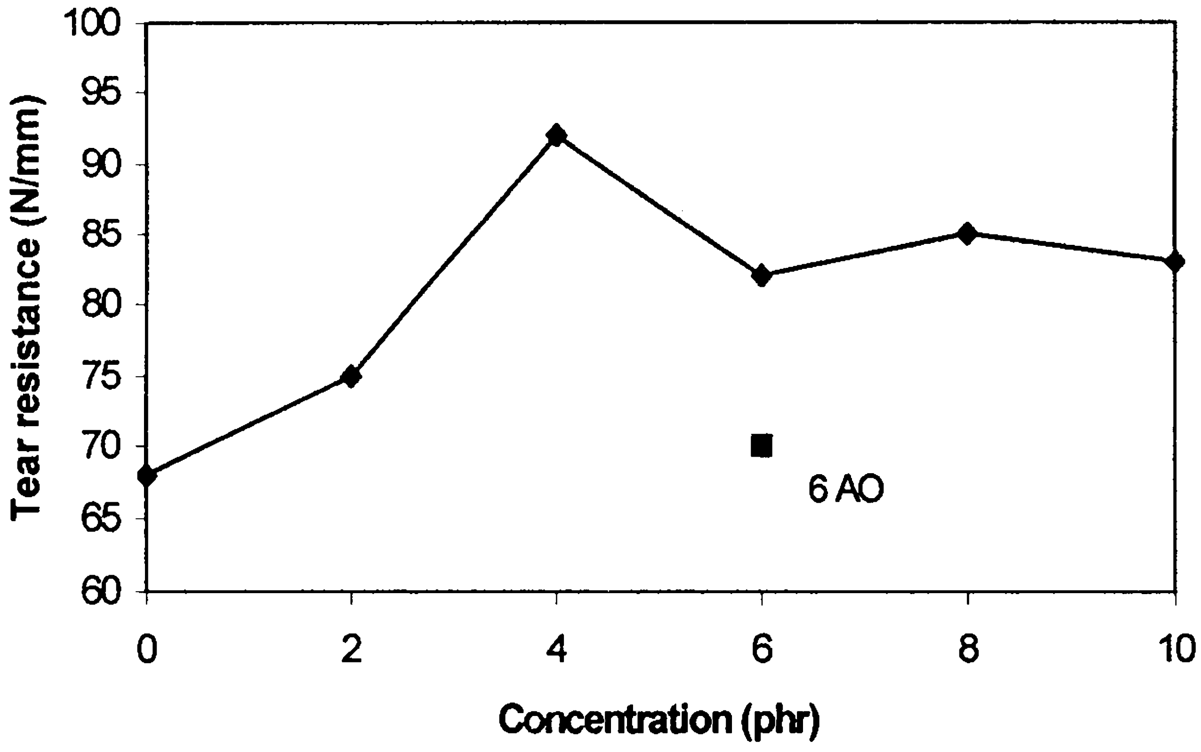


Table 4.4.1 Cure characteristics and tensile strength of aged and unaged samples

Sample composition	Scorch time (t_{10}) Min	Cure time (t_{90}) Min	Cure rate Nm/min.	Tensile strength (M.Pa)	
				Unaged	Air aged
6 phr aromatic oil	2.7	10.4	0.0617	21.80	15.00
0 phr plasticizer	2.3	8.10	0.0877	21.90	14.10
2 phr rubber seed oil	2.6	10.4	0.0603	25.40	17.90
4 „	2.7	10.6	0.0621	27.25	23.60
6 „	2.8	10.7	0.0594	26.20	21.80
8 „	2.6	10.6	0.0579	25.10	20.10
10 „	2.7	10.6	0.0522.	24.00	18.90

Table.4.4.2 Abrasion resistance, compression set,De Mattia flex resistance , heat build up and resilience of vulcanizates.

Sample composition	Abrasion loss (% loss in volume)	Compression set. (%)	Flex resistance (Cycles)	Heat build up (^{0}F)	Resilience (%)
6 phr aromatic oil	4.1	44.3	41000	92	40
0 phr plasticizer	4.1	41.2	72000	97	41
2 phr rubber seed oil	3.9	39.1	49000	96	45
4 ,,	4.0	37.3	56000	99	48
6 ,,	4.2	29.5	112000	100	45
8 ,,	4.0	27.2	116000	103	45
10 ,,	4.1	25.6	133000	105	43

4.5 Punnal oil as a multipurpose additive in SBR

Punnal oil (calophyllum inophyllum) is tried as multipurpose additive in styrene butadiene rubber. SBR is compounded according to formulations given in Table 4.1.1 Wherever punnal oil is used, it is used as a substitute for aromatic oil and stearic acid. The properties of the compounds and vulcanizates with different loadings of punnal oil were compared with that of the control mix with aromatic oil and that without any plasticizer.

Results and discussion

Fig. 4.5.1 shows the flow curves of the compounds with different loading of punnal oil, obtained form the Brabender plasticorder as (torque/rpm) representing viscosity vs rpm representing shear rate . All the compounds are pseudoplastic. It is seen that compounds with 6 phr punnal oil, and the control mix with the same loading of aromatic oil have almost similar viscosity, showing that punnal oil is comparable with aromatic oil in the plasticization of SBR . While linseed oil, soyabean oil and castor oil are less plasticizing in SBR due to the aromatic side chain present in the rubber molecule, the results shown by rubber seed oil and punnal oil may be clearly due to the difference in composition of these oils. As already mentioned in the previous section, rubber seed oil is different from other oils, having hexabromide fatty acids as a constituent and this may be the reason for its slightly better performance with SBR. In the case of punnal oil, the difference with other oils is in the content of non glyceride components. The oil is found to contain a considerable amount of heterocyclic aromatic polycyclic compounds, especially coumarine derivatives. The presence of these aromatic polycyclic compounds and also the lower unsaturation of the oil may be the reason for the comparatively better plasticizing action of this oil with SBR . The cure behaviour of the compound is also similar to their flow behaviour (Fig 4.5.2). The cure curves of compounds with 6 phr punnal oil coincides with the control mix with 6 phr aromatic oil. The mix without plasticizer shows a higher viscosity and torque compared to all other mixes.

Table 4.5.1 shows the cure time and scorch time of the compounds. It is seen that cure time gradually decreases with increase in oil content. It may be noted that cure time of compounds with lower concentrations (2-4 phr) of oils are higher than that of the control mix . This is not the case with highly plasticizing oils as seen in the case of such oils with NBR; where even at 2 phr level they give lower cure time than that of the control mix. So this difference in behaviour may be due to the lower percentage of unsaturated fatty acids in the oil, which are considered to be better co activators than stearic acid.

Fig. 4.5.3 shows the variation of tensile strength of vulcanizates with different loadings of punnal oil. The tensile strength of vulcanizates increases upto a concentration of 6 phr and then start decreasing. But vulcanizates with punnal oil always show a higher value of tensile strength, than those with the same loading of aromatic oil. This shows that the oil covulcanizes with the elastomer, along with better filler incorporation. The lowering in tensile strength with increase in oil content is seen to be marginal. This may be due to the lower factice formation, as is expected from the lower unsaturation in the oil . The vulcanizate without plasticizer also shows a higher tensile strength than the mix with aromatic oil.The variation in tear resistance (Fig 4.5.4) and modulus (Fig 4.5.5) are also similar to the variation in tensile strength, and is supported by the variation in crosslink density (Fig 4.5.6) The elongation at break is inversely proportional to the cross link density (Fig 4.5.7).The ageing resistance of the vulcanizate with punnal oil shows little improvement compared to the control mix. The tensile strength of aged and unaged samples are compared in Table 4.5.1.

The compression set of the vulcanizates (Table 4.5.2) and heat build up (Table .4.5.2) are unaffected by substitution of aromatic oil with punnal oil. But abrasion resistance (Table 4.5.2), De Mattia flex resistance (Table 4.5.2) and resilience (Table 4.5.2) showed improvements. The vulcanizate without plasticizer showed slight diadvantage in heat build up and resilience but a marginal increase in compression set. These variations can be explained on a similar way to oils discussed earlier.

Conclusion

Use of punnal oil imparts improvements in properties like, tensile strength, tear resistance abrasion resistance, DeMattia flex resistance and resilience to SBR vulcanizates. Processability of the compound is unaffected while cure rate is increased. 5-6 phr punnal oil is an optimum concentration that can advantageously substitute 6 phr aromatic oil and 2 phr stearic acid in SBR vulcanizates. Further punnal oil being very cheap, the cost of the compound can also be reduced.

FIG4.5.1 FLOW CURVE

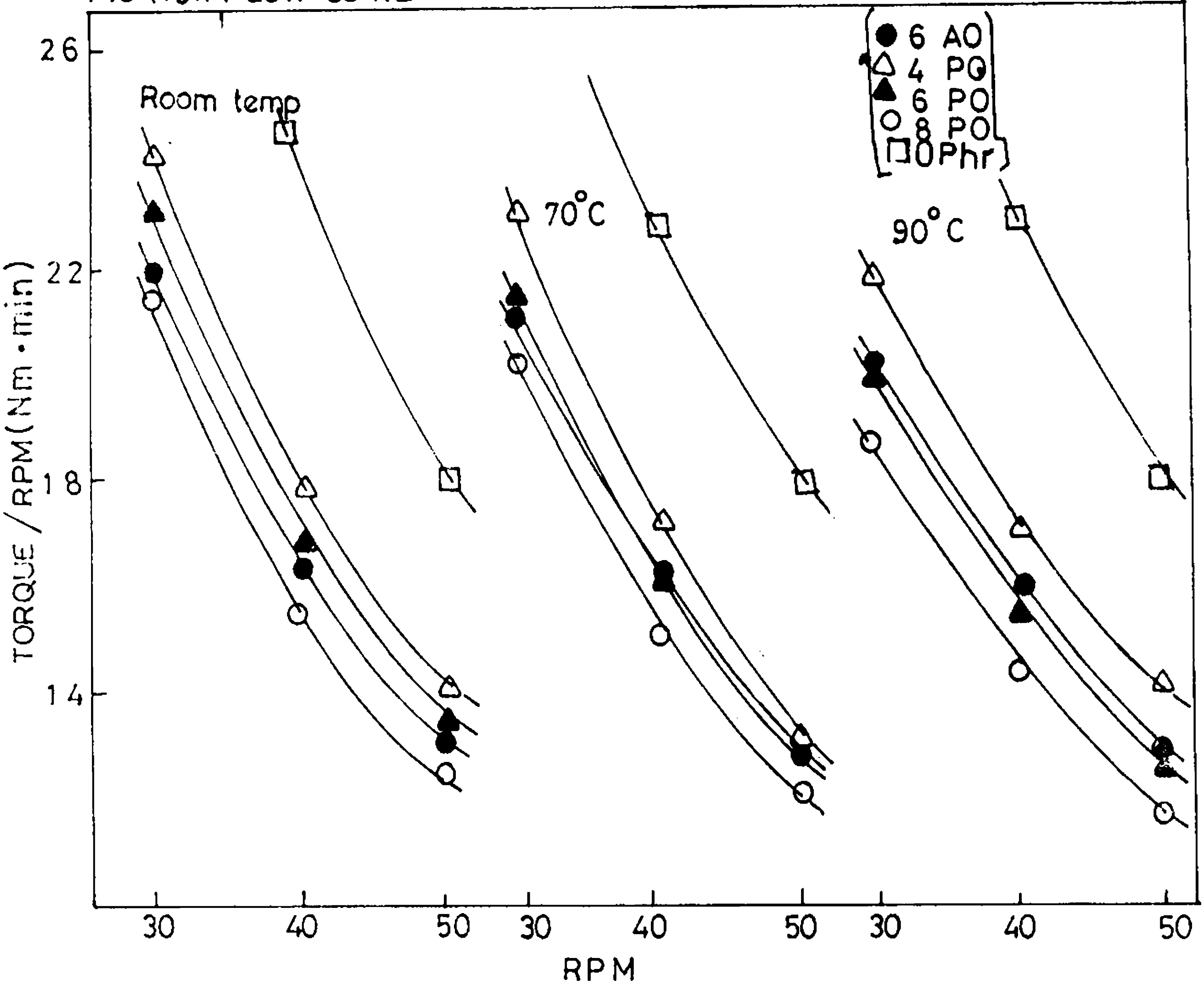


FIG4.5.2 CURE CURVE

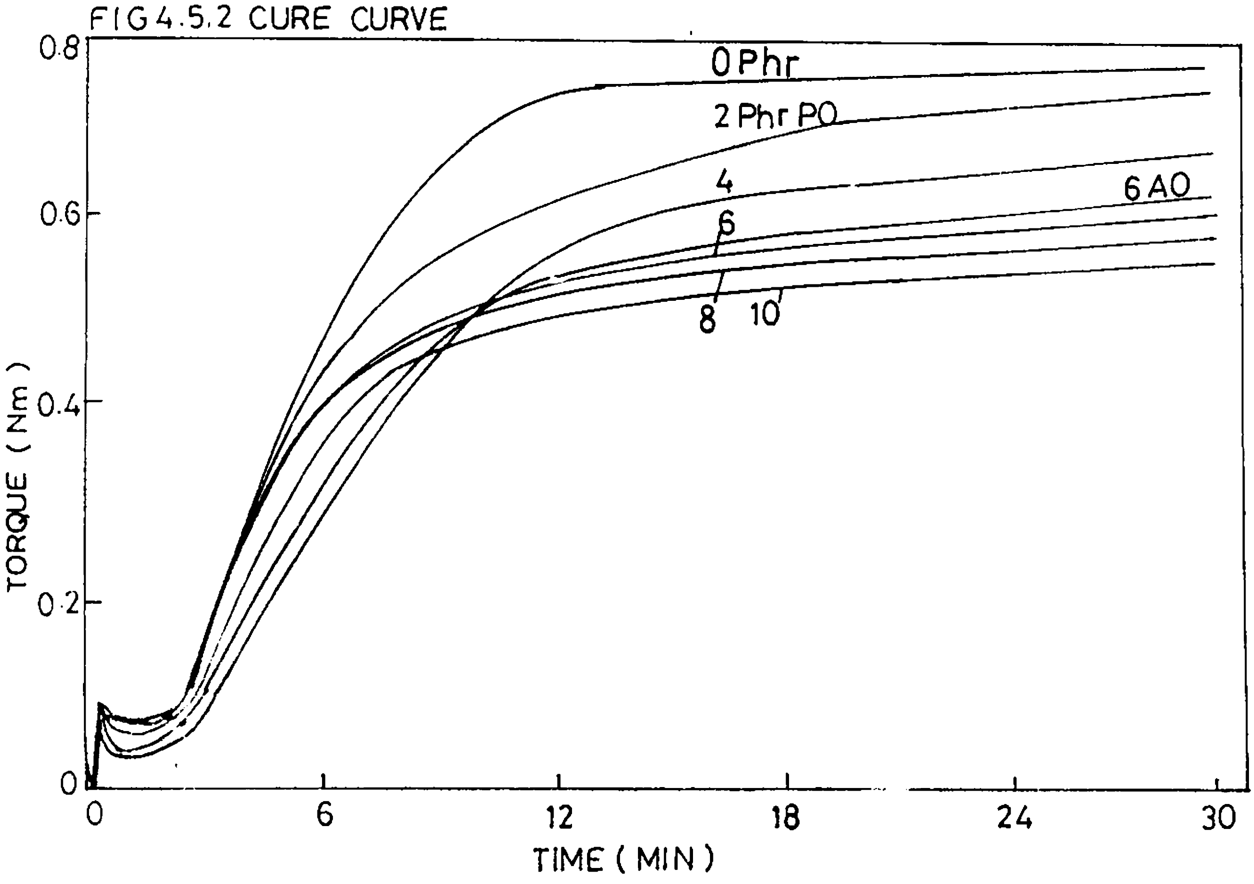


Fig.4.5.3 VARIATION OF TENSILE STRENGTH WITH DOP AND PUNNAL OIL

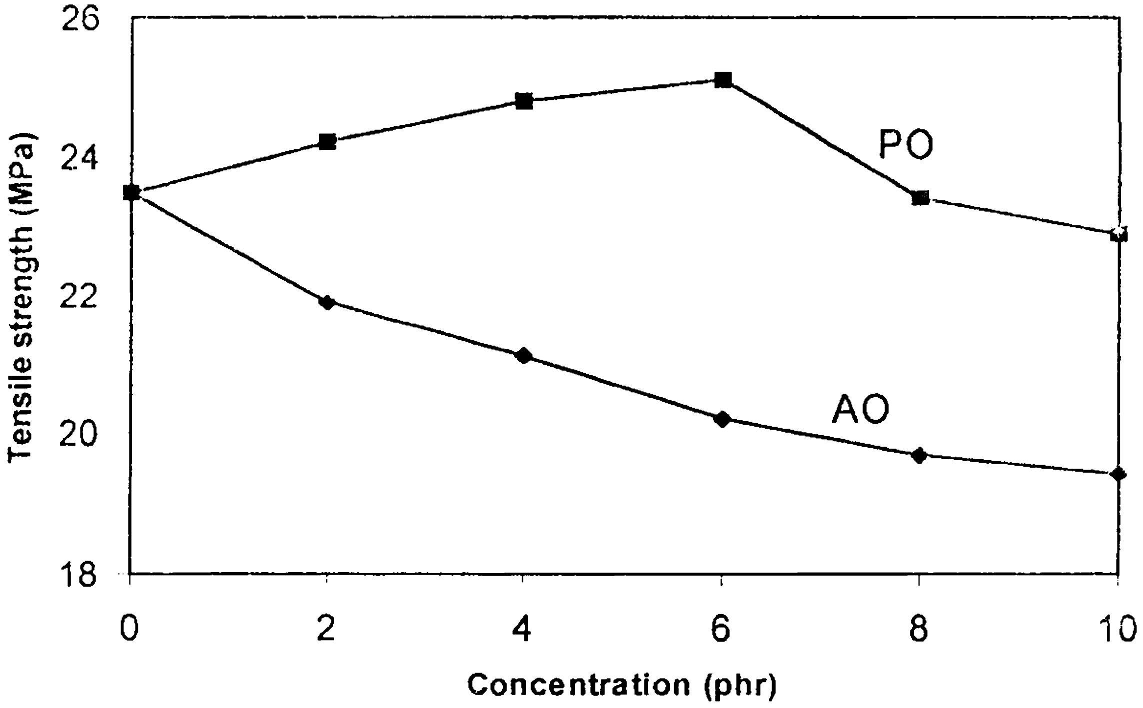


Fig.4.5.4 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT

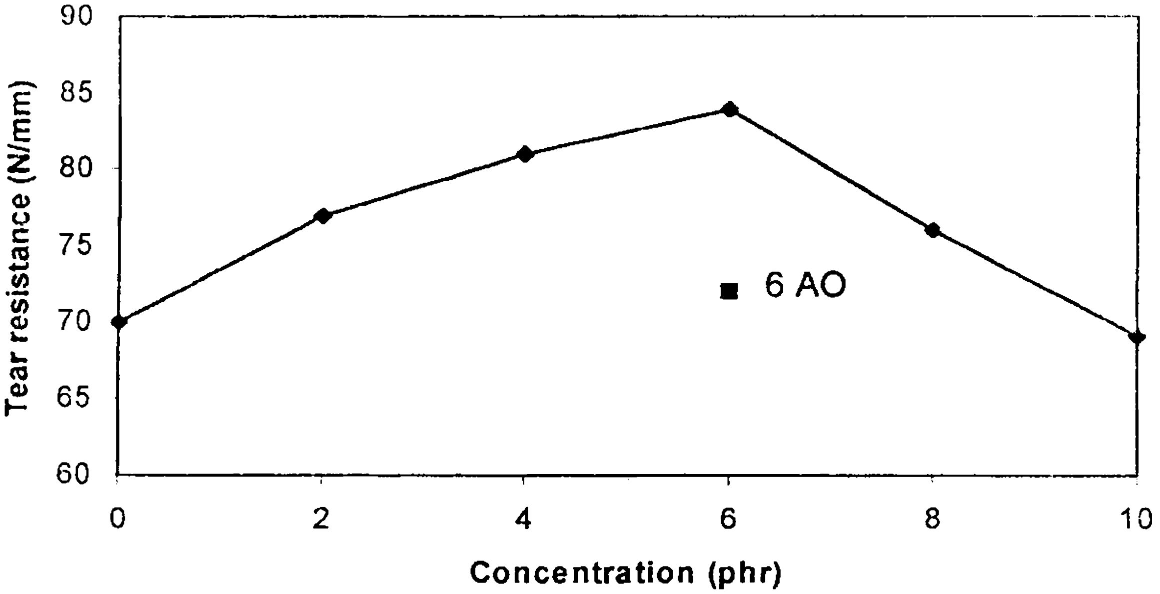


Fig 4.5.5 VARIATION OF MODULUS WITH OIL CONTENT

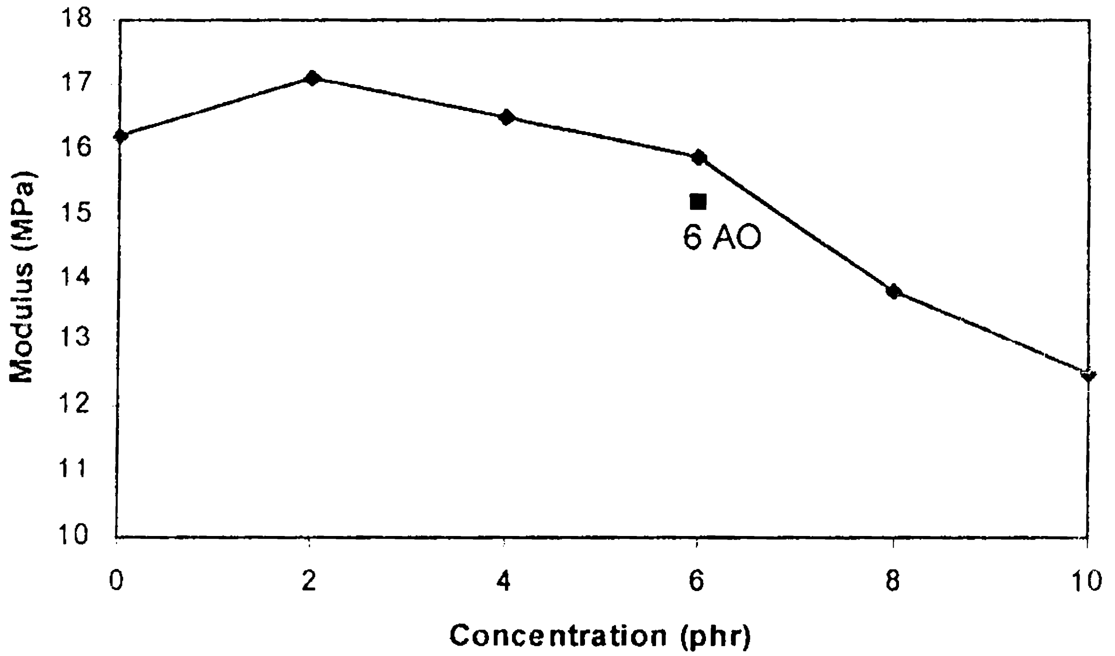
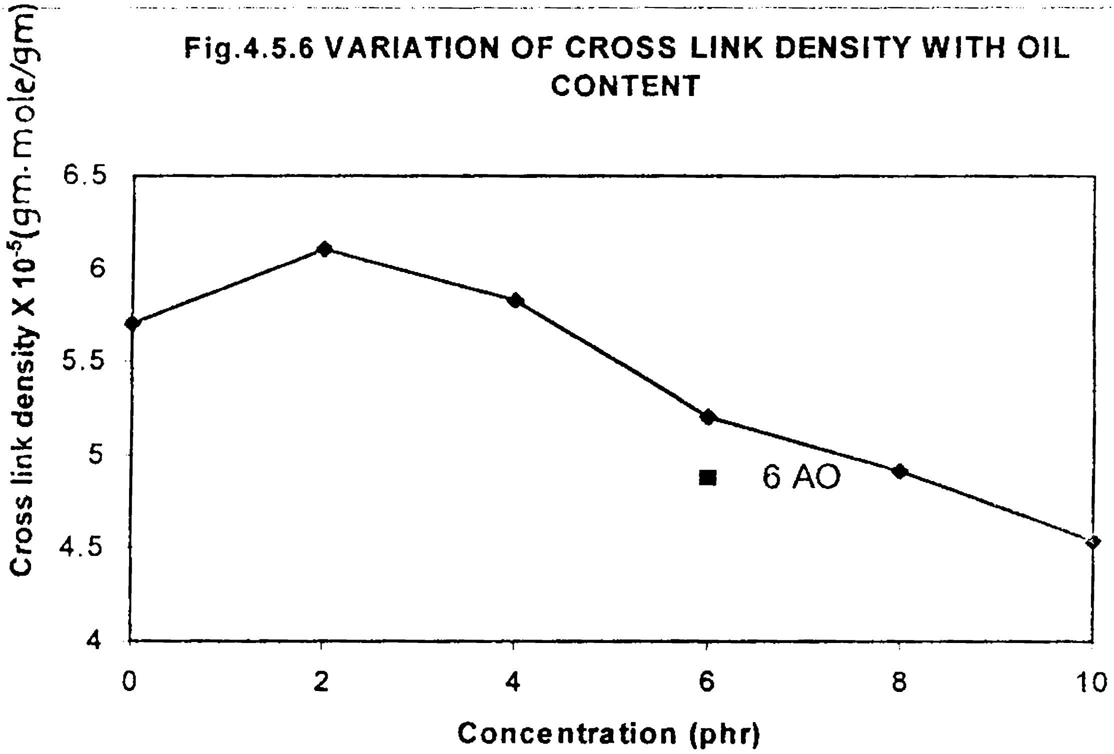


Fig.4.5.6 VARIATION OF CROSS LINK DENSITY WITH OIL CONTENT



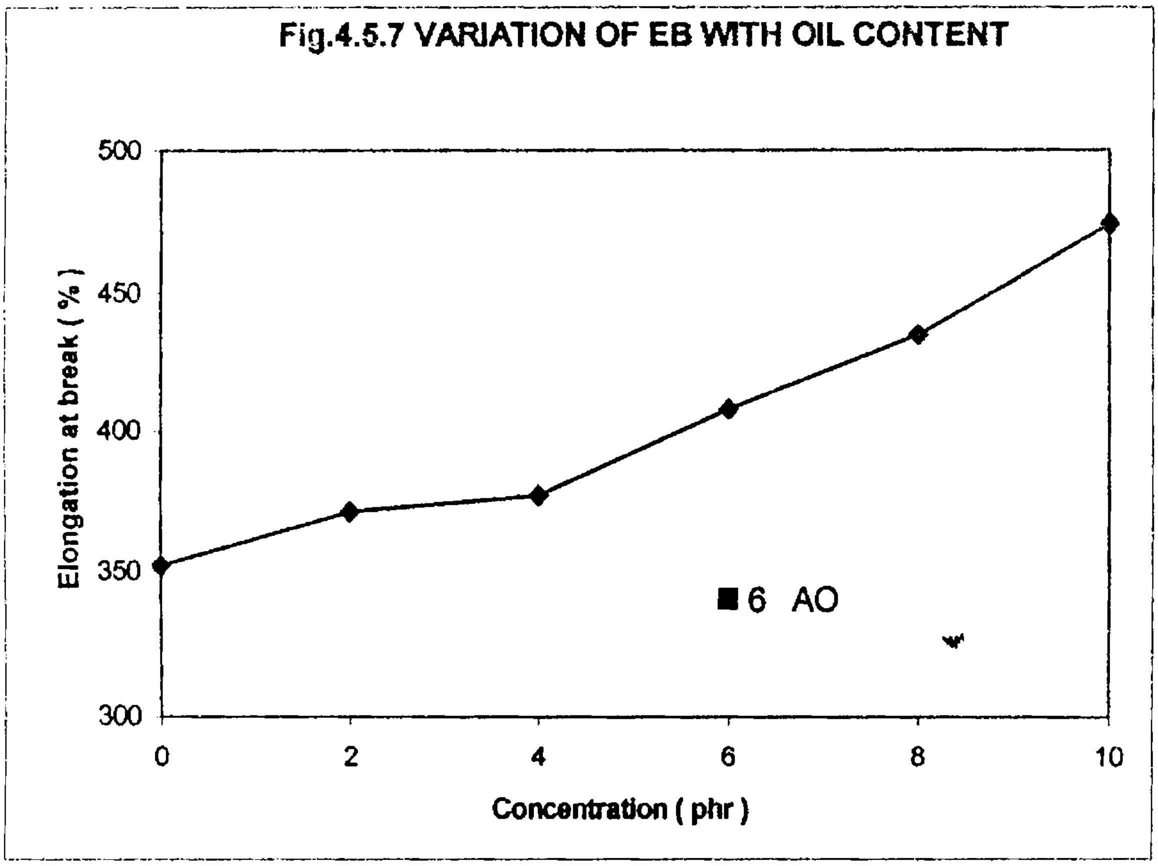


Table 4.5.1 Cure characteristics of the compounds and tensile strength of aged and unaged vulcanizates.

Sample composition	Scorch time (t_{10}) Min	Cure time (t_{90}) Min	Cure rate Nm/min.	Tensile strength (M.Pa)	
				Unaged	Air aged
6 phr aromatic oil	2.1	9.0	0.0769	20.20	14.10
0 phr plasticizer	2.3	8.1	0.0877	21.90	14.10
2 phr punnal oil	2.4	10.5	0.0658	24.20	18.40
4 ,,	2.2	9.2	0.075	24.80	19.20
6 ,,	2.3	7.5	0.0961	25.10	18.90
8 ,,	2.2	7.2	0.098	23.40	17.60
10 ,,	2.2	7.2	0.098	22.90	17.10

Table.4.5.2 Abrasion resistance, compression set,De Mattia flex resistance , heat build up and resilience of vulcanizates.

Sample composition	Abrasion loss (% loss in volume)	Compression set. (%)	Flex resistance (Cycles)	Heat build up (^{0}F)	Resilience (%)
6 phr aromatic oil	4.1	44.3	46000	92	39
0 phr plasticizer	4.1	41.2	72000	97	41
2 phr punnal oil	3.7	42.9	57000	94	42
4 ,,	3.6	45.1	76000	93	42
6 ,,	3.8	44.5	125000	93	43
8 ,,	3.9	45.3	192000	92	42
10 ,,	3.9	45.6	213000	92	42

CHAPTER V

STUDIES ON THE EFFECT OF VEGETABLE OILS ON THE CURE CHARACTERISTICS AND VULCANIZATE PROPERTIES OF NATURAL RUBBER (NR)

Natural rubber (NR) commonly obtained from the latex of hevea braziliensis, contain approximately 94% rubber hydrocarbons 3% protein and 3% other materials including fatty acids and resins. Purified natural rubber hydrocarbon is a long chain polymer made of cis 1,4- poly isoprenoid units and the average molecular weight ranges form 2-5 lakh (87). Natural rubber has high structural regularity and crystallizes on stretching. The strain-induced crystallization gives it the unique high tensile strength in gum vulcanizates. The superior building tack green strength, high resilience and excellent dynamic properties make it, the preferred polymer in many areas.

Products of desired properties are prepared by compounding the rubber with selected ingredients. They are usually processing aids, vulcanizing agents, accelerators, activators, age resisters, fillers and miscellaneous ingredients like retarders, blowing agents, antiabrasives, colourants etc.

Process aids will be considered as those materials included in a rubber mix primarily to reduce the time and energy required in processing. At the same time they help the dispersion of dry materials, give smoother stocks, improve extrusion rates and in some instances increase the homogenity of blended rubbers.

The most widely used processing oils are aromatic and naphthenic oils. But as already mentioned in previous chapters industry are in search for better substitute for them. Vegetable oils are triesters of glycerol with long chain fatty acids. Many of their properties including boiling point, viscosity and non staining nature make them suitable as process aids. The combined fatty acid or free fatty acid in them are better substitute for stearic acid, as co activator; Raw vegetable oils generally contains phenolic compounds like tocopherols, which can function as antioxidants. So vegetable oils can be tried as a multipurpose additive in rubber. In the present study vegetable oils like, linseed, soyabean castor, rubber seed, and punnal oil are tried as multipurpose ingredient in natural rubber.

5.1 Linseed oil as a multipurpose additive in natural rubber

Natural rubber is compounded as per formulation given in Table 5.1.1. Wherever linseed oil is used it is used as a substitute for aromatic oil and stearic acid. The results reported are the average of at least five specimens. The properties of the compound and vulcanizate are compared with that of the controll mix with aromatic oil and that of the mix without any plasticizer.

Results and discussion

Fig 5.1.1 shows the flow behaviour of compounds with different loadings of linseed oil obtained from the Brabender as (torque/rpm) representing viscosity vs rpm representing shear rate. All the compounds were psuedoplastic. It is seen that incorporating linseed oil in place of aromatic oil considerably reduces the viscosity of the compounds.The flow curves of compounds with 2 phr linseed oil is very close to that of the control mix with 6 phr aromatic oil. This shows that linseed oil is highly plasticizing in NR. It may also be noted that only very little variation in viscosity is shown by compounds with different loadings of oil. This high reduction in viscosity shows that linseed oil considerably reduces the rubber-rubber interaction The cure behaviour of the compounds are also similar to their flow behaviour (Fig 4.1.2). The cure curves of compound with 2 phr linseed oil is very close to that of the control mix with 6 phr aromatic oil. The compound without plasticizer shows a higher viscosity and torque compared to all other mixes with aromatic oil or linseed oil. The cure rate is highly enhanced by substituting linseed oil for aromatic oil and stearic acid (Table 5.1.2). Compound with 6 phr linseed oil is found to have cure time 30% less than that of the control mix with the same loading of aromatic oil. This reduction in cure time is explained by the activation of the rubber molecule by reduction in their intermolecular force by the oil. This view is again supported by the lowest cure rate shown by the compound without plasticizer.

Fig 5.1.3 shows the variation of tensile strength of vulcanizates with different loadings of linseed oil. It is to be noted that the change in concentration of the oil does not affect the tensile strength of vulcanizates. It may also be noted that all the vulcanizates with 2 to 10 phr oil, have almost similar tensile strength with that of the control mix containing 6 phr aromatic oil and also with that of the mix without plasticizer.

This behaviour of linseed oil in natural rubber is different from its behaviour with NBR and SBR. So before going into the reasons for this behaviour let us look into the variation in modulus (Fig 5.1.4) and cross link density (Fig 5.1.5) of the vulcanizates. The modulus and crosslink densities of vulcanizates with linseed oil show considerably higher value than that of the control mix. As shown generally by oils that reduces the viscosity of the mix, the values gradually decreases with increase in oil content. Though the variation in modulus and cross link densities is explained on the basis of their mutual dependence, their variations are not reflected on the tensile strength as expected. In this situation, also considering the very high plasticizing action of the oil, it is presumed that the expected increase in tensile strength due to the covulcanization of the oil is nullified by the plasticiser effect on tensile strengths. And also it is to be assumed that, the values of crosslink densities of all the vulcanizates are above the upper limit above which it has little effect on tensile strength.

The variation of elongation at break is as expected and is inversely proportional to the variation in cross-link density (Fig 5.1.6). The tear resistance of the vulcanizates also shows little variation, similar to tensile strength and is explained on a similar line (Fig 5.1.7).

The ageing resistance of the vulcanizates is improved by substituting linseed oil for aromatic oil. Tensile strengths of aged and unaged samples are given in Table 5.1.2 This improved ageing resistance may be due to the presence of unsaturated fatty acid which protect the elastomer from oxidation. The vulcanizate without plasticizer is seen to be poor in ageing resistance similar to the controll mix with aromatic oil. The abrasion resistance of the vulcanizates with linseed oil showed little variation with that of the control mix (Table 5.1.2). But the compression set is seen to be improved as can be seen from Table 5.1.2. The De Mattia flex resistance is improved considerably (Table

5.1.2) and the resilience marginally improved (Table 5.1.2), while heat build up is not affected (Table 5.1.2). The increase in flex resistance can be explained on a similar way to SBR discussed in the previous section. The vulcanizate without plasticizer shows a higher value for its heat build up, and a comparable value for flex resistance with that of the control mix.

Conclusion

Linseed oil is a very good multipurpose additive in natural rubber. It gives better processability for the compound with reduced cure time. Though tensile strength , tear resistance, abrasion resistance and heat build up showed no variation Other vulcanizate properties like ageing resistance, compression set, De Mattia flex resistance, and resilience are improved. 2-4 phr linseed oil is an optimum concentration which can advantageously substitute 6 phr aromatic oil and 2 phr stearic acid in natural rubber vulcanizates. Further the use of the toxic aromatic oil can be avoided. Though processing is difficult, vulcanizate without plasticizer showed disadvantage only in ageing resistance and heat build up.

FIG 5.1.1 FLOW CURVE

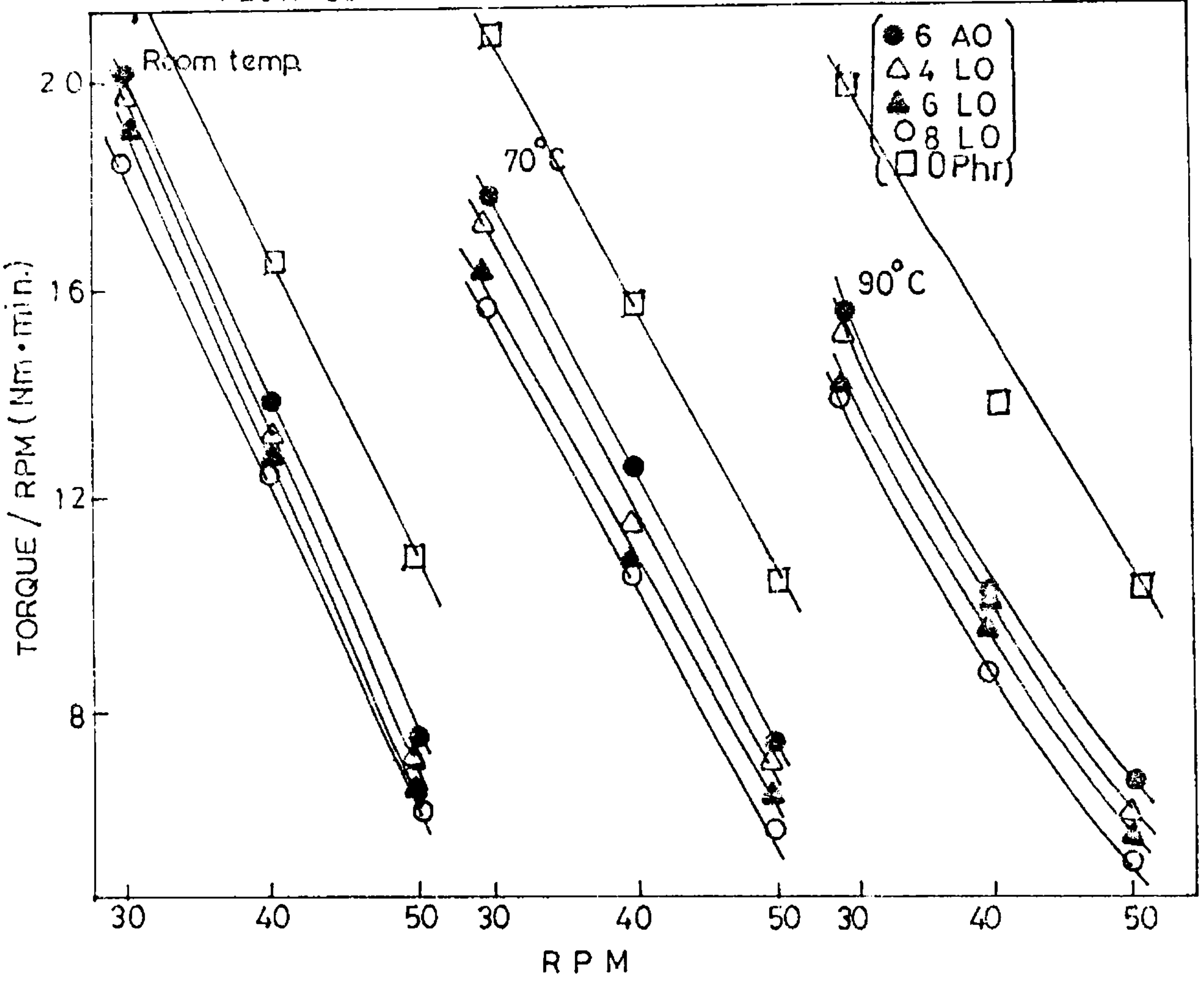


FIG 5.1.2 CURE CURVE

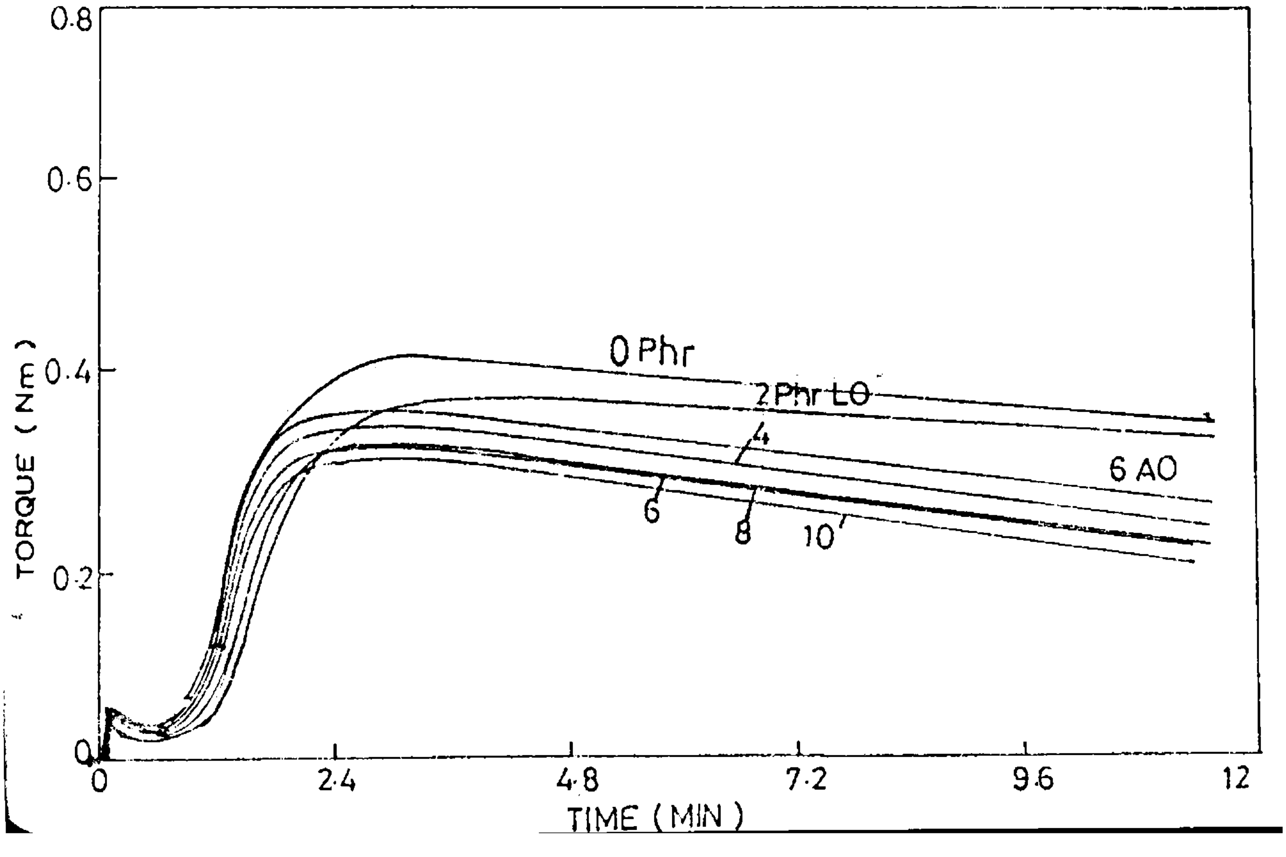


Fig.5.1.3 VARIATION OF TENSILE STRENGTH WITH AO AND LINSEED OIL

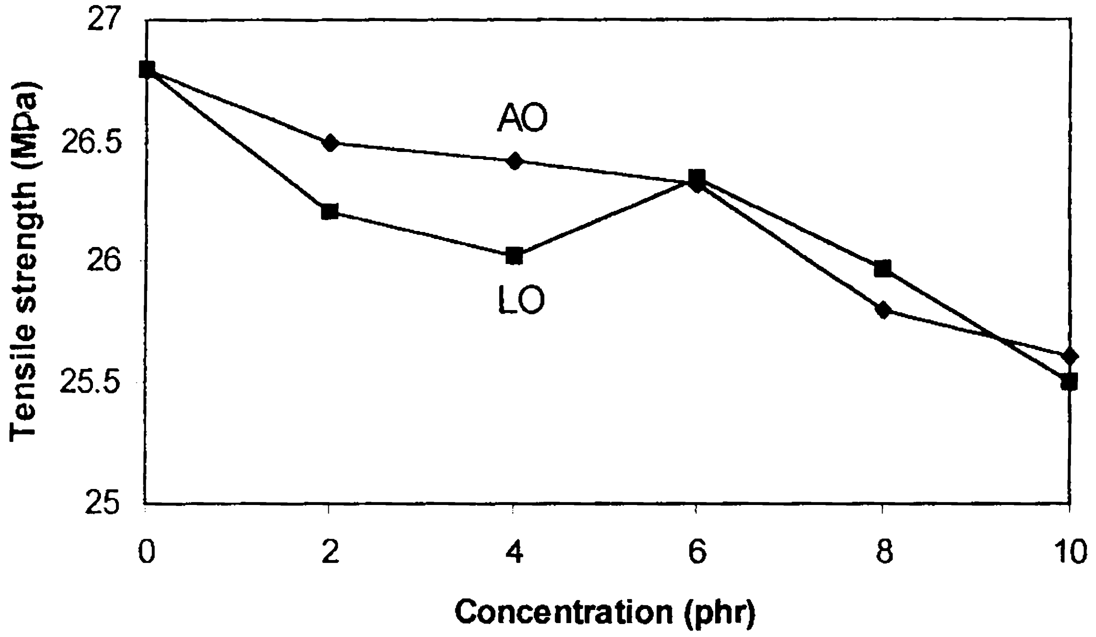


Fig.5.1.4 VARIATION OF MODULUS WITH OIL CONTENT

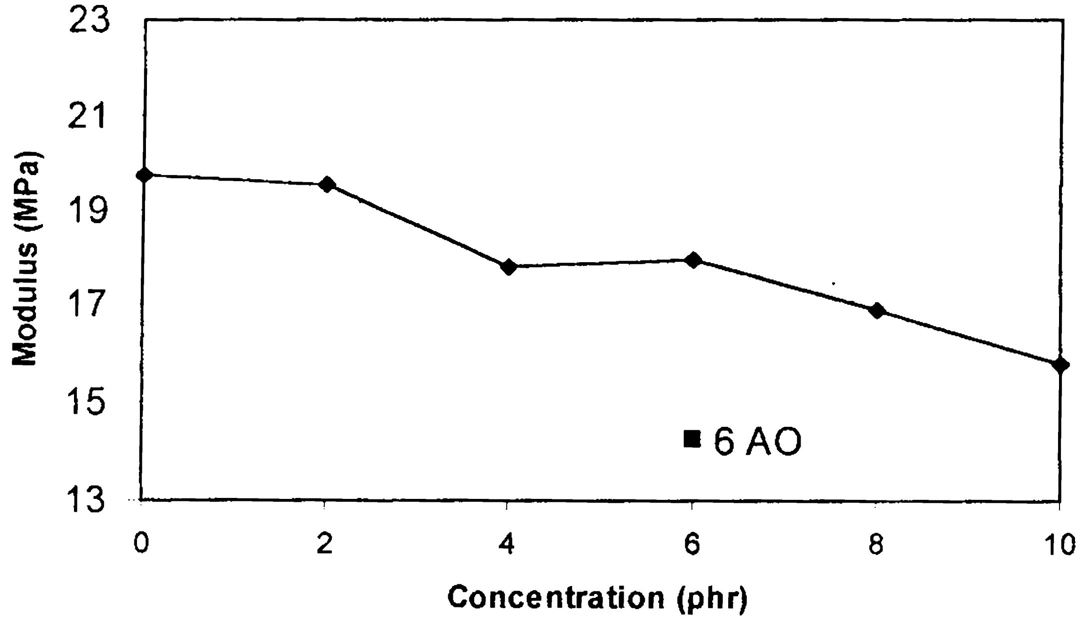


Fig.5.1.5 VARIATION OF CROSS LINK DENSITY WITH OIL CONTENT

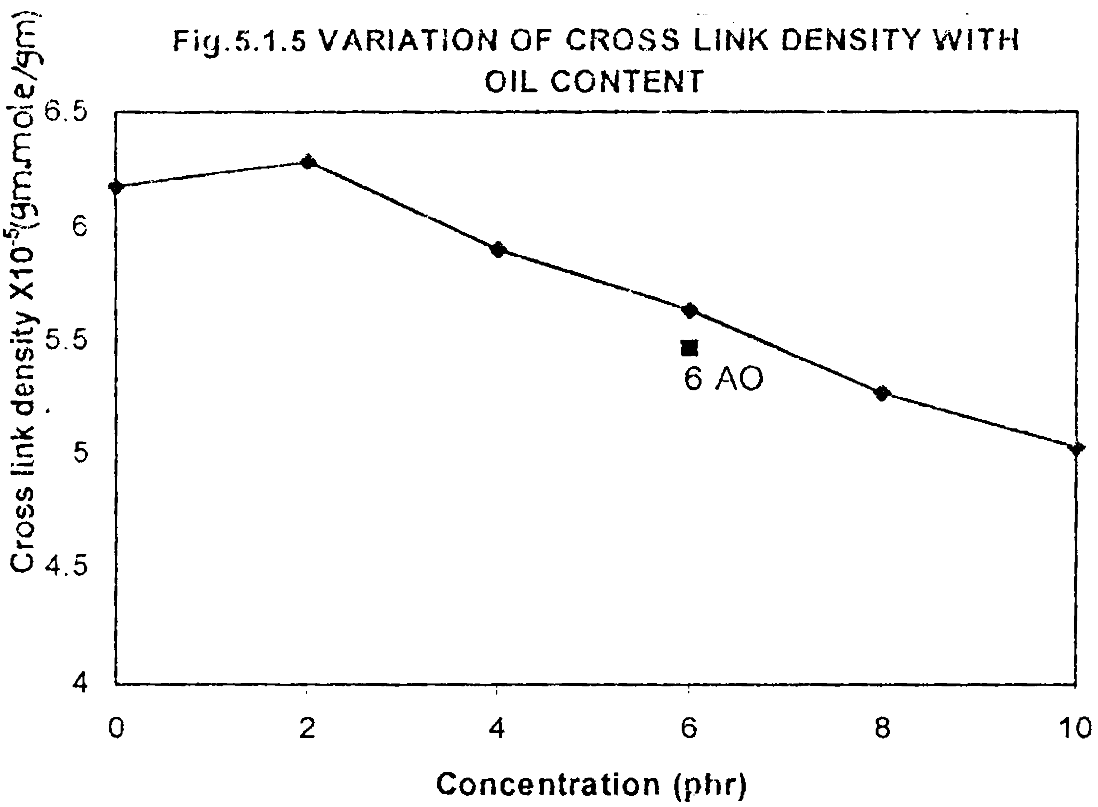


Fig.5.1.6 VARIATION OF EB WITH OIL CONTENT

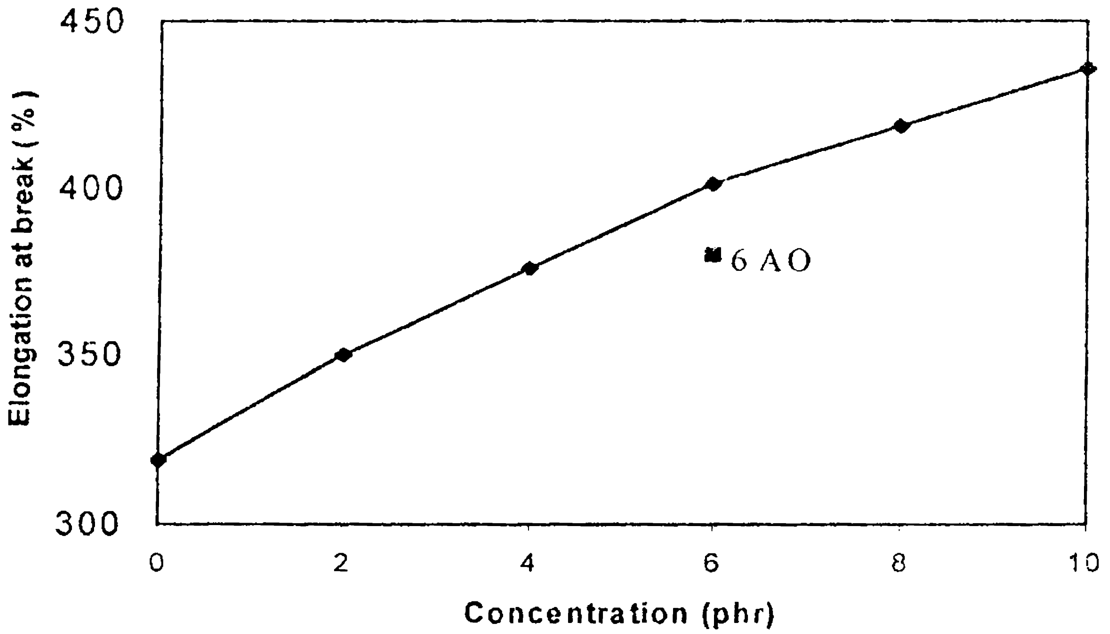


Fig.5.1.7 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT

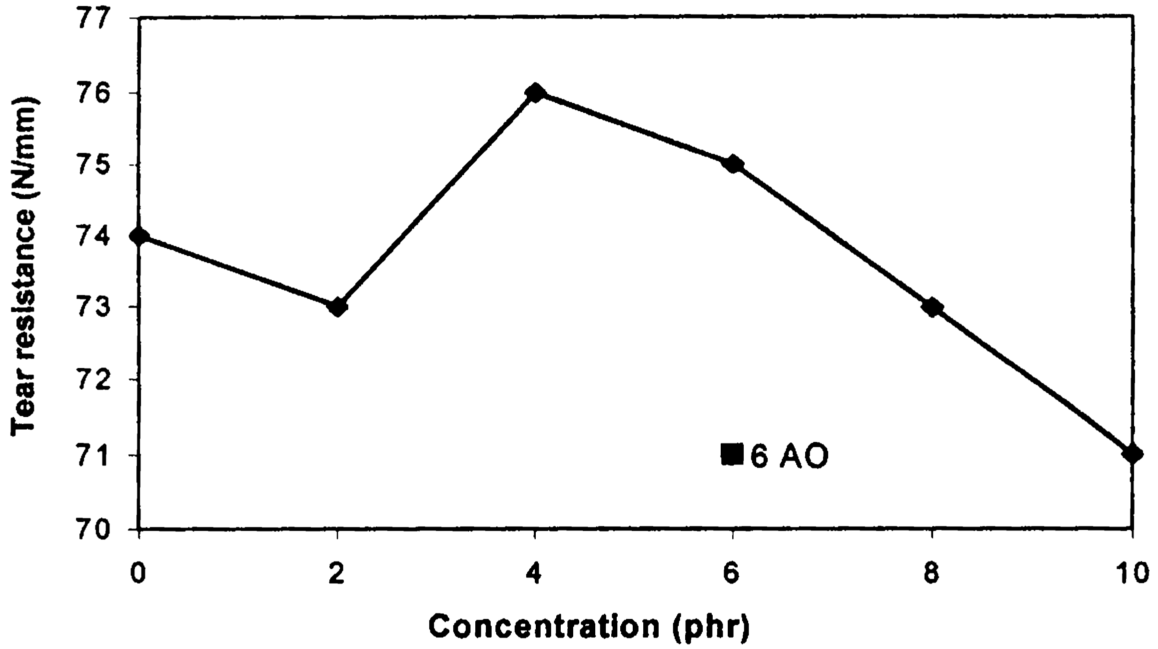


Table 5.1 Formulation

NR	100 phr.
HAF	50 „
Zinc oxide	5 „
Stearic acid	2 „
MBTS	1 „
TMTD	0.2 „
Sulphur	1.5 „
Vulcanox HS	1 „
Vulcanox 4020	0.5 „
Aromatic oil	6 phr

Table 5.1.2 Cure characteristics of the compounds and tensile strength of aged and unaged vulcanizates.

Sample composition	Scorch time (t_{10}) Min	Cure time (t_{90}) Min	Cure rate Nm/min.	Tensile strength (M.Pa)	
				Unaged	Air aged
6 phr aromatic oil	1.64	3.04	0.2553	26.32	12.33
0 phr plasticizer	1.60	3.40	0.1725	26.30	12.40
2 phr linseed oil	1.28	2.20	0.3583	26.20	17.55
4 „	1.32	2.20	0.3695	26.02	15.33
6 „	1.32	2.20	0.3390	26.34	17.43
8 „	1.32	2.16	0.3667	25.97	14.06
10 „	1.32	2.16	0.3621	25.50	14.53

Table.5.1.3 Abrasion resistance, compression set, De Mattia flex resistance , heat build up and resilience of vulcanizates.

Sample composition	Abrasion loss (% volume)	Compression set. (%)	Flex resistance (cycles)	Heat build up (^{0}F)	Resilience (%)
6 phr aromatic oil	2.7	28.8	120000	77	37
0 phr plasticizer	2.9	27.5	118000	81	40
2 phr linseed oil	3.0	23.8	142000	79	41
4 „	2.9	20.5	175000	78	40
6 „	2.9	23.4	235000	79	40
8 „	2.9	21.2	365000	77	39
10 „	2.8	23.1	430000	80	40

5.2 Soyabean oil as a multipurpose additive in natural rubber

NR is compounded as per formulation given in Table 5.1.1. Whenever linseed oil is used it is used as a substitute for aromatic oil and stearic acid. The properties of the compound and vulcanziates were compared with that of the control mix with aromatic oil and the mix without plasticizer.

Fig 5.2.1 shows the flow behaviour compounds obtained from the Brabender plasticorder as (torque/rpm) representing viscosity vs rpm representing shear rate. All the compounds are pseudo plastic. It is to be noted that, viscosities of the compounds with varying amounts of soyabean oil are only marginally separated from that of the control mix showing that even small amounts of oil (2-4phr) is enough to give a comparable viscosity with that shown by 6 phr aromatic oil. The cure curves of the compounds also show a similar behaviour (Fig 5.2.2). Compounds with 2-6 phr oil, and the control mix are having a comparable torque; but compounds with soyabean oil always showing a higher cure rate as can be seen from Table 5.2.1. It may also be noted that variation in oil content has little effect on the cure time, as shown by linseed oil. This shows that soyabean oil is comparable to linseed oil in its plasticizing action towards NR. The mix without plasticizer shows higher viscosity,.higher torque and lower cure rate compared to all other mixes.

Fig 5.2.3 shows the variation of tensile strength with concentration of soyabean oil and aromatic oil. When vulcanizates with aromatic oil shows a gradual but marginal decrease with increase in concentration of aromatic oil, almost very little variation is shown by compounds with soyabean oil. The tensile strength of vulcanizates with 2-10 phr soyabean oil have almost the same value as that of the control mix with 6 phr aromatic oil. But as in the case of linseed oil, it should be noted that, there is difference in the values of modulus (Fig 5.2.4) and cross link density (Fig 5.2.5). At an oil concentration of 2-4 phr level, their values are higher than that of the control mix with 6 phr aromatic oil and as the concentration of the oil further increases a marginal decease in their values is seen. This shows that the behaviour of soyabean oil towards NR is similar to that shown by linseed oil and can be explained similar to linseed oil. The vulcanizate without plasticizer shows a slightly higher tensile strength than any of the other mixes. The variation of tear resistance is similar to tensile strength and is explained on a similar line (Fig 5.2.6). The elongation at break is as expected and gradually increases with oil content (Fig 5.2.7)

The ageing resistance of the vulcanizates are improved and varies directly with oil content (Table 5.2.1). But the vulcanizate without plasticizer showed a poor ageing resistance when comparable with that of the control mix with aromatic oil. The abrasion resistance (Table 5.2.2), resilience (Table 5.2.2) and De Mattia flex resistance (Table 5.2.2) are improved , while heat build up (Table 5.2.2) is unaffected. But there is a slight disadvantage in compression set (Table 5.2.2). The vulcanizate without plasticizer shows slightly higher compression set and heat build up along with a marginally lower flex resistance.

Conclusion

Substitution of aromatic oil with soyabean oil reduces the viscosity of NR compounds with increased cure rate. The vulcanizate properties like ageing resistance, abrasion resistance, resilience and De Mattia flex resistance are improved, while tensile strength, tear resistance and heat build up are unaffected. 2-4 phr soyabean oil is an optimum concentration which can advantageously substitute 6 phr aromatic oil and 2 phr stearic acid in NR vulcanizates.

FIG 5.2.1 FLOW CURVE

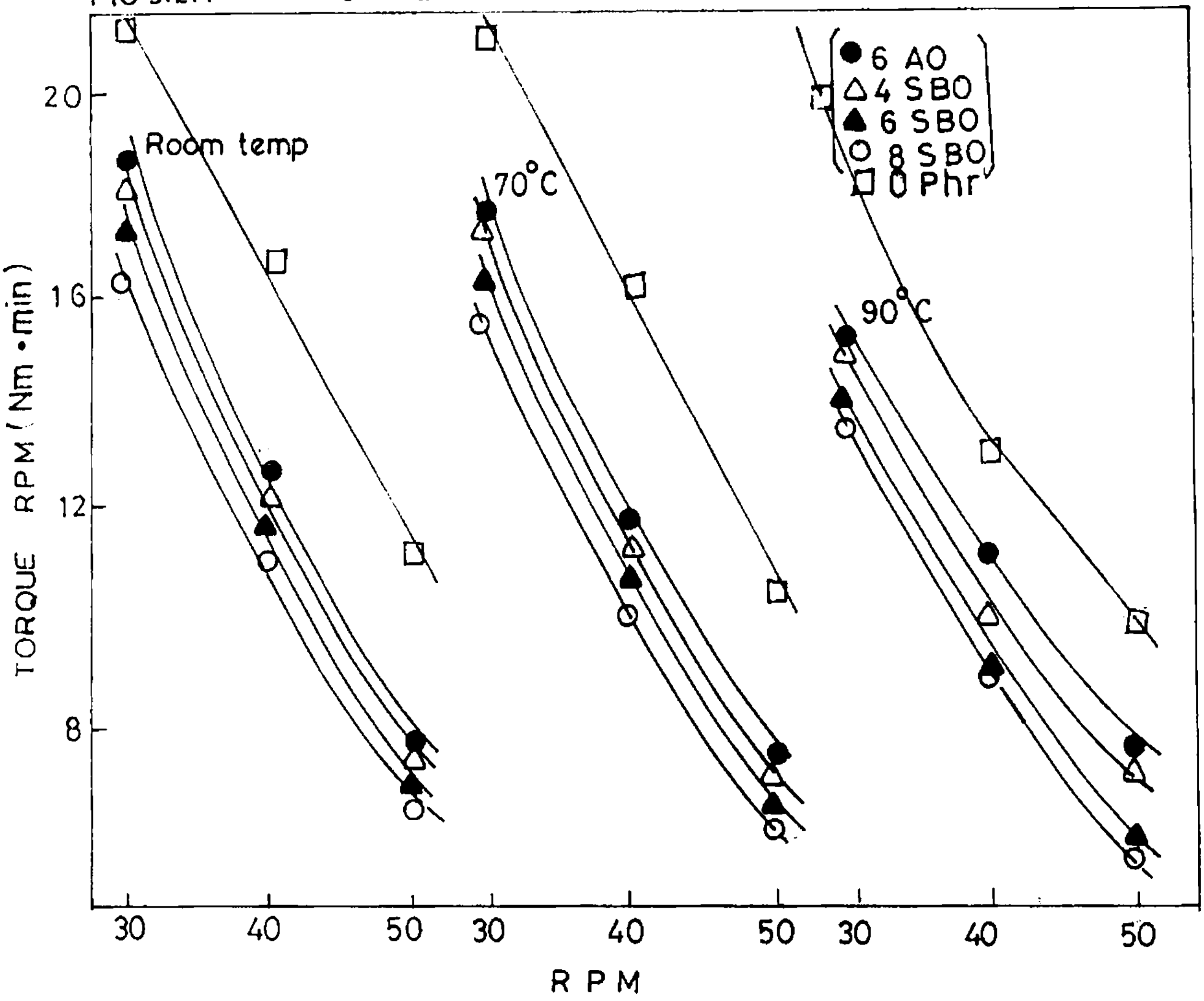


FIG. 5.2.2 CURE CURVE

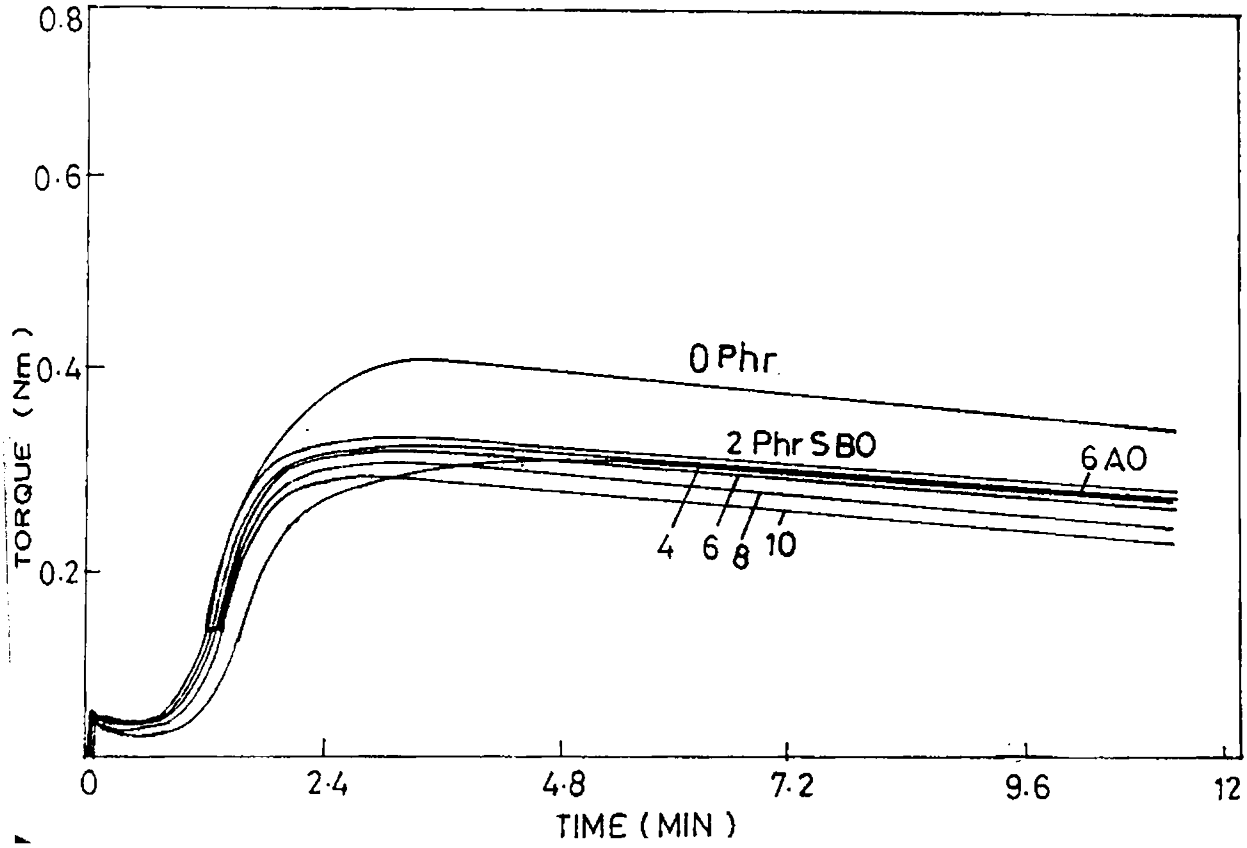


Fig.5.2.3 VARIATION OF TENSILE STRENGTH WITH AROMATIC OIL AND SBO

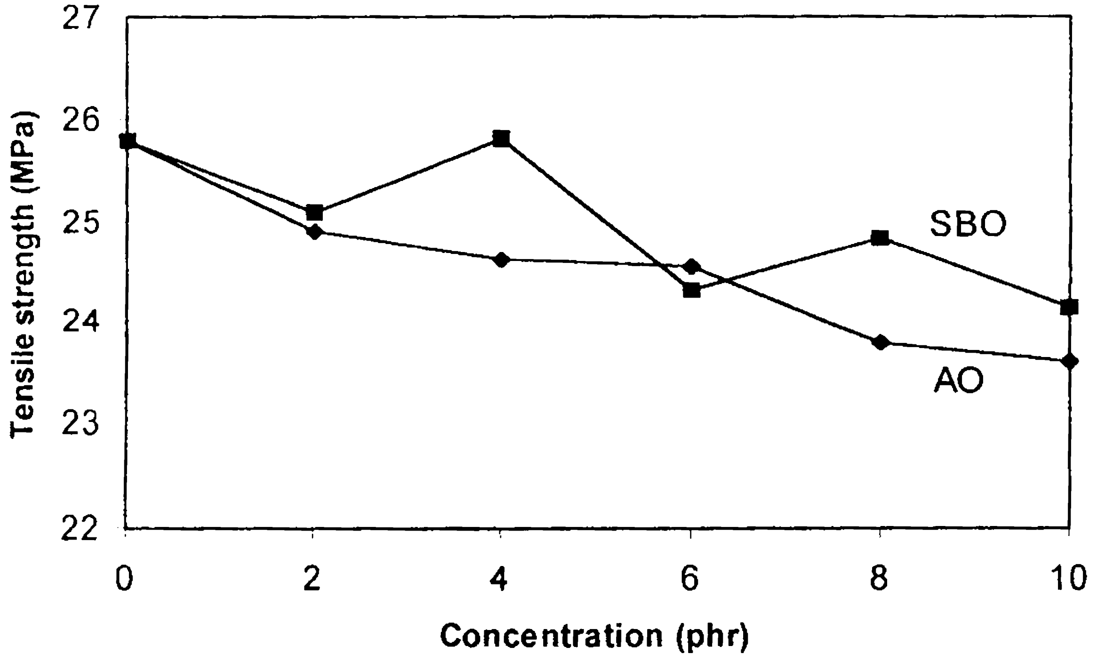


Fig 5.2.4 VARIATION OF MODULUS WITH OIL CONTENT

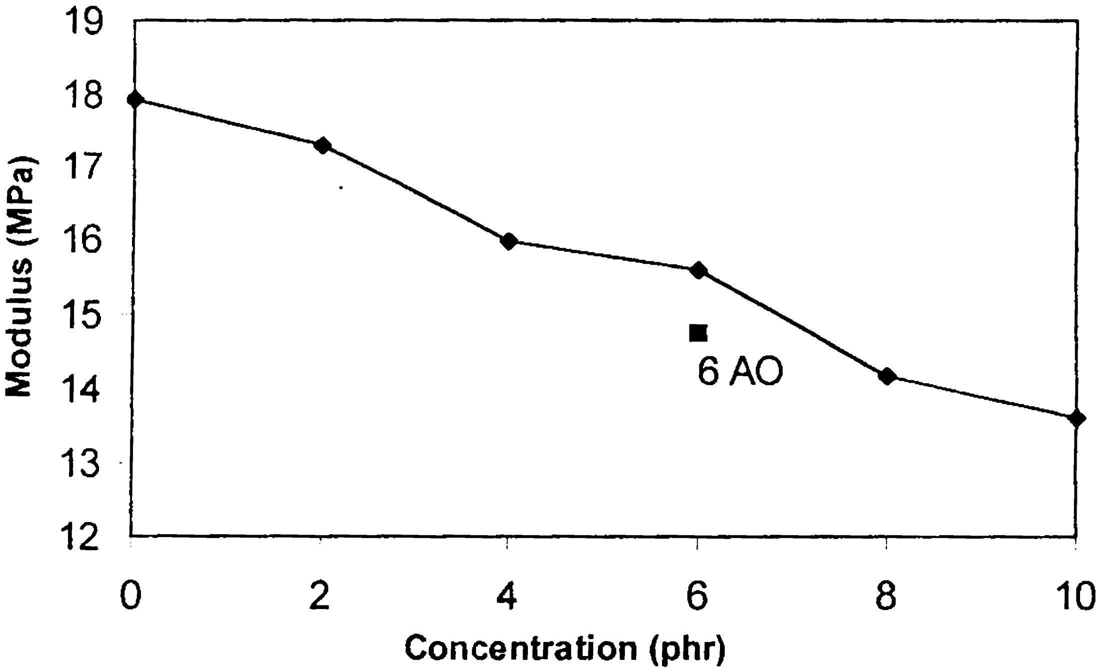


Fig 5.2.5 VARIATION OF CROSS LINK DENSITY WITH OIL CONTENT

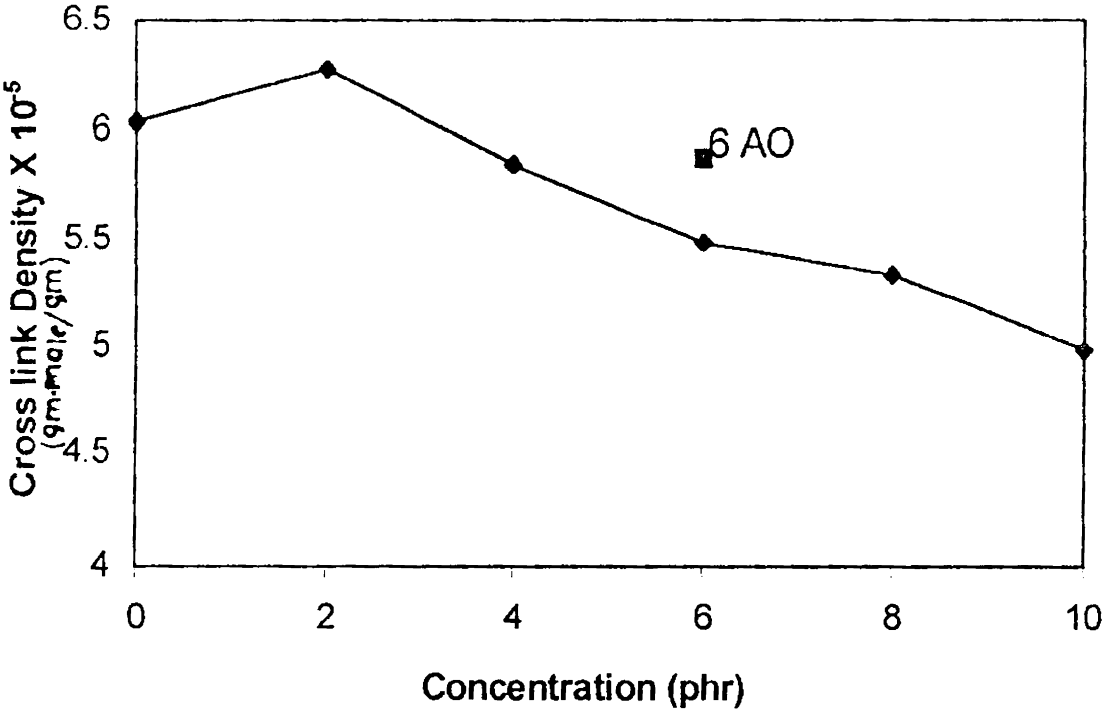
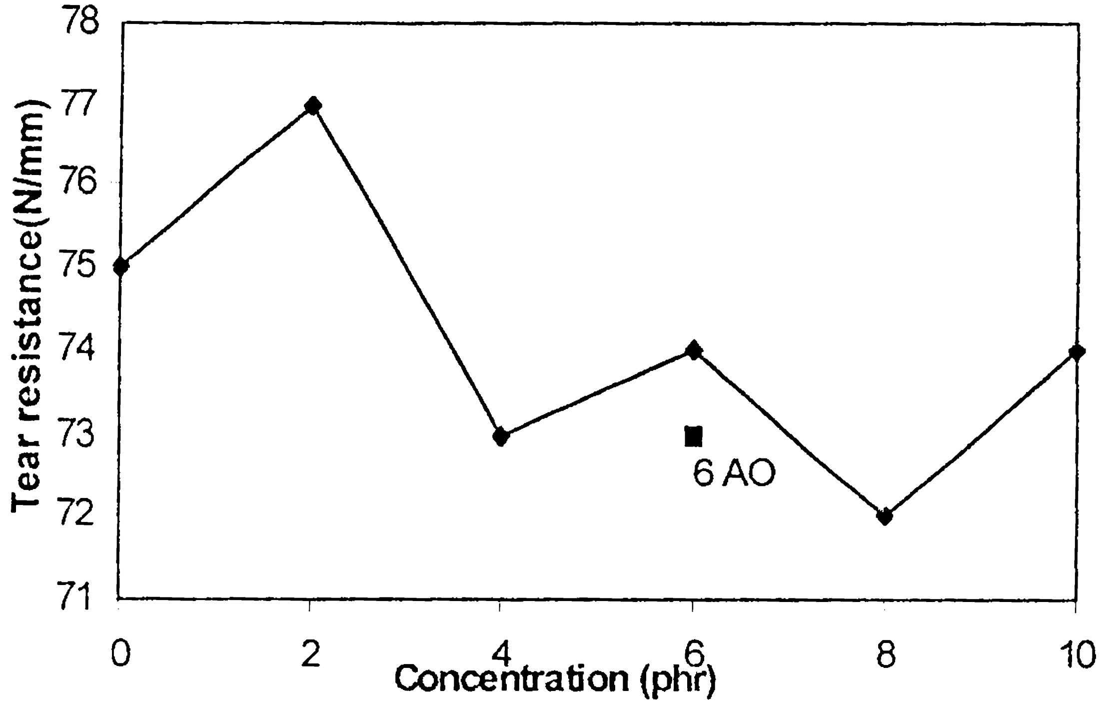


Fig 5.2.6 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT



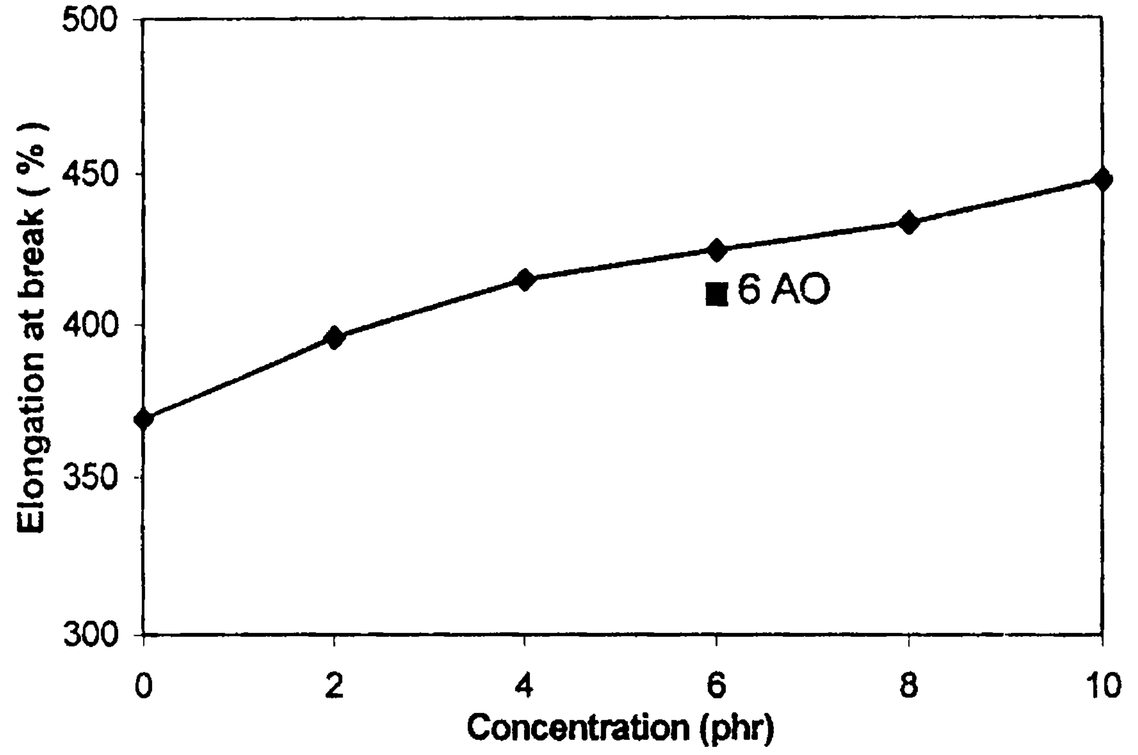


Fig.5.2.7 VARIATION OF EB WITH OIL CONTENT

Table 5.2.1 Cure characteristics of the compounds and tensile strength of aged and unaged vulcanizates.

Sample composition	Scorch time (t_{10}) Min	Cure time (t_{90}) Min	Cure rate Nm/min.	Tensile strength (M.Pa)	
				Unaged	Air aged
6 phr aromatic oil	1.60	3.24	0.1852	24.54	10.50
0 phr plasticizer	1.60	3.41	0.1725	26.30	12.13
2 phr soyabean oil	1.32	2.28	0.3260	25.08	13.95
4 ,,	1.36	2.36	0.3032	25.82	14.44
6 ,,	1.40	2.36	0.3117	24.30	14.58
8 ,,	1.40	2.36	0.3148	24.83	16.15
10 ,,	1.40	2.36	0.2868	24.14	15.70

Table.5.2.2 Abrasion resistance, compression set,De Mattia flex resistance , heat build up and resilience of vulcanizates.

Sample composition	Abrasion loss (% volume)	Compression set. (%)	Flex resistance (Cycles)	Heat build up (^{0}F)	Resilience (%)
6 phr aromatic oil	3.3	22.8	130000	77	39
0 phr plasticizer	2.9	27.5	118000	81	40
2 phr soyabean oil	2.9	25.3	135000	79	41
4 „	2.9	24.3	199000	79	42
6 „	2.9	25.6	203000	78	43
8 „	2.7	30.2	342000	77	42
10 „	2.7	30.8	279000	77	42

5.3 Castor oil as a multipurpose additive in natural rubber

NR is compounded as per formulation give in Table 5.1.1.Wherever castor oil is used, it is used as a substitute for aromatic oil and stearic acid. The properties of the compounds and vulcanizates were compared with that of the control mix with aromatic oil and the mix without any plasticizer.

Results and discussion

Fig 5.3.1 shows the flow behaviour of compounds with varying amounts of castor oil and that of the control mix. All the compounds are highly pseudo plastic. Viscosities of the compounds are highly reduced by the incorporation of castor oil. The viscosity of compound with 2 phr castor oil is marginally lower than that of the control mix with 6 phr aromatic oil. This shows that castor oil is highly plasticizing in NR, and is in contrast to its behaviour with NBR and SBR. Compared to linseed oil, soyabean oil, rubber seed oil or punnal oil, castor oil was found to be least plasticizing, with NBR and SBR. But with NR, castor oil is more plasticizing than these oils. This may be possibly due to the absence of polar side chains on the rubber molecule. The polar -CN group on adjacent chains of nitrile rubber form strong hydrogen bond with the hydroxyl group of ricinoleic acid, which in turn will reduce the mobility of rubber chains causing a higher viscosity for the compounds. The same hydroxyl group highly reduces the Van der Waal's forces between adjacent rubber chains of NR due to repulsive forces between the hydrocarbon chain of the rubber and the polar hydroxyl group. This causes an increase in free volume in the rubber matrix reducing the viscosity of the compound. The compound without plasticizer shows higher viscosity than any of the other mixes.

The cure behaviour of the compounds are also similar to their flow behavior. The cure curve of compound with 2 phr castor oil is very close to that of the control mix with 6 phr aromatic oil (Fig 5.3.2). It may also be noted that there is a considerable reduction in cure time, when aromatic oil is substituted with castor oil. The behaviour of castor oil towards cure rate of compounds is also in contrast to that shown by it in NBR and SBR. Whereas the cure time of NBR and SBR compounds showed a marginal increase with increase in castor oil content, the cure time of NR compounds, ,marginally decreases with increase in oil content (Table 5.3.1). The compound without plasticizer shows the highest torque and cure time compared to all other mixes.

Under these circumstances, it is worthwhile to compare these oils in connection with their behaviour towards the viscosity and cure time of the compounds.

Oils which reduce the viscosity are seen to have reduced the cure time also. The reduction in viscosity of compounds is correlated to the interaction of the oils with the elastomer, as shown in earlier discussions. But viscosity of any substance depends on the intermolecular attraction and any material which reduces the intermolecular force will also reduce its viscosity. Castor oil reduces the viscosity of natural rubber compounds by acting as lubricant like other oils and additionally by creating more "free volume" by repelling the adjacent rubber chains. This additional decrease in viscosity seems to be parallel with the reduction in cure time. So this faster cure rate at low viscosity clearly explains, that the molecules are in a more activated state due to reduced intermolecular force, when viscosity is low. The compound without plasticizer shows the lowest cure rate compared to all other mixes.

Fig. 5.3.3 shows the variation of tensile strength with concentration of castor oil and aromatic oil. Castor oil shows a marginal increase in tensile strength with increase in oil content as against the behaviour of linseed oil and soyabean oil. But the variation in modulus (Fig 5.3.4) and cross-link densities (Fig 5.3.5) are not similar to the variation in tensile strength. Their variations are mutually supporting, and have a higher value at lower concentrations of the oil, which marginally decreases with increase in oil content. So as in the case of linseed oil and soyabean oil, the cross link densities may be above the limit which can influence the tensile strength. The tear resistance shows a higher value at lower concentration of oil (Fig.5.3.6) and is explained by the variations in crosslink density. The variation of elongation at break is inversely proportional to the variation in cross link density as expected (Fig 5.3.7).

The ageing resistance of vulcanizates is also increased by incorporation of castor oil and varies directly with the oil concentration (Table 5.3.1) The vulcanizate without plasticizer is comparable with that of the controll mix in ageing resistance. The abrasion resistance of the vulcanizates showed little variation (Table 5.3.2) and the compression set showed a marginal decrease (Table 5.3.2) when aromatic oil is substituted with castor oil. But variation in oil content have little effect on this properties. The De Mattia flex resistance is increased and increases gradually with increase in oil content (table 5.3.2).This variation in flex resistance can be explained on a similar way to oils discussed earlier. The rebound resilience is marginally increased (Table 5.3.2) while heat build up showed a marginal decrease (Table 5.3.2). The vulcanizate without plasticizer shows a slightly lower compression set and higher heat build up along with a comparable flex resistance with that of the mix with aromatic oil.

Conclusion

Castor oil is a good substitute for aromatic oil in natural rubber. It highly reduces the viscosity of the compounds along with reduction in cure time. Though no much improvement is seen in the tensile strength and abrasion resistance, there are advantages in properties like tear resistance ,De Mattia flex resistance, compression set, resilience and heat build up. 2-3 phr castor oil can advantageously substitute 6 phr aromatic oil in NR vulcanizates

FIG 5.3.1 F LOW CURE

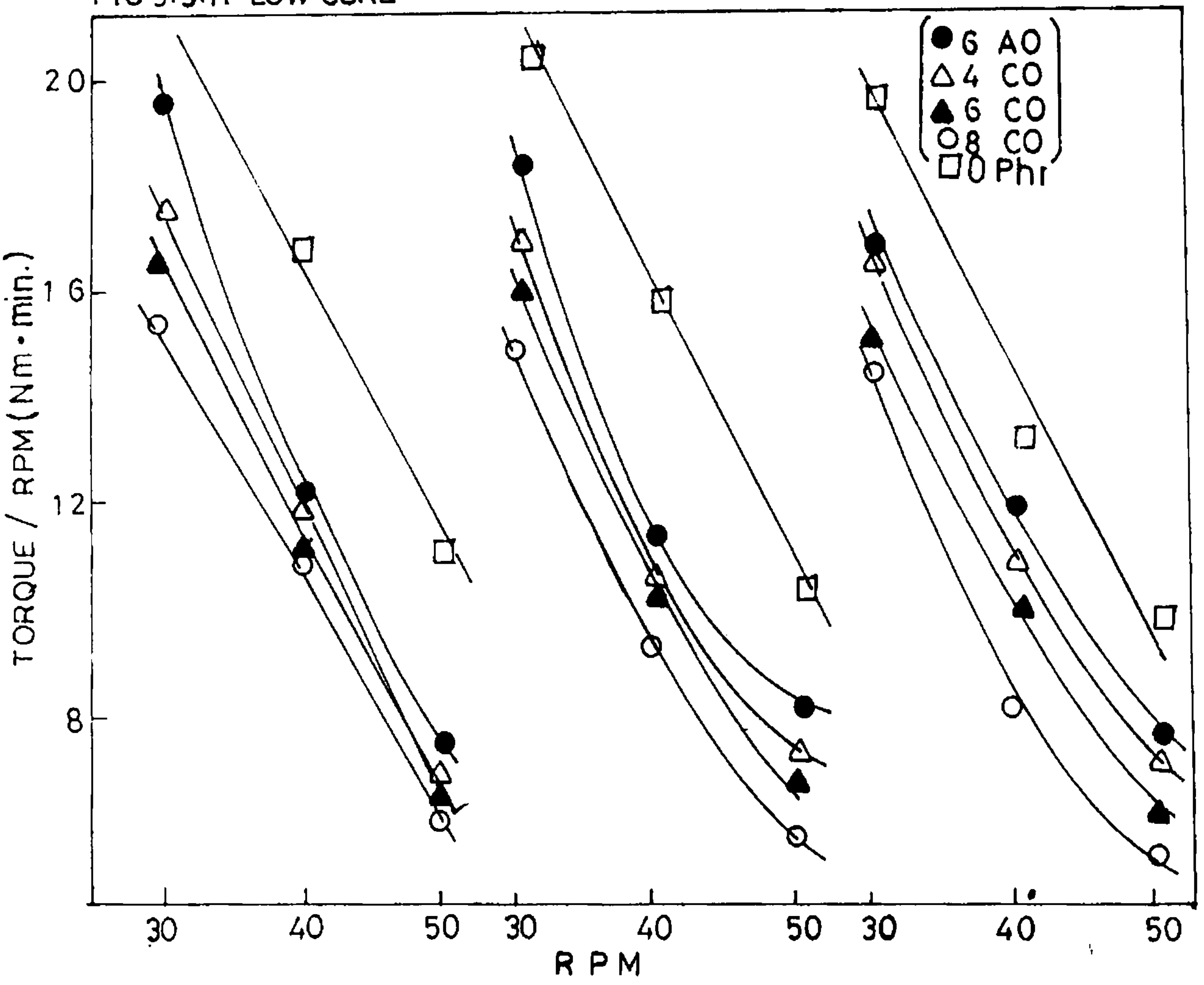


FIG.5.3.2 CURE CURVE

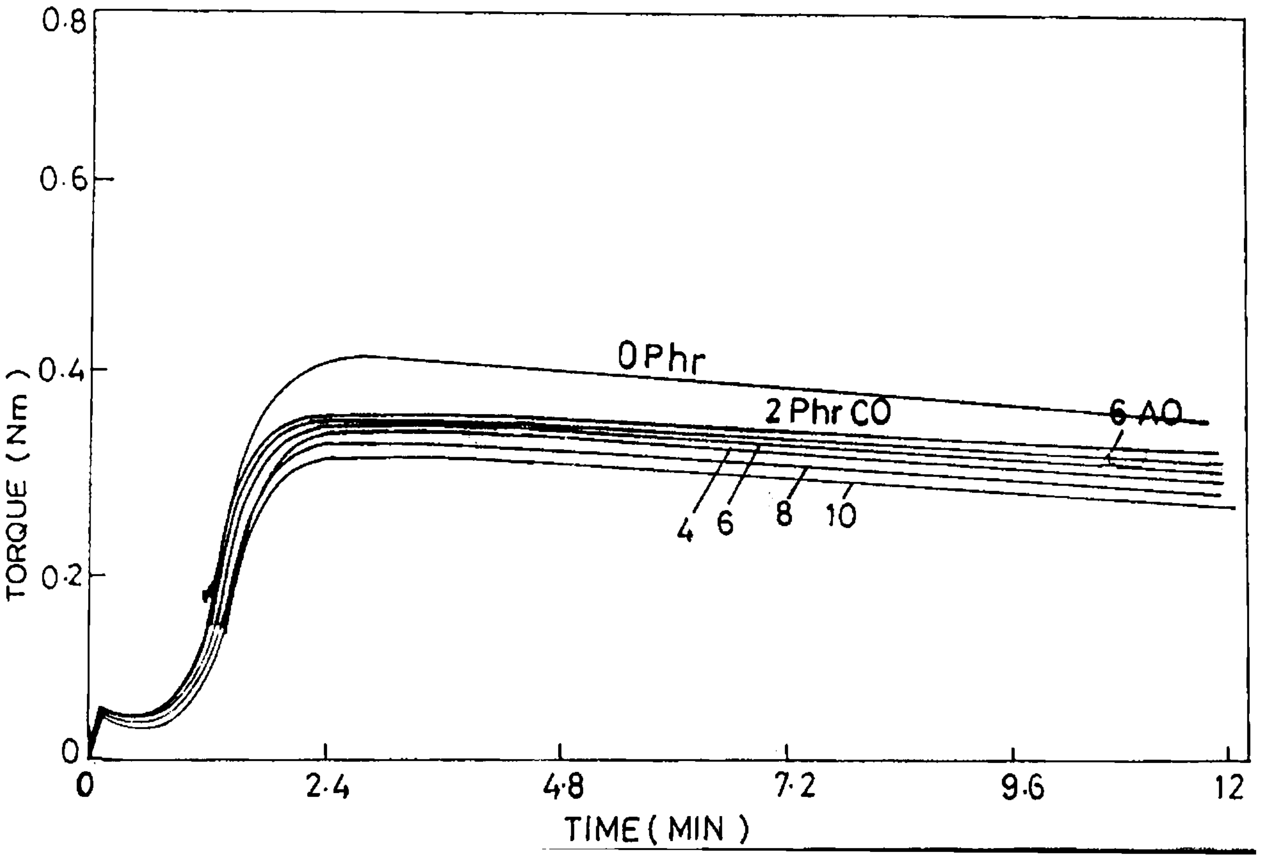


Fig.5.3.3 VARIATION OF TENSILE STRENGTH WITH AROMATIC OIL AND CASTOR OIL

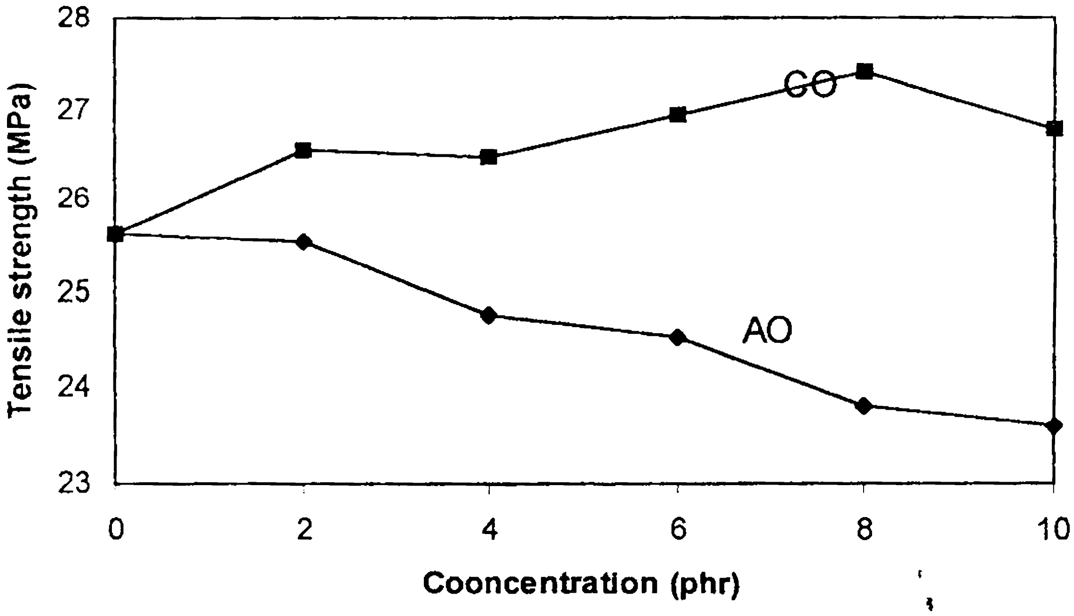
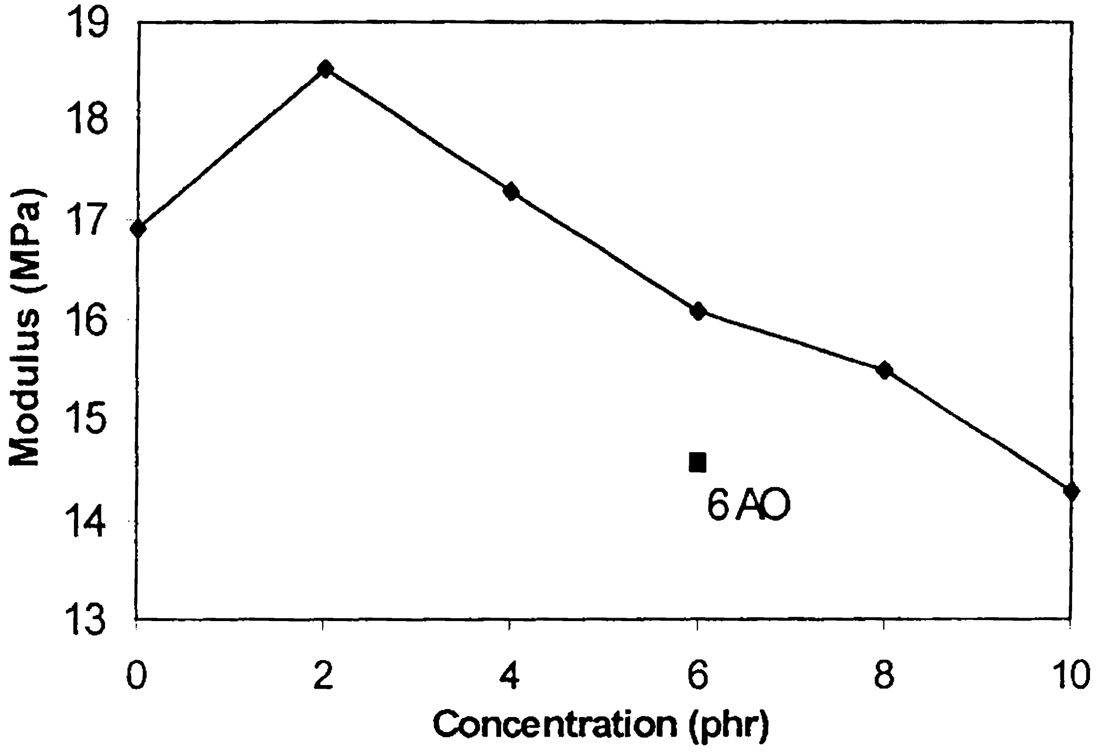


Fig.5.3.4 VARIATION OF MODULUS WITH OIL CONTENT



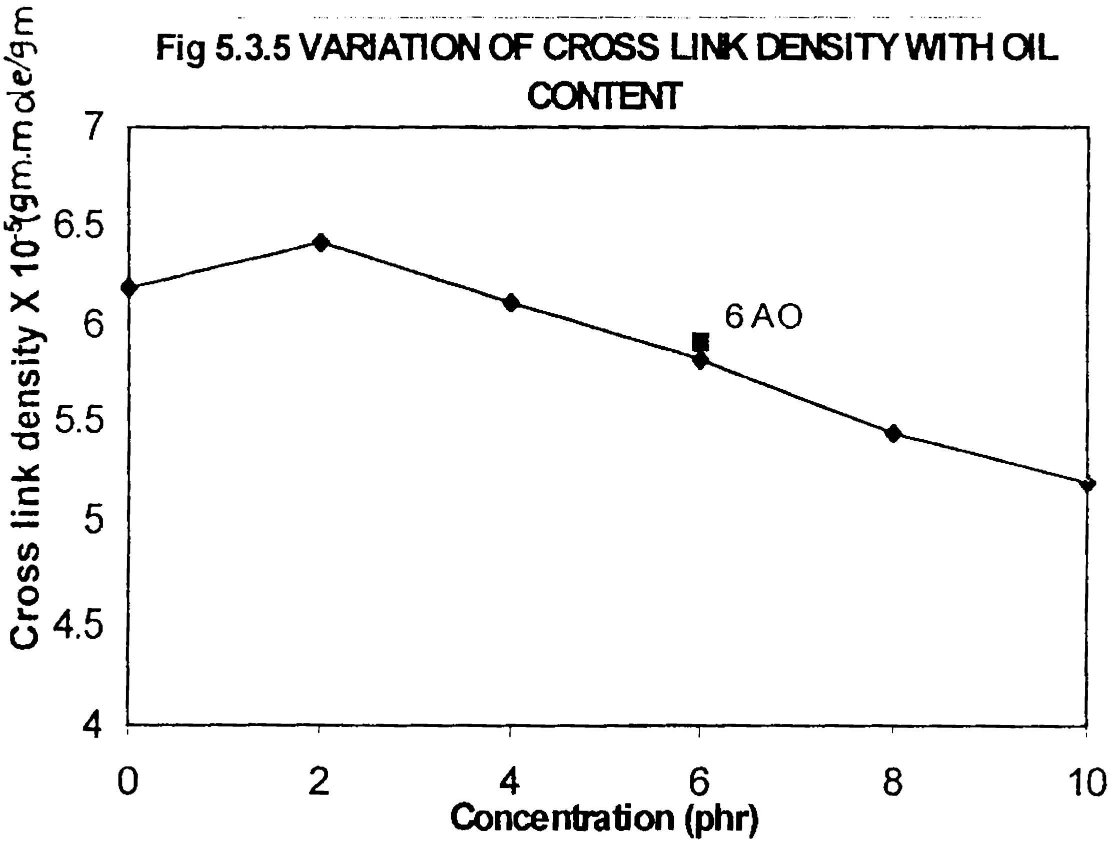


Fig 5.3.5 VARIATION OF CROSS LINK DENSITY WITH OIL CONTENT

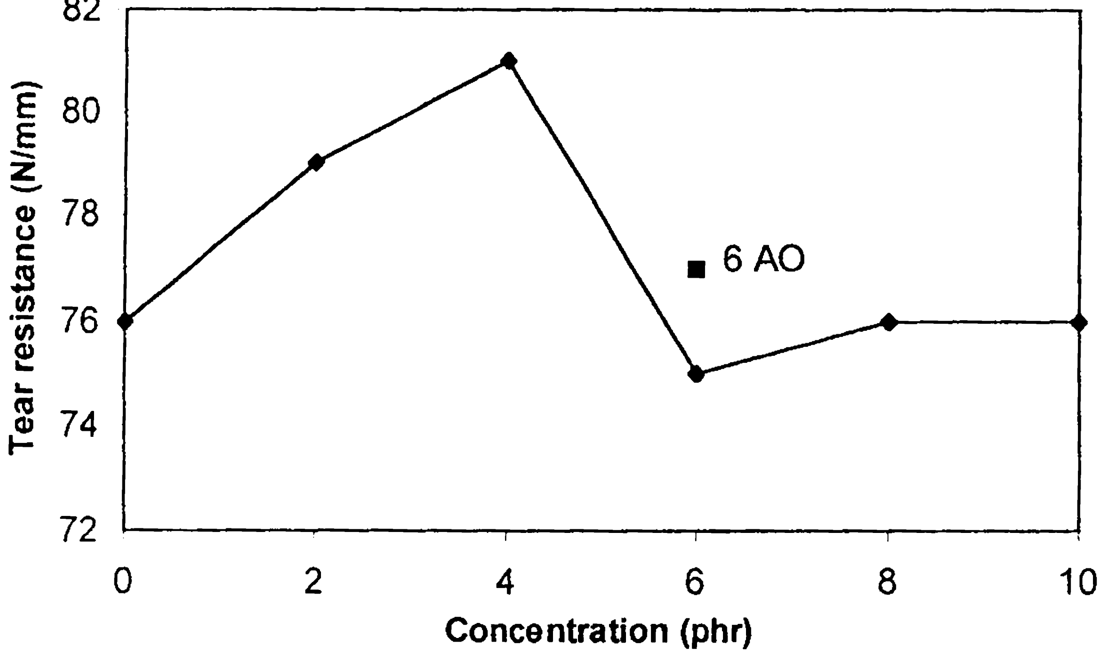


Fig.5.3.6 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT

Fig 5.3.7 VARIATION OF EB WITH OIL CONTENT

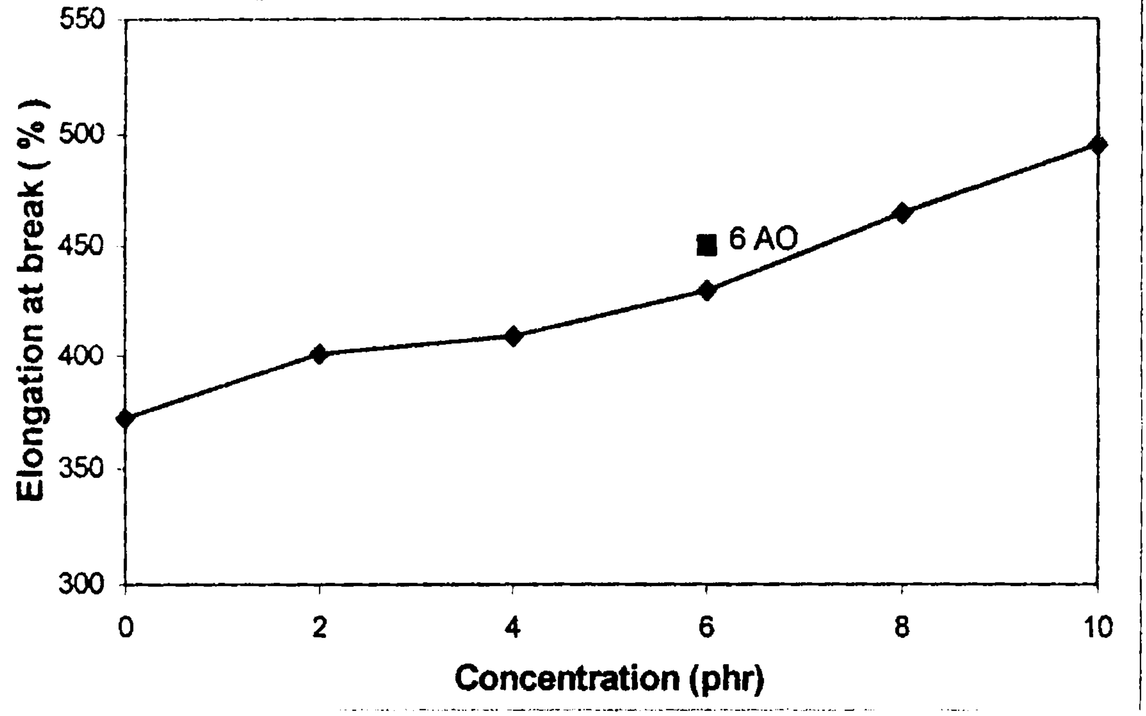


Table 5.3.1 Cure characteristics of the compounds and tensile strength of aged and unaged vulcanizates.

Sample composition	Scorch time (t_{10}) Min	Cure time (t_{90}) Min	Cure rate	Tensile strength (M.Pa)	
				Unaged	Air aged
6 phr aromatic oil	1.52	2.88	0.2459	24.54	11.81
0 phr plasticizer	1.60	3.40	0.1725	26.32	12.40
2 phr castor oil	1.74	2.20	0.3478	26.56	17.38
4 „	1.24	2.16	0.3526	26.48	18.76
6 „	1.24	2.20	0.3239	26.93	15.69
8 „	1.16	2.08	0.3656	27.40	18.83
10 „	1.24	2.20	0.3107	26.79	22.33

Table.5.3.2 Abrasion resistance, compression set,De Mattia flex resistance , heat build up and resilience of vulcanizates.

Sample composition	Abrasion loss (% volume)	Compression set. (%)	Flex resistance (cycles)	Heat build up (^{0}F)	Resilience (%)
6 phr aromatic oil	2.6	33.0	117000	78	38
0 phr plasticizer	2.9	27.5	118000	81	40
2 phr castor oil	2.5	30.8	128000	77	40
4 „	2.4	29.2	147000	77	40
6 „	2.6	30.1	192000	76	41
8 „	2.5	29.8	217000	75	39
10 „	2.5	30.0	279000	76	39

5.3 Rubber seed oil as a multipurpose additive in natural rubber

Natural rubber is compounded as per formulation given in Table 5.1.1. Wherever rubber seed oil is used it is used as a substitute for aromatic oil and stearic acid. The properties of the compounds and vulcanizates were compared with those of the control mix.

Results and discussion

Fig 5.4.1 shows the flow curves of compounds obtained from the Brabender plasticoder. The flow behaviour of the control mix with 6 phr aromatic oil is in between that of the compounds with 6 and 8 phr rubber seed oil, but closer to the compound with 8 phr rubber seed oil. This shows that rubber seed oil is slightly less plasticizing than aromatic oil, in natural rubber compounds. Also it may be noted that all other oils discussed earlier are more plasticizing than aromatic oil. This may be due to the crystalline hexabromide fatty acids present in the oil which may have stronger interaction with the oil. Fig 5.4.2 shows the cure behaviour of the compounds. As in the case of their flow curves, the cure curve of the compound with 8 phr rubber seed oil is very close to that of the control mix with 6 phr aromatic oil. The compound without plasticizer shows a higher viscosity and torque compared to other mixes with aromatic oil or rubber seed oil. Incorporation of rubber seed oil considerably reduces the cure time. Though cure time is very low at low concentration of oil, from there it gradually increases, with increase in oil content (Table 5.4.1). This higher rate at low concentration of oil may be due to the higher activity of unsaturated fatty acids and also due to the activation of the rubber molecule by decreasing their intermolecular attraction by the oil. The increase in cure time with increase in oil content may be due to the increase in intermolecular distance as more and more oil molecules enter in between the adjacent rubber molecules. The compound without plasticizer shows a lower cure rate compared to all other mixes.

Fig 5.4.3 shows the variation of tensile strength with varying concentration of rubber seed oil. A considerable increase in tensile strength occurs when aromatic oil is replaced with rubber seed oil. When vulcanizates with conventional plasticizer show a gradual decrease in tensile strength with increase in their concentration, vulcanziates with rubber seed oil show a different behaviour. The tensile strength of vulcanizates gradually increases up to a concentration of about 8 phr, and then start slowly decreasing. But vulcanizates with rubber seed oil always show greater (25-30%) tensile strength when aromatic oil is replaced with the same loading of rubber seed oil. It should also be noted that the increase in tensile strength with rubber seed oil is substantial compared with the other oils discussed earlier. The main reason for the increased tensile strength may be the ability of unsaturated vegetable oil to covulcanize with the elastomer; but above a certain concentration, the oil itself may get cross linked (factice formation) simultaneously with covulcanization, which reduces the strength of the vulcanizates. This variation in strength can be related partially to the variation in cross link density, and also to the better filler incorporation. But the very high increase in strength compared to other oils may be due to the presence of hexabromide fatty acid which may have some effect on the strength of the vulcanizate. The vulcanizate without plasticizer shows a slightly higher tensile strength than the mix with aromatic oil.

Fig 5.4.4 show the variation of modulus of the vulcanizates with oil concentration. As expected modulus varies directly with crosslink density (Fig 5.4.5). The variation in tear resistance is similar to the variation in tensile strength and modulus and is explained on a similar line (Fig 5.4.6). Variation in elongation at break is inversely proportional to the variation in modulus and crosslink density (Fig.5.4.7).

The antioxidant nature of the oil is proven by the ageing studies of the vulcanizates. The tensile strength of the aged and unaged samples are given in Table 5.4.1. Vulcanizates with rubber seed oil show very high ageing resistance and that without plasticizer shows lower ageing resistance compared to the mix with aromatic oil. The compression set of vulcanizates with different loadings of oil are compared with that of the control mix. It is seen that incorporation of rubber seed oil or variation in its concentration do not affect the set (Table 5.4.2). Abrasion loss of the vulcanizates gradually decreases with increase oil content (Table 5.4.2)

The De Mattia flex resistance of the vulcanizates are considerably increased by the incorporation of rubber seed oil (Table 5.4.2), along with increased rebound resilience (Table 5.4.2). The increase in flex resistance can be explained on a similar way to oils discussed earlier. The heat build up of the vulcanizates seems to be unaffected (Table 5.4.2). Vulcanizate without plasticizer showed a lower value for its abrasion loss and compression set, but a small increase in heat build up.

Conclusion

Rubber seed oil is a good substitute for aromatic oil in natural rubber vulcanizates. Though there is a slight disadvantage in processability, cure time is considerably reduced. The tensile strength, tear resistance, abrasion resistance, De Mattia flex resistance, ageing resistance and resilience of the vulcanizates are improved, whereas heat build up and compression set are unaffected. 6-8 phr oil seems to be the optimum concentration of rubber seed oil, which can substitute 6 phr aromatic oil and 2 phr stearic acid in NR vulcanizates.

FIG 5.4.1 FLOW CURVE

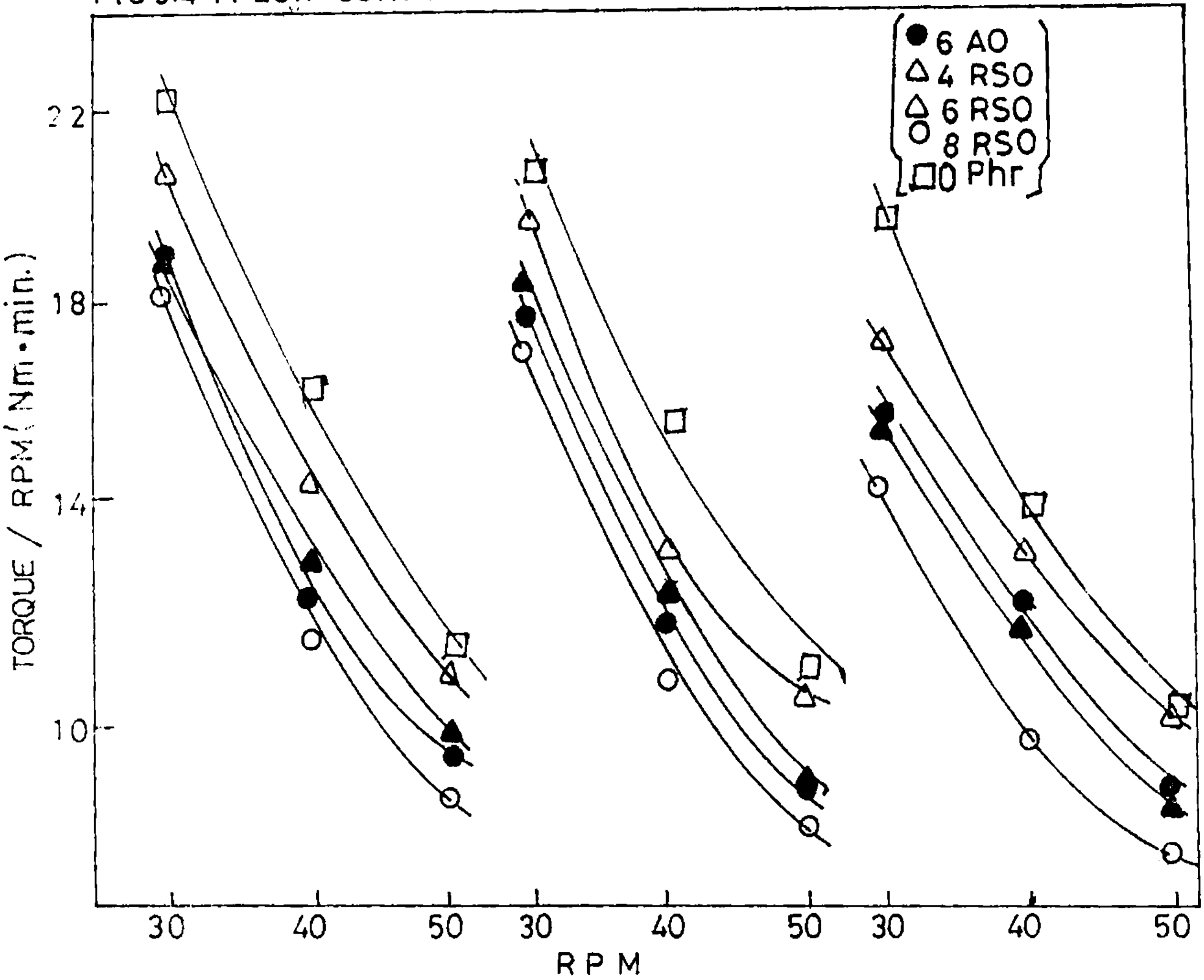


FIG 5.4.2 CURE CURVE

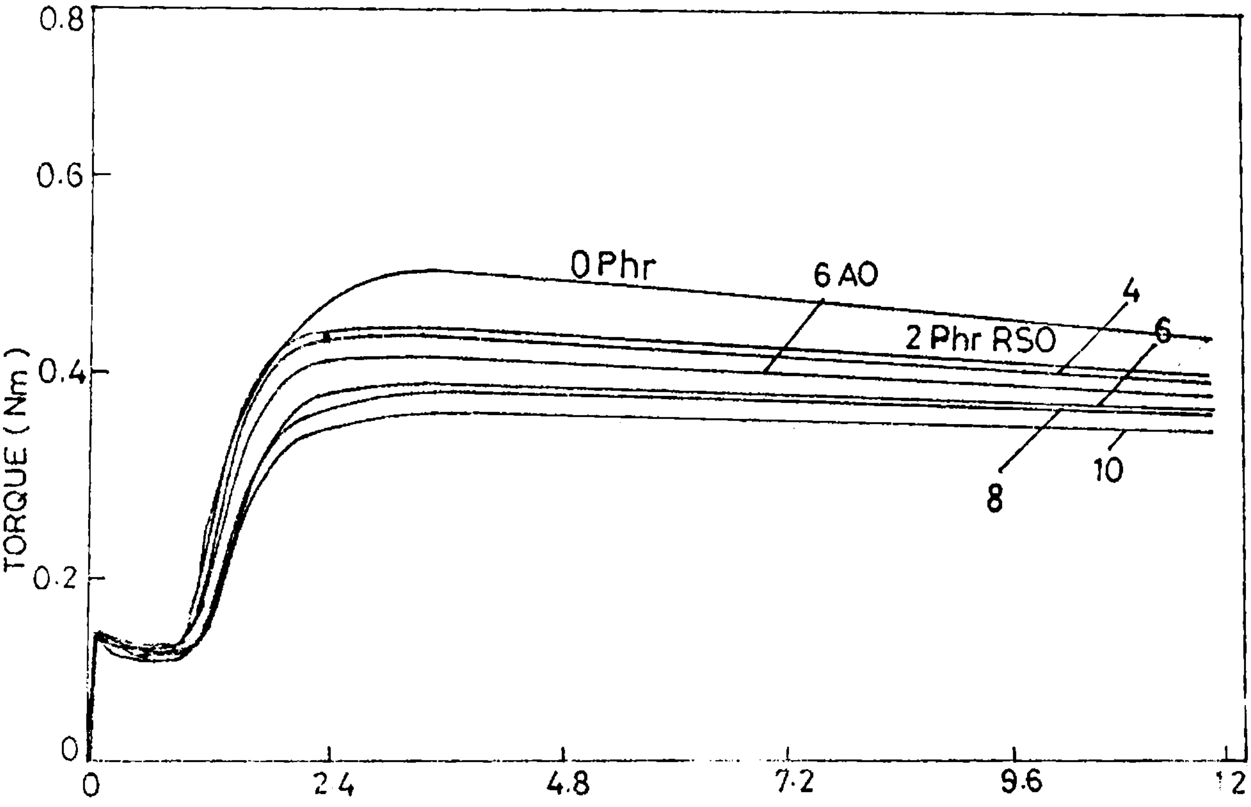


Fig.5.4.3 VARIATION OF TENSILE STRENGTH WITH AROMATIC OIL AND RSO

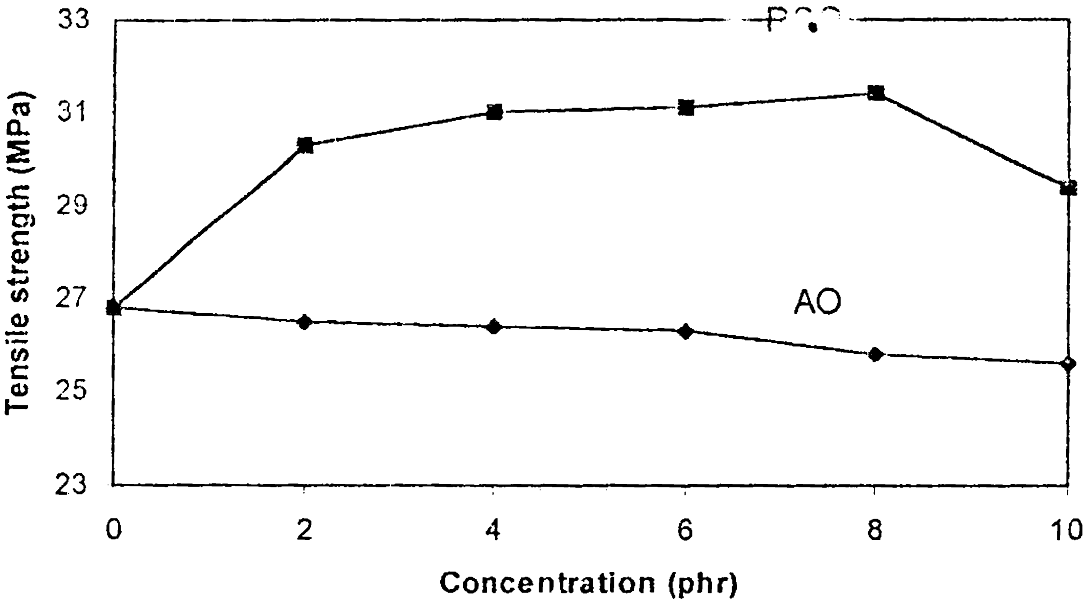


Fig.5.4.4 VARUIATION OF MODULUS WITH OIL CONTENT

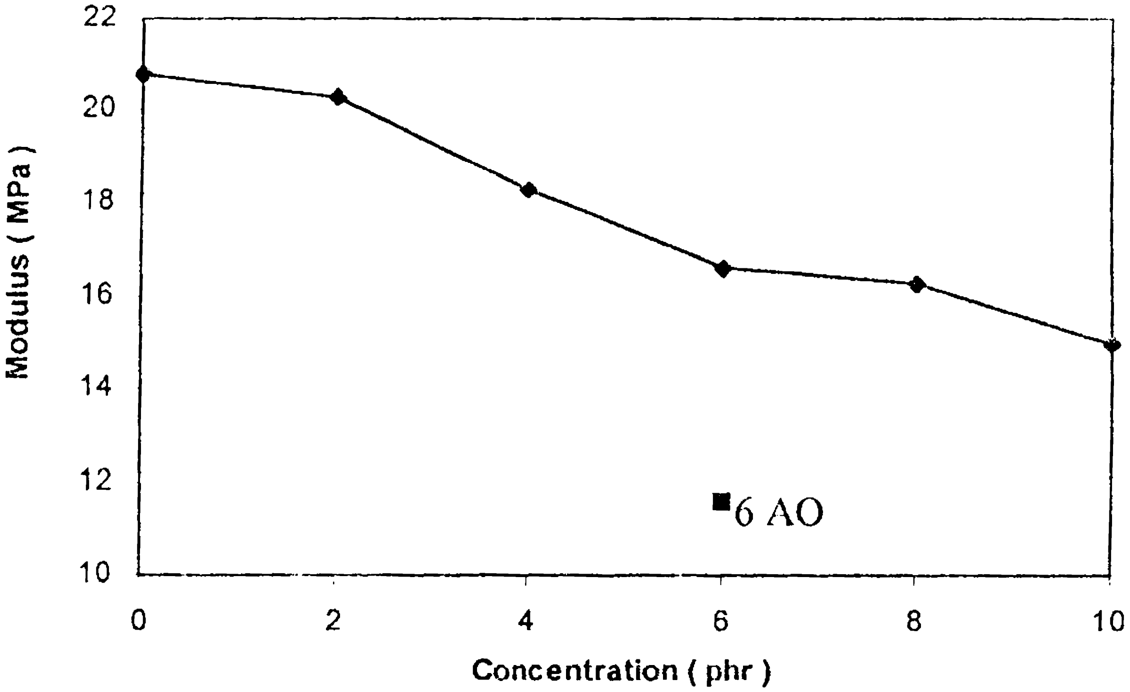


Fig.5.4.5 VARIATION OF CROSS LINK DENSITY WITH OIL CONTENT

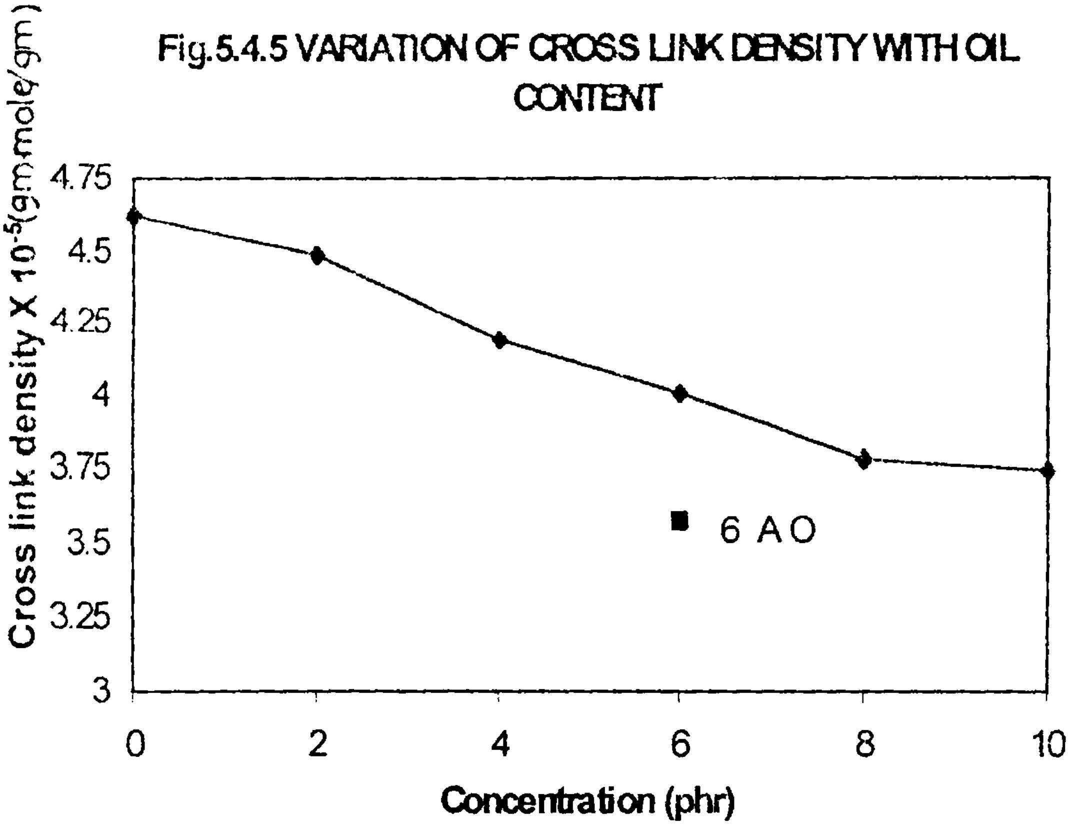
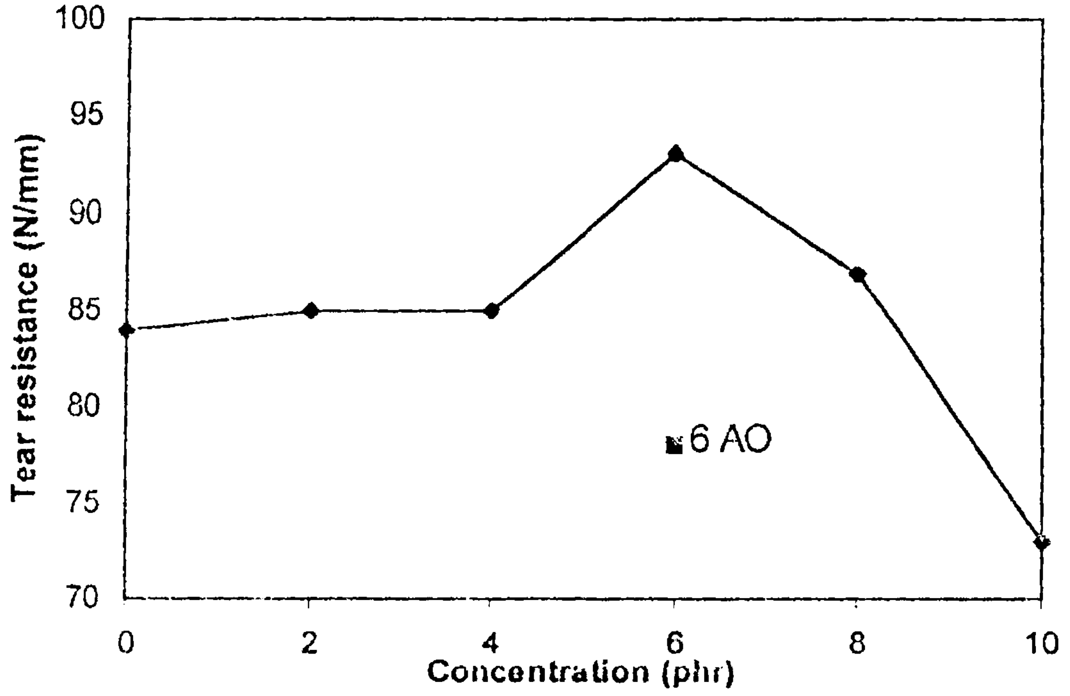


Fig.5.4.6 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT



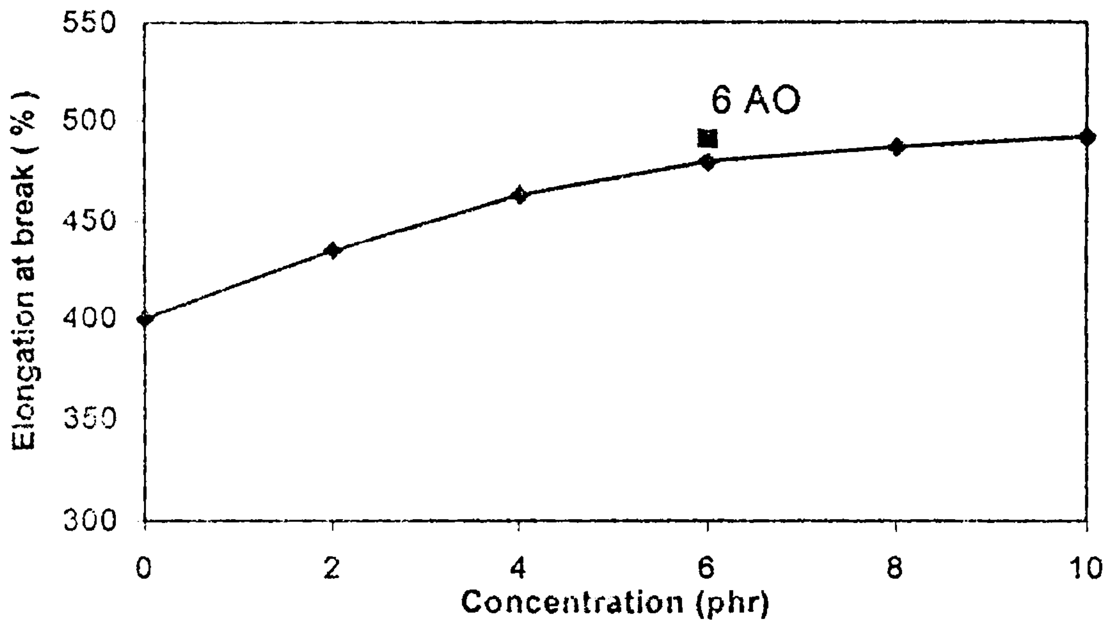


Fig. 5.4.7 VARIATION OF EB WITH OIL CONTENT

Table 5.4.1 Cure characteristics of the compounds and tensile strength of aged and unaged vulcanizates.

Sample composition	Scorch time (t_{10}) Min	Cure time (t_{90}) Min	Cure rate Nm/min.	Tensile strength (M.Pa)	
				Unaged	Air aged
6 phr aromatic oil	1.40	2.72	0.2633	24.50	12.71
0 phr plasticizer	1.60	3.40	0.1732	26.32	12.40
2 phr rubber seed oil	1.12	2.00	0.4472	30.30	22.30
4 „	1.20	2.20	0.3686	31.00	24.90
6 „	1.24	2.32	0.3404	31.10	26.30
8 „	1.28	2.44	0.3005	31.40	25.30
10 „	1.32	2.52	0.2762	29.40	21.20

Table.5.4.2 Abrasion resistance, compression set,De Mattia flex resistance , heat build up and resilience of vulcanizates.

Sample composition	Abrasion loss (%volume)	Compression set. (%)	Flex resistance (cycles)	Heat build up (^{0}F)	Resilience (%)
6 phr aromatic oil	3.94	47.5	112000	77	37
0 phr plasticizer	2.91	27.5	118000	81	40
2 phr rubber seed oil	3.66	46.8	135000	80	45
4 „	3.48	46.7	146000	78	44
6 „	3.43	44.7	168000	74	45
8 „	3.23	48.1	192000	77	46
10 „	3.04	50.3	282000	81	42

5.5 Punnal oil as a multipurpose additive in natural rubber

NR is compounded as per formulation given in Table 5.1.1 Wherever punnal oil is used, it is used as a substitute for aromatic oil and stearic acid. The properties of the compounds and vulcanizates were compared with that of the control mix with aromatic oil and also with the mix without plasticizer.

Results and discussion

Fig 5.5.1 compares the flow behaviour of compound at different loadings of punnal oil, with that of the control mix with 6 phr aromatic oil and the mix without plasticizer. The flow curve of the control mix with 6 phr aromatic oil is in between that of the curves with 6 and 8 phr punnal oil. Punnal oil is slightly less plasticizing than aromatic oil, and about 7-8 phr oil is necessary to give a comparable viscosity for the compound, with that of the control mix. Fig. 5.5.2 shows the cure curves of compounds. As in the case of their flow curves, the cure curve of the control mix and that with 6 and 8 phr punnal oil are very close. The cure time of the compounds are reduced by substituting aromatic oil with punnal oil (Table.5.5.1. But it shows a gradual increase with increase in oil content. This variations are similar to that shown by rubber seed oil and can be explained on a similar line.The compound without plasticizer shows higher viscosity, torque and cure time compared to all other mixes.

Fig. 5.5.3 shows the variation of tensile strength of the vulcanizates with varying amounts of rubber seed oil and aromatic oil. As the tensile strength of vulcanizates with aromatic oil shows a gradual decrease, vulcanziates with punnal oil shows an initial increase at low concentration of the oil and then start decreasing. But vulcanizates with punnal oil always show a higher value than that of the control mix with 6 phr aromatic oil. The increase in tensile strength is due to the increase in crosslink density and may also be due to better filler incorporation and covulcanization.The lowering of tensile strength with increase in concentration of the oil is also marginal, and may be due to the lower amount of factice formation, due to the lower unsaturation of the oil. The variation in modulus (Fig 5.5.4) and cross link density (Fig 5.5.5) are similar and support the variation in tensile strength. The vulcanizate without plasticizer shows an equal value for the tensile strength with that of the mix with aromatic oil.

The variation in tear resistance is similar to the variation in tensile strength (Fig 5.5.6), and the elongation at break gradually increase with oil content (Fig 5.5.7). These variations are explained by the variation in crosslink density.

The air resistance of the vulcanizates shows a slight improvement as can be seen from the tensile strength of the aged and unaged samples given in Table 5.5.1. This improvement in ageing resistance may be due to the presence of an appreciable amount of non saponifiable matter including sterols and also due to the presence of unsaturated fatty acids in the oil. The ageing resistance of the vulcanizate without plasticizer is seen to be slightly lower than the mix with aromatic oil. The abrasion resistance of the vulcanizates is not much affected by substituting aromatic oil with linseed oil. The increase in concentration of the oil also does not affect the abrasion resistance (Table 5.5.2). The compression set of the vulcanizates with varying amounts of punnal oil showed little variation with the control mix (Table 5.5.2). Table 5.5.2 shows the De Mattia flex resistance of the vulcanizates and the control mix. It is to be noted that, punnal oil imparts very high flex resistance to the vulcanizates compared to aromatic oil. The increase in flex resistance can be explained in a similar way to oils discussed earlier. The resilience of the vulcanizates, also show an increase (Table 5.5.2) where as heat build up seems to be unaffected (Table 5.5.2) The vulcanizate without plasticizer shows lower compression set and flex resistance, but a slightly higher heat build up compared to all other mixes.

Conclusion

Punnal oil can advantageously substitute for aromatic oil in NR vulcanizates. Though the viscosity of the compounds is marginally higher than that with aromatic oil, cure time is marginally reduced. Use of punnal oil increases the tensile strength, tear resistance, ageing resistance and resilience of the vulcanziates, at the same time not affecting the compression set, abrasion resistance and heat build up. The optimum concentration of punnal oil is found to be 6-8 phr, which can advantageously substitute 6 phr aromatic oil and 2 phr stearic acid in NR vulcanizates. Further the cost of the compound can also be reduced by use of the cheap punnal oil.

FIG 5.5.1 FLOW CURVE

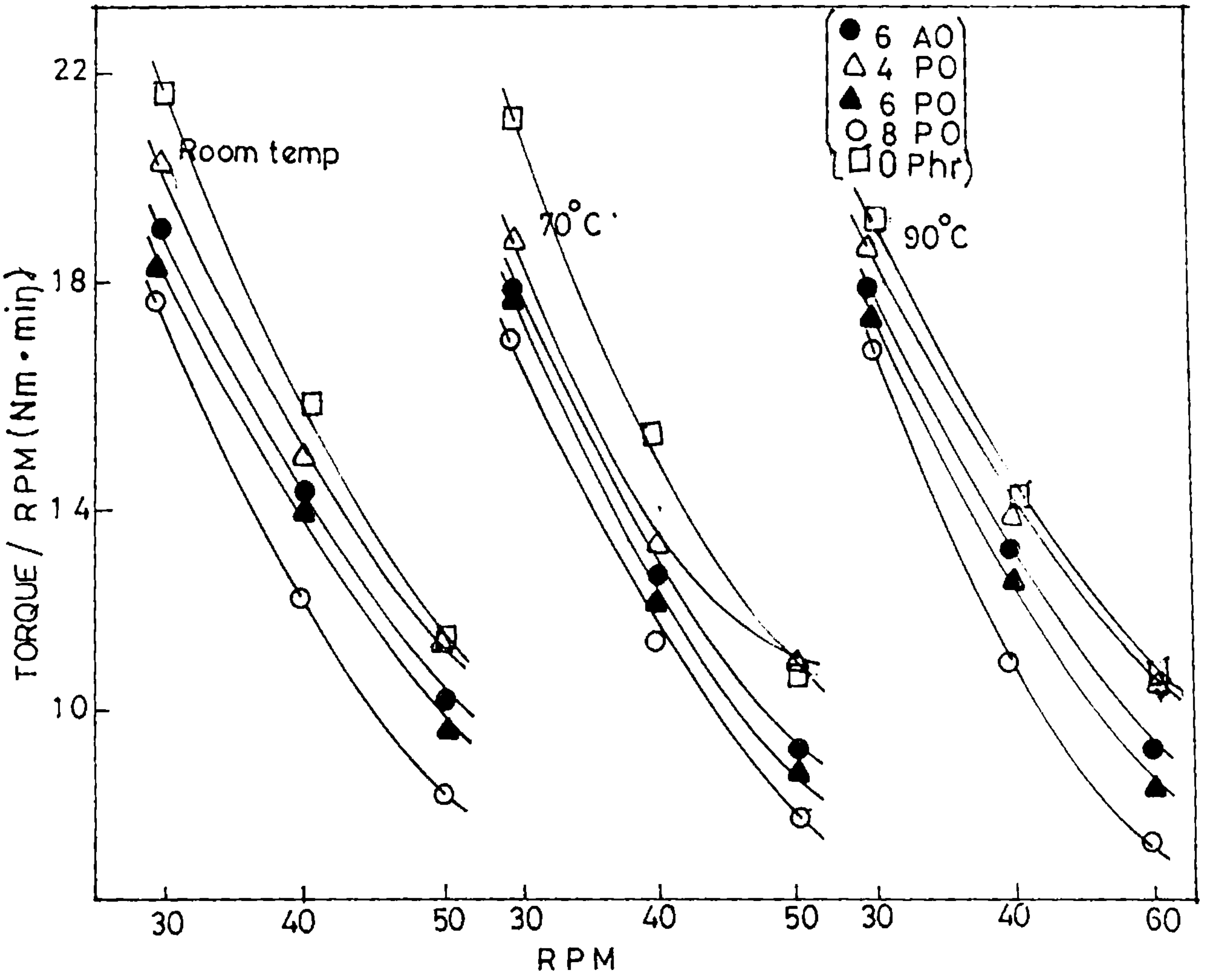


FIG 5.5.2 CURE CURVE

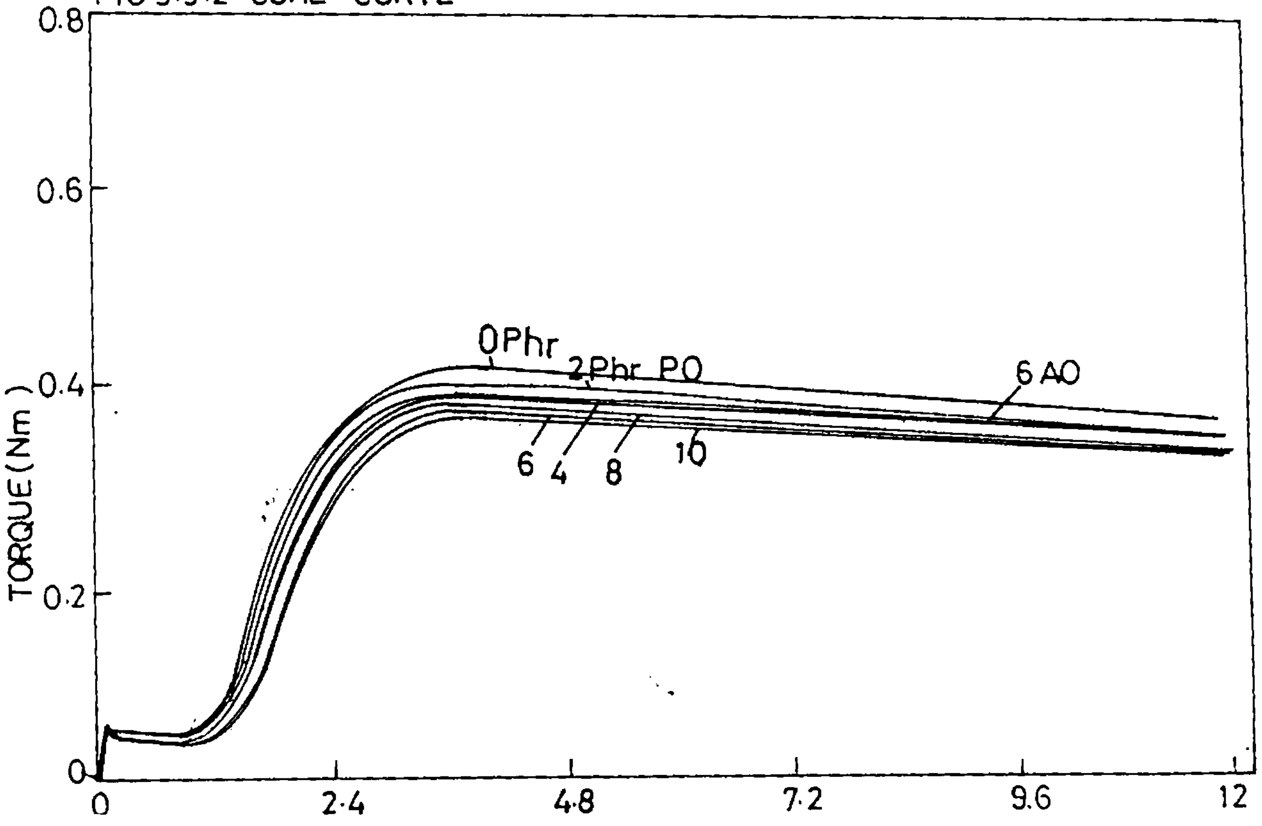


Fig.5.5.3 VARIATION OF TENSILE STRENGTH WITH AROMATIC OIL AND PUNNAL OIL

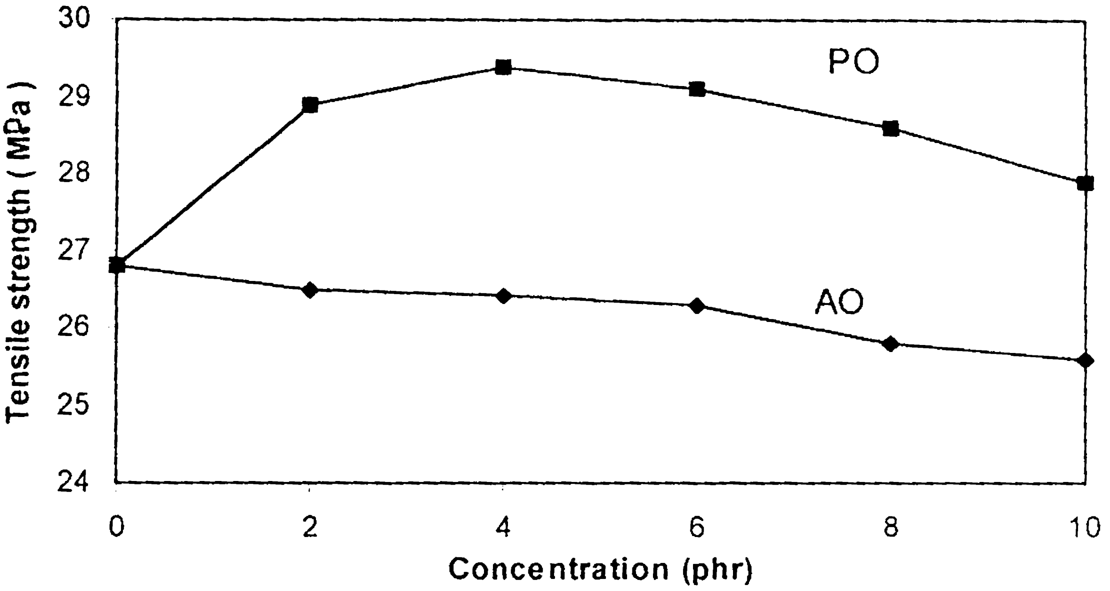
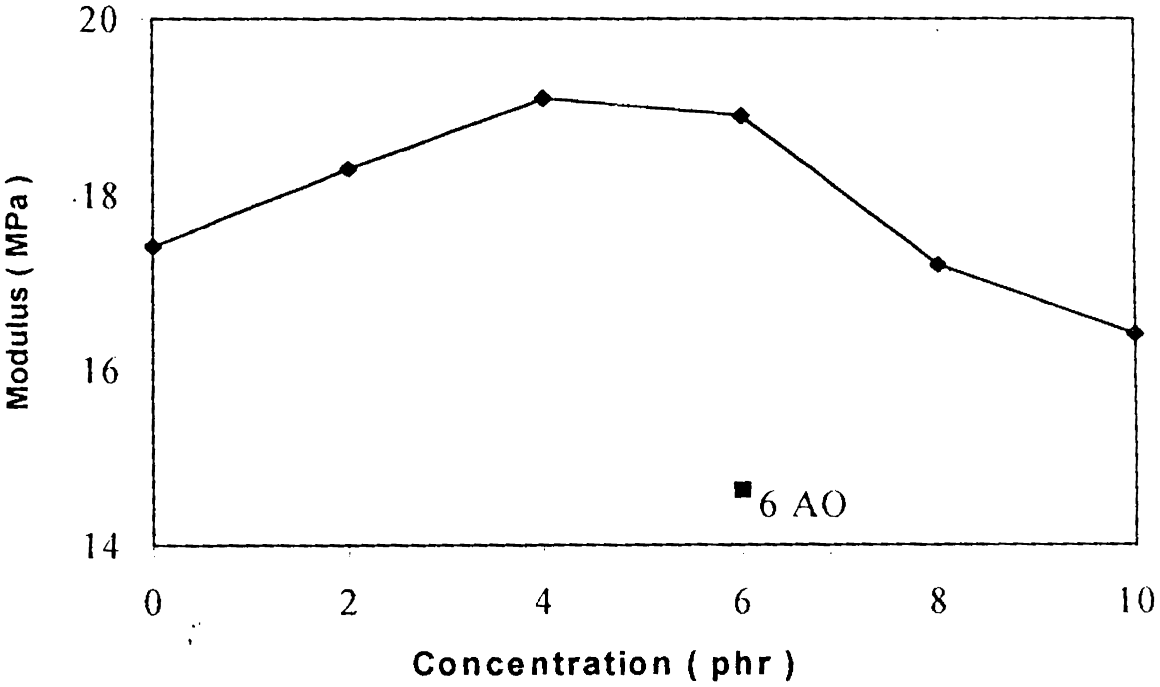


Fig.5.5.4 VARIATION OF MODULUS WITH CONTENT



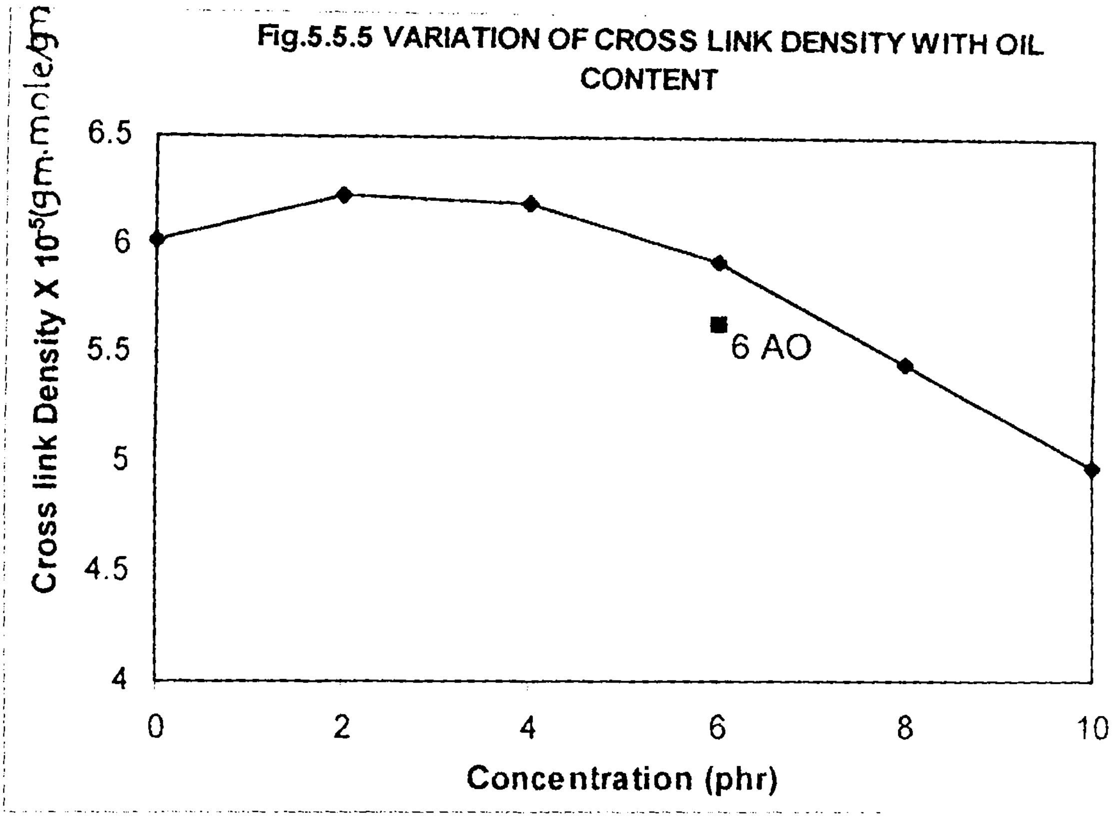


Fig.5.5.5 VARIATION OF CROSS LINK DENSITY WITH OIL CONTENT

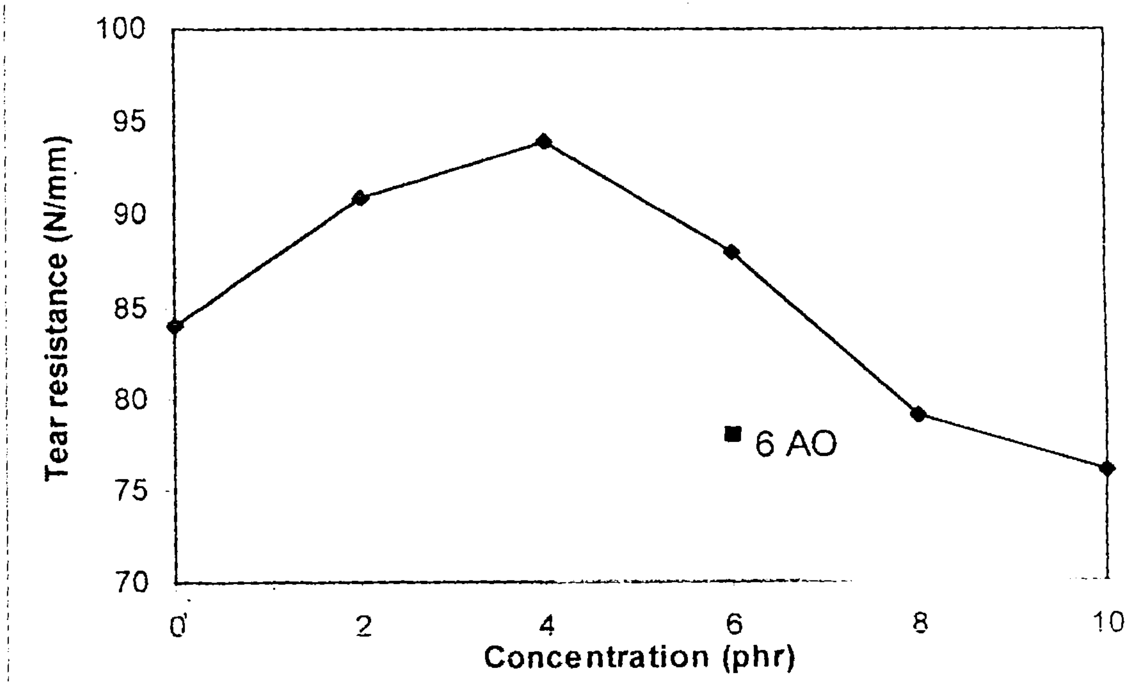


Fig.5.5.6 VARIATION OF TEAR RESISTANCE WITH OIL CONTENT

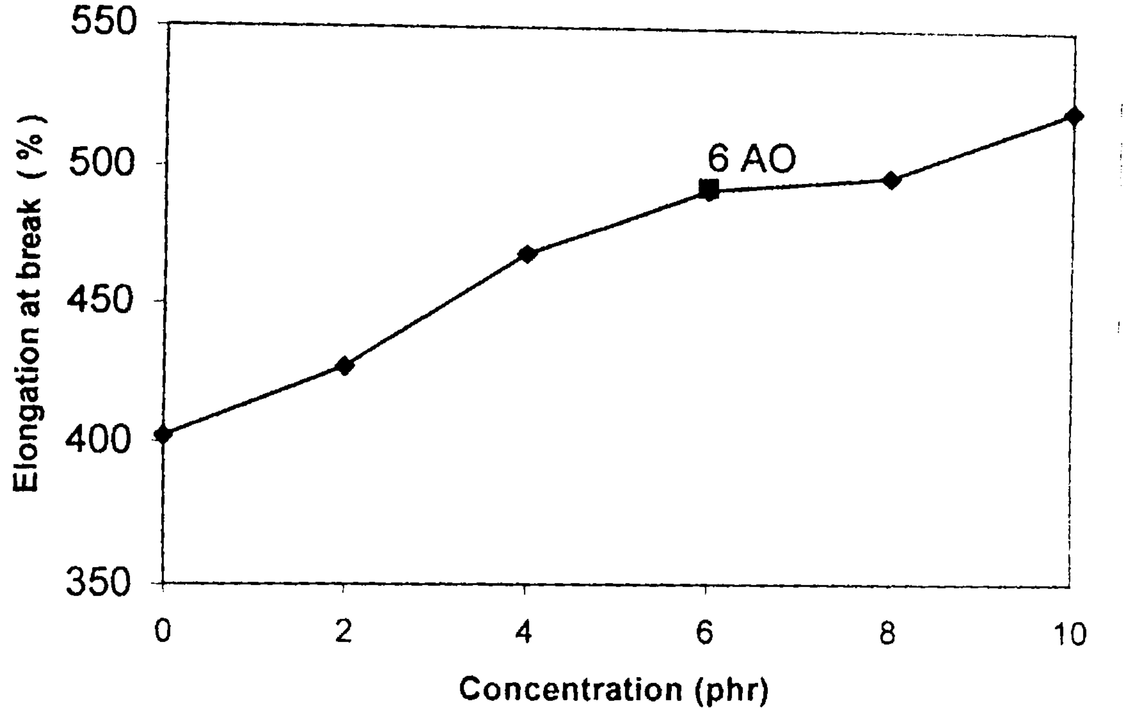


Fig.5.5.7 VARIATION OF EB WITH OIL CONTENT

Table 5.5.1 Cure characteristics of the compounds and tensile strength of aged and unaged vulcanizates.

Sample composition	Scorch time (t_{10}) Min	Cure time (t_{90}) Min	Cure rate Nm/min.	Tensile strength (M.Pa)	
				Unaged	Air aged
6 phr aromatic oil	1.40	2.40	0.3110	26.50	13.10
0 phr plasticizer	1.60	3.40	0.1725	26.32	12.40
2 phr punnal oil	1.00	2.00	0.3380	28.90	17.20
4 „	1.00	2.10	0.3045	29.40	18.10
6 „	1.10	2.20	0.3091	29.10	18.90
8 „	1.10	2.30	0.2958	28.60	17.90
10 „	1.20	2.40	0.2958	27.90	16.80

Table.5.5.2 Abrasion resistance, compression set,De Mattia flex resistance , heat build up and resilience of vulcanizates.

Sample composition	Abrasion loss (%volume)	Compression set. (%)	Flex resistance (cycles)	Heat build up (°F)	Resilience (%)
6 phr aromatic oil	3.1	47.1	130000	78	38
0 phr plasticizer	2.9	27.5	118000	97	40
2 phr punnal oil	3.1	46.2	132000	80	40
4 „	3.1	47.8	199000	80	40
6 „	2.9	48.2	199000	79	39
8 „	2.9	48.0	230000	78	40
10 „	3.0	48.5	239000	78	39

CHAPTER VI

STUDIES ON THE EFFECT OF VEGETABLE OIL ON THE PROPERTIES OF SOME TYPICAL RUBBER PRODUCTS

As already seen in previous chapters, the vegetable oils used are generally good substitutes for the conventional plasticizers and stearic acid, in individual elastomers like NBR SBR and NR. So it is worthwhile to try these oils in some typical rubber products. The products selected for the study are tyre tread, microcellular soles, and sponge.

6.1. Studies on the effect of using vegetable oils on the properties of tyre tread

Experimental

NR/PB blend is compounded as per formulation given in Table 6.1.1. Whenever vegetable oils are used it was used as a substitute for aromatic oil. Mixes with varying amounts of different oils were prepared and the properties compared with those of the control mix.

Results and discussion

The behavior shown by the NR/PB blend towards these oil is almost similar to that shown by NR. The flow behavior of the compounds showed that the viscosities of the compounds are marginally lower in the case of castor oil, and marginally higher in the case rubber seed oil and punnal oil; whereas linseed oil and soyabean oil gave a comparable viscosity with that of the control mix. But the lowering in viscosity shown by oil in the blend is not so prominent as they have shown with NR. This may be due to the presence of BR in the blend. It may be noted that when linseed oil, soyabean oil and castor oil decreased the viscosity of NR compounds , with castor oil showing the maximum, rubber seed oil and punnal oil slightly increased the viscosity. If this variations are decreased to a certain limit, it coincides with their behaviour in the NR/PB blend. So it is clear that the behaviour of these oils in BR is either opposite or to a small extent on the same line, to their behaviour with NR. Since NR and PB have the same molecular back bone and differ only in angular methyl group, the influence of the angular methyl group on the action of these oils is well established. It is now clear that the behaviour of these oils in the NR/PB blend is similar to their behaviour in NR, but reduced to a small extent by the presence of PB. The cure behavior of the compounds are also similar to their flow behavior. But all the oils show decrease in cure time as can be seen from Table 6.1.2. Though NR/PB blend shows a higher cure time compared to the NR mixes, the decrease in cure time can be explained on a similar way to NR mixes.

Table 6.1.3 shows the tensile strength of vulcanizates with varying amounts of vegetable oils and that of the control mix. When linseed oil, soyabean oil and castor oil showed a marginal increase, rubber seed oil and punnal oil gave a considerable increase in tensile strength. But the tensile strength of the blends are lower than that of NR with the same loading of oils. This shows that the properties of the blend are the average of the properties of the individual elastomers. The variations in tensile strength can be explained on a similar way to that of NR. The tear resistance of the vulcanizates also show a similar trend (Table 6.1.3). The ageing resistance is slightly improved with all the oils (Table 6.1.3) as shown by them in individual elastomers and can be explained similar to that.The abrasion resistance of the vulcanizates are not affected by the oils (Table 6.1.3). The De Mattia flex resistance is highly improved with all the oils, whereas heat build up is unaffected (Table 6.1.4). The increase in flex resistance is a general behaviour of oils as seen in previous chapters. But why unusually very high value is shown by punnal oil, is yet to be understood The compression set showed a slight disadvantage with linseed and soyabean oil, but other oils do not affect this property (Table 6.1.4). Vulcanizates with all the oils showed a marginal increase in resilience (Table 6.1.4).

Conclusion

All the oils tried are good substitutes for aromatic oil in tread compounds. Many of the properties are improved or unaffected by almost all oils. The only disadvantage seen is the marginal lowering of processability by rubber seed oil and punnal oil..5-7 phr oils are found to be the optimum concentration which can advantageously substitute 7 phr aromatic oil and 2 phr stearic acid in tyre tread compounds.

Table.6.1.1 Formulation

NR	70 phr
BR	30 „
ZnO	5 „
Stearic acid	2 „
HAF	55 „
MOR	1 „
Sulphur	2.25 „
Vulcanox 40 20	0.75 „
Vulcanox HS	0.5 „
Aromatic oil	7 „

Table 6.1.2 Cure characteristics of the compound

	Sample composition															
	Linseed oil (phr)			Soyabean Oil (phr)			Castor oil (phr)			Rubber seed oil (phr)			Punnal oil (phr)			Aromatic Oil (phr)
	5	7	9	5	7	9	5	7	9	5	7	9	5	7	9	7
Scorch time (min)	2.7	2.8	2.7	2.8	2.8	2.6	2.3	2.4	2.4	2.7	3.0	2.9	2.6	2.8	2.7	3.1
Cure time (min)	6.7	6.9	6.8	6.8	7.0	6.5	5.6	5.8	5.8	7.2	7.5	7.8	7.2	7.9	7.7	8.4

Table 6.1.3 Tensile strength tear strength and abrasion resistance

Sample No	Composition	Tensile strength (MPa)		Tear strength (N/mm)	Abrasion loss (% volume)
		Unaged	Aged		
1	7 phr Aromatic oil	20.85	10.39	69	2.8
2	„ Lineed oil	21.2	13.12	72	2.7
3	„ Soyabean oil	21.9	13.45	74	2.9
4	„ Castor oil	22.0	15.61	71	2.9
5	„ Rubber seed oil	25.13	14.90	76	2.7
6	„ Punnal oil	25.42	16.21	79	3.2

Table 6.1.4 De Mattia flex resistance, compression set and resilience of vulcanizates

Sample No	Composition	De Mattia flex resistance (cycles)	Compression set (%)	Resilience (%)
1	7 phr Aromatic oil	60,000	36.4	39
2	„ Lineed oil	2,25,000	39.7	41
3	„ Soyabean oil	2,64,000	38.9	40
4	„ Castor oil	3,10,000	37.1	41
5	„ Rubber seed oil	2,92,000	35.9	40
6	„ Punnal oil	9,00,000	36.8	39

6.2 Studies on the effect of vegetable oils on the properties of microcellular soles

NR is compounded as per formulation given in Table 6.2.1. Wherever vegetable oils are used, it was used as a substitute for paraffinic oil and stearic acid. The properties of the vulcanizates with different oils were compared with those of the control mix with paraffinic oil.

Table 6.2.2 gives the flex resistance of the soles with different loadings of different oils and that of the control mix with paraffinic oil. It may be noted that linseed oil considerably increases the flex resistance, whereas it is adversely affected by soyabean oil, castor oil and rubber seed oil. Punnal oil seems to have little effect on the flex resistance. This shows that the behaviour of these oils on M.C. soles is different from that shown towards conventional vulcanizates. When De Mattia flex resistance of the vulcanizates are considerably increased by all the oils, their behavior towards M.C. soles is seen to depend on their drying nature. It may also be considered that the effect of flexing will be different in a cellular structure and in a matrix. In a cellular structure, flex resistance mainly depends up on the thickness of the cell wall, whereas in a matrix it depends on many properties including plasticization and the density of crosslinks. Linseed oil, the drying oil, preferentially self vulcanizes to form factice, which softens the sole, and hence the flex resistance is increased. The semi drying oils have both the possibilities for self vulcanization and co vulcanization in NR compounds. This additional cross linking may have a disadvantage in the flexing due to increased hardness of soles. Punnal oil seem to act mainly as a lubricant like paraffinic oil and hence little difference is seen in flex. The abrasion resistance of the soles are not much affected by these oils (Table 6.2.2)

Conclusion

Drying oils are good substitute for paraffinic oil in M.C. soles. They give better flex resistance. They are also non staining. Paraffinic oil can be advantageously substituted with an equal amount of linseed oil or punnal oil in M.C. soles

Table 6.2.1 Formulation

NR	70 phr
HSR	30 „
ZnO	4.5 „
Stearic acid	6 „
Clay	80 „
Crumb	50 „
Silica	10 „
Vulcafor F	1.2 „
Sulphur	2.3 „
SP	1.0 „
Paraffinic Oil	5.0 „
DNPT	6.0 „

Table 6.2.2 Flex resistance and abrasion loss of soles with oils.

Sample No	Composition	Flex resistance (cycles	Abrasion loss (% volume)
1	5 phr Paraffinic oil	44,000	8.5
2	„ Lineed oil	52,000	7.6
3	„ Soyabean oil	42,000	8.9
4	„ Castor oil	36,000	9.1
5	„ Rubber seed oil	27,000	8.6
6	„ Punnal oil	44,000	9.3

6.3. Studies on the effect of vegetable oils on the properties of NR sponge

Experimental

NR is compounded as per formulation given in Table 6.3.1. Whenever vegetable oils are used it is used as a substitute for naphthenic oil and stearic acid. The properties of the sponges with vegetable oils were compared with those of the control mix with naphthenic oil. The compression deflection, compression set and ageing resistance are measured as per ASTM D 1056.

Table 6.3.2 compares the compression deflection, compression set and ageing resistance of the natural rubber sponge with the same loading of aromatic oil and vegetable oils. It is seen that vegetable oils generally improve the compression deflection of sponge. This increase may be due to the additional crosslinks formed by the covulcanization of the oil with the elastomer. Though compression deflection is improved the oils are seen not to affect the compression set. The ageing resistance is also not affected by the substitution of naphthenic oil with vegetable oils, as can be seen from the values of compression deflection of the unaged and aged samples.

Conclusion

Vegetable oils are good substitutes for naphthenic oil in natural rubber sponge. They improve the compression deflection, without affecting the compression set and ageing resistance.

Table. 6.3.1 Formulation

NR	100 phr
ZnO	5 „
Stearic acid	6 „
$CaCO_3$	15 „
$NaHCO_3$	12 „
DNPT	1.0 „
Naphthenic oil	15 „
MBTS	1.0 „
TMTD	0.15 „
Sulphur	2.5 „
Vulcanox HS	0.5 „
Vulcanox 40 20	0.5 „

Table 6.3.2 Compression deflection of unaged and aged samples and compression set

Sample No	Composition	Compression Deflection (psi)		Compression set (%)
		Unaged	Aged	
1	Naphthenic oil	2.31	1.05	7.3
2	Lineed oil	3.30	1.92	7.0
3	Soyabean oil	3.15	2.01	7.4
4	Castor oil	2.97	1.92	7.5
5	Rubber seed oil	3.17	2.02	7.4
6	Punnal oil	3.07	1.89	7.4

CHAPTER VII

SUMMARY AND CONCLUSION

The first chapter gives an introduction about oils and fats. Their general structure and specifications like SV, IV etc are explained. The major industrial uses of oils and fats are discussed in detail. The effect of the fatty acid composition of the oil and the alkali used, on the nature of the soaps is briefly discussed. The classification of oils based on unsaturation and the use of oils in paints and varnishes are briefly discussed. The film drying mechanism of oils are discussed in detail. The production of various chemicals derived from oils is summarised. A detailed survey of the use of vegetable oils in the field of polymers is given in this chapter. Majority of the references cited shows its use as plasticizers. So a discussion about the theories of plasticization, along with a survey of different types of materials used as plasticizer like, petroleum oil, pine products, esters and vegetable oils, is attempted. As the present work is on the use of vegetable oils, like linseed, soyabean, castor, rubber seed and punnal oil, in elastomers a detailed survey of their earlier uses is made. The survey also includes the use of derivatives of the oils in the field of plastics and rubbers. The anticipated suitability of these oils as multipurpose additive in elastomers is established by evaluating their V.G.C. and other properties like free fatty acid content and non-glyceride components. The principal objectives of the present study are pointed out briefly.

Chapter II gives the specifications of all the materials used in the study and summarises the different experimental techniques used in the study. The flow behaviour of the compounds were studied using Brabender plasticorder, the cure characteristics were studied using Elastograph, and the physical properties of the vulcanizates were studied using Universal

Testing Machine. The abrasion resistance of the vulcanizates were studied using a DIN abrader as per DIN standard. The compression set of the vulcanizates was determined as per ASTM D 395. The rebound resilience test was carried out as per ASTM D-2632, The ageing resistance was studied as per ASTM 573-88. The chemical crosslink density was determined by equilibrium swelling methods. The heat build up of the vulcanizates was studied using Goodrich flexometer

Chapter III gives a general introduction about nitrile rubber. NBR is classified in to three categories based on the ACN content. The properties of the elastomer depends on the ACN content. The general behaviour of the elastomer during compounding and curing is discussed. NBR is compounded basically like natural rubber. But as the solubility of sulphur is lower in NBR sulphur is added first during compounding. The cure rate of NBR is also fast. Since NBR is polar, usually esters like DOP or DOS are used as plasticizers. A detailed study of the use of linseed oil, soyabean oil, castor oil, rubber seed oil and punnal oil in ntirile rubber compounding is given in this chapter. These oils are used in place of DOP and stearic acid and the properties of the compound and vulcanizates are evaluated. Linseed oil marginally lowers the viscosity of the compound along with higher cure rate compared to DOP. The tensile strength, modulus, and tear resistance of the vulcanizates are improved by the substitution of DOP with linseed oil. It also decreases the leachability and reduces blooming, by maintaining, the air and oil resistance of the vulcanizates. 2-5 phr linseed oil is found to be an optimum concentration that can substitute 6 phr DOP and 2 phr stearic acid in NBR vulcanizates.

Substitution of DOP with soyabean oil also is seen to be advantageous. The processability of the compound is increased, and cure time is reduced. The cure rate is proportional to the oil concentration. The tensile strength, modulus and tear resistance are increased, along with reduced compression set, blooming and leachability. The oil resistance is improved, while air resistance is unaffected. 4 phr soyabean oil is found to be the optimum concentration which can substitute 6 phr DOP and 2 phr stearic acid in nitrile rubber vulcanizates.

Substitution of DOP with castor oil increases the viscosity of the mix. The theoretical aspects relating to this is discussed. The cure time is increased. But castor oil gives appreciable increase in tensile strength, tear resistance, and ageing resistance with reduced leachability to the vulcanizates. 5-6 phr castor oil is the optimum concentration, which gives advantages in properties, if lower processability can be ignored.

Rubber seed oil, gave a comparable viscosity and cure characteristics to NBR with that of DOP. Tensile strength, tear resistance and modulus of the vulcanizates are increased, along with ageing resistance leachability and blooming are reduced, but compression set is slightly increased. 4-6 phr rubber seed oil is found to be the optimum concentration, that can substitute 6 phr aromatic oil and 2 phr stearic acid in NBR. Punnal oil is also found to be a good substitute for DOP in NBR vulcanizates. The oil gives advantage in processability, cure time, with improvements in physical properties like tensile strength, tear resistance, modulus and compression set. It also reduces leachability and blooming. The optimum concentration of punnal oil is found to be 3-5 phr that can advantageously substitute 6 phr aromatic oil and 2 phr stearic acid in NBR vulcanizates.

Chapter IV deals with a detailed study of the effect of vegetable oils on the cure characteristics and vulcanizate properties of SBR. A brief discussion about the elastomer and the compounding methods adopted, are summarised in this chapter. Linseed oil is tried as a substitute for aromatic oil and stearic acid. It marginally increases the viscosity and cure time of the compounds. Though an improvement in ageing resistance resilience and De Mattia flex resistance are observed, it marginally affects tensile strength, tear resistance, abrasion resistance and compression set. Properties like heat build up, modulus and elongation are unaffected. Linseed oil cannot be considered as a potential additive for SBR particularly as a replacement for aromatic oil. Substitution of aromatic oil with soyabean oil marginally affects the processability. It improves the vulcanizate properties like ageing resistance, De Mattia flex resistance and abrasion resistance. The tensile properties and compression set are unaffected. The cure rate also is unaffected 6-8 phr soyabean oil can substitute 6 phr aromatic oil and 2 phr stearic acid in SBR vulcanizates with the benefit of avoiding aromatic oil and balancing the advantages and disadvantages in properties of compounds and vulcanizates. Castor oil is not a good additive for SBR. Though improvement is seen in cure time and De Mattia flex resistance, all other properties are adversely affected or unaffected. Rubber seed oil is found to be an advantageous substitute for aromatic oil in SBR. It gives appreciable increase in properties like tensile strength, tear resistance De Mattia flex resistance, and rebound resilience to SBR vulcanizates. The compression set of the vulcanizates is reduced while cure rate and ageing resistance are increased. The optimum concentration of rubber seed oil is found to be 5-6 phr that can advantageously substitute 6 phr aromatic oil and 2 phr stearic acid in SBR vulcanizates. Punnal oil imparts improvement in properties like, tensile strength, tear resistance and abrasion resistances, De Mattia flex resistance and resilience to SBR vulcanizates. Processability of the compound is unaffected, while cure rate is increased. 5-6 phr punnal oil is found to be the optimum concentration. Chapter V deals with the effect of vegetable oils on the cure characteristics and vulcanizate properties of natural rubber. Linseed oil is a very good multipurpose additive in natural rubber. The processability is increased and cure time is decreased. The tensile strength, tear resistance, abrasion resistance, and heat build up are unaffected other vulcanziates properties like ageing resistance, compression set, De Mattia flex resistance and resilience are improved. 2-4 phr linseed oil is an optimum concentration, which can advantageously substitute 6 phr aromatic oil and 2 phr stearic acid in natural rubber vulcanizates. Substitution of aromatic oil with soyabean oil reduces the viscosity of NR compounds with increased cure rate. The oil improves the vulcanizate properties like ageing resistance, abrasion resistance resilience and De Mattia flex resistance, while tensile strength, tear resistance and heat build up are unaffected. 2-4 phr soyabean oil is found to be the optimum concentration. Castor oil is seen to be most plasticizing in NR compared to other oils. Along with high reduction in viscosity, the cure time also is reduced. The theoretical aspects of this phenomenon are discussed later. Though no much improvement is seen in tensile strength tear resistance and abrasion resistance, advantages is seen in properties like De Mattia flex resistance, compression set, resilience and heat build up. Th optimum concentration is seen to be 2-3 phr. Rubber Seed oil is a good substitute for aromatic oil in natural rubber vulcanizates. Though there is a slight disadvantage in processability, cure time is considerably reduced. The tensile strength, tear resistance abrasion resistance, De Mattia flex resistance ageing resistance and resilience of the vulcanizates are improved, whereas heat build up and compression set are unaffected. The optimum concentration is found to be 6-8 phr that can substitute 6 phr aromatic oil and 2 phr stearic acid in NR vulcanizates. Punnal oil is also found to be a good substitute for aromatic oil in natural rubber. Though it marginally increases the viscosity, cure time is marginally reduced. The tensile strength, tear resistance ageing resistance, and resilience of the vulcanizates are increased without affecting the compression set, abrasion resistance and heat build up. 6-8 phr is the optimum concentration, that can substitute 6 phr aromatic oil and 2-phr stearic acid.

Chapter VI deals with the effect of vegetable oils on the properties of some typical rubber products. Substitution of aromatic oil with vegetable oils show mixed effect on the viscosities of the compounds. Castor oil marginally lowered the viscosity while rubber seed oil and punnal oil marginally increased the viscosity. Linseed and soyabean oil do not affect the viscosity. The cure time of the compounds are lowered by all the oils tried.

Tensile strength of tread is marginally increased by linseed oil soyabean oil and castor oil, whereas it is considerably increased by rubber seed oil and punnal oil. Tear resistance also showed a similar variation.De Mattia flex resistance is considerably increased and ageing resistance is marginally improved by all the oils. All the oils moderately improve the resilience. The heat build up of the vulcanizates are not affected by the oils. Linseed oil is found to be a good substitute for paraffinic oil in microcellular soles. It considerably increases the flex resistance without affecting the abrasion resistance. Punnal oil also can be used in M.C soles as it does not affect any of the properties. But soyabean oil , castor oil and rubber seed oil are found to decrease the flex resistance of the soles. All the vegetable oils tried are found to be good substitutes for aromatic oil in natural rubber sponge. They improve the compression deflection, without affecting the compression set and ageing resistance.

The summary of the effect of all these oils on the cure characteristics and vulcanizate properties of NBR, SBR, and NR are given in the following chart.

SUMMARY OF THE ADVANTAGES AND DISADVANTAGES IN PROPERTIES BY USE OF VEGETABLE OILS

	OIL	P	CT	TS	TR	M	EB	AR	FR	CS	R	HB	AA	OA	L	B
NBR	LO	↑	⬆	⬆	⬆	⬆	⬆			↑			=	=	⬆	⬆
	SBO	↑	⬆	⬆	⬆	⬆	⬆			↑			=	↑	⬆	⬆
	CO	⬇	⬇	⬆	⬆	⬆	⬆			↓			↑	↑	⬆	⬆
	RSO	=	=	⬆	⬆	⬆	⬆			↓			↑	↑	⬆	⬆
	PO	↑	↑	⬆	⬆	⬆	⬆			↑			=	=	⬆	⬆
SBR	LO	↓	↓	↓	↓	↓	↑		⬆	-	↑		↑			↑
	SBO	↓	=	=	=	=	↑	↑	⬆	↑	=	=	↑			↑
	CO	↓	↑	=	=	=	=		⬆	-	=	=	=			↑
	RSO	=	↑	⬆	⬆	⬆	⬆	=	⬆	⬆	⬆	↓	↑			↑
	PO	=	↑	⬆	⬆	⬆	⬆	↑	⬆	=	⬆	=	=			↑
NR	LO	⬆	⬆	=	=	=	⬆	=	⬆	↓	⬆	=	↑			↑
	SBO	⬆	⬆	=	=	=	↑	⬆	⬆	↓	↑	=	↑			↑
	CO	⬆	⬆	=	=	=	=	=	⬆	↑	↑	↑	↑			↑
	RSO	↓	⬆	⬆	⬆	⬆	=	⬆	⬆	=	⬆		↑			↑
	PO	↓	↑	↑	↑	↑	=	=	⬆	=	⬆		↑			↑

P = Processability

CT = Cure time

TS = Tensile Strength

TR = Tear Resistance

M = Modulus

EB = Elongation at Break

AR = Abrasion Resistance

FR = DeMattia flex resistance

CS = Compression set

R = Resistance

HB = Heat Build up

AA = Air Ageing Resistance

OA = Oil Ageing Resistance

L = Leachability

⬆ = Advantage

↑ = Moderate Advantage

⬇ = Disadvantage

↓ = Slight disadvantages

- Unaffected

Structure dependence of plasticizer action and effect on cure rate

A major out come of the present study is the establishment of the relation between processability and cure rate, and the relation of both with the structure of the elastomer and the plasticizer. It is generally known that the viscosity of any material is lowered where intermolecular force is reduced. Processability of any elastomer is achieved by reducing the viscosity, for which processing aids or plasticizers are used. Along with the major theories of plasticization viz. 1. The solvation theory 2. Lubricity theory 3. Gel theory and 4. Free volume theory. It is also mentioned that viscosity is reduced when intermolecular attraction between the polymer is reduced. The different intermolecular interaction in a compound are the Elastomer-Elastomer (EE interaction), the plasticizer-plasticizer (PP interaction) and the Elastomer Plasticizer interaction (EP interaction). Any plasticizer is considered to be good, when the EE interaction and the EP interaction are lower than the original EE interaction or PP interactions. The usual interactive forces between molecules are the Van der Waals' force, the London force and the hydrogen bond. Hydrogen bond is the strongest among them. A material can highly affect the viscosity if it can produce or break hydrogen bonds. Use of castor oil as ingredient in Nitrile rubber, highly increases the viscosity of the compounds. This is due to the strong hydrogen bond formed between cyano nitrogen of the elastomer and the hydroxyl hydrogen of the plasticizer. The same castor oil highly reduces the viscosity of natural rubber. This is because of the repulsive force between Elastomer and plasticizer which in turn reduces the EE interaction. This theory is against the solvation theory, according to which, a plasticizer is compatible with the polymer, when they are of same nature (like dissolves like). But the conclusion that a good plasticizer may not be a good solvent or may not be compatible with the elastomer is supported by the above observations.

Plasticizer effect on cure rate

The same observation correlates the plasticizing ability to cure rate. The rate of any reaction depends on the activation energy of the molecules taking part. A plasticizer due to it structure can activate or deactivate a polymer molecule. When the plasticizer, which is non compatible with the polymer enters in to the polymer, the polymer-polymer interaction is reduced, and the molecule become activated, and the cure rate will be faster, as in the case of castor oil in NR. The action of castor oil in NBR is in the opposite direction. It forms strong hydrogen bond with adjacent elastomer molecule, reducing the energy of the reacting molecule, and the cure rate is lowered.

So it is concluded that a plasticizer, which increases the polymer-polymer interaction or polymer-plasticizer interaction, is a poor plasticizer, and it will reduce the cure rate. On the other hand a chemically non compatible plasticizer will reduce the intermolecular forces of attraction, between the elastomer molecules, activating it, which results in highly reduced viscosity and increases cure rate.

REFERENCES:

1. A.E.Rheineck, ***J. Paint. Techn.*** 44, 35-54 (1972.)
2. K. Hultzsch ***J. Prakt. Chem.*** 158, 275 (1941).
3. H.J. Richtler, Challenges to a Mature Industry Henkel KGaA, Dusseldorf, 1983.
4. Z.W. Wicks, Jr. and F.N. Jones in Z.W. Wicks, F.N.Jones and S.P. Pappas eds. ***Organic Coating Science & Techn.*** Vol. 1, John Wiley & Sons. Inc. New York 1992, Chapter 9.
5. A.E. Rheineck and R.O. Austin in R.R. Mayers and J.S. Long eds. ***Treatise on Coatings.*** Vol. 1. Part. 2, Marcel Decker Inc. New York 1968, Chapter- 4.
6. D.N. Rampky and J.A. Hasnip. ***J.Oil. Colou. Chem. Assoc.*** 59, 356-62 (1976).
7. O,S,Privett, W.O. Lundberg, N.A. Khan, W.E. Tolberg and D.H. Wheeler, ***J. Am. Oil Chem. Soc.*** 30, 61, (1953).
8. S.A. Harrison and D.H. Wheeler, ***J. Am. Chem. Soc.*** 76, 2379, (1974).
9. O.S. Privett, and C.J. Nickel. ***J.Am. Oil. Chem. Soc.*** 33, 156 (1956).
10. O.S. Privett. ***J. Am. Oil. Chem. Soc.*** 36, 507 (1959).
11. R.N.Faulkner, ***J. Appl, Chem.*** 8, 448-58 (1958).
12. R.R. Allen and F.A. Kummerow. 2, ***J. Am. Oil. Chem. Soc*** 8, 101 (1951).
13. A.E. Rheineck and S.C.G. Peng, ***Official Digest.*** 36, 878 (1964).
14. L.A.O' Neill, ***Chem Ind,*** 384 – 387 (1954)

15. Ludwig et. Al. ***Indian Rubber World*** 53 , 173, (1945)

16 Files, E ; A Basic Look at Fluid Effect on Elastomers. ***Rubber and Plastic News*** (1991).

17. Stephens .H.L, Plasticizer Theory- An Overview Based on the works of Doolittle, Bueche and Ferry, ***Educational Symposium No. 10,*** ACS Rubber Division, May 1993.

18. Nakamura, M. et. al., Paper No. 80 presented at 150th ACS Technical Meeting.

19. Fultz, W.C. et. al. Paper No, 37 Presented at 151st ACS Technical Meeting.

20. Barlow, F.W. ***Rubber Compounding***, Marcel *Decker* Inc. (1993).

21. Onotsuka, Michio; Asahina, Mitsuo; Japan 60, 30, 577 (cl , 25, H 35) 03 Oct. Appl. 20 Nov. 1965. 8 pp.

22. Smith, Walter, Lindel, Stanly.M; Ger Offen. 2, 005, 244 (cl. C. 09 j) 06 Aug 1970 U.S. Appl. 03 Feb. 1969, 17 pp.

23. Aoki, Akira, Ibaragi, Toshio; Yamada, Tsuyoshi; Honda Makoto; Japan , 77, 62, 363 (cl. c. 08 L 53/ 02), 23 May 1977. Appl. 75/ 137, 749, 18th Nov.1975, 8 pp.

24. Abdul Barry, E.M., Badran B.M, Khalifa W.H, Yahia .A.A; ***Elastomerics*** , **110** **(11)** 38 – 42 (1978)

25. Clark Lawrence; Ger. Offen. DE, 3, 738, 335 (cl c 08 L 13/ 00) 26 May 1988 U.S Appl. 931, 389, 17 Nov. 1986 13 pp.

26. Boccaccio. G ***Colloq. Lippochim. Ind. Son. Avenir Cote Petrochim (Actes)*** 52 – 60 (1980) (Published 1981).

27. Clark, Lawrence; Ger Offen DE 3, 738,335 (cl, C 08 L 13/00) 26 May Appl. 931,389 17 Nov. 1986, 13 pp.

28 Yahia. A.A. Badran B.M, Ismail M.N. ***Rubber World***, 197 (1) 37-39 (1987)

29. Richard. A, Pryde Everett.H. US Public Patent (cl 260 . 30 4 R c 08K) 17 Feb. 1976. Appl. B. 485060, 01 Jul. 1974. 7 pp

30. Frankel Edwin. N. Pryde Everett . H. US Pat. Appl. 699, 920, 25th June 1976, 28 pp Avail NTIS.

31. Kaneshige,Yoduke; Sanuki, Kenichi; Nakamoto, Yutako; ***Toyo Soda Kemkya*** 19 (1) 13 – 31 (1975).

32. Saito, Yukihiro; Kitayama, Hiroshi; Ueckusa, Kenji; Suzuki, Takoshi. Japan Kokai, Tokyo Koho JP 63, 264, 648 [88, 264,648] (cl c 08 L 11/00) 01 Nov. 1988. Appl. 87 /98, 896, 22 April 1987, 3 pp.

33. Veichewa .I., Bashdarov.D, Dzhgarova.E, ***Plaste Kausch*** **36 (4),** 123 – 6 (1989).

34. Union Carbide Corp. Brit. 793, 595. (1958).

35. Waldo.C. Ault and Reuben. O. Feuge. US, 2, 895,966, July 21st 1959.

36. Samuel. E. Brillhart and Aloin. N. Gray, US ,2, 426, 858, Sept. 2, 1947.

37. Bevilacqua Edward. M. US, 3, 658, 743 (cl 260- 23.5 A; c 08 d) 25 April 1972, Appl. 33, 480, 30 April 1970.

38. Lee Charles.W. US 3, 661, 874 (cl 260- 80. 3 c, 08 f), May 1972, Appl. 33479, 30 April 1970, 4 pp.

39. Gorbatova. K.A, Balyatskaya .ON, Setnikove .L.P, Gul. V.E, ***Izu. Vysch. . Ucheb Zaved, Khim Khim Technol.*** **16 (12)** 1879-84 (1973)

40. Blackshaw and George Colin. Brit. UK. Pat. Appl. 2, 025,428 (cl c 08 K 5 / 15) 23 Jan 1980. Appl. 307, 575 17 Jul. 1978, 6 pp

41. Asahi, Japan Kokai. Tokyo Koho 80, 62, 947 (cl c 08 L 25/12) 12 May 1980

Appl. 78/ 135, 894, 06 Nov. 1978, 7 pp.

42. Rudolf Ditmar, ***Gummi Zug*** **41**, 535-6, (1926).

43. Zeng Ziangsheng; Li Huilin; Xu, Xi. Famiong Zhuanli Shengking Gongkai Shomingshu CN 1,078, 482 (cl c 08 L 23/ 16) 17 Nov. 1993. Appl. 92, 108, 111, 03 May 1992

44. Hammond Thimothy; Liggal, John Jameison ,Montader James Henry; Webb Andrews PCT Int. Appl. W.O 9428061 (cl c 08 K 5/ 00) 08 Dec. 1994. GB Appl. 93/ 11,399, 02 June 1993, 33 pp.

45. Hamilton, Harry Joseph; Hurley Peter John; PCT. Int. Appl. W.O, 98 39,382 (cl c 08 K 5/ 00) 11Sept. 1998. IE. Appl. 280, 15 April 1977,48 pp.

46. Ando Sachio ; Japan Kokai, Tokyo Koho. JP. 09, 300, 543 [97, 300, 543] (cl B 32 B 27/08), 25 Nov. 1997. Appl. 96/ 143, 771, 13 May 1996, 3 pp.

47. Yoshihide, Kakimoto, Repts , Osaka Ind. Research. Inst. Japan 19. No.9 (1929)

48. Yasaki, Takao; Noro, Masataka; Japan Kokai Tokyo Koho, 78, 139, 657 (cl c 08 L 23/ 02) 06 Dec. 1978. Appl. 77 / 54, 554, 12 May,1972, 5pp.

49. Jain,Ajai. K; Bhatnagar, Rajendra. K. ***Indian Journal of Techn*** **8 (2)** 62 – 4 (1970).

50. Bhatnagar, Rajendra.K; Jain Ajai. K. Indian, 105,490, 22 Aug. 1970, Appl. 28 May 1966, 15 pp.

51. Dewan, Rajendra Kumar; Jain, Ajai Kumar; Indian, IN 159,311 (cl c 08 B 27/ 50) 02 May 1987, Appl. 83 / DE 62, 02 Feb. 1983, 12 pp.

52. Fagade N.B, Banerjee M.S, Millus. W, ***Elastomerics*** **113 (7)** 35 – 40 (1981).

53. Walker George. E, US, 3,438,971, (cl 260- 23.7; c 08 f c 09 d)

15 April 1969, Appl., 03 Sept. 1965, 22 June 1967, 5 pp.

54. Sing, Surinder; Chandran, D.V; Jain A.K; Bhatnagar R.K; ***Popular Plastics*** **14,(7),** 39 – 44 (1969)

55. Kubens Roff; Ger Offen 1,804,364 (cl c 08 G), 21 May 1970, Appl. 22 Oct 1968, 8 pp.

56. Gardner, John. C; William Harold; S.African, 70,01,714, 10 March 1971, Brit. Appl., 13 March 1969, 12 pp.

57. Jurkovski, Boleslaw; Roswadowski, Stanislaw; ***Polimery*** (Warsaw) **22 (5)** 171 - 4

(1977) (Poli.).

58. Tikhvinskii, S.S; Kasyanova.A.A; ***Kozh. Obuvn. Prom. St.*** **20 (7)** 34 - 6 (1978) (Russ.).

59. Kotaki Koju; Kobayashi Saloshi; Tagashira Yutaka; Nishijima Akio; Jpn Kokai Tokkyo Koho, JP, 05,59,310 [93,59,310] (cl c 09 D5/20), 09 May 1993. Appl. 91/ 250,278, 04 Sept. 1991.

60. Kotaki, Koju; Kabayashi, Saloshi; Tagashira Yutaka; Nishijima, Akio; Jpn Kokai Tokkyo Koho JP. 05,112,742 [93,112,742] (cl c 09 D 5/20), 07 May 1993. Appl. 91/229,522 21 Oct. 1991, 12 pp.

61. Redfarn, Cyril.A, Can. CA, 1,238,750 (cl c 08 L 61/ 28) 28 Jan 1998. Appl., 440,049 31 Oct. 1983 12 pp.

62. Jacob Joan; Ciobanu, Constantin, Rom. RO 90,62 b (cl A 63 B41/08) 29 Nov. 1986. Appl. 114,924 19 June 1984, 2 pp.

63. Makaruk, Lessele, Damenska, Irena Gozdz.B. ***Polymery***, **19 (2)** 87-8 (1874).

64. Matyushova V.G, Rusakor O.T; Tremut V.M, Doroshenko N.P.***Plast. Massy***

G§310

60 (4) (1970).

65. Nishnik, .V.V; Solomko V.P; Pelishcnko, S.S; Lutchitskaya N.B; Pavlyuchenka' A.I, ***Sint. Fiz. Khim. Polim.*** **16,** 56 – 60 (1975).

66. Jurkouski, Boleslaw; Kledzik, Maria; ***Polymery*** **25** (5) 189-95 (1980).

67. Eka .O.U. ***West Afr. Jour. Biol. Appl. Chem.*** **20 (3)** 45-54 (1977)

68. Okieimen, Felix .E; Ebhoaye Justin.E; ***Polym. Prepr. (Am. Chem. Soc. Div. Poly. Chem.)*** **34 (2)** (227-8 (1993)

69. Bangaruswamy, S; Obonukul E.J. ***Journal Leather Res.*** **3** (1) 4 – 7 (1985).

70. Patel Paulin. N; Raval D.A; Mannari .V.M; Int. ***J. Polym. Mater.*** **39** **(3 - 4)**

213 – 225 (1998).

71. Patel Paulin N; Raval D.A; Mannari. V.M; Peter .P; ***J. Sci. Ind. Res.*** 57 (2) 70-78 (1998).

72. Dunn P.D; Perera. E.D.I.H; ***Common, Eur. Communities*** [Rep] EUR 1985,

EUR 10024, *Energy Biomass* 1172- 6.

73. Hemavathy. J ; Prabhakar K.V ***J.A.O.C.S*** **67 12)** (955-7 (1990).

74. Games D.E, ***Tetrahedron Letters*** **31** 3187 – 90 (1972)

75. Murthi V.V.S ; Kumar P.S ; Sampath Seshadri T.R, ***Indian Journal of Chem.***

10 (3) 255-7, (1980).

76. Gautier, J; Kunesh.G; Polonsky, J, ***Tetrahedron Letters*** **27** , 2715-18 (1972)

77. Gunstone F.D ; Steward, S.R; Cornelius , J.A; Hammonds T.W; ***J. Sci. Food Agr.*** **23, (1)** 53-60 (9172).

78. Sicchowski J. ***Riv. Ital. Sosfanje Grasse*** . **48 (9)** 502 – 504 (1981).

79. Khafisov. R.Kh; Khrapova N.G; Sakaeva R.*F; Izh. Vyssh. Uchebn. Zaved; Pishch. Technol.* **2** 29- 34 (1979).

80. Guld borg, Merethe; ***Frezenius Z Anal. Chem.* 309 (2)** 117-122 (1982).

81. Tanaka, Akio, ***Yakagalea* 37 (9)** 736 – 9 (1988).

82. Delaveau. P Hotallier Fair, Vaguette, ***J. Plant Med. Phytother,* 5 (4)** 324 – 6 (1971)

83. Dunn, J.R, and Blackshaw G.C, ***NBR; Chemistry and markets,*** Energy Rubber Group Educational Symposium, Dallas, TX, Sept. 24 , 1985 p. 11.

84. Borodina .I ; Nikitin. A, ***Technological properties of synthetic rubbers of USSR-*** Manufacture, Goskhinizdat (1952).

85. Dinsmore . R.P, Juvein R.D, ***Synthetic Rubbers*** , G.S Whitby , (Ed), John Wiley & Sons, New York (1954).

86. Corish P.J ; Palmer M.J, IRI Conference, Loughborough (1959).

87. C.G. Williams ; Proc. Royal Soc. 10, 516 (1860), ***J. Chem. Soc.*, 15, 110** (1867).

88. B.Ellis and G.N. Welding, *Techniques of Polymer Science*, Society of Chemical Industry, London, **17, 45-62,** (1964)

89. D.S. Campbell, *J. Appl. Polym. Sci.,* **13 , 1201,** (1969).

90. D.S. Campbell and B. Saville, *Proc. Int. Rubb. Conf.* , Brigton, **1**, (1967)

LIST OF PUBLICATIONS FROM THIS WORK

1. V.Nandanan, Rani Joseph and D.Joseph Francis
   "Linseed oil as multipurpose additive in NBR vulcanizate"
   Journal of Elastomers and Plastics **28** 326 – 34 (1996).

2. V.Nandanan, Rani Joseph and A.P.Kuriakose
   "Vegetable oils as plasticizer for nitrile rubber"
   Proceedings of the National Rubber Conference, Indian Rubber Institute, Feb. 1997, Mumbai.

3. V.Nandanan, Rani Joseph and K.E.George
   "Rubber seed oil : A multipurpose additive in NR and SBR compounds"
   Journal of Applied Polymer Science **72** 487 – 92 (1999).