UTILIZATION OF RICE BY-PRODUCTS IN RUBBER

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CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by **Sri Ganapathy Rajendran** under my supervision and guidance. No part of this work reported in this thesis has been presented for any other degree from any other Institution.

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DECLARATION

I hereby declare that the work presented in this thesis is based on the original work done by me under the guidance of Dr.A.P.Kuriakose, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology and no part of this thesis has been presented for any other degree from any other Institution.

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Ganapathy Rajendran

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Chapter 1

INTRODUCTION

Rice is the staple food of about half of the human race.[1,2] The world area under paddy is about 93 million hectares producing more than 466 million metric tonnes of this crop. China contributes upto 38% of the world rice production on 24% of the world's rice growing area and India contributes 17% of the production on 28% of the area.[3] It is the single most important crop in India whose economy is dominated by agriculture.[4] Rice is a covered cereal and in the thrashed grain (rough rice) the kernel is enclosed in a tough silicious hull, which renders it unsuitable for human consumption as such.[5] Most of the agricultural commodities including rice have got to be processed in one form or the other before consumption. In the case of paddy, milling is an important link in the post harvest system as it converts the paddy into the consumable form. India has three rice milling systems: The traditional huller rice mill, the under run disc sheller rice mill and the modern rice mill.[6] The objective of rice milling is to remove the hull, the bran and germ with minimum breakage of the starchy endosperm.[7] The huller mill combines both dehusking and polishing process in one operation. Therefore the by-products, viz. husk, bran and germ are mixed together and obtained as huller bran. The oil content of huller bran is 4 to 6%.[8,9] In the under run disc sheller rice mill, disc sheller is used for dehusking and either a huller or cone polisher is used for polishing the dehusked rice. The shelling efficiency of disc sheller is normally 75 to 80% and remaining paddy is recovered for reprocessing. Husk is powdered to some extent during dehusking and as a result the fine husk finds its way into the bran. The oil content of the sheller bran is 10 to 15%.[8,9] The modern rice mill consists of cleaner, rubber roll sheller, paddy separater, polisher and grader. Husk is removed by rubber roll sheller and bran is removed when polished through cone polisher. As a result, the by-products obtained are pure husk, pure bran and brokens. Generally the brokens are again added to the milled rice before consumption. Hence the by-products in modern rice milling system are husk and bran only. The oil content of the modern rice mill bran is 20 to 30%.[10] Rice bran oil and rice husk ash are derivatives obtained from bran and husk.

1.1 RICE HUSK

Rice husk is a fibrous nondigestive material representing about 20% of the dried paddy. Silica is highly concentrated in the outer layer which is coated with a thick cuticle and surface hairs. The inner region of the husk is fibrous and striated and is composed of elongated hypodermal fibres. The mid region contains only little of silica.[11-13] Rice husk is generally straw or gold in colour. Some rice husk may be reddish brown, shades of purple, sooty black, russet or white.[14] The length of the rice husk is about 5-10 mm and the width varies from 2.5 to 5 mm. The bulk density value ranges from 96 to 160 kg/m^3.[15,16] Grinding can raise the bulk density from 192 to 208 kg/m^3. The high concentration of opaline silica present in the outer layer of rice husk results in its effective hardness. The major carbohydrates present in the husk are cellulose and hemicellulose. Hemicellulose, chiefly pentosan, is a glucoxylan which can be hydrolysed to xylose.[17] Starch is apparently absent although small amounts are noted in some varieties. The composition of rice husk is given in Table 1.1.

The crude protein content of rice husk is about A higher protein value reflects some bran contamination in it. The lipid content ranges from 0.39 to 2.98%.[18] The lipids from rice husk contain unsaponsifiable matter

Table 1.1

Composition of rice husk[30,31]

Constituent	Percentage
Moisture	14
Crude proteins	1.9-3
Crude fat	0.3-2.98
Crude fibre	34.5-45.9
Available carbohydrate	26.5-29.8
Ash	13.2-21

and free fatty acids 4 times higher than those from rice bran and rice caryopsis.[19] There is evidence that a large part of the lignin is chemically combined with the hemicellulose and that the middle lamella of the cell walls may contain upto 70% of the lignin associated with pentosans and a little cellulose.[20] Lignin is present in the range of 19.20 to 24.47% in rice husk.[21] The levels of thiamine, riboflavin and niacin in rice husk are 0.84 to 2.4; 0.62 to 0.93 and 14 to 39.5 μ/g respectively.[22-24] Total acids extracted from rice husk is upto 58 meq/kg of which about 30 meq is organic acids.[25] Oxalic and citric acids are the major organic acids present. The other acids present in minor quantities are acetic, fumaric, malic, succinic and some aromatic acids. The aromatic acids are ferulic, vanillic, p-coumaric, sinapic, p-hydroxy benzoic, salicylic and indole acetic acids.[26,27] Ash which constitutes the inorganic portion varies from 13 to 21% of the weight of husk.

Treatment of rice husk (60 mesh) at 120°C for 30 min. with 2% sulfuric acid at an acid husk ratio of 6 ml/g gave 19% xylose, 2.8% arabinose and 1.5% glucose.[28] Furfural can be prepared by acid hydrolysis of rice husk. The hydrolysis of husk (0.5 M sulfuric acid) using superheated steam at 185°C and 1.165 mpa pressure in a batch reactor resulted in 7-9% yield of furfural with upto 1% acetic acid in 1 to 2 hr.[29] The elemental composition of rice husk is given in Table 1.2.

Table 1.2

Elemental composition of rice husk[32-33]

Constituent	Percentage
Carbon	17.7-42.1
Hydrogen	4.8-5.3
Nitrogen	0.5
Oxygen	31.7-40
Sulfur	0.07-0.12

1.2 RICE BRAN AND RICE BRAN OIL

The composition of rice bran depends on a variety of factors associated with the rice grain itself and the milling process. The major factors associated with the rice grain are: (1) average chemical composition; (2) thickness of anatomical outer layers; (3) size and shape of the grains and (4) resistance of grain to breakage and abrasion.

Major factors associated with the milling process are: (1) processing methods and machines and (2) milling conditions. Reported data can also vary because of differences in analytical techniques used by different authors. A general composition of rice bran is given in Table 1.3. Huller bran is lower in protein and fat content and higher in fibre and ash content. The composition of

Table 1.3

Chemical composition of rice bran[34]

Constituent (% dry basis)	Minimum	Maximum
Protein	6.7	17.2
Fat	4.0	30.0
Fibre	6.2	26.9
Ash	8.0	22.2
NFE (Nitrogen free extract)	33.5	53.5

sheller bran strongly depends on the type of sheller. The under run disc sheller produces bran of higher protein and fat content and lower fibre content than the rubber roll huller. The type of machine used in the hulling step also has an influence on the composition of the bran removed in subsequent whitening. The rubber roll huller produces undamaged brown rice from which a bran richer in fat will be removed. The under-run disc sheller removes some germ and outermost layer rich in oil. In multistep milling, the bran from latter cones is higher in nitrogen free extract and lower in protein, fat, fibre and ash.[35]

Rice bran oil is extracted from the bran. This potentially important material has shown remarkable growth during the postwar period, but has still not been widely and profitably exploited in most under developed rice producing countries. The main technical problem is rapid deterioration of the oil in the bran after separation from the brown rice and the subsequent reduction in oil quality. Oil extracted from stored rice bran contains a high percentage of free fatty acids. This can be prevented by stabilization of bran either by heat treatment or by physico chemical methods. But these methods have not been commercially applied extensively. As a result, most of the rice bran oil produced in India is in a crude form.

The oil extraction process consists of three steps: (1) pre-treatments like drying, cleaning, thermal treatment; (2) extraction by pressure or by solvent and (3) recovery and post extraction treatments. Thermal treatment is responsible for stabilising the rice bran to avoid oil deterioration. The activity of a lipolytic enzyme may be destroyed in the bran by heat treatment at 95-100°C for 3 min.[36-38] This thermal treatment also eliminates the fines problem by increasing the particle size and altering the physical characteristics of the particles with a 'crisping' or hardening effect. Gastrock[39] studied a process of mildly cooking the bran which made the material easier to extract and which gave a better yeild of oil. Other processes, with small differences in bran moisture content, heating time and temperature, drying conditions etc. have also been described.[40-43]

1.3 EXTRACTION OF RICE BRAN OIL

Mechanical and solvent methods of oil extraction from rice bran have been practiced for many years especially the latter since World War II, due to higher oil recovery. The two important mechanical methods currently employed are batch production by hydraulic press and continuous production by the use of expellers. The former operates with an open type press at a pressure of about 281 kg/cm^2; the latter is a closed type press with a pressure of 1406 to 2812 kg/cm^2. The amount of oil left in the residue approximates 6 to 12% and 4 to 8% under hydraulic pressing and expeller conditions respectively.

Solvent extraction includes batch type, battery type and continuous method. Batch type is the oldest system using one or more extractors in which the pretreated raw material is placed; hexane from the solvent tank is pumped to the extraction vessel and the solvent level is maintained to percolate the bran and dissolve the oil. The miscella pass through the filter to the evaporator for desolventizing. In battery extraction, sometimes called a semicontinuous system, the fresh solvent is applied only to 1st batch, while the miscella obtained is used to treat the contents of all the other extraction vessels following in order in a counter current system. Continuous extraction is an ideal system achieving the highest economy of labour and materials. It is suitable and economical for a capacity of 50 to 200 MT per day or more.

A filtration extraction process for rice bran has been reported by Graci.[44] Its difference from the conventional solvent extraction system is that the major facility was designed with a series of unit operations of filtration through a continuous horizontal rotary vacuum filter to separate the concentrated miscella from the residual meal. The advantages of this process include rapid filtration rate, low fines content in the miscella, good oil extractability, high capacity, low solvent to meal ratio, low solvent content in the solvent extracted bran, better quality of oil and meal products and low cost.

Fatty acids are the most important constituents of oils and fats. In rice oil, there are 3 major fatty acid components viz. palmitic, oleic and linoleic acids and 5 minor constituents : myristic, palmitoleic, stearic, linolenic and arachidic acids. The composition of the fatty acids of rice bran oil is given in Table 1.4.[45] It has been shown that the variety of rice influences the amount of oil obtained but the fatty acids of the oil had more or less the same general composition.[46] It has been indicated that the oil from bran-polish and from milled rice extracted with petroleum ether have similar fatty

Table 1.4

Fatty acid composition of rice bran oil[45]

Constituent	Percentage
Saturated	
Myristic	0.4-1
Palmitic	12-18
Stearic	1-3
Unsaturated	
Oleic	40-50
Linoleic	29-42
Linolenic	tr-1
Palmitoleic	0.2-0.4

acid composition.[47] However, milled rice oil extracted with chloroform and methanol has a higher linoleic acid content and lower oleic acid than oil extracted with petroleum ether. The presence of phospholipids including phosphatidylethanolamine, phosphatidylcholine and phosphatidylinositol has also been demonstrated in rice bran oil. The fatty acids of phospholipids include linoleic 45.18%, oleic 34.02%, plamitic 16.62% stearic 1.82%, plamitoleic 1.54% and myristic 0.82%.[48]

There are also some unsaponifiable components other than fatty acids in the rice oil. The amount of this unsaponifiable matter is approximately 3 to 8% in raw oil. One of these components is tocopherol (vitamin-E) which comprises 2 to 5% of crude oil. It is a natural antioxidant preventing fat deterioration. Another of the unsaponifiable component is oryzanol, which is obtained from alkali washed raw oil.[49,50] Crude oil contains 2-3% oryzanol. It is reported that this substance has an effect similar to that of vitamin E in expediting human growth, facilitating blood circulation and stimulating hormonal secretion. A medicine known as OZ has been developed from oryzanol in Japan.[51]

Sterols can be recovered from rice bran oil by means of esterification and saponification. Sterols in rice bran oil have been found in amounts upto 5% in which β-sitosterol is the most abundant.[52] Campesterol, stigmasterol and β-sitosterol in the sterol fractions and cycloartanol and 2,4-methylene-cycloartanol in the triterpene fractions have been the results of the action of lipase which give undesirable high free fatty acid levels in the oil.[53,54]

It is important to note that unrefined oil will keep much longer than refined oil. This is due to the former containing higher levels of tocopherols which protect the oil against atmospheric oxidation and rancidity. Oil stored in tin cans show relatively higher rate of increase in free fatty acid concentration than does oil stored in PVC or polyethylene containers.[55] Commercial grade of azelaic acid can be obtained in yields of 10 to 25% by ozonolysis of rice bran oil.[56] A simple and effective method to recover ferulates from rice bran oil has also been reported.[57] A product of gummy wastes from rice bran oil processing mixed with defatted rice bran or wheat bran without additives is an excellent animal feed. It contains crude protein (17.7%) and crude lipids (1.9%) and has a digestability index of 49.2.[58] The main food use for rice oil with low free fatty acids is as cooking oil after refining, bleaching and deodorization.[59,60] A dried granular form of baking yeast has been made by using compressed yeast or yeast concentrate mixed with rice bran oil, monoglycerides, sorbitol fatty acid ester, soyabean oil and alum. This oil can also be used as a pan-release agent in the baking industry, brominated to an essential oil stabilizer and soft drink clarifier, or sulfonated to emulsifiers, wetting and dispersing agents. Pre-treated rice containing 0.1-0.5% rice oil is useful for sake brewing by fermentation.[61]

1.4 RICE HUSK ASH

The use of rice husk ash has found commercial success in the manufacture of specialised bricks known as silex in Italy and porasil in Canada.[62] Slaked lime added to the ash at 3-15% by weight reacted with silica of the ash during firing to provide a vitreous calcium silicate bond. Rice husk ash can also be used as a silica source in the glass and ceramic industries.[63] Ceramic specimens have been prepared from rice husk ash (75-85%) and basic oxides such as those of sodium, boron, calcium and aluminium. The raw materials are fired at 800-1000°C in a furnace, crushed and ground to desired shape, sieved through 300-400 mesh and finally sintered at 700-900°C. Concrete building blocks may be prepared from partly ashed rice husk and cement with added soil.[64] Rice husk ash and lime (1:2) were mixed with nine parts (by weight) of soil and then with water, and blocks were moulded at a pressure of 21 kg/cm^2 and cured at 45-50°C for 24 hrs.

Rice husk ash can be used as a processing aid in filtration, adsorption or coagulation of impurities in water. A filtering medium consisting of 80 cm thick each of shredded coconut fibre and burnt rice husk ash has been used for purification of water.[65] The coconut fibre reduced turbidity and removed suspended solids; burnt rice husk ash achieved the polishing stage in reducing turbidity, removed bacteria and also produced water with acceptable taste, colour and odour. A hydraulic cement can be made by grinding together lime with 20-30% rice husk ash.[66] The setting and hardening characteristics of rice husk ash cement are similar to normal portland cement. Rice husk ash is a potential source of sodium silicate also.[67] Rice husk charcoal is advantageously used to improve soil for seedling horticulture and truck gardening. Seed bed soil containing 20 to 30% husk charcoal substantially increases the tensile strength of rice seedlings with respect to their mechanical transplanting. Charcoal briquettes may be readily prepared from rice husk by a carbonization process followed by briquetting. Zinc oxide may be used in place of zinc chloride as an activator of the carbon for the preparation of activated carbon from carbonised rice husk.[68]

Rice husk ash can be used as an absorbent of oil and a covering to provide an antiskid surface.[69] It acts as a colloidal catalyst carrier and as an abrasive such as in cleaning powder, tooth paste etc. Together with clay it acts as an absorbent for potassium permanganate which is used as a scrubber for ethylene to delay ripening of fruits in transit.[70]

Amorphous silica in the ash from rice husk fired below 700°C is 95% pure. It has been used in developing laboratory scale process for preparing solar grade silicon.[71] The reduction of prepurified rice husk ash silica to silicon with magnesium and by a carbothermic process provides an economic one step conversion of silica to silicon.[72,73]

1.5 USE OF RICE BY-PRODUCTS IN PLASTICS AND RUBBER

Few instances of use of rice by products in plastics and rubber have been reported in the literature. Wills et al.[74] used surface modified husk in polyolefins and prepared products like polyethylene films, moulded window frames, shutters etc. Polypropylene resin compositions containing husk as one of the components has been reported by Monshige Akira and others.[75] Chand et al.[76] reported the preparation of rice husk ash filled polyester resin composites. It was found that the tensile strength and impact strength of the rice husk ash (RHA) polyester resin composites decreased with increasing RHA content. Mehta and Pith[77] developed a specially designed burning equipment for burning the husk to produce heat energy under conditions such that the residual ash which is essentially silica continues to be in an amorphous form. The burning time and temperature are controlled so that the cellular structure of the husk is not disrupted and the silica thus produced is in a reactive form. The silica ash as produced by this process is in the form of a soft material, characterised by high surface area, cellular structure and non-crystalline form. The pulverised ash is found to be a good reinforcing material for rubber compounds containing 50-100 parts of ash by weight to 100 parts of styrene butadiene rubber (SBR). These vulcanizates show mechanical properties superior to those given by commercially available silica or clay fillers. Properties of rubber compounds containing rice husk ash are comparable to those obtained by using medium thermal blacks as reinforcing agents. Based on a synthetic rubber viz. SBR, the relative mechanical properties from different reinforcing fillers are compared. It is evident from the data that the strength, elasticity and hardness of rubber compounds made with rice husk ash are further improved by slight modification of the compound compositions such as by introducing silane or by using a combination of rice husk ash and a commercial carbon black (HAF black). They have reported that among the advantages of using rice husk ash as a filler are: (1) ash incorporates readily into the rubber compounds, and (2) curing is somewhat quicker when compared with carbon black.

The use of rice husk ash is not limited to the SBR type synthetic rubber alone. Good quality rubber products based on other types of synthetic rubbers have also been made in the laboratory.[77] An interesting observation was that 60 parts of ash by weight to 100 parts of natural rubber gave a product with unexpectedly superior mechanical properties, ie., 207 kg/cm^2 tensile strength and 63 kg/cm^2 elastic modulus at 300% strain level.

A detailed work was later taken up by Haxo and Mehta[78] by using the above ash of 325 mesh. The effect of increased loading of RHA on SBR vulcanizates was also studied. In addition to SBR, use of RHA in other rubbers like natural rubber, neoprene and nitrile rubber was also undertaken. In most cases the RHA was used at moderately high loadings. The results show that practical compounds of these rubbers can be prepared.

Chatterjee[79] reported that burning of rice husk in the air produced ash with high silica content and he used this ash as a semi-reinforcing filler in natural rubber and compared the properties with china clay as filler. Rai and coworkers[80] also undertook similar studies in SBR and NR. They used begasse ash also as a filler and found that rice husk ash was better as a reinforcing filler compared to begasse ash at any filler loading presumably due to the higher content of silica and lower content of iron and aluminium in the former. The reinforcing activity of rice husk ash in SBR was found to be comparable to that of medium thermal black. Louis et al.[81] used rice husk ash and hydrated silica from the ash as fillers in SBR and measured the dielectric properties of the vulcanizates at 1592 Hz at room temperature.

1.6 THE SCOPE AND OBJECTIVES OF THE PRESENT STUDY

The function of the processing oil in rubber compounding is to provide better processability during the addition of fillers. They act as lubricants between the rubber chain molecules and improve the processing properties. Generally processing oils are rubber soluble at the processing temperature. However they readily exude at relatively low levels and thereby reduce the tackiness of the rubber compound. The efficiency of the processing oil depends on their chemical structure and physical properties as well as on the type of rubber used. The physical properties of the processing oils are important for practical applications in high processing and application temperatures. High boiling point, low vapour pressure and chemical stability are necessary. The gel point is important for the elastic properties of the vulcanizate at low temperature while viscosity influences the hardness.

The most widely used processing oils are aromatic and naphthenic. Use of vegetable oils in rubber compounding has also been reported.[82] Certain unsaturated oils such as linseed, rapeseed and Safflower oils were used in neoprene rubber to improve properties like low temperature flexibility and tear resistance. Vegetable oils are also used for producing factice by treating with sulphur.

The use of rice bran oil has not so far been reported as processing oil in the rubber industry. In the present study we used rice bran oil as processing oil in place of aromatic/naphthenic oil. Apart from high cost of the above conventional processing oils, they are reported to have toxic effects also. There is a report[82] which classifies untreated naphthenic oil as carcinogenic. Similarly, oils containing more than 0.1 per cent polynuclear aromatics are considered carcinogenic. In view of the above facts we thought it worth while to try the use of rice bran oil as a processing aid in the compounding of natural rubber and styrene butadiene rubber (SBR 1502). The use of rice bran oil as processing aid is advantageous as it is comparatively cheaper than other processing oils and is devoid of any toxicity.

The vulcanization characteristics and vulcanizate properties of natural rubber differ from synthetic rubbers in many respects including variation of receipe for compounding. Compared to NR, synthetic rubbers require higher proportion of accelerator with a corresponding reduction in the amount of sulphur. Also synthetic rubbers do not stress crystallise as much as natural rubber and hence green strength and tensile properties of gum vulcanizates of NR are better than those of synthetic rubbers. It was in view of such variations in processing and vulcanizate properties of NR vis-a-vis synthetic rubbers, it was decided to use natural rubber (NR) and a typical synthetic rubber viz. styrene butadiene rubber (SBR 1502) for this investigation.

Rubber compounding also involves the use of activators. Activators are substances which increase the effect of accelerators. By far the most popular activator system is zinc oxide and stearic acid where stearic acid acts as co-activator. The amount of stearic acid used will vary from 1 to 3 parts on rubber. Rubber grade stearic acid is rather a mixture of fatty acids, typically containing about 60% stearic, 21% palmitic and 9% myristic acid. In general these fatty acids are necessary in small amounts as vulcanization activators. Larger amounts would give a plasticising effect but affect tackiness negatively. Increasing amounts of fatty acids also reduce the rate of vulcanization.

As reported earlier rice bran oil contains higher fatty acids like oleic, linolenic, palmitic etc. In the present study, we made an attempt to utilize these fatty acids present in rice bran oil as co-activator in rubber vulcanization. Different mixes were prepared using NR and SBR in standard formulations with and without stearic acid and along with rice bran oil. Variation in processing characteristics, cure and vulcanizate properties etc. of the different mixes were evaluated.

Rubbers which can be vulcanized with sulphur are susceptible to attack by oxygen. This oxidation reaction may be initiated by different external factors each giving rise to an essentially different form of degradation. The unsaturation in diene rubbers make it possible to cure them with sulphur, but at the same time present a sensitivity toward oxygen, ozone and other reactive substances. Higher temperatures make these effects more noticeable. In the presence of oxidation catalysts like Cu and Mn compounds, these ageing phenomena occur rapidly. Since unreacted double bonds are present in the vulcanizates the possibility exists of further reaction with sulphur causing hardening (post vulcanization). In rubber compounds these degradation processes can be retarded by addition of chemicals that are commonly called age resistors (antioxidants, antiozonants etc). Antioxidants are added to rubber mixtures in amounts of 1-3 phr (parts per hundred rubber). The degree of the protection depends primarily on the nature of the antioxidant. Amines and phenols are the largest group of antioxidants used in rubber industry.

Rice bran oil contains phenols like tocopherol and oryzanol. The amount of tocopherol in rice bran oil ranges from 2 to 5%.[83] Tocopherols are potent antioxidants and the antioxidant property depends upon the presence of free phenolic hydroxyl group. Chemically they are chroman derivatives.[84] They function as antioxidants in human body also in that they inhibit the oxidation of unsaturated lipids by molecular oxygen. Natural oils and fats are known to have much greater resistance to oxidation than pure glycerides and it is also observed that vegetable oils are more resistant to oxidation than those of animal origin. This stability effect can eventually be traced to the tocopherols.[85]

In the present study we also made an attempt to utilise the tocopherol and oryzanol in rice bran oil as antioxidants in NR and SBR mixes. Compounds were prepared with rice bran oil, and with and without conventional antioxidants. The ageing resistance of these vulcanizates were evaluated and the results compared with those of the control mixes.

Phenolic acids like ferulic, vanillic, ρ-coumaric, sinapic, ρ-hydroxy benzoic, salicylic and indoleacetic acids and oryzanol are present in rice husk.[26,27] Eventhough different phenols have been extracted from rice husk, their use in rubber compounding as antioxidant has not been reported. The use of these phenols, obtained by hot extraction method, as antioxidant in rubber also forms part of the present study. Different formulations in NR gum, SBR gum, NR filled and SBR filled compounds were tried and the cure characteristics of the different mixes and physical properties of the vulcanizates (both before and after ageing) were evaluated.

The use of fillers is of utmost importance inorder to obtain the desired properties of rubber vulcanizates. One can produce soft, filler free NR vulcanizates of high tensile strength because of its high stress crystallisation. But for most applications the use of fillers is more or less desirable or necessary in synthetic rubber vulcanizates. The fillers should most often be looked upon as quality enhancing materials and not as cost cutting ones alone. This is true both for the processing properties of the unvulcanized compound as well as for the properties of the vulcanizates. Fillers are generally classified as reinforcing, non-reinforcing and semi-reinforcing types. Reinforcing fillers improve the tensile strength, abrasion resistance, tear resistance etc. besides changing the viscosity of compound.

In India rice husk is generally used as a fuel and after incineration, the ash is the by-product. Eventhough some work on the use of rice husk and rice husk ash in the compounding of rubber has been reported, a systematic study on the cure characteristics, vulcanizate properties etc. of the different systems is lacking. An attempt in the above lines is also made in this thesis. Use of rice husk as such and at different particle size was tried as filler in both NR and SBR vulcanizates. All the mixes prepared in these different filler studies were evaluated for their cure characteristics and also vulcanizate proporties.

The black ash obtained from rice husk contains approximately 50% carbon, 49% silica and 1% other minerals. This black ash was tried as a filler in the preparation of different rubber compounds and their properties were evaluated.

Trials were also made using this black ash along with a conventional filler viz. carbon black at different levels of loading. Carbon and silica were separated from the black ash using caustic soda solution.[86] Experiments were also carried out using the separated carbon and silica separately as fillers in NR and SBR compounds.

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Chapter 2

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

Styrene-butadiene rubber (SBR)

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

Volatile matter, percent by mass	0.75
Total ash, percent by mass	0.50
Bound styrene content, (percent by mass)	25.0

Compounding ingredients

1. Zinc oxide (activator)

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°C)	0.5%

2. Stearic acid (Co-activator)

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

Melting point	65°C
Acid number	200
Iodine number	9.05
Specific gravity (g/cm^3)	0.85
Ash	0.1%

3. Mercaptobenzthiozyl disulphids (MBTS) (Accelerator)

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

Specific gravity (g/cm^3)	1.34
Melting point	165°C

4. Tetramethyl thiuram disulphide (TMTD) (Accelerator)

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

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

5. Sulphur (Crosslinking agent)

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%

6. Fillers

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

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

Precipitated silica (vulkasil-S) was of commercial grade and was supplied by Rubo Chem Industries, Kottayam. It had the following specifications.

pH (5% aq. solution)	6.3
Specific gravity (g/cm^3)	2.03
SiO_2 hydrate on dried samples (min)	90%
Nitrogen free surface	175 ±15 m^2/gm
Loss on heating (105°C, 2 hrs)	5.5%

7. Process oils

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

Aniline point (°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 (°C)	-20
Aniline point (°C)	-78
Viscosity gravity constant	0.87
Aromaticity as %	20

Rice bran oil was supplied by Tamil Nadu Agro Industries Corporation, Thanjavur. It had the following specifications:

Colour (Y + 5R, 1 cm cell)	37
Moisture and volatile matter (% w/w)	0.8
Flash point (°C)	210
Free fatty acid (% oleic acid)	44
Iodine value (wij's)	92
Unsaponifiable matter (% w/w)	4.2

Refractive index (40°C)	1.46
Phosphatides (% w/w)	1.8
Wax (% w/w)	3.5
Hydroxyl value	11
Chlorophyl content (ppm)	2

Other additives

Coumarine indene resin and silane coupling agent were of rubber grade. Hexamethylene tetramine, resorcinol, sodium hydroxide, phenolphthalein and styrenated phenol were all of analytical quality.

Solvents

Solvents used in the study viz., toluene, n-hexane, methanol, chloroform, diethlene glycol (DEG) and ethanol were all of analytical grade.

2.2 STUDY OF THE PROCESSABILITY OF THE COMPOUNDS USING BRABENDER PLASTICORDER

Brabender plasticorder has been widely used for measuring processability of polymers.[1,2] This torque rheometer is essentially a device for measuring the torque generated due to the resistance of a material to mastication or flow under preselected conditions of shear and temperature. The heart of the torque rheometer is a jacketed mixing chamber 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 two 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°C. 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 to obtain a torque - time curve or a plastogram.

The nature of shear in the plasticorder is similar to that encountered in practical processing operations such as extrusion or milling. Blyler and Daane[3] observed that the power law relationship between rotor torque and rotor speed is reminiscent of the power law relationship often found between shear stress and shear rate, and with a few assumptions derived the equation,

$$M = C(n)KS^{n}$$

where, M is the torque

n the power law index

C(n) a function weakly dependent on n

K a constant and

S the rotor speed.

The slope of the plot of log n vs. log S gives the power law index. Also torque/rpm of the Brabender plasticorder represents viscosity and the activation energy for viscous flow can be measured from it if log (torque/rpm) is plotted against 1/T. The activation energy at constant rpm obtained by this procedure should correspond to the flow activation energy at constant shear rate.

In the present study, the processability of natural rubber/styrene butadiene rubber using rice bran oil was compared with that of conventional processing aids viz., aromatic oil and naphthenic oil. Rubber was first mixed for 4 minutes at 30 rpm in the plasticorder with roller mixing heads at room temperature (30°C). Activator and accelerator were then added within 2-3 minutes. Carbon black mixed with rice bran oil/aromatic oil was then added followed by sulphur. The total mixing time was 14 minutes.

In the case of silica, the same procedure in sequence and time was followed. Instead of aromatic oil, naphthenic oil was used in these mixes. Diethylene glycol and silane coupling agent were also added. Rice bran oil, aromatic oil and naphthenic oil were added at different phr levels and based on the torque values, the oil quantity required was optimised.

2.3 MIXING AND HOMOGENIZATION OF THE RUBBER COMPOUNDS

Mixing and homogenization of elastomers and compounding ingredients was done on a laboratory size (15x33 cm) two roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through the nip (0.002x100)". Then it was given two passes through the nip of (0.002x10)" and allowed to band at the nip of (0.002x55)". The temperature of the rolls was maintained at 60±5°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 temperature were controlled during the process.

2.4 DETERMINATION OF CURE CHARACTERISTICS

The cure characteristics of the mixes were determined using a Goettfert 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 oscilated through a small deformation angle (±0.2°). The frequency is 50 oscillations per minute. The torque is measured on the lower oscillating die half. A typical elastograph cure curve is shown in Fig.2.1. The important data taken from the torque-time curve are:

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

ii) Maximum torque: This is maximum torque recorded after the curing of the mix is completed.

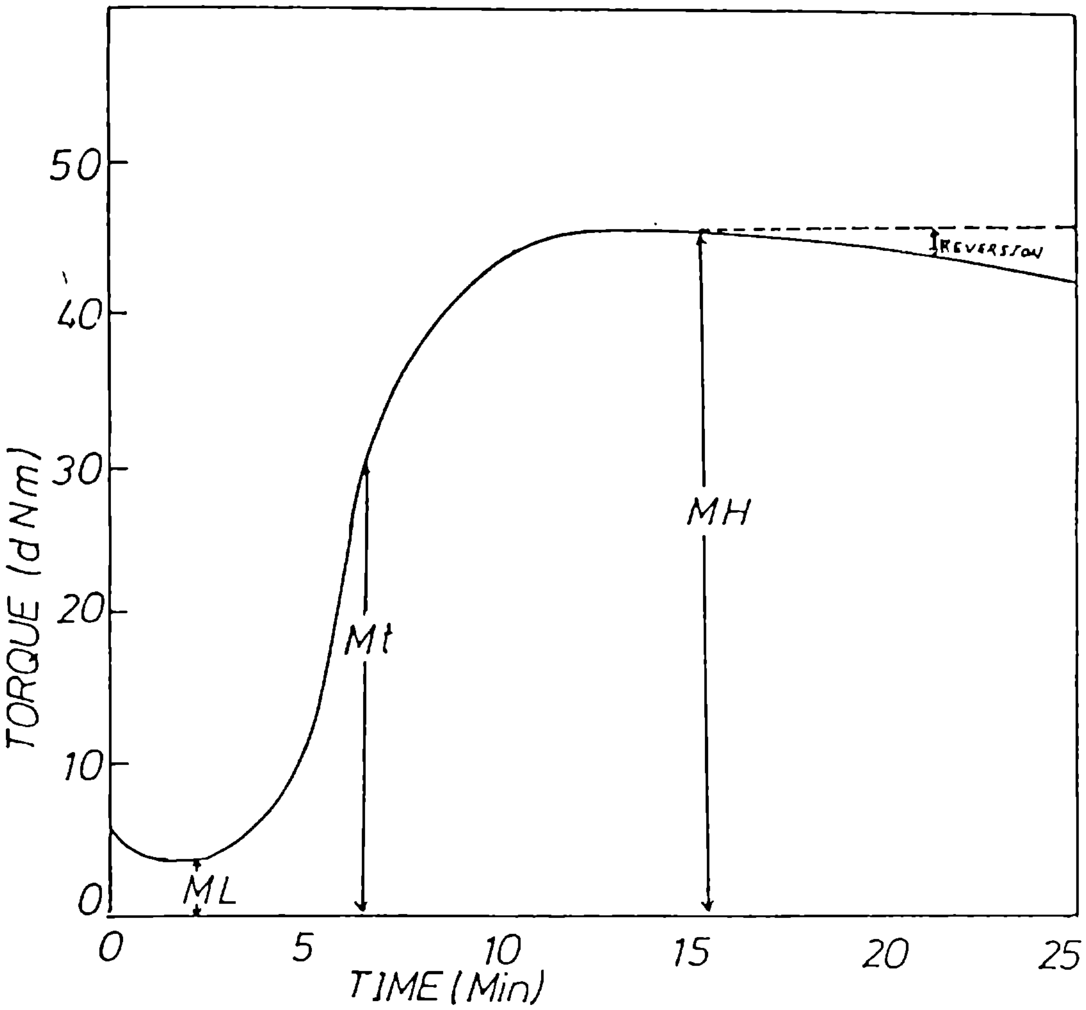

Fig.2.1 Analysis of a typical cure curve to find out various cure parameters of a rubber mix

M_H - Maximum torque M_L - Minimum torque

M_t - Torque at any specified time

iii) Scorch time: This is the time taken for 10% vulcanization.

iv) Optimum cure time: This is the time taken for attaining 90% of the maximum torque.

v) Cure rate: Cure rate is determined from the following equation.

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

where, L_{max} and L_{min} are the maximum and minimum torque and t_{90} and t_{10} 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 moulding on a single day light, electrically heated press having 30x30 cm platens at a pressure of 11.764 MPa on the mould. The rubber compounds were vulcanized upto their respective optimum cure time at 150°C and 160°C for NR and SBR respectively. Mouldings were cooled quickely 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 mouldings.

2.6 PHYSICAL TESTS ON THE 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 the tests were carried out at 28±2°C. Samples were punched out from compression moulded sheets using a dumb-bell die (C-type). The thickness of the narrow portion was measured by bench thickness guage. 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° angle test pieces. The samples were cut from the compression moulded 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°C.

c) Hardness

The hardness (Shore A) of the moulded samples was determined using Zwick 3114 hardness tester in accordance with ASTM D 2240 (1981). The tests were performed on unstressed samples of 30 mm diameter and 6 mm thickness. A load of 12.5 N was applied and the readings were taken after 10 seconds of indentation after firm contact had been established with the specimen.

d) 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°C. 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:

$$\text{Compression set (\%)} = \frac{t_o - t_1}{t_o - t_s}$$

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

e) Abrasion resistance

The abrasion resistance of the samples was determined using a DIN abrader (DIN 53516). Sample 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 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 abravise surface. The abrasion loss was calculated as follows:

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

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

f) Rebound resilience

Dunlop tripsometer (BS 903, pt-22, 1950) was used to measure rebound resilience. The sample was held in position by applying vacuum. It was conditioned by striking with the indenter six times. The indenter was then allowed to strike the sample three times and recorded the highest reading of the three to the nearest 0.05° as the angle of rebound. The temperature of the specimen holder and the sample was kept constant at 35°C. Rebound resilience was calculated as follows:

$$\text{Rebound resilience (\%)} = \frac{1 - \cos\theta_2}{1 - \cos\theta_1} \times 100$$

where θ_1 and θ_2 are the initial and rebound angles respectively, θ_1 was 45° in all cases.

g) <u>Ageing studies</u>

Ageing studies were carried out according to ASTM D 573-88. Dumb-bell samples were kept in an air oven at 100°C for 24 hours in the case of NR and at 100°C for 72 hours in the case of SBR. Physical properties like tensile strength, elongation at break, modulus etc. were measured after ageing. Knowing the values of these tests before ageing, the retention of these properties was calculated for assessing the effect of ageing.

h) Density

Density of the samples was determined as per ASTM D 297 (1981). In this method the weight of the specimen in air was first noted and then the specimen was immersed in water and its loss of weight in water was determined. The density is given by,

$$\frac{\text{Weight of specimen in air x density of water}}{\text{Weight loss of specimen in water}}$$

2.7 CHEMICAL TEST METHODS

Extraction of phenols from husk

Soxhlet extraction apparatus was used for extracting oil and phenols from husk. Husk (2 kg) of CR 1009 variety was cleaned, pulverised and sieved through 50 mesh sieve. 25 g of sieved husk was wrapped in filter paper and placed in the tube of the extractor which was then connected with the condenser. A plug of cotton was placed on the top of the thimble to prevent the pulverised samples from floating out as the solvent rises and being carried into the flask during the siphoning. The sample was first extracted with n-hexane to remove the oil from the husk. The oil content was then determined. Then the sample was further extracted with a 1:1 mixture of chloroform and methanol.[4] The heating was controlled in such a way that the solvent siphoned over about 5 to 6 times an hour. After the extraction was completed, the solvent was distilled off. The residue was dissolved in minimum quantity of methanol, filtered through a filter paper (Whatman No.40, qualitative) methanol was removed and then dried at 80°C (yield 1%).

Separation of carbon and silica from black ash

The black ash for the preparation of carbon and silica was obtained by controlled burning of husk at 700±10°C for 10 min in a muffle furnace.[5] Caustic soda solution (2 litres, 10%) and black ash (450 gm)[6,7,8] were taken in a stainless steel vessel and heated to 97-98°C for 30 min with intermitent stirring. One litre of water was further added at the end of heating and stirred. Dilute sodium silicate solution thus obtained was allowed to settle for 30 min and the supernatent liquid filtered through a cotton cloth. The strength of sodium silicate solution was determined by using hydrometer (25 Baume). The filtrate was added with 1:1 HCl slowly till gel was formed. The gel ($SiO_2.H_2O$) was washed with water till it was free from salt and dried. It was then pulverised, sieved through the appropriate sieves and used for the experiments. The chemical reactions involved in the separation of silica may be represented as;

$2NaOH + SiO_2 \qquad Na_2SiO_3 + H_2O$

$Na_2SiO_3 + 2HCl \qquad H_2SiO_3 + 2NaCl$

$H_2SiO_3 \qquad SiO_2 + H_2O$

Two litres of water was added to the stainless steel vessel containing residual carbon and was neutralised with dilute hydrochloric acid. This was filtered and the residue was repeatedly washed with water. The carbon thus obtained contains minerals also. The minerals were removed by heating the residue with 1:1 HCl at 100°C for 1 hour. It was filtered and residue was washed acid free and dried. The carbon obtained as above was pulvarised and used for the experiments after sieving through appropriate sieves.

Estimation of free fatty acids in rice bran oil[9]

Alcoholic solution of rice bran oil containing fatty acids was volumetrically estimated using standard alkali. Alcohol was boiled on a waterbath for 5 minutes to remove dissolved gases and neutralised by adding dilute sodium hydroxide using 3 drops of phenophthalein until a pale pink colour was obtained. Rice bran oil was weighed into a flask, 50 ml of the hot neutralised alcohol was added and the mixture boiled on a water bath for 5 minutes. While still hot, the solution was titrated with 0.1 N sodium hydroxide solution until the pale pink colour was restored. Free fatty acid is expressed as oleic acid as it is the predominent acid in rice bran oil. Based on the above titre value, the free fatty acid was calculated.

Determination of chemical crosslinks of the vulcanizates[10-12]

The concentration of crosslinks (crosslink density) of the vulcanizates was determined from the equilibrium swelling data as follows:

Samples of approximately 0.3 g were cut and kept to swell in solvent (toluene) for 24 hrs. The outer portion of the swollen samples was then dried using a filter paper and weighed. It was then placed inside the oven at 60°C for 24 hrs. to remove toluene. The deswollen weight was determined. The volume fraction of rubber in the deswollen network was then calculated by the method reported by Ellis and Welding[10] from the following equation

$$Vr = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_o\rho_s^{-1}}$$

where, T = weight of the test specimen; D = deswollen weight of the test specimen; F = weight fraction of insoluble component; A_o = weight of the absorbed solvent corrected for the swelling increment; ρ_r = density of test specimen; ρ_s = density of solvent.

In the case of vulcanizates containing filler the value of V_r obtained as above were converted into V_ro by means of an equation derived by Porter.

$$\frac{V_ro}{V_r} = 0.56\ e^{-z} + 0.44$$

where, V_r is the volume fraction of rubber without the filler, Z is the weight of the filler divided by total weight of all ingredients, and V_ro is the volume fraction of rubber with filler. This value was then substituted in the Flory Rehner equation in place of V_r to obtain the crosslink density.

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Chapter 3

RICE BRAN OIL AS A NOVEL COMPOUNDING INGREDIENT IN SULPHUR VULCANIZATION OF NATURAL RUBBER

Natural rubber which is commonly obtained from the latex of hevea brasiliensis, contains approximately 94% rubber hydrocarbon, 3% protein and 3% of other materials including fatty acids and resins. Purified natural rubber hydrocarbon is a long chain polymer made up of cis 1,4-polyisoprenoid units and the average molecular weight ranges from 2-5 lakhs.[1] Due to its high structural regularity,natural rubber tends to crystallise on stretching. The strain induced crystallization gives it the unique high tensile strength in gum or non-filler vulcanizates. Natural rubber is the preferred polymer in many areas because of its superior building tack, green stock strength, better processing properties, high resilience and excellent dynamic properties.

In rubber industry, compounding and vulcanization transforms raw rubber into a range of materials suitable for applications as diverse as tyres and tubes, building mounts, hot water bottles and chemical plant linings.

Depending upon demand, these products will also vary in such properties as stiffness, resilience and durability. Compounding of rubber involves the addition of processing aids, vulcanizing agents, accelerators, activators, age resistors, fillers, and miscellaneous ingredients like retarders, colours, blowing agents, antiabrasives, odorants etc. As the present study concentrates more on process oils coactivators and antioxidants, these topics may be discussed in a little more detail especially in connection with natural rubber compounding.

Process aids will be considered as those materials included in a rubber mix primarily to reduce the time and energy required in processing. However, at the same time they help with dispersion of dry materials, give smoother stocks, improve extrusion rates and in some instances increase the homogeneity of blended rubbers. The most widely used processing oils are aromatic and naphthenic but use of vegetable oils in rubber compounding has also been reported. Vulcanizing agents are the chemicals that are required to crosslink the rubber chains into the network that gives the desired physical properties in the final product. Accelerators reduce the vulcanization time by increasing the rate of vulcanization. Accelerator activators form chemical complexes with accelerators and thus aid in obtaining maximum benefits from an accelerator system by increasing the vulcanization rate and improving the final product properties. Zinc oxide is the most common activator and it is generally used in combination with a fatty acid to form a rubber soluble soap in the rubber matrix. Fatty acid functions as a coactivator. The mechanism by which this complex speeds up the cure has not been well understood and results to date indicate its complexity. It is presumed that zinc oxide reacts with stearic acid to form zinc stearate which is soluble in the rubber and in this form facilitate the crosslinking process. It is essential to have the zinc ions in soluble form. Stearic acid or other fatty acids used also serve as lubricants between the polymer chains and allow easier flow of the compound in shear. Both ends of the stearic acid molecule help processing. The paraffinic end provides the lubricating effect while the acid group along with other functions absorbs the pigments on the surface. Although stearic acid is by far the most common fatty acid used, others like oleic acid may also be used.

Age resistors are used in rubber compounding to reduce ageing processes in the vulcanizates. Ageing is normally caused by chain scission, crosslinking or some form of chemical alteration of the polymer chains. Consequently, the age resistors used must be capable of reacting with the agents causing ageing, prevent or slow the polymer breakdown to improve the anti-ageing qualities and to extent the service life of the product involved. Amines and phenols are generally used as antioxidants and they function by slowing down the oxidative degradation of rubber products.

Rice bran is obtained as a by-product in rice milling and it has been a potential source of oil containing 20-25 percent on the weight of bran. The oil obtained from rice bran is good quality edible oil, but the free fatty acid (FFA) of the rice bran oil increases if the bran oil is not extracted immediately after milling. This is due to the presence of lipolytic enzyme in rice bran which becomes active just after milling. Actually rice bran does not contain more lipase than other oil bearing materials such as groundnut, but fine particle size (0.32 mm) and porosity is responsible for the quick hydrolysis of oil resulting in the development of FFA. With the increase of FFA in rice bran oil, the oil becomes inedible and the refining cost prohibits the high FFA oil for edible purpose. The rise in FFA is 3-10% in parboiled bran and 40-70% in raw rice bran within a week's time after production while the initial value of FFA is only 1-3%.[2,3]

A characteristic feature of rice bran oil is the presence of fatty acids, unsaponifiable matter, phosphatides and wax.[4] The composition of fatty acids is 40-50% oleic, 20-42%, linoleic, 13-18% plamitic, 1-3%, stearic, 0.4 to 1% myristic and 0-1% linolinic acids. The unsaponifiable matter[5] that comes from the glyceride portion of the oil consists of phytosterol, tocopherol, squalene, oryzanol and naphthene group of hydrocarbons. The unsaponifiable matter that comes from the wax is mostly esters of long chain fatty acids and long chain alcohols. Phosphatides[6] mainly contain lecithin and is present to the order of 0.6%. Lecithins are mixed esters of glycerine and choline with fatty acids and phosphoric acid. Tocopherol functions as an antioxidant[7] in human body in that it inhibits the oxidation of unsaturated lipids by molecular oxygen. The natural oils and fats are known to have a much greater resistance to oxidation than pure glycerides and it is also observed that vegetable oils are more resistant to

$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH$

Oleic acid

$CH_3-(CH_2)_4-CH=CH-CH_2-CH=CH-(CH_2)_7-COOH$

Linoleic acid

$CH_3-(CH_2)_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_6-COOH$

Linolenic acid

$CH_3-(CH_2)_{16}-COOH$

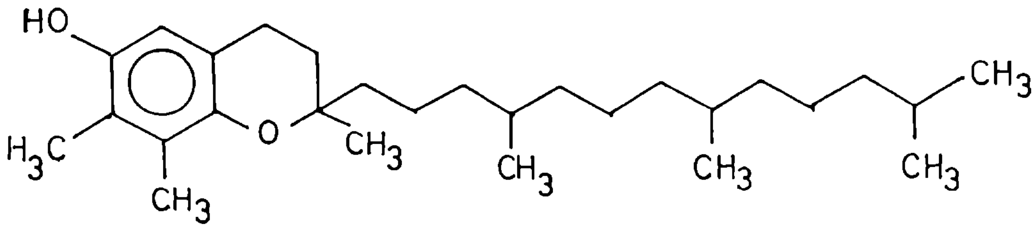
Stearic acid

$CH_3-(CH_2)_{14}-COOH$

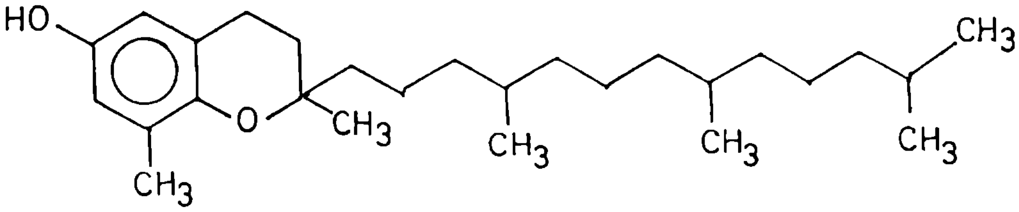
Palmitic acid

$CH_3-(CH_2)_{12}-COOH$

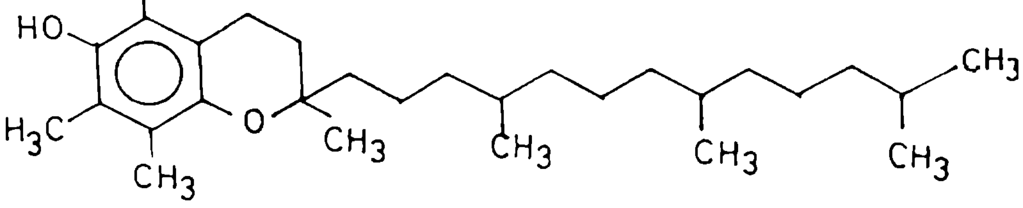
Myristic acid



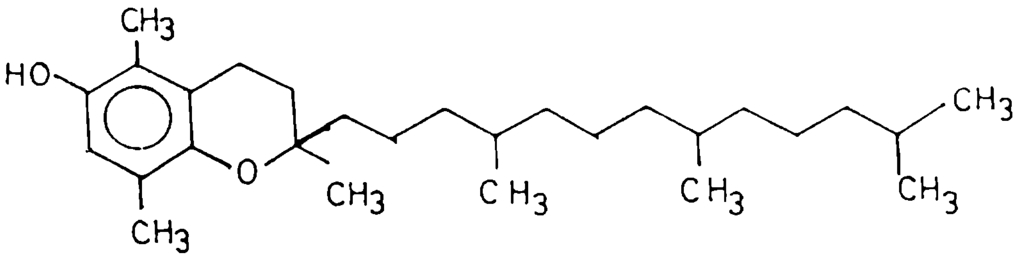
α-Tocopherol



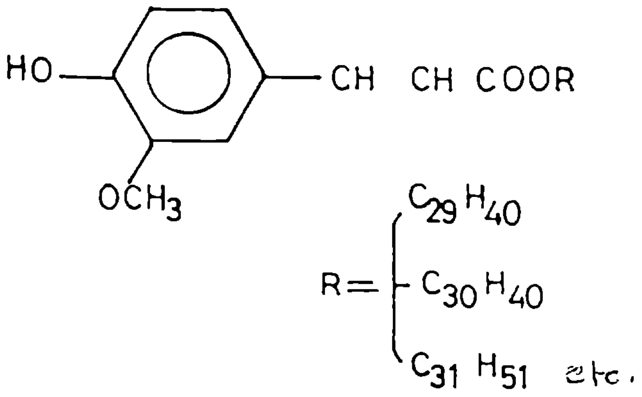
β-Tocopherol



γ-Tocopherol



δ -Tocopherol



Oryzanol

oxidation than those of animal origin. This stability effect can eventually be traced to the tocopherols.[8] It is reported that rice bran oil contains upto 3 to 5% tocopherol.[9]

In view of the fact that rice bran oil contains good amount of higher fatty acids and reasonable amount of natural antioxidants, it was thought worthwhile to try this oil as a substitute for;(1) processing oil (2) co-activator and (3) antioxidant for natural rubber compounding. The study becomes all the more important because petroleum oils used as processing aids are becoming prohibitively costly whereas rice bran oil is available at much cheaper rates in India. It is also worthwhile to note that many antioxidants used in rubber industry are reported to have toxic effects while natural rice bran oil is devoid of any toxicity.

In the present study we used a sulphur accelerated system for the vulcanization of natural rubber using rice bran oil as indicated above. Both carbon black and precipitated silica were tried as fillers and aromatic/ naphthenic oil was used as processing aid in the control mixes. The mixes obtained from these different formulations were evaluated for their cure characteristics. The vulcanizates prepared were evaluated for their tensile and other physical properties. In order to study the variation in physical properties of the different vulcanizates, the total chemical crosslink density was also estimated. Also studied was the variation in processing characteristics brought about by the incorporation of the rice bran oil with the help of a Brabender plasticorder. The results obtained in the above experimental mixes were compared with those of the control mixes. The optimum quantity of the rice bran oil required in the different formulations has also been derived.

In this study, we also made an attempt to utilize the fatty acids present in rice bran oil as co-activator in these natural rubber vulcanization studies. Different mixes were prepared using NR in standard formulations using rice bran oil and with and without stearic acid. Variation in processing characteristics, cure and vulcanizate properties etc. of the different mixes were evaluated. In the next part of the study we made an attempt to utilize the tocopherol and oryzanol present in rice bran oil as antioxidant in NR mixes. Compounds were prepared with rice bran oil, and with and without conventional antioxidants. The ageing resistance of these vulcanizates were evaluated and the results compared with those of the control mixes.

EXPERIMENTAL

Natural rubber comforming to ISNR-5 having specifications given in chapter 2 was used in the present study. Zinc oxide, stearic acid, mercapto benzothiazyl disulphide (MBTS), tetramethyl thiuram disulphide (TMTD), sulphur, carbon black (HAF-330), precipitated silica (Vulkasil) aromatic oil, naphthenic oil, diethylane glycol (DEG) and silane coupling agent used are all of rubber grade. Rice bran oil obtained from Tamil Nadu Agro Industry Corporation, Thanjavur having the specifications given in Table 3.3 was used in the study.

Brabender plasticorder PL-3S was used for studying the processing characteristics of the mixes. The processability of natural rubber using rice bran oil was compared with that of conventional aromatic oil/naphthenic oil. NR was first mixed for 4 min. at 30 rpm in the plasticorder with roller mixing heads at room temperature. Activator and accelerator were then added within 2-3 min. Carbon black mixed with rice bran oil/atomatic oil was then added followed by sulphur. The total mixing time was 14 min. The formulation of the mixes is as given in Table 3.1 except for the fact that the oil levels were varied. To optimise the requirement of oil, rice bran oil and aromatic oil were first used at 3, 5 and 7 phr levels each. A higher torque was obtained in the case of mixes in which 3 phr of rice bran oil/aromatic oil was added. But acceptable torque was obtained in the case of 5 and 7 phr levels. So it is evident that an oil level of 5 phr each can be taken to be optimum for carbon black filled natural rubber compounds (Fig.3.1 and 3.2) in a Brabender plasticorder. But it may be noted that in the mixing mill the oil level required was only 3 phr due to the higher shearing force encountered in the mill.

The same procedure in sequence and time was followed in the case of silica and the receipe for these mixes is also given in Table 3.1. Instead of aromatic oil, naphthenic oil was used in these mixes. Rice bran oil/naphthenic oil was added at 3, 5, 7 and 9 phr levels each. DEG (diethylene glycol) and silane coupling agent were also added. An acceptable torque value was obtained in the case of 7 and 9 phr of the oil only. Hence 7 phr of the oil is taken to be optimum in these silica filled compounds. The Brabender torque curves obtained for these mixes are given in Fig.3.3 and 3.4.

The conventional system of rubber vulcanization was used in the present study (Table 3.1). Mix I contains carbon black and mix II contains precipitated silica. Mixes IA & IB contain aromatic oil, mixes IIA and IIB contain nephthenic oil while mixes IC, ID, IIC and IID contain rice bran oil. Mixes IA and IIA contain no antioxidant but other compounding ingredients are added as usual. IB and IIB contain 1 phr each of styrenated phenol as antioxidant. In IC & IIC no stearic acid and antioxidant are added. ID and IID contain antioxidant but no stearic acid.

The mixes were prepared on a laboratory size two roll mixing mill (30x15 cm) at a friction ratio of 1:1.25 according to the procedure given in ASTM D 3285-88. The cure characteristics of the various mixes at 150°C were evaluated using Goettfert Elastograph (Model No.65.85) as per ASTM D 1646 (1981). The cure properties obtained are given in Table 3.2. The cure curves of the carbon black filled compounds are given in Fig.3.5 and those of silica filled compounds are given in Fig.3.6.

The procedure adopted for vulcanization, estimation of different physical and chemical properties of the vulcanizates etc. are as reported in chapter 2. Vulcanization was carried out in an electrically heated hydraulic press of 18x18 inch platens maintained at 150°C and at a pressure of 11.764 Mpa. Tensile and other physical properties of the vulcanizates were determined as per relevant ASTM procedures and the results obtained are reported in Table 3.4. The crosslink density of the different vulcanizates was determined and these results are also reported in Table 3.4. The ageing studies are carried out as per ASTM D 573-88.

RESULTS AND DISCUSSION

1. Processability

The quantity of rice bran oil and aromatic/ naphthenic oil required for the various compounds was optimised in a Brabender plasticorder. The mixes were then prepared in a two roll mixing mill and it is found that a lower dosage of both oils is sufficient for processing in the mill due to the higher shearing force during the operation of two roll mill compared to Brabender plasticorder. 3 ml each of rice bran oil/aromatic oil was found sufficient in carbon black filled compounds while 5 ml of rice bran oil/naphthenic oil was required for the silica compounds. Based on the processing characteristics thus estimated and also on vulcanizate properties it is evident that rice bran oil can be effectively used as processing oil in the different natural rubber systems included in the present study.

2. Cure characteristics

The cure curves of NR-carbon black and NR-silica systems are given in Fig.3.5 and 3.6 respectively. Optimum cure time, cure rate index scorch characteristics etc. are given in Table 3.2. From the cure curves, it can be seen that the maximum torque developed is more in mixes containing rice bran oil compared to those containing aromatic oil/naphthenic oil in both carbon black and silica filled systems. In the carbon black filled systems, there is not much variation in the induction time, scorch time and optimum cure time of the mixes when rice bran oil is used compared with the control mixes. More or less the same trend is noticed in the case of mixes containing silica also. It is evident that the use of rice bran oil tends to give a higher torque value without much affecting the cure characteristics in both these systems of vulcanization. In the mixes where fatty acid and antioxidant were substituted also, there is not much variation in the cure characteristics presumably due to the presence of the higher fatty acids and antioxidants in rice bran oil.

3. Crosslink density

The total chemical crosslink density of the vulcanizates was evaluated for both carbon black and silica filled systems. The results obtained are given in Table 3.4. Systems containing carbon black and rice bran oil showed higher crosslink density values than those with aromatic oil. This is also evidenced by the slight increase in tensile strength values for the former systems. But in the case of silica filled systems, the crosslink density values did not show much variation between rice bran oil and naphthenic oil. The higher crosslink density values obtained in the carbon black filled vulcanizates can be attributed to the better interaction between the rubber and filler in the case of carbon black compared to silica.[10] Rice bran oil shows a positive effect in this interaction.

4. Tensile and other physical properties

Tensile and other physical properties obtained for the vulcanizates from the various systems are given in

Table 3.4. From the table it is seen that the initial tensile strength is slightly higher for the vulcanizates containing rice bran oil than for those containing aromatic oil for the carbon black filled systems. But a corresponding increase is not noticed for the modulus values. Elongation at break is maximum for the mix containing rice bran oil with the conventional antioxidant. But the differencesin tensile strength, elongation at break and modulus are only marginal among the mixes. The mixes containing rice bran oil with and without antioxidant and the mixes containing aromatic oil with antioxidant on heat ageing retained more or less same level of tensile properties. Retention of tensile properties is less in the mix containing aromatic oil without antioxidant.

In the case of silica filled systems, slightly higher tensile strength is noticed in the mix containing rice bran oil without antioxidant. This is followed by the mix containing naphthenic oil with antioxidant, rice bran oil with antioxidant and finally naphthenic oil without antioxidant. Modulus at 200% elongation is higher for the mix containing naphthenic oil compared to the one containing rice bran oil. Elongation at break is maximum for the mix containing naphthenic oil without antioxidant.

Elongation is intermediate for the mixes containing rice bran oil. As expected tensile values for silica filled vulcanizates are lesser than those containing carbon black.[11] The percentage retention of tensile properties on heat ageing is quite high for the mixes containing rice bran oil with and without antioxidant and also for the mix containing naphthenic oil with antioxidant. In contrast, poor retention of tensile properties is noticed for the mix containing naphthenic oil without antioxidant. It can be noted that the presence of rice bran oil in carbon black and silica filled systems of NR provide ageing resistance comparable to that of styrenated phenol. As suggested earlier, the antioxidant property of rice bran oil may be attributed to the presence of tocopherol and oryzanol in this oil.[12]

Other physical properties of the vulcanizates studied are hardness, compression set, resilience, tear strength and abrasion resistance. In the case of carbon black systems, hardness, compression set and resilience are found to be more or less the same for the mixes containing aromatic oil and rice bran oil. The same trend is observed in silica filled systems also. The higher values of tear strength obtained for the mixes containing rice bran oil compared to those containing aromatic oil is in agreement with their higher crosslink density values[13] (Table 3.4). In the case of silica filled systems, tear strength is more or less same for the vulcanizate samples from all the mixes. It may be noted that the crosslink density values of these mixes are also more or less the same. In the estimation of abrasion loss also both carbon black and silica filled vulcanizates showed almost similar values for rice bran oil and aromatic oil/naphthenic oil.

CONCLUSION

The results of this study indicate that raw rice bran oil can be used in natural rubber compounding where sulphur accelerator system is used. It is seen that this oil can replace the processing oil, fatty acid and antioxidant in a natural rubber compound without much affecting the processibility and cure characteristics of the mixes and the physical properties of the vulcanizates. Apart from low cost of the rice bran oil, there will be energy saving also during processing. This is all the more important because the mineral oils used at present as processing aids in rubber are becoming prohibitively costly in India while rice bran oil (non-edible) is available at much cheapter rates. The results also suggest that conventional antioxidants used for rubber compounding which are known to be somewhat toxic can also be replaced with rice bran oil. The high free fatty acid rice bran oil which is at present used mainly in soap industry can advantageously be used in the rubber industry.

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Table 3.1 Formulation of mixes containing carbon black and precipitated silica

Mix	IA	IB	IC	ID	IIA	IIB	IIC	IID
Natural rubber	100	100	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4	4	4
Stearic acid	1.5	1.5	--	--	1.5	1.5	--	--
Mercapto benzothiazyl disulphide (MBTS)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Tetramethyl thiuram disulphide (TMTD)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Styrenated phenol	--	1.0	--	1.0	--	1.0	--	1.0
Carbon black (HAF N330)	50	50	50	50	--	--	--	--
Precipitated silica (Vulkasil)	--	--	--	--	50	50	50	50
Aromatic oil	3	3	--	--	--	--	--	--
Naphthenic oil	--	--	--	--	5	5	--	--
Rice bran oil	--	--	3	3	--	--	5	5
Diethylene glycol	--	--	--	--	2	2	2	2
Silane coupling agent (Si 69)	--	--	--	--	2	2	2	2
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Table 3.2 Cure characteristics of mixes containing carbon black and precipitated silica (at 150°C)

Mix	IA	IB	IC	ID	IIA	IIB	IIC	IID
Optimum cure time t_{90} (min.)	5.1	5.1	5.2	5.2	4.8	4.8	4.9	4.9
Scorch time t_{10} (min.)	2.1	2.1	2.1	2.1	1.6	1.6	1.7	1.7
Cure rate index	31.33	31.33	31.12	31.12	31.25	31.25	31.25	31.25
Induction time (min.)	0.98	0.98	0.98	0.98	0.96	0.96	0.96	0.96

Table 3.3: Characteristics of the crude rice bran oil[4,5,6,14,15]

Colour (Y + 5R, 1 cm cell)	37
Moisture and volatile matter (% w/w)	0.8
Flash point (°C)	210
Free fatty acid (% oleic acid)	44
Iodine value (Wij's)	92
Unsaponifiable matter (% w/w)	4.2
Refractive index (40°C)	1.46
Phosphatides (% w/w)	1.8
Wax (% w/w)	3.5
Hydroxyl value	11
Chlorophyll content (ppm)	2

Table 3.4: Physical properties of vulcanizates

Parameter	IA	IB	IC	ID	IIA	IIB	IIC	IID
Tensile strength (MPa) BA	25.33	25.44	25.48	25.56	20.05	20.45	21.04	20.25
Tensile Strength (MPa) AA	13.56	19.93	19.64	19.88	10.19	15.15	15.12	15.06
Elongation at break (%) BA	442	438	431	446	600	662	640	622
Elongation at break (%) AA	231	319	309	311	290	368	369	363
Modulus at 200% (MPa)	8.84	8.67	8.45	8.33	3.74	3.25	2.64	2.65
Tear strength (N/mm)	90.20	91.25	95.90	95.20	61.05	61.90	60.35	61.11
Compression set (%)	35.40	35.52	35.74	35.76	54.10	55.00	54.72	54.80
Hardness (Shore A)	64	64	64	64	68	67	67	67
Abrasion (cm^3/hr)	7.680	7.664	7.612	7.407	7.710	7.690	7.740	7.760
Resilience (%)	54.43	54.11	55.08	55.08	53.15	54.11	54.11	54.43
Crosslink density (mmol/kg)	70.30	73.01	75.40	78.29	67.00	67.87	68.02	68.42

BA - Before ageing, AA - After ageing.

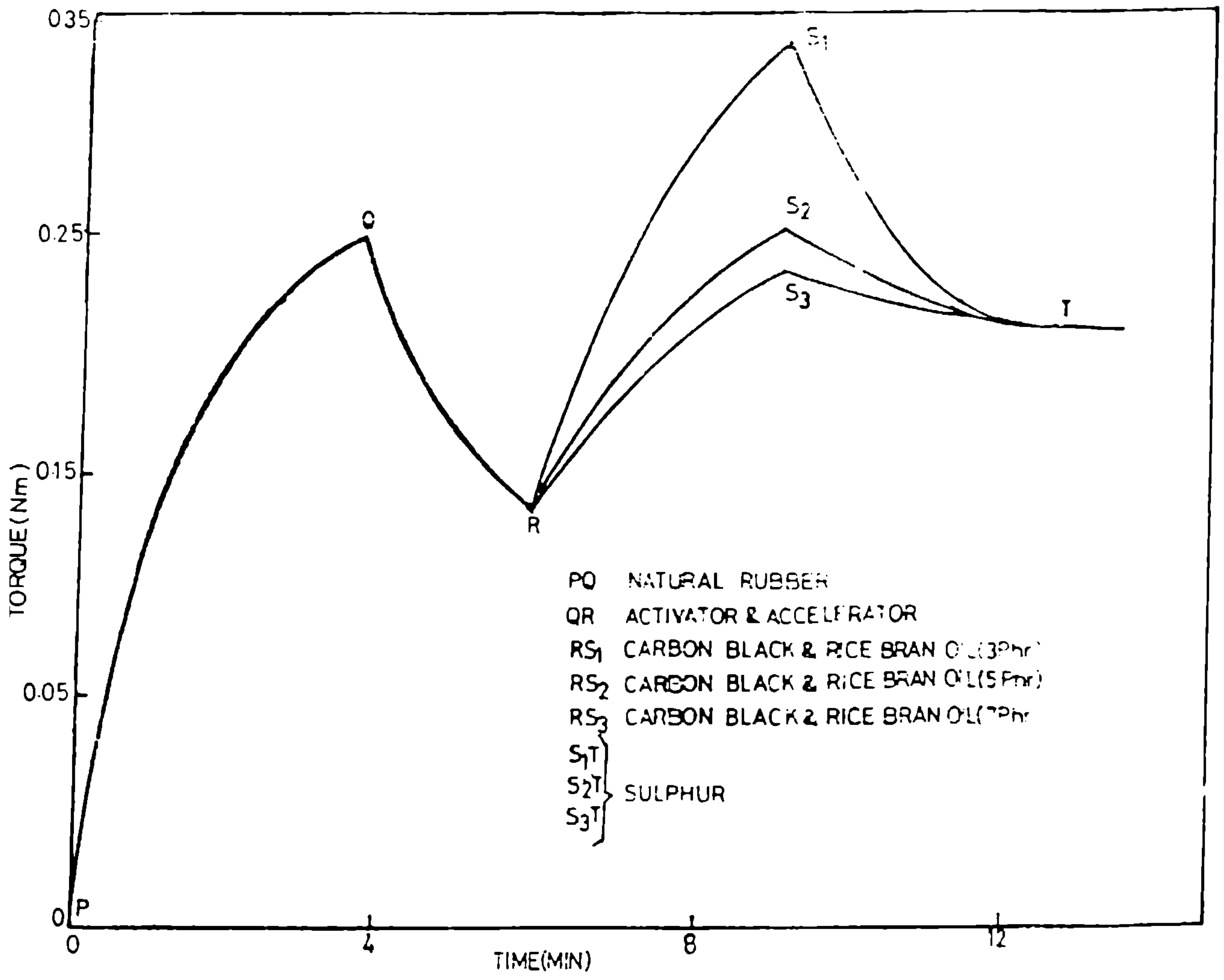


Fig.3.1 Variation of Brabender torque with rice bran oil in the carbon black filled system

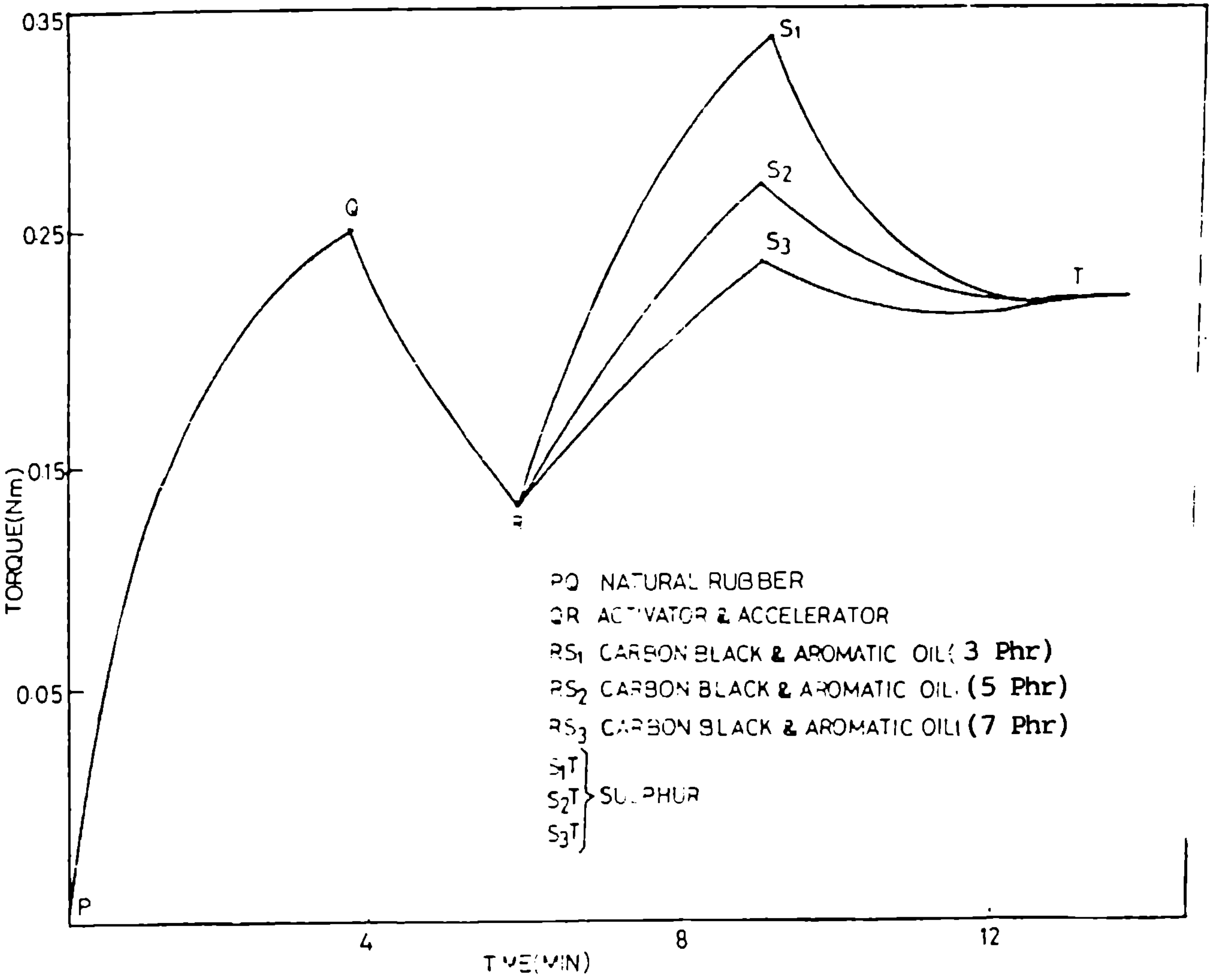


Fig.3.2 Variation of Brabender torque with aromatic oil in the carbon black filled system

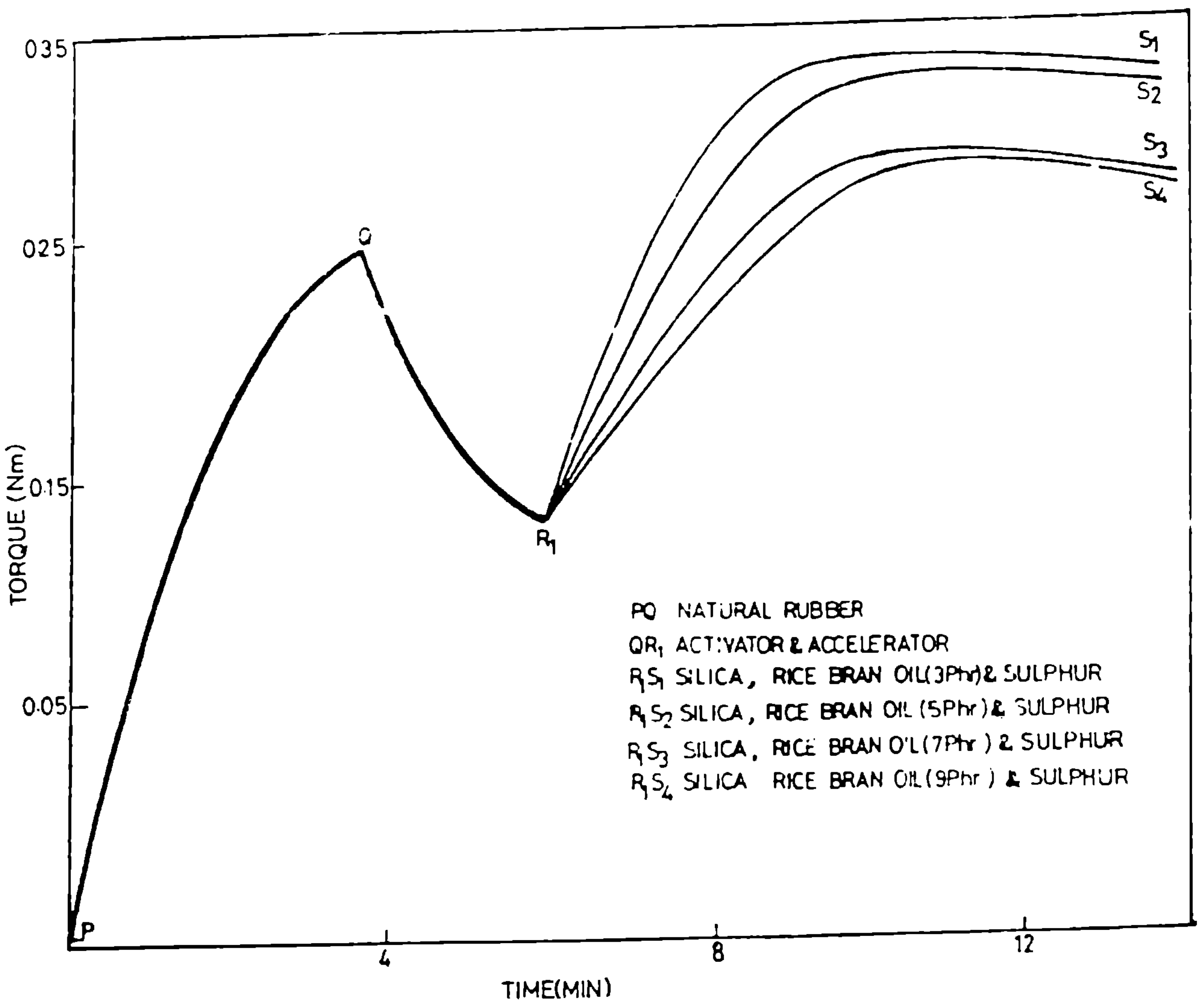


Fig.3.3 Variation of Brabender torque with rice bran oil in the silica system

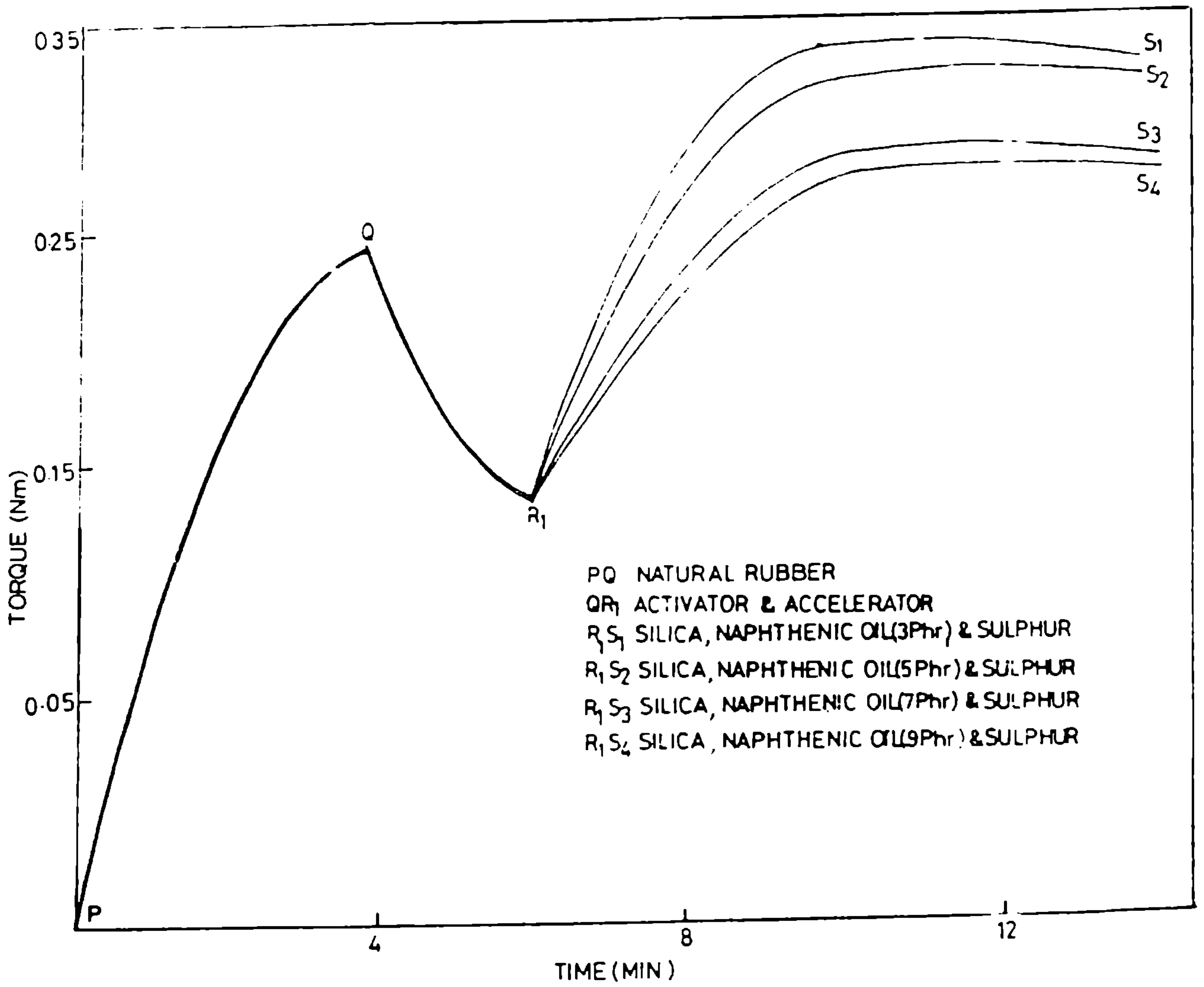


Fig.3.4 Variation of Brabender torque with varying amounts of naphthenic oil in the silica system

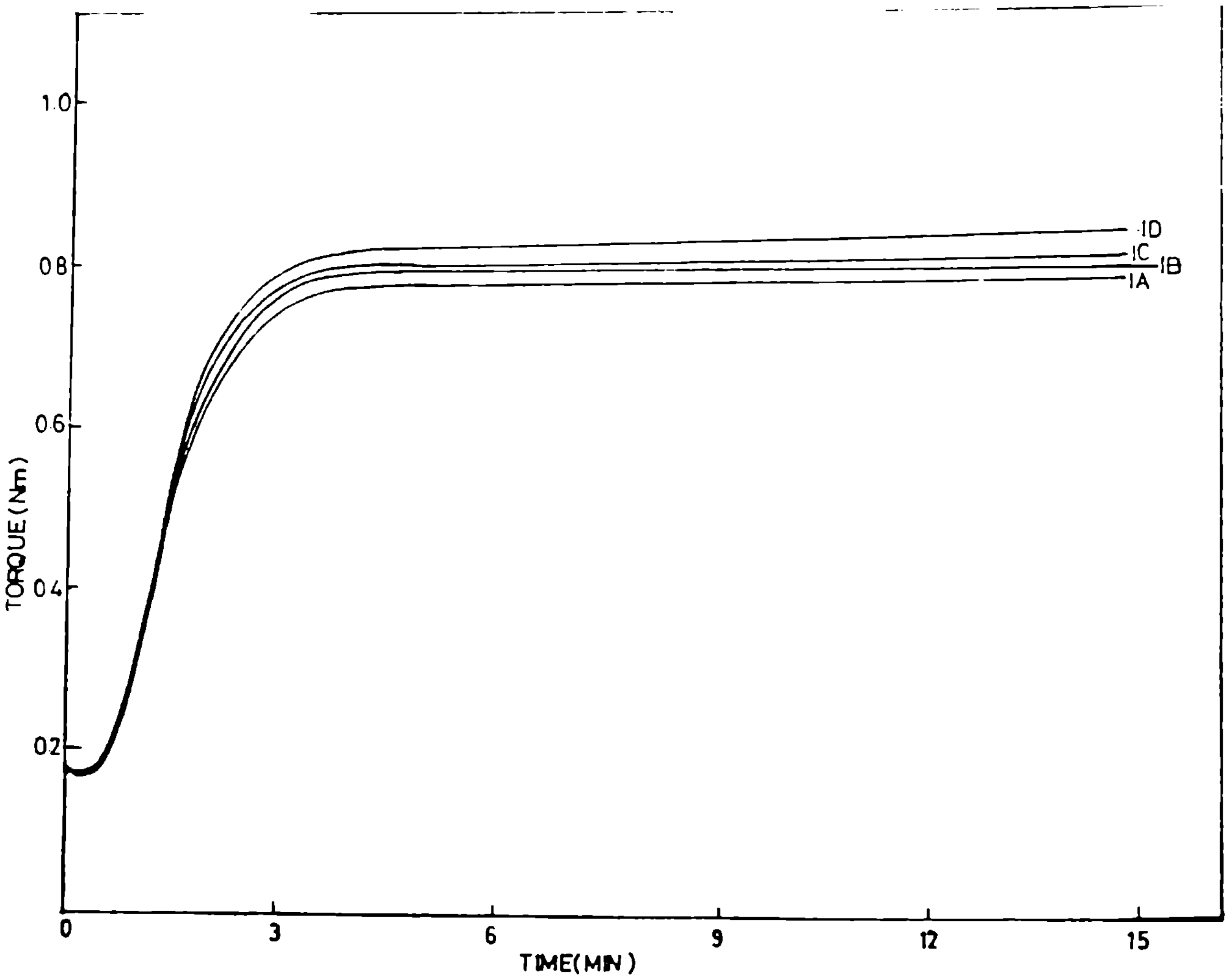


Fig.3.5 Cure curves of the mixes containing carbon black in rice bran oil/aromatic oil

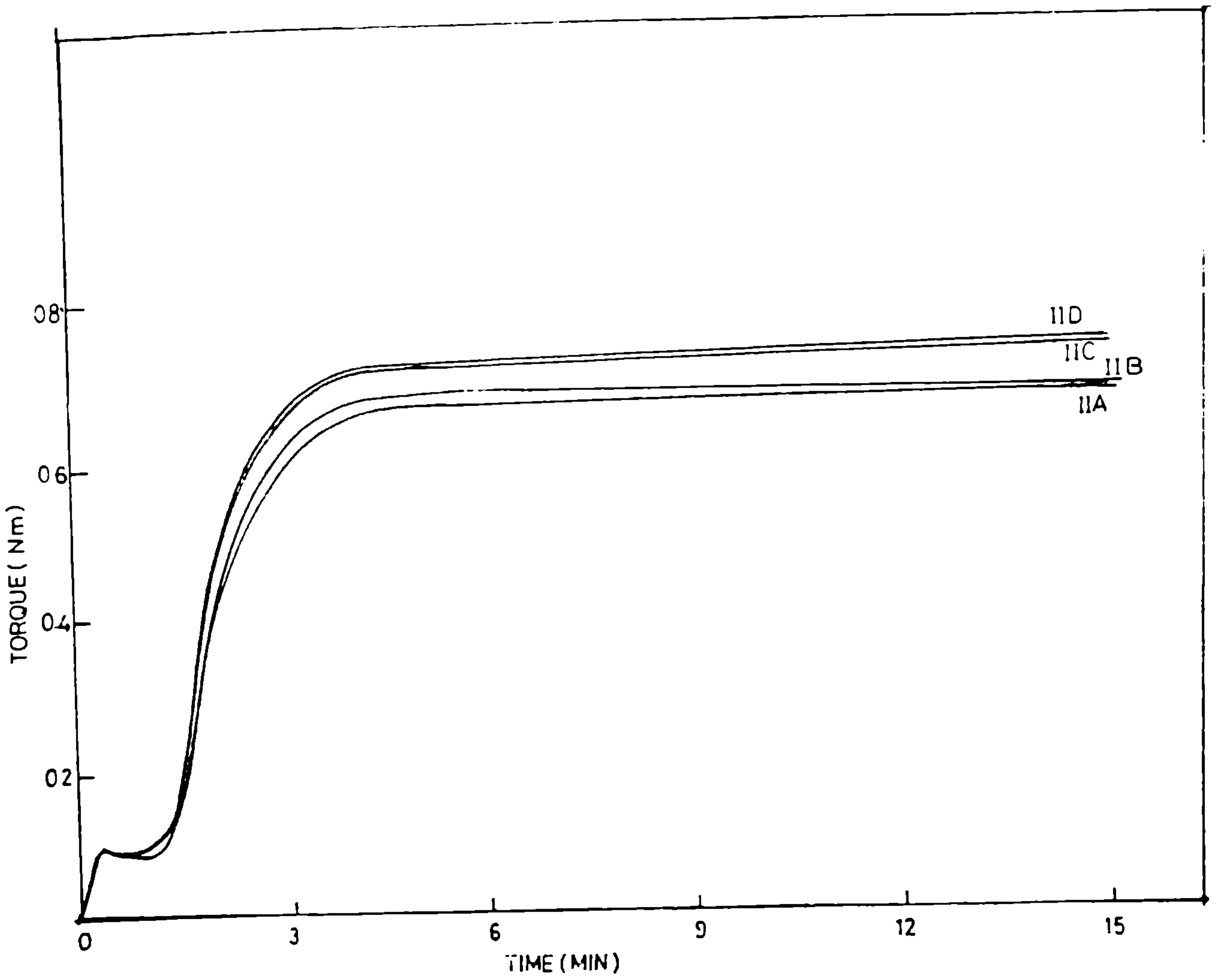


Fig.3.6 Cure curves of the mixes containing silica in rice bran oil/naphthenic oil

Chapter 4

USE OF RICE BRAN OIL IN THE COMPOUNDING OF STYRENE BUTADIENE RUBBER

In view of the fact that we got encouraging results on the use of rice bran oil in the compounding of natural rubber, we thought it worthwhile trying this oil in the vulcanization studies on a synthetic rubber. This study was undertaken mainly because a lot of differences are encountered in the compounding and vulcanization of natural rubber vis-a-vis synthetic rubbers. For example, compared with natural rubber, synthetic rubbers are more uniform in quality and compounds are more consistent in both processing and product properties. They are also supplied at viscosity ranges which facilitate good dispersion of ingredients and ease of flow in extrusion, calendering and moulding. This provides savings in both energy consumption and time and hence on costs. It is also to be noted that mill mixing of synthetic rubbers is more difficult compared to natural rubber.

Synthetic rubbers lack tack and green strength and this is of consequence in tyre building, particularly with radial tyres. Whilst natural rubber is crystalline with a

Tm of about 50°C, synthetic rubbers are more or less amorphous. Although crystallinity in natural rubber is reduced by the presence of crosslinks and of fillers and other additives, it still crystallises on extension giving a rubber of good tensile strength, even with gum stocks. On the other hand gum vulcanizates of the synthetic rubbers are generally weak and it is essential to use reinforcing fillers such as fine carbon black to obtain products of high strength.

We selected styrene butadiene rubber for the present study. It is a copolymer of styrene and butadiene, manufactured by polymerising them under controlled conditions of reaction using different techniques of polymerisation. Both cold and hot polymerised SBR are marketed in numerous varieties under various trade names.[1] These brands differ from one another in the relative proportions of butadiene and styrene, content of different initiating agents, emulsifiers, oils, fillers etc. and temperature of polymerisation. The unsaturation in SBR is less than that in natural rubber and the double bonds are less active chemically than the double bonds of the isoprenoid unit in NR. Hence SBR rubbers are slower curing than natural rubber, and either more accelerator or a more active accelerator system is required.[2] Scorch problems are less likely with SBR than with natural rubber stocks. In SBR, plastization before mixing with other ingredients is not necessary.

The molecular irregularity and large pendant group in SBR prevent crystallization on stretching. This will result in lower green strength and gum tensile strength. To overcome this type of behaviour of SBR, incorporation of fine reinforcing fillers is required. Dinsmore[3] reported that the ratio of tensile strength of black filled to that of gum vulcanizate is 10 to 5 for vulcanizates of SBR. It requires some optimum filler loading for properties such as wear and tear resistance.[4] Viscosity of SBR is also of special importance regarding its processibility. Lower viscosity grades band more easily on mills, incorporate fillers and oil more readily, show less heat generation during mixing, are more easily calendered, and often give a higher extrusion rate than the higher viscosity grades. On the other hand, the higher viscosity SBR's have better green strength, tend to give less porosity in the vulcanizate and at the same time accept higher filler and oil loadings, which is attractive pricewise. The higher the molecular weight of SBR, the higher the resilience of the vulcanizate and there is generally an improvement in the mechanical properties, particularly tensile strength and compression set. However, the differences in vulcanizate properties of high and low molecular weight SBR's can be largely eliminated through the choice of active fillers in the rubber compound.

Both NR and SBR require mastication prior to compounding. The mastication of SBR has to be done comparatively for longer time compared to NR and it can be carried out at low temperature. The increase of temperature during mastication leads to degradation of NR to some extent. On the other hand, SBR is not degraded much due to increase of temperature during mastication. The concentration of zinc oxide and stearic acid used are the same for both NR and SBR whereas the concentration of accelerator and sulphur used are varied for both rubbers. SBR requires higher temperature for vulcanization compared to NR.

The reinforcing carbon blacks and white fillers give the same level of mechanical properties for SBRs as for NR vulcanizates. The relative order of activity of fillers is the same in SBR as in NR, but the degree of reinforcement of the fillers is higher in SBR than in NR. Tear resistance of SBR is still inferior. The elastic properties are also poorer compared to NR. The compression set depends to a great measure on the compound formulation, the cure condition and the specific test method. Through proper compounding and at optimum cure, it is possible to obtain very low values of compression set. The dynamic fatigue resistance and heat ageing resistance of SBR vulcanizates surpass NR vulcanizates. Abrasion resistance is also better compared to NR.

SBR is predominantly used in combination with BR (polybutadiene) for the production of car and light truck tyres. For heavy truck and high speed tires, SBR is practically not used at all because of the higher dynamic heat build up in comparison with NR, IR or BR.

As in the case of natural rubber, sulphur vulcanization of SBR involves heating it with accelerator, activator, co-activator, anti-oxidant, filler processing oil etc. to obtain products of required properties. 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 alongwith zinc oxide and is the usual co-activator. Antioxidants are added to reduce ageing processes in the vulcanizates. Amines or phenols are generally used as antioxidants. Fillers are incorporated to improve the physical properties and/or to reduce the cost of final product. The function of the processing oil is to provide better processability during the addition of fillers. Aromatic or naphthenic oil is the usual processing oil used in the rubber industry.

SBR used for the present 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, moulded and extruded products, footwears, coated fabric etc. In our studies with SBR also we used sulphur accelerated system for the vulcanization using rice bran oil in place of aromatic oil/naphthenic oil and without stearic acid and antioxidant. The results obtained from these mixes were compared with different control formulations. Since green strength and tensile properties are poor in SBR gum formulations, experiments were carried out with reinforcing fillers viz., carbon black (HAF) and precipitated silica (vulkasil). The variation in processing characteristics brought about by the incorporation of rice bran oil was studied with the help of a Brabender Plasticorder. The optimum quantity of rice bran oil required in the different formulations has also been derived. The mixes were evaluated for their cure characteristics and the vulcanizate samples were evaluated for tensile and other physical properties. It is to be noted that definite relationships exist between chemical structure of the vulcanizates and their physical and mechanical properties. So the total chemical crosslink density of the vulcanizates was also estimated to understand the variation in tensile properties among the different mixes. Also studied was the heat ageing resistance of the vulcanizates of both control as well as experimental samples.

EXPERIMENTAL

The elastomer used in this study was synaprene 1502 having specifications reported in Chapter 2. Other compounding ingredients viz., zinc oxide, stearic acid, mercaptobenzthiazyl disulphide (MBTS), tetramethyl thiuram disulphide (TMTD), sulphur, carbon black (HAF), precipitated silica (vulkasil), aromatic oil, naphthenic oil, silane coupling agent (Si-69) and diethylene glycol are of rubber grade. Rice bran oil (FFA 44%) was obtained from Tamil Nadu Agro Industries Corporation, Thanjavur. Specifications of all these ingredients used in the study are reported in chapter 2.

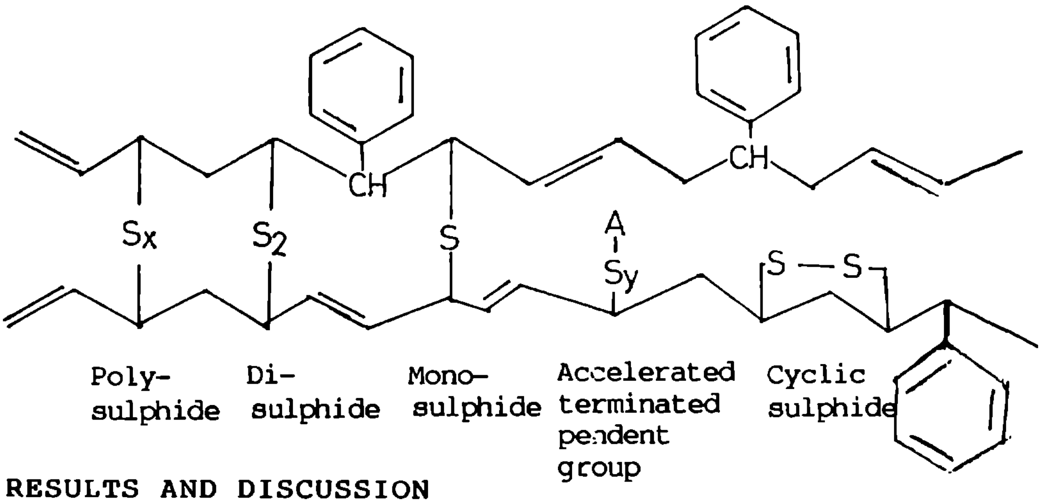
The processing characteristics of the above SBR with rice bran oil and with aromatic/naphthenic oil as control was studied in a Brabender plasticorder (PL 3S). Processibility is generally concerned with the readiness of the rubber to take up substantial quantities of filler alongwith processing oil, usually in an internal mixer. One quantitative way of studying this is to follow the power consumption pattern during internal mixing. Beach et al.[5] suggested that a useful criterion was the time interval between loading the mixer and observing the second peak in the power consumption-mixing time curve. The use of an internal mixer for such studies is clearly not an ideal laboratory situation and subsequently Meder and May[6] found that similar data was obtainable using a Brabender plasticorder, and in this case measuring the time to the second peak in the torque-time curve.

In our studies, the speed of the roller mixing heads in the Plasticorder was 30 rpm. First SBR was passed six times in a two roll mill at a nip gap of 0.8 mm to get a thin sheet. This was then cut into small strips before feeding into the Brabender plasticorder. The total mixing time was 16 min with the following break-up. SBR was masticated within 4 min followed by adding activator and accelerator within 3 min. Carbon black mixed with rice bran oil was then added within 8 min and finally sulphur within 1 min. The formulations of the different mixes is as given in Table 4.1 except for the fact that the oil levels were varied. For the control mixes the same procedure was repeated by replacing rice bran oil with aromatic oil. In order to optimise the quantity of oil required, rice bran/aromatic oil was added at 5, 10 and 15 phr levels each. The addition of 10 and 15 phr of oil resulted in proper mixing of the filler with rubber whereas 5 phr of oil was insufficient for proper mixing. This is indicated by the relevant torque values. It may be noted that substantial reduction in torque is noticed (Fig.4.1 & 4.2) when 10 phr of oil was used instead of 5 phr in these carbon black filled compounds. Hence it may be concluded that 10 phr of rice bran oil/aromatic oil is optimum for carbon black filled SBR compounds.

In silica filled compounds rice bran oil/ naphthenic oil was initially tried at 5, 10, 15 and 20 phr levels each. The procedure followed was the same as in the case of carbon black mixes. DEG and silane coupling agent were added alongwith silica while feeding into the plasticorder. The addition of 5 and 10 phr of rice bran oil/naphthenic oil resulted in higher torque values whereas an acceptable torque was obtained in the case of 15 and 20 phr levels of oil. Substantial reduction in torque was noticed when 15 phr of oil was used (Fig.4.3 & 4.4). So 15 phr can be taken to be optimum level of oil requirement in silica filled compounds.

The formulation of the mixes are designed in such a way as: (1) to study the effect of rice bran oil as a processing aid and (2) to evaluate the fatty acids and phenols present in this oil as co-activator and antioxidant respectively. The conventional system of SBR vulcanization was followed. Compounding was done in a laboratory size two roll mixing mill at a friction ratio of 1:1.25 as per details given in ASTM D 3185-88. During the mixing of NR in two roll mill, a band was easily made within three passes whereas SBR required six passes to make a band. Due to the higher shearing force in the mill compared to the plasticorder only lower dosage of oil was sufficient for mill mixing during the addition of fillers. Thus only 5 ml of rice bran oil/aromatic oil in carbon black filled compounds and 7 ml of rice bran oil/naphthenic oil in silica filled compounds were found to be sufficient when compounding was done in the mixing mill. The composition of different mixes is given in Table 4.1. The fillers viz. carbon black and precipitated silica were incorporated at 50 phr level each. Reference mixes contain stearic acid as co-activator and styrenated phenol as antioxidant. Mix I contains carbon black and mix II contains precipitated silica. Mixes IA and IB contain aromatic oil while IIA and IIB contain naphthenic oil. Mixes IC, ID, IIC and IID contain rice bran oil. IA and IIA contain no antioxidant but other compounding ingredients are added as usual. IB and IIB contain styrenated phenol as antioxidant. Mixes IC and IIC contain neither stearic acid nor antioxidant. ID and IID contain antioxidant but no stearic acid.

The cure characteristics of the various mixes at 160°C were evaluated using Goettfert elastograph (model 67.85) as per ASTM D 1646 (1981). Details of the procedure is as reported in Chapter 2. The cure properties of the mixes are given in Table 4.2. Cure rate index, induction time, optimum cure time and elastograph scorch time are reported therein. Vulcanization was carried out in an electrically heated press of 18"x18" platens maintained at 160°C and at a pressure of 11.764 Mpa. Tensile strength, elongation at break, hardness, compression set, resilience etc. were determined as per the relevant ASTM procedure given in Chapter 2. Ageing studies on the vulcanizates was carried out (ASTM D 573) at 100±1°C for 72 hrs in an air oven. The concentration of chemical crosslinks (crosslink density) of the different vulcanizates was determined from the swelling method reported earlier. Total crosslinks include mono, di, and poly sulphides etc.[7] A typical crosslinked structure for rubber is given below:



RESULTS AND DISCUSSION

In the initial part of the study, variation in the processing characteristics brought about by using rice bran oil instead of the usual conventional oils in this synthetic rubber compounding was studied by using the Brabender plasticorder. The quantity of rice bran oil/aromatic oil/naphthenic oil required for the various mixes is also optimised. But in actual practice, the compounds were prepared in two roll mill and it is found that lower dossages of oil ie. 5 ml each of rice bran oil/aromatic oil in carbon black filled compounds and 7 ml each of rice bran oil/naphthenic oil in silica filled compounds are found to be sufficient for processing in two roll mill. This is due to the higher shearing force of the mixing mill compared to plasticorder. Based on the processing characteristics, both in the Plasticorder and in the mixing mill, it is seen that rice bran oil can be used for processing the above mixes similar to the conventional oils viz. aromatic or naphthenic. Estimation of cure characteristics of the mixes and physical properties of the vulcanizates reported later in this chapter also indicate that rice bran oil does not have any adverse effect in these vulcanization reactions.

The cure curves of SBR-carbon black and SBR-silica systems are given in Figs.4.5 and 4.6 respectively. The relevant cure characteristics are given in Table 4.2. It is seen that the maximum torque developed is more in the mixes containing rice bran oil compared to those containing aromatic/naphthenic oil. There is no appreciable variation in the induction time, scorch time and optimum cure time of the mixes when rice bran oil is used in place of other processing oils both in carbon black and silica filled compounds. Thus it is evident that rice bran oil can be advantageously used as a processing aid in place of the other conventional processing oils and that the cure characteristics of the system is not affected by this change. The higher torque value observed with rice bran oil when used with antioxidant will indicate better mechanical properties of the vulcanizates. In mixes which do not contain fatty acid and antioxidant (but with rice bran oil) also not much variations is observed in the cure characteristics. It can also be reasonably assumed that the higher fatty acids and phenols present in rice bran oil can act as co-activator and antioxidant respectively. This is further proved by the evaluation of tensile and other physical properties (before and after ageing) reported in the subsequent sections.

Mechanical properties of the vulcanizates evaluated are given in Table 4.3. As in the case of natural rubber, in SBR also the initial tensile strength is slightly higher for the mixes containing rice bran oil compared to the control mixes. Elongation at break is more or less same for the mixes containing rice bran oil and these containing aromatic oil. Slightly lower modulus values are observed for the mixes containing aromatic oil. The mixes containing rice bran oil without and with antioxidant and the one containing aromatic oil with antioxidant retained more or less same level of tensile properties after ageing. Comparatively poor retention of tensile properties is noticed in the mix containing aromatic oil without antioxidant. It is evident that the phenols present in rice bran oil impart antioxidant properties to the vulcanizates in the systems containing this oil. In the case of silica filled compounds also higher tensile strength is noticed (before ageing) for the mixes containing rice bran oil compared to naphthenic oil systems. Elongation at break is less for the vulcanizates from these mixes. The percentage retention of tensile properties on heat ageing is higher for the mixes containing rice bran oil with and without antioxidant in silica filled compounds. The same trend is noticed for the mix containing naphthenic oil with antioxidant. But comparatively poor retention of tensile properties is noticed for the mix containing naphthenic oil without antioxidant. In silica filled compounds, the reversion resistance is generally poor.[8] But in our studies, the reversion resistance behaviour was found to be more or less same both in carbon black and silica filled compounds. It is evident that the presence of rice bran oil in carbon black and silica filled systems of styrene butadiene rubber provides ageing resistance comparable to that of styrenated phenol. As suggested earlier, the antioxidant property of rice bran oil may be attributed to the presence of the different phenolic derivatives in this oil.

Hardness, compression set, resilience, tear strength and abrasion resistance of the vulcanizates were also evaluated as per relevant ASTM procedures mentioned in chapter 2. The results indicate that the value of tear strength, compression set, hardness and abrasion loss are more or less same for the mixes containing rice bran/aromatic oil in carbon black filled systems and rice bran oil/naphthenic oil in silica filled systems. Resilience is slightly higher for the mixes containing aromatic oil compared to those containing rice bran oil.

The total chemical crosslink density was evaluated for the vulcanizates of both carbon black and silica systems. The results are reported in Table 4.3. In the carbon black filled compounds, mixes containing rice bran oil showed higher crosslink density compared to the aromatic oil systems and this resulted in a higher tensile strength values for the former system. In the case of silica filled systems also there is marginal increase in crosslink density for the rice bran oil containing mixes. Filled vulcanizates which are known to give higher crosslink density values are generally having better interaction between rubber and filler. The results indicate that rice bran oil has a positive effect in this interaction.

CONCLUSIONS

From the results obtained in this study it is evident that raw rice bran oil can be advangageously used in the compounding and sulphur vulcanization of a synthetic rubber like SBR also. This oil can replace the conventional processing oils like aromatic and the naphthenic types. Fatty acid and antioxidant in an SBR compound can also be replaced with rice bran oil. Evaluation of cure and processing characteristics of the mixes containing rice bran oil and those containing conventional processing aids like aromatic/naphthenic in the different systems under review also indicate that rice bran oil does not have any adverse effect on these properties. Study on the physical properties of the vulcanizates (before and after ageing) also point to more or less similar conclusions. Apart from the non-toxic nature of the rice bran oil, it is also comparatively cheaper than aromatic/naphthenic oils used in rubber compounding. The co-activator and antioxidant properties exhibited by this oil can be attributed to the presence of higher fatty acids and phenols in it.

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Table 4.1: Formulation of mixes containing carbon black and precipitated silica

Mix	IA	IB	IC	ID	IIA	IIB	IIC	IID
Styrene butadiene rubber	100	100	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4	4	4
Stearic acid	1.5	1.5	--	--	1.5	1.5	--	--
Mercaptobenzothiazyl disulphide (MBTS)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Tetramethyl thiuram disulphide (TMTD)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Styrenated phenol	--	1.0	--	1.0	--	1.0	--	1.0
Carbon black (HAF N330)	50	50	50	50	--	--	--	--
Precipitated silica (Vulkasil)	--	--	--	--	50	50	50	50
Aromatic oil	5	5	--	--	--	--	--	--
Naphthenic oil	--	--	--	--	7	7	--	--
Rice bran oil	--	--	5	5	--	--	7	7
Diethylene glycol	--	--	--	--	2	2	2	2
Silane coupling agent (Si. 69)	--	--	--	--	2	2	2	2
Sulphur	2	2	2	2	2	2	2	2

Table 4.2: Cure characteristics of mixes containing carbon black and precipitated Silica (160°C)

Mix	IA	IB	IC	ID	IIA	IIB	IIC	IID
Maximum torque (Nm)	0.73	0.75	0.78	0.79	0.90	0.93	0.96	0.98
Minimum torque (Nm)	0.08	0.08	0.08	0.08	0.09	0.09	0.09	0.09
Optimum cure time t_{90} (min.)	7.5	7.7	7.7	7.7	7.4	7.4	7.3	7.3
Elastographic scorch time, t_{10} (min.)	2.6	2.6	2.6	2.6	1.8	1.8	1.8	1.8
Cure rate index	20.4	19.6	19.6	19.6	17.8	17.8	18.1	18.1
Induction time (min.)	1.5	1.5	1.5	1.5	1.0	1.0	1.0	1.0

Table 4.3: Physical properties of vulcanizates

Parameter	IA	IB	IC	ID	IIA	IIB	IIC	IID
Tensile strength (MPa) BA	24.19	24.32	24.60	24.68	21.62	21.70	21.86	21.98
Tensile strength (MPa) AA	10.45	14.15	14.55	14.55	10.04	14.70	14.71	14.90
Elongation at break (%) BA	386	388	384	385	521	530	524	526
Elongation at break (%) AA	98	122	120	132	103	205	216	218
Modulus at 200% (MPa)	9.17	9.20	9.27	9.28	6.40	6.42	6.45	6.45
Tear strength (N/mm)	58	59	58	58	60	60	60	61
Compression set (%)	23.16	22.47	22.94	22.51	37.72	37.64	38.09	37.63
Hardness (Shore A)	64	64	64	64	67	67	67	67
Abrasion loss (cm^3/hr)	6.149	6.250	6.199	6.161	7.094	7.088	6.906	7.094
Resilience (%)	53.14	53.14	52.49	52.49	51.87	51.56	51.26	51.56
Crosslink density (mmol/kg)	79.80	80.62	81.34	82.23	80.10	80.27	81.66	82.65

BA - Before ageing, AA - After ageing.

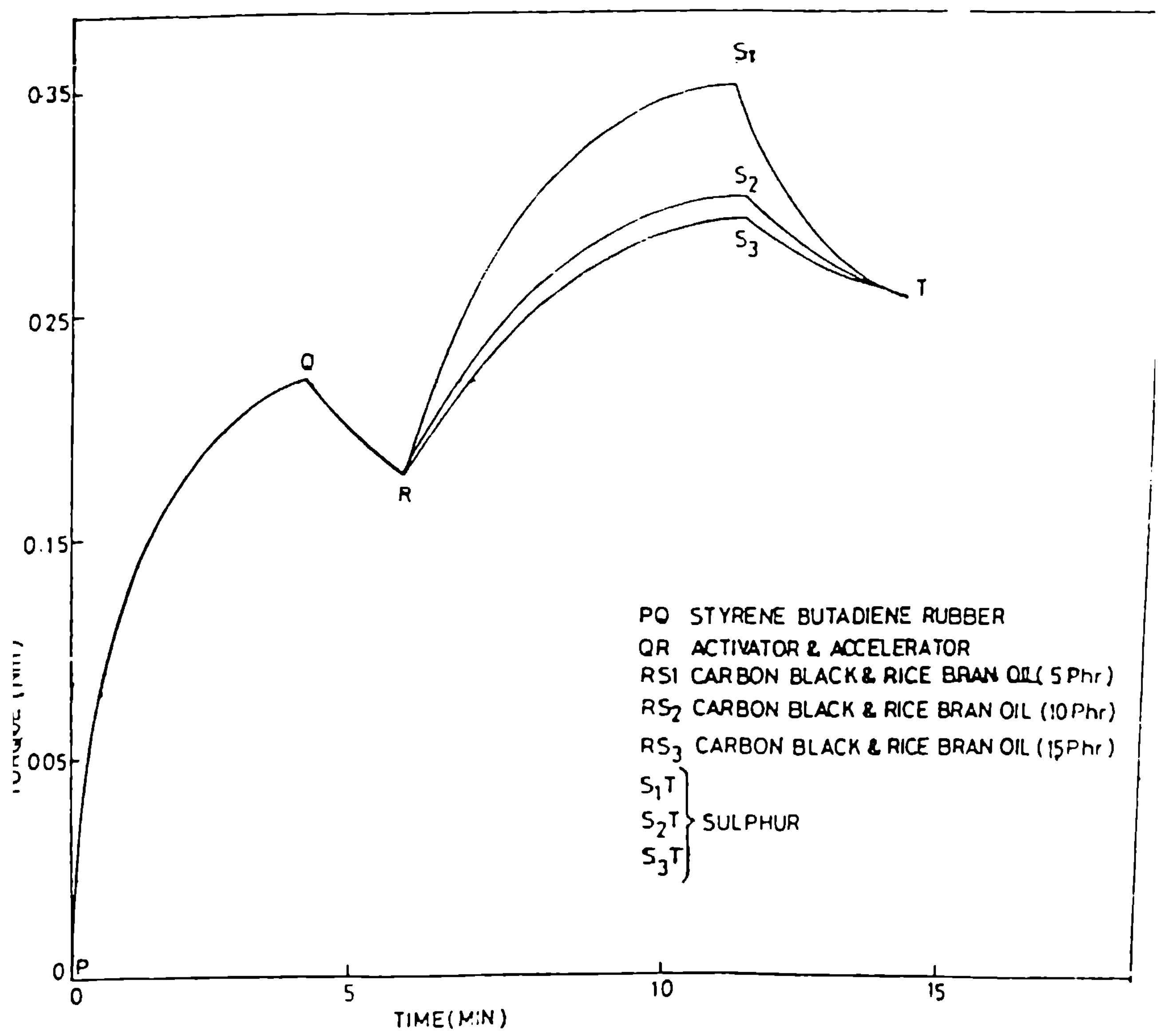

Fig.4.1 Brabender torque variation with rice bran oil in the carbon black filled systems of SBR.

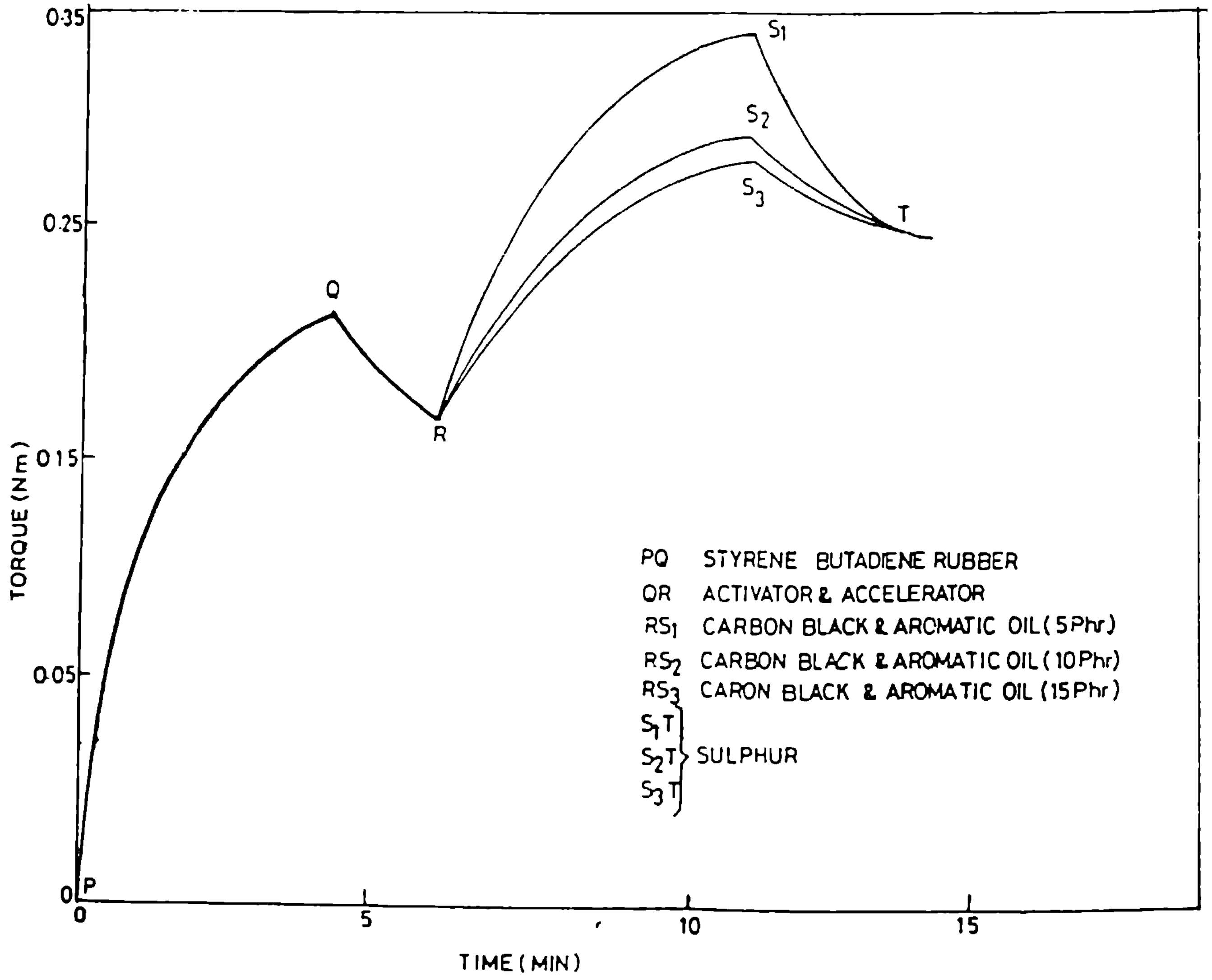

Fig.4.2 Brabender torque with aromatic oil in the carbon black systems of SBR

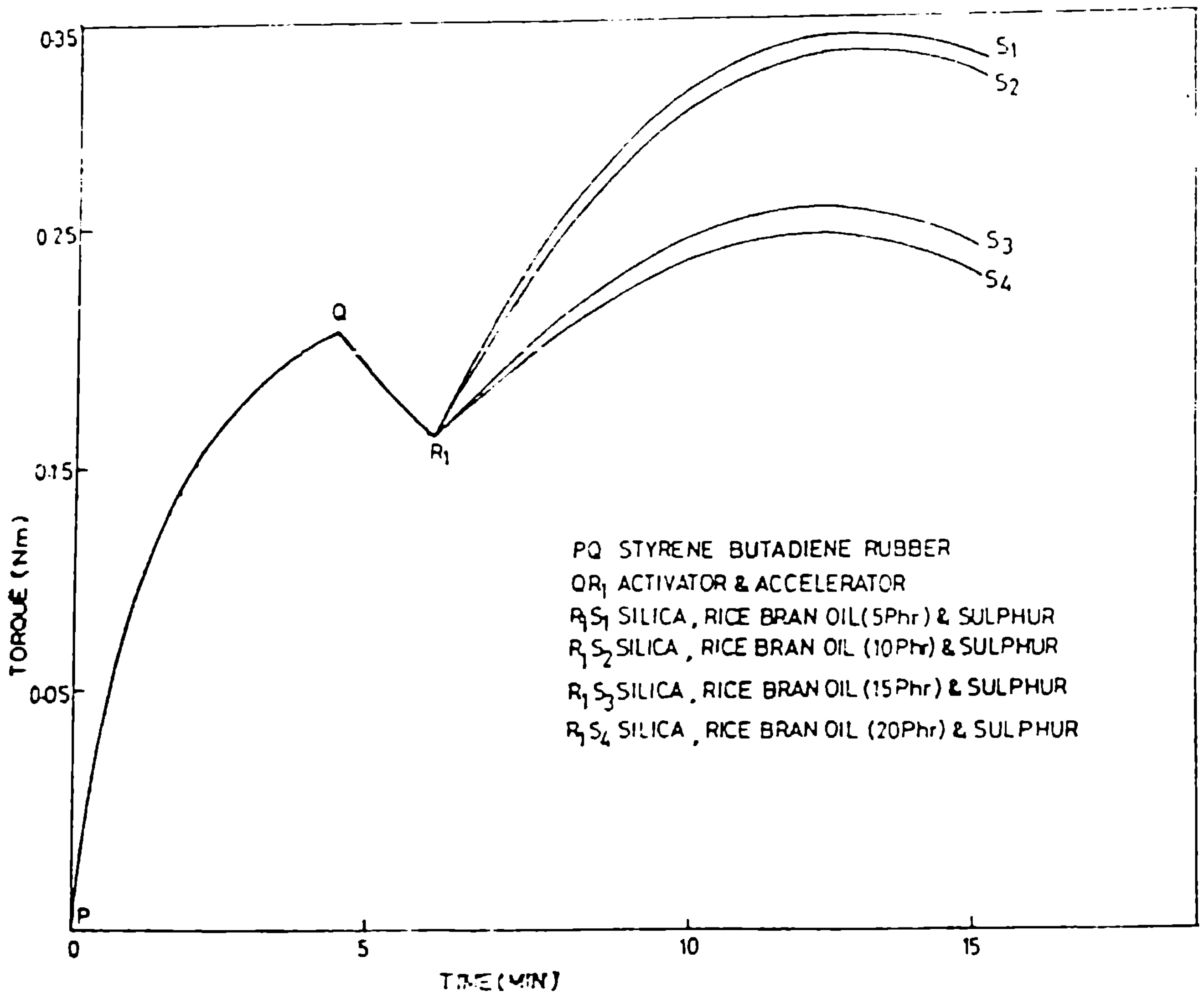

Fig.4.3 Variation of torque with rice bran oil in silica systems

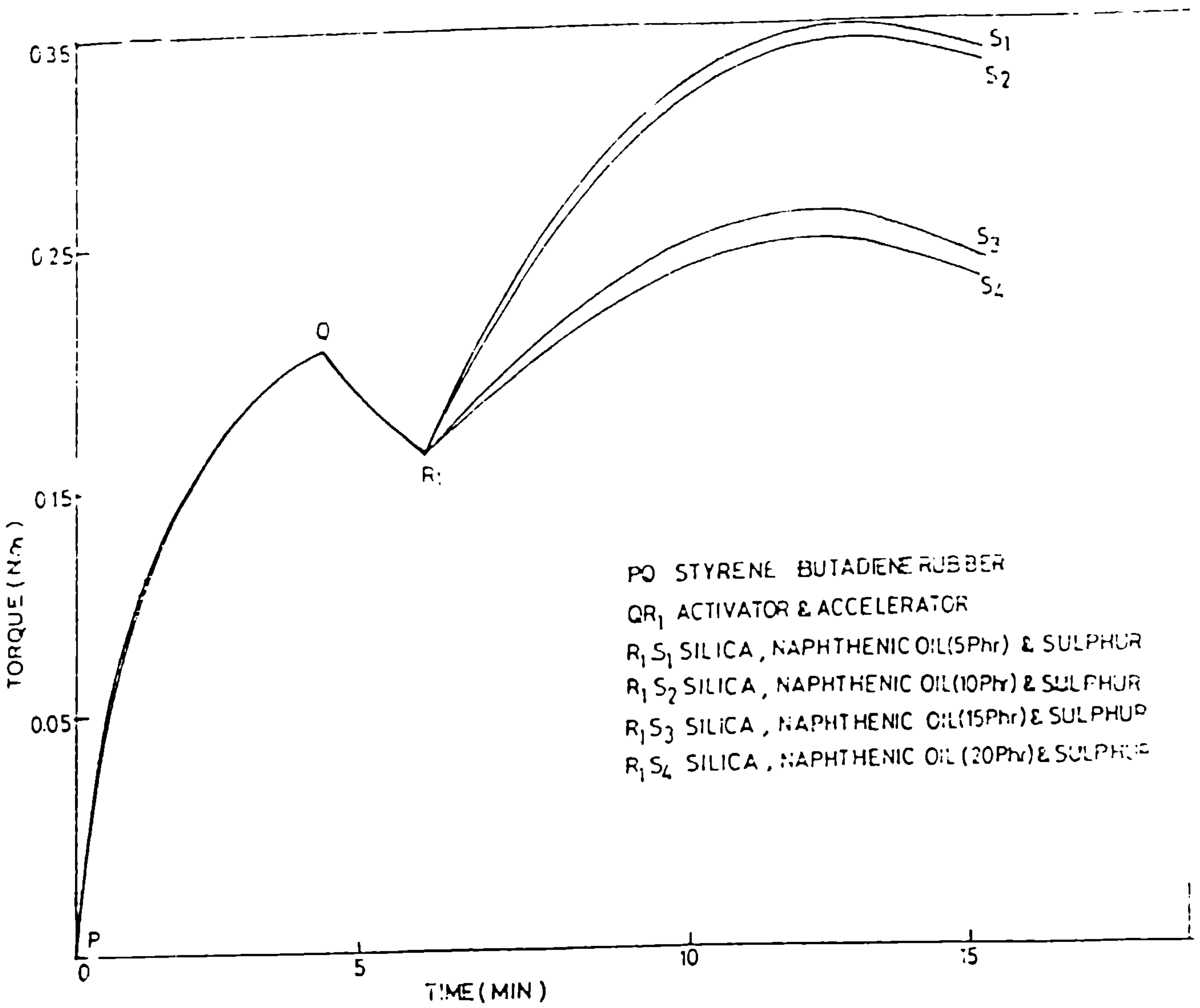

Fig.4.4 Brabender torque variation with varying amounts of naphthenic oil in the silica compounds of SBR

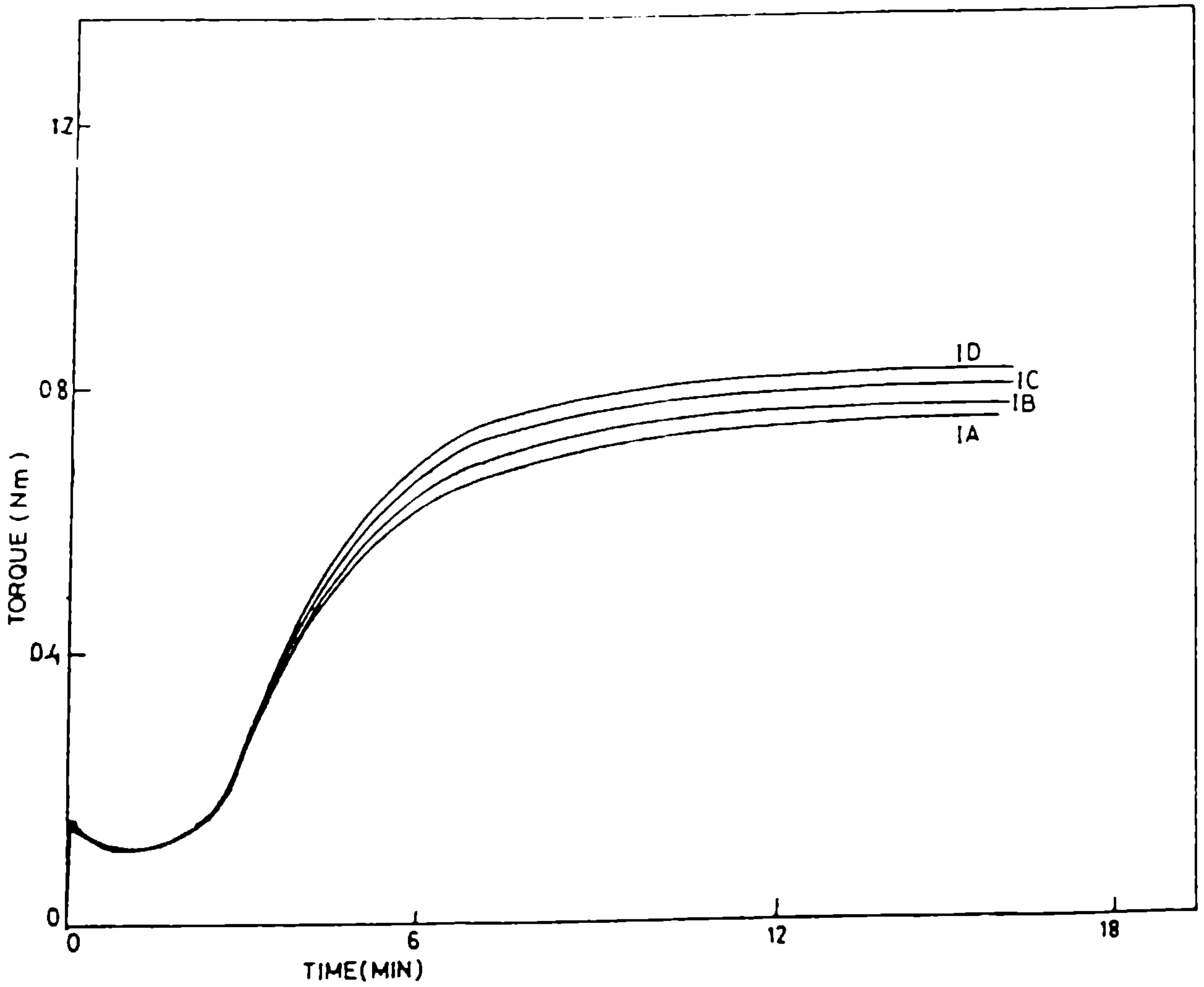

Fig.4.5 Cure curves of the carbon black mixes in rice bran oil and aromatic oil systems

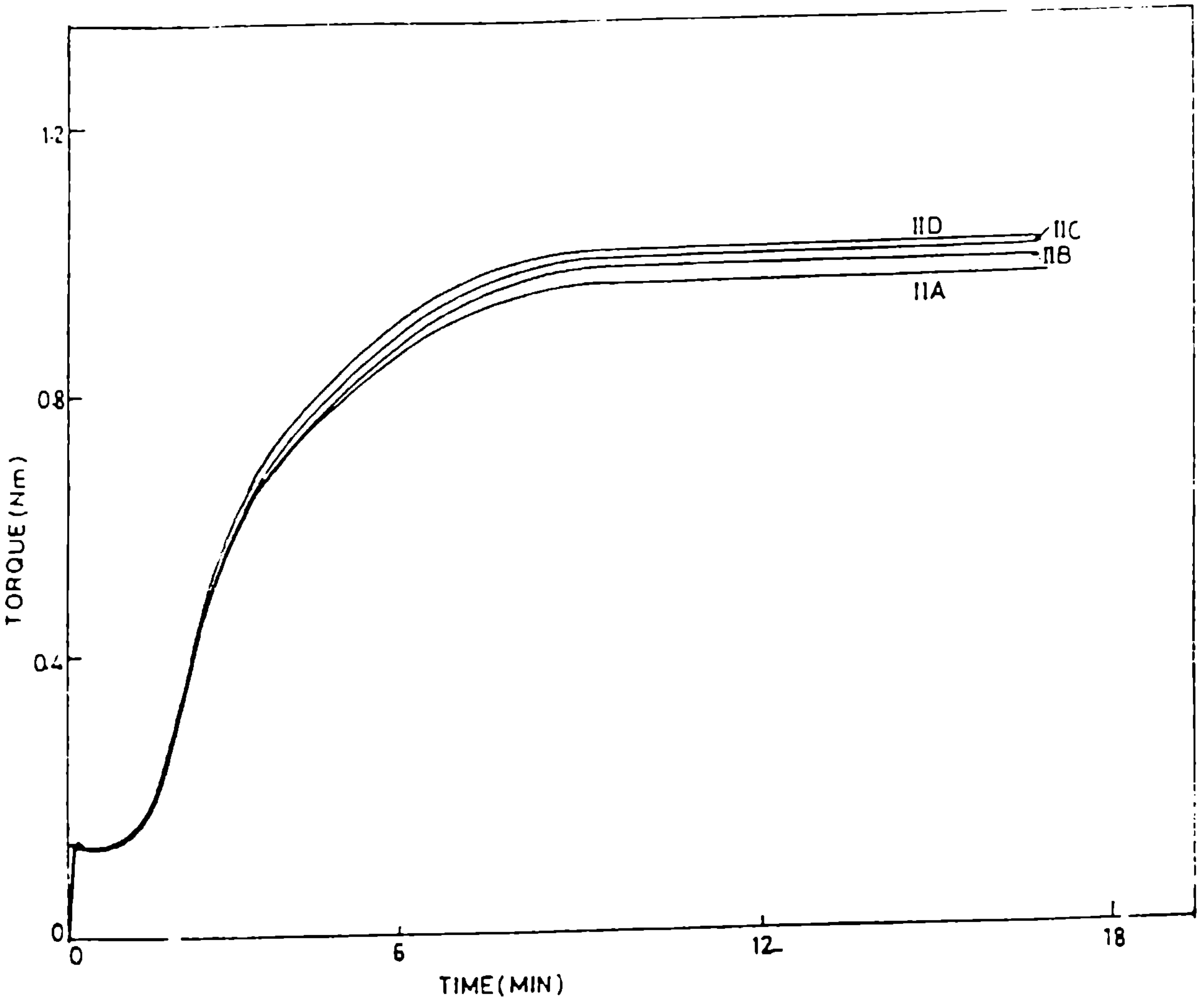

Fig.4.6 Cure curves of the silica filled mixes in rice bran oil and naphthenic oil

Chapter 5

USE OF RICE HUSK AND ITS BY-PRODUCTS IN VULCANIZATION STUDIES ON NATURAL RUBBER

In India, about 20 million tonnes of rice husk are produced annually. Rice husk consists of the outer shell covering of the rice kernel and it forms 16-25% by weight of the paddy. It is used as a fuel in husk fired furnaces for heating air and this hot air is used for drying either moist or parboiled paddy.[1] This hot air is also used for generating steam in areas where parboiling process is practised. Apart from using husk as a fuel, it can be used for preparing chemicals like silicon carbide[2] and silicon tetrachloride.[3] Chemicals like acetic acid, propionic acid, phenol and cresol can also be obtained by destructive distillation of husk. The major chemical components of rice husk are cellulose, lignin, silica and pentosan and minor components are fat, protein and phenols.[4] The phenols/phenolic acids present in rice husk is a mixture of ferulic, vanillic, p-coumaric, sinapic, p-hydroxyl benzoic, salicyclic and indoleacetic acids. The free phenols range from 77 to 390 μg per gram depending upon the life of the rice seed and its storage period.[5-7] Though there are reports on the extraction of phenols from husk, there is no mention in the literature on the use of these phenols in the polymer industry. There is also no report on a systematic study on the use of husk as a filler in rubber eventhough many short fibres[7,8] were tried as filler in rubber compounding.

In rice mills, black ash is available as a by-product after incinerating the husk in the furnace The ash is used for the production of humidifier plates, insecticides[9] and also as a preservative for straw.[10] The black ash contains approximately 50% carbon, 49% silica and 1% other minerals whereas white ash contains 90 to 95% silica, 1% other minerals and 4-9% carbon. The carbon and silica present in the black ash cannot be separated by using sodium hydroxide solution due to the presence of crystalline silica which is formed as a result of uncontrolled burning of husk in the furnace.[11] For separating carbon and silica, the black ash has to be produced by controlled burning of the husk at 700°C.[12] The black ash as such available in rice mills and the carbon and silica separated from black ash have not been used so far as fillers in rubber eventhough white ash has been used for this purpose earlier.[13] As this chapter mainly deals with the use of phenols extracted from rice husk as antioxidant and husk and husk ash as fillers in natural rubber a brief description on the application of antioxidants and fillers in natural rubber is attempted here.

Ageing is a collective term for changes in property of materials that occur on longer term storage that lead to partial or complete degradation. These changes can occur in the form of degradation, embrittlement, rotting, softening and fatigue processes, static crack formation and the like. Uncured and cured rubber are especially prone to such ageing effects. The unsaturation in diene rubbers make it possible to cure with sulphur but at the same time present a sensitivity towards oxygen, ozone and other reactive substances. These reactions cause changes in the rubber. Since soft rubbers based on diene structure contain free double bonds, they remain sensitive to the above agents even after vulcanization. Higher temperature makes these effects more noticeable. In the presence of oxidation catalysts like Cu and Mn compounds, these ageing phenomena occur rapidly. All these effects lead to various forms of destruction summarily called "ageing". There is therefore no single process of ageing but various forms of degradation processes that exhibit different end results.

The stability of vulcanizates against single or combined action of degrading agents is primarily determined by the type of rubber affected. Diene rubbers are attacked considerably more by oxygen and especially by ozone than saturated rubbers. The latter are, for that reason, quite stable towards oxygen and ozone. Diene rubbers based on isoprene are less stable because of the electron donating influence of the methyl group than those based on butadiene. The crosslinking system too has a considerable influence on the ageing and heat stability of elastomers. EV-systems and sulphur free crosslinking agents have a better resistance to ageing and are more heat stable. The type and amount of fillers used also have considerable influence on the stability of vulcanizates. In any given rubber compound the degradation due to oxidation can be retarded by addition of chemicals that are summarily called antioxidants. The degree of protection depends primarily on the type and composition of the antioxidants used.

The majority of commercially available antioxidants are classified into two groups viz. amines and phenols. The amines generally used are derivatives of aniline or diphenyl amine. These materials are referred to as staining antioxidants as they tend to discolour non-black vulcanizates on exposure to light. Their volatility is also important for their effectiveness as antioxidants. The volatility depends strongly on the molecular structure. The least volatile antioxidant generally yield the highest high temperature resistance. DNPD (N,N'-di β-naphthyl-p-phenylene diamine) is one of the least volatile antioxidants. Methyl SDPA (Methyl styrenated diphenyl aniline), TMQ (Trimethyl 1,2-dihydroquinoline) etc. are other examples. Sufficiently good heat ageing is also obtained with other p-phenylenediamines as long as they have high molecular weight. The phenols generally used are the substituted types. Styrenated phenol, 2,6-di-tert, butyl p-cresol, 2,4-dimethyl 6-tert. butyl phenol, 2,4-dimethyl 6 - methyl cyclohexyl phenol etc. are examples of this class. Phenols are non-staining in nature. Among the bifunctional phenols, 2,2'-methylene-bis (4-methyl-6-tert. butyl phenol) gives excellent protection against the action of oxygen. Trifunctional phenols for eg. tri-1,1,3 (2'-methyl 4-hydroxy-5 - tert. butyl phenyl) butane is used mainly for rubber that is processed at higher temperatures. The completely non-discolouring antioxidant (for eg.

styrenated phenol) has to be added to rubber as much as 2 phr. The resulting protection is always more apparent in NR than in synthetic rubbers, partly because of the inherent better ageing stability of synthetic rubbers and partly because of the added stabiliser during the manufacture of synthetic rubber.

Based on the reinforcement given to the rubber compound by the fillers, they may be classified into reinforcing, nonreinforcing and semi-reinforcing types. These can also be classified as carbon blacks and light coloured fillers. Different varieties of carbon black include furnace black, channel black and thermal black. Furnace black is most widely used. Thermal blacks have in recent years been replaced by suitable furnace blacks because of economical and ecological factors, often with suitable changes in receipe. The light coloured fillers include colloidal silica, calcium and aluminium silicate, alumina gel, kaoline, silica, talcum chalk etc. Aside from these, anisotropic fillers like short fibres are also in use. Most carbon blacks, colloidal silica and very small particle size silicates belong to the high and medium activity fillers while chalk belong to the inactive types. Eventhough NR vulcanizates with good tensile strength can be produced without filler because of its stress crystallisation, use of fillers is necessary for almost all the product applications. Fillers are certainly required for synthetic rubber vulcanizates and they can give property improvement in many ways. This is true both for the processing properties of the unvulcanized compound and for the vulcanizates.

The main effects of filler characteristics on vulcanizate properties are their particle size, surface activity, structure and porosity. Small particle size results in higher tensile strength, higher hysteresis, higher abrasion resistance, higher electrical conductivity and higher Mooney viscosity. They have minor effects on extrusion shrinkage and modulus. An increase in surface activity (physical adsorption) results in higher modulus at higher strains (300% upwards), higher abrasion resistance, higher 'bound rubber' and lower hysteresis. An increase in persistent structure results in lower extrusion shrinkage, higher modulus at low and medium strains, higher Mooney viscosity, higher hysteresis and longer incorporation time. Higher electrical and heat conductivity are found for high structure blacks. Porosity results in higher viscosity and higher electrical conductivity in the case of carbon blacks. Fillers are also known to influence the crosslinking reaction during vulcanization. Those fillers which only lead to small increases in viscosity of the compound and otherwise reduces the mechanical properties of the vulcanizates are not reinforcing and they may be called non-reinforcing or inactive types. In contrast, reinforcing fillers lead to dramatic changes in viscosity of the compound and increase the tensile properties of the vulcanizates.

Few instances of use of rice husk and rice husk ash in plastics and rubber have been reported in the literature. The use of surface modified husk in products like polyethylene films, moulded window frames, shutters etc. have been reported.[14] Polypropylene resin compositions containing husk as one of the components and polyester resin composites containing rice husk ash has also been reported.[15] It was found that the tensile and impact strength of the rice husk ash polyester resin composites decreased with increasing rice husk ash content. Thermal ash (85% silica) alone and alongwith conventional fillers has been tried in NR compounding.[16] These investigations were carriedout to compare thermal ash with conventional fillers like china clay, whiting and carbon black (HAF). The results indicated that the maximum torque value of the mix was obtained with thermal ash compared to all other fillers except carbon black. The cure rate was the highest with the thermal ash filled system. The tensile strength and the modulus were the lowest with thermal ash but the hardness values were comparable with other fillers.

In view of the fact that ordinary black ash from rice mills contains both carbon and silica, we thought this ash is worth trying as a filler in rubber. Eventhough there are few reports on the utilization of rice husk and rice husk ash (specially prepared white ash) in the polymer industry a systematic study on the subject is lacking. Also there are no reports whatsoever on the use of phenols extracted from rice husk in rubber compounding. In this context, we made an exhaustive study on the utilization of rice husk and rice husk ash (black ash) as fillers and phenols extracted from rice husk as antioxidant respectively in the vulcanization studies on natural rubber. Also studied was the effect of carbon and silica separated from black ash as a filler. All the fillers tried were used in different particle size and at various filler loadings. The experimental details of this investigation is reported below.

EXPERIMENTAL

The elastomer used in the present study is Natural rubber (ISNR-5). Activator (zinc oxide), accelerators (MBTS, TMTD), co-activator (stearic acid), fillers (carbon black, precipitated silica), processing oils (aromatic oil, naphthenic oil), diethylene glycol, silane coupling agent, vulcanising agent (sulphur) and styrenated phenol used had specifications reported in earlier chapters. Chloroform, methanol, n-hexane, CI resin, hexamethylene tetramine and resorcinol are of analytical grade. Phenols extracted from rice husk by method reported earlier has been used. Rice husk was used as such and also after pulverising and sieving onto different mesh size. Rice husk ash was also used as such and in different mesh size. Carbon and silica from rice husk ash was prepared as per procedure detailed earlier.

Soxhlet extraction procedure was followed for extracting oil and phenols from husk. Sample was first extracted with n-hexane to remove the oil from the husk. This was further extracted with 1:1 mixture of chloroform and methanol. After the extraction was completed, the solvent was distilled off and the residue obtained was dissolved in minimum quantity of methanol. Methanol was then removed and sample dried at 80°C.

The black ash for the separation of carbon and silica was obtained by controlled burning of husk at 700±10°C for 10 min. in a muffle furnace. Sodium hydroxide solution and this black ash were heated to 97-98°C for 30 min. with intermittent stirring. Water was added at the end of heating and stirred. The strength of sodium silicate solution thus obtained was determined by using a hydrometer. The gel ($SiO_2.H_2O$) obtained by acidification of the filtrate was washed with water salt free and dried. It was then pulverised, sieved and used for the experiments.

Water was added to the residual carbon after removal of silica and it was then neutralised with dilute hydrochloric acid. This was filtered and the residue was repeatedly washed with water. The minerals remaining in the carbon was then removed by heating the residue with 1:1 HCl at 100°C for 1 hour. After filtration again the residue was washed acid free and dried. The carbon thus obtained was pulverised and used for the experiments at the required mesh size.

In this study, the rice husk was used as such and also at different mesh size, viz. 50, 100 and 200. The different formulations used in these experiments are given in Table 5.1. Coumarone indene (CI) resin and resorcinol with hexamine were also tried in some of the mixes. Resorcinol with hexamine and CI resin are known to promote adhesion between rubber and filler and thereby improve tensile properties.[17] All the above mixes were evaluated for the cure characteristics and the vulcanizates were tested for the different tensile properties. The details are discussed under results and discussion.

The mixture of phenols extracted from rice husk was tried as antioxidant in NR gum, NR-carbon black and NR-silica filled systems using the formulation given in Table 5.2. The control mixes containing styrenated phenol were also prepared and their properties compared with those of the mixes containing antioxidant from husk. The cure characteristics of the mixes, tensile and other physical properties, ageing resistance, crosslink density etc. of the vulcanizates were evaluated.

The black ash from rice mills was used as such at 25, 50 and 100 phr filler loadings. Pulverised black ash at 50, 100, 200 and 300 mesh size were also used at filler loadings of 25, 50 and 100 phr. The detailed formulation for the above mixes are given in Table 5.3. The black ash (100 mesh) was also used along with CI resin and with hexamine and resorcinol. This black ash with conventional carbon black (HAF) at different levels of loading was also tried. The formulation for these mixes is given in Table 5.4. Carbon and silica separated from black ash at 300 mesh size was also tried as filler at 25 and 50 phr. Formulation for these mixes are given in Table 5.5. Cure characteristics of these mixes and tensile properties of the vulcanizate samples from all mixes were evaluated and compared with the control formulations.

The vulcanization system used was of conventional type. The preparation of mixes, determination of cure properties, preparation of vulcanized sheet for test samples, determination of tensile and other physical properties like compression set, resilience, tear strength, hardness etc. were all carried out as per relevant ASTM procedures described in chapter 2. The ageing studies and crosslink density determination were also carried out as per relevant procedures discussed earlier.

RESULTS AND DISCUSSION

Cure Characteristics

The cure curves of the mixes containing 25, 50 and 100 phr of rice husk as such as a filler are given in Fig.5.1. Similarly the cure curves of those mixes containing rice husk of 50, 100 and 200 mesh at 25, 50 and 100 phr levels of loading are given in Fig.5.2. The different cure characteristics of the mixes evaluated are given in Table 5.6. From the results it is clear that the torque developed is minimum for the mixes containing 25 phr of rice husk and is maximum for the mixes containing 100 phr of rice husk. Slightly higher torque and a slight reduction in cure time is observed when the husk used is in smaller particle size. Cure curves of the mixes containing 50 phr of rice husk of 100 mesh with cumarone indene resin and with resorcinol and hexamine are given in Fig.5.3. The CI resin seems to have no influence on the torque as well as on cure time where as resorcinol and hexamine prolonged the cure time with some increase of torque. The different cure characteristics of the mixes are given in Table 5.6. As far as induction time and scorch time are concerned, it was 3.5 min and 4.3 min respectively for the mixes containing 25, 50 and 100 phr of husk as such as filler whereas it was in the range of 3.1 to 3.4 min for the other mixes containing 25, 50 and 100 phr of husk of different particle size. Optimum cure time was 7.2 to 7.5 min for the former mixes whereas it was in the range of 7.0 to 7.4 min for the latter set of experiments. The induction time for the mixes containing husk with CI resin and with resorcinol and hexamine was 3.3 and 2.1 min respectively. The scorch time for the above mixes was 4.2 and 2.5 min while optimum cure time was 7.2 and 8.4 min respectively.

The cure curves of NR gum, NR-carbon black and NR-silica compounds containing phenols from rice husk and those containing styrenated phenol (control) are given in Fig.5.4. Optimum cure time, cure rate index and scorch characteristics are given in Table 5.7. From the cure curves, it can be seen that the torque developed was maximum in mixes containing antioxidant from rice husk compared to those containing styrenated phenol. There was not much variation in the induction time, scorch time and optimum cure time among the different mixes. It is evident that the addition of phenolic antioxidant from rice husk does not have any adverse effect on the cure characteristics in NR gum, NR-carbon black and NR-silica systems. The different cure values obtained are comparable to those obtained from control mixes.

The cure curves of the mixes in which black ash was used as such at 25, 50 and 100 phr filler levels are given in Fig.5.5. Similarly the cure curves of the mixes containing black ash of 50, 100, 200 and 300 mesh at 25, 50 and 100 phr filler levels are given in Fig.5.6. Optimum cure time, cure rate index, scorch time etc. of the above mixes are given in Table 5.8. It is seen that the particle size of the black ash has a positive role in reducing the cure time of the mixes. In general it may be stated that finer the particle size, the lesser is the cure time of the mix. As expected, the torque value increases as the filler loading increases.The cure curves of the mixes containing 50 phr of black ash (100 mesh) with CI resin and with resorcinol and hexamine are given in Fig.5.7. As in the case of husk, the CI resin has not much effect on the cure time and on the torque developed whereas the addition of resorcinol with hexamine had increased the cure time. The different cure characteristics of the above mixes are reported in Table 5.9.

The cure curves of the mixes containing black ash (100 mesh) alongwith conventional carbon black (HAF) mixed in different proportions are given in Fig.5.8. Cure characteristics of the above mixes are given in Table 5.9. The mix containing black ash alone has the minimum torque and the torque value increases as the ratio of the conventional carbon black in the mix increases. Mix containing HAF black alone showed the maximum torque value. The cure time was maximum for the mix containing black ash and minimum for the one containing HAF black at 50 phr level.

The cure curves of the mixes containing carbon and silica (separated from black ash) as filler at 25 and 50 phr levels are given in Fig.5.9. The different cure properties evaluated are given in Table 5.10. From the table it is seen that the cure time for the mix containing carbon is higher compared to the mix containing conventional carbon black at the same filler loading (See Table 5.9 also) whereas it is more or less same for silica separated from black ash and conventional silica (See Table 5.7 also).

Crosslink density

The crosslink density values of the compounds containing antioxidant from husk and those with styrenated phenol are given in Table 5.12. From the results, it is seen that crosslink density value is highest for carbon black filled compounds followed by silica filled and then unfilled vulcanizates. A slightly higher crosslink density is noticed for the mixes containing antioxidant from husk compared to the control mixes. But this difference is only marginal among the mixes of NR gum, NR-carbon black and NR-silica. These differences in crosslink density values are also reflected in the results of physical properties reported later in this section.

Tensile and other physical properties

The tensile properties of the vulcanizate samples containing husk as a filler are given in Table 5.11. From the table, it is clear that the husk does not give reinforcement to the vulcanizates. Among the different mixes, tensile strength is better for the samples containing finer particles of husk (100 and 200 mesh). The results obtained in the case of mixes containing CI resin and resorcinol with hexamine are also given in Table 5.11. The data indicate that the tensile strength increases with the incorporation of these resins. The cumerone indene resin had better effect on tensile strength compared to resorcinol and hexamine and the latter had comparatively higher torque values.

In the second part of this study, phenols extracted from husk was used as antioxidant in NR gum, NR-carbon black and NR-silica systems using styrenated phenol as control. The tensile and other physical properties obtained for these various mixes are given in Table 5.12. From the table, it is clear that in the case of gum formulations, the initial tensile strength for the mix containing styrenated phenol was higher compared to the mix containing phenolic antioxidant from husk. Elongation was higher for the mix containing antioxidant from husk. The tensile properties of the samples after ageing are also given in Table 5.12. Regarding the after ageing properties, the retention of tensile properties was better for the mix containing antioxidant from husk compared to the reference mix in NR gum compounds. In the case of carbon black filled systems, the initial tensile strength was better for the reference mix compared to the mix containing antioxidant from husk. As expected, a reverse trend is noticed for elongation values. The retention of tensile strength on heat ageing was better for the mix containing antioxidant from husk. Almost the same trend in initial tensile strength, elongation at break values and after ageing properties is noticed for silica filled compounds also. The results are indicative of the fact that the phenols extracted from rice husk shows a strong antioxidant character in NR gum, NR-carbon black and NR-silica systems. The initial tensile strength, elongation at break and the modulus values of the vulcanizates and their after ageing properties are not adversely affected by the incorporation of this phenolic mixtures in to the rubber compound.

Some of the other physical properties of the vulcanizates evaluated are hardness, compression set, tear strength, resilience and abrasion resistance. Hardness and abrasion loss values did not show significant variation among the different mixes. The tear strength was higher for the mixes containing antioxidant from husk compared to the reference mixes in all the systems.

In the next part of the study, the tensile properties of the vulcanizates containing black ash alone, black ash with resin and black ash alongwith conventional carbon black (HAF) were evaluated. The results obtained for the mixes containing black ash alone are given in Table 5.13. Tensile strength was found to be better for the compound containing 25 phr of black ash compared to 50 and 100 phr levels irrespective of the particle size of the ash used indicating that this ash cannot give reinforcement to the vulcanizates. As expected, tensile strength is higher for the compounds containing finer particles of black ash. The results of the experiments using CI resin and resorcinol with hexamine are given in Table 5.14. The data indicate that the addition of these resins slightly increased the tensile strength of the vulcanizates. An increase in elongation and a decrease in modulus value was observed in the case of CI resin whereas a reverse trend was observed in the case of resorcinol and hexamine. The results also indicate that the increase of tensile strength is directly proportional to the amount of conventional black (HAF) added to the black ash.

In the 4th set of experiments, carbon and silica separated from black ash was used as fillers at 25 and 50 phr levels of loading. The results of tensile and other physical properties (of 25 phr filler level) obtained in these experiments are given in Table 5.15. The values of tensile properties show that this carbon and silica do not have reinforcing effect under conditions used in these experiments. At the same time not much adverse effect is noticed on the cure characteristics of the mixes or on the processability parameters. Hence this carbon and silica separated from black ash can be used as fillers in rubber products of medium or low tensile strength. For getting higher reinforcement further chemical treatment of the fillers will be necessary.

CONCLUSION

Rice husk and rice husk ash were used as fillers in NR compounding. The effect of variation of particle size and of filler loading was investigated. Also studied was the reinforcing effect of carbon and silica separated from black ash. The mixture of phenols extracted from husk has been tried as antioxidant and the results viz., cure characteristics and vulcanizate properties (both before and after ageing) were compared with those of control mixes containing styrenated phenol in gum and filled vulcanizates. When phenols from husk was used as antioxidant in different mixes, it is seen that there is not much variation in cure characteristics compared with the control mixes. At the same time antioxidant protection given by the phenols is comparable with styrenated phenol. On evaluation of the different tensile properties also these phenols do not show any adverse effect.

With regard to the use of husk and black ash as fillers in natural rubber it is seen that much reinforcement is not effected by incorporation of these in different formulations. But when these fillers are used in smaller particle size some reinforcement effect is noticed. The reinforcement can further be increased to some extent by incorporation of resorcinol and hexamine. But significant reinforcement could be obtained when black ash is used along with conventional black (HAF) in different proportions. Husk and husk ash do not have any adverse effect on processing or curing characteristics of the mixes. So these fillers can be used in NR mixes when product requires only low or medium tensile strength. Also tried was the separation of carbon and silica from black ash and trying them separately as fillers. Even though no adverse interference is seen in the cure properties of the mixes, the reinforcement character of this carbon and silica is seen to be minimal. To obtain higher reinforcement further chemical treatment may be necessary. At the same time they can be used as non-reinforcing or semi-reinforcing fillers.

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Table 5.1 Formulation of mixes containing husk as such and at different particle sizes

Mix	IA	IB	IC	IIA	IIB	IIC	IIIA	IIIB	IIIC	IVA	IVB	IVC	VA	VB
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Styrenated phenol	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mercaptobenzothiazyl disulphide	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Tetramethyl thiuram disulphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Husk (As such)	25	50	100	—	—	—	—	—	—	—	—	—	—	—
Husk (50 mesh)	—	—	—	25	50	100	—	—	—	—	—	—	—	—
Husk (100 mesh)	—	—	—	—	—	—	25	50	100	—	—	—	—	—
Husk (200 mesh)	—	—	—	—	—	—	—	—	—	25	50	100	—	—

Table 5.1 contd.

Mix	IA	IB	IC	IIA	IIB	IIC	IIIA	IIIB	IIIC	IVA	IVB	IVC	VA	VB
Husk (100 mesh) with CI resin	—	—	—	—	—	—	—	—	—	—	—	—	50	—
Husk (100 mesh) with resorcinol and hexamine	—	—	—	—	—	—	—	—	—	—	—	—	—	50
Aromatic oil	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0	5.0	5.0
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Table 5.2 Use of phenols obtained from husk as antioxidant in filled and unfilled vulcanizates of natural rubber

Mix	VIA	VIB	VIIA	VIIB	VIIIA	VIIIB
Natural rubber	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
Mercaptobenzthiazyl disulphide	0.8	0.8	0.8	0.8	0.8	0.8
Tetramethyl thiuram disulphide	0.2	0.2	0.2	0.2	0.2	0.2
Styrenated phenol (control)	1.0	—	1.0	—	1.0	—
Phenols from husk	—	1.0	—	1.0	—	1.0
Carbon black (HAF 330)	—	—	50	50	—	—
Precipitated silica (vulkasil)	—	—	—	—	50	50
Aromatic oil	—	—	5	5	—	—
Naphthenic oil	—	—	—	—	5	5
Diethylene glycol	—	—	—	—	2	2
Silane coupling agent	—	—	—	—	2	2
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

Table 5.3 Formulation of mixes containing black ash of different particle size

Mix	IXA	IXB	IXC	XA	XB	XC	XIA	XIB	XIC	XIIA	XIIB	XIIC	XIIIA	XIIIB	XIIIC
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Styrenated phenol	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mercaptobenzothiazyl disulphide	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Tetra methyl thiuram disluphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Black ash (As such)	25	50	100	--	--	--	--	--	--	--	--	--	--	--	--
Black ash (50 mesh)	--	--	--	25	50	100	--	--	--	--	--	--	--	--	--
Black ash (100 mesh)	--	--	--	--	--	--	25	50	100	--	--	--	--	--	--
Black ash (200 mesh)	--	--	--	--	--	--	--	--	--	25	50	100	--	--	--
Black ash (300 mesh)	--	--	--	--	--	--	--	--	--	--	--	--	25	50	100
Aromatic oil	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Table 5.4 Formulation of mixes containing black ash with resin and black ash with carbon black (HAF)

MIX	XIVA	XIVB	XVA	XVB	XVC	XVD	XVE
Natural rubber	100	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sterenated phenol	1	1	1	1	1	1	1
Mercaptobenzthiazyl disulphide	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Tetramethyl thiuram disulphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Black ash (100 mesh) with CI resin	50	--	--	--	--	--	--
Black ash (100 mesh) with resorcinal + Hexamine	--	50	--	--	--	--	--
Black ash (100 mesh)	--	--	50	--	--	--	--
Black ash with carbon black (HAF)(75:25)	--	--	--	50	--	--	--
Black ash with carbon black (50:50)	--	--	--	--	50	--	--
Black ash with carbon black (25:75)	--	--	--	--	--	50	--
Carbon black (HAF alone)	--	--	--	--	--	--	50
Aromatic oil	5	5	5	5	5	5	5
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Table 5.5 Formulation of mixes containing carbon and silica separated from black ash

M I X	XVIA XVIA	XVIB	XVIIA	XVIIB
Natural rubber	100	100	100	100
Zinc oxide	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5
Sterenated phenol	1	1	1	1
Mercaptobenzthiazyl disulphide	0.8	0.8	0.8	0.8
Tetramethyl thiuram disulphide	0.2	0.2	0.2	0.2
Carbon black (300 mesh)	25	50	--	--
Silica (300 mesh)	--	--	25	50
Aromatic oil	2.5	5.0	--	--
Naphthenic oil	--	--	2.5	5.0
Diethylene glycol	--	--	2	2
Silane coupling agent	--	--	2	2
Sulphur	2.5	2.5	2.5	2.5

Table 5.6 Cure characteristics of mixes containing husk of different particle size (cured at 150°C)

Cure characteristics	MIX No.													
	IA	IB	IC	IIA	IIB	IIC	IIIA	IIIB	IIIC	IVA	IVB	IVC	VA	VB
Optimum cure time t_{90} (min.)	7.2	7.4	7.5	7.1	7.3	7.4	7.0	7.2	7.3	7.0	7.1	7.2	7.2	8.4
Elastographic scorch time t_{10} (min.)	4.3	4.3	4.3	4.2	4.2	4.2	4.1	4.1	4.1	4.0	4.0	4.0	4.2	2.5
Cure rate index	34.48	32.25	31.25	34.48	32.25	31.25	34.48	32.25	31.25	33.33	32.26	31.25	33.33	16.94
Induction time (min.)	3.5	3.5	3.5	3.4	3.4	3.4	3.3	3.3	3.3	3.1	3.1	3.1	3.3	2.1

Table 5.7 Cure characteristics of mixes containing phenolic antioxidants from husk

Cure characteristics	MIX NO.					
	VIA	VIB	VIIA	VIIB	VIIIA	VIIIB
Optimum cure time t_{90} (min.)	6.2	6.1	5.1	5.1	5.0	5.0
Elastographic scorch time t_{10} (min.)	3.5	3.4	2.0	2.0	2.2	2.2
Cure rate index	37.03	37.03	32.26	32.26	35.71	35.71
Induction time (min.)	3.1	3.0	1.3	1.3	1.4	1.4

Table 5.8 Cure characteristics of mixes containing black ash of different particle size (at 150°C)

Cure characteristics	MIX No.														
	IXA	IXB	IXC	XA	XB	XC	XIA	XIB	XIC	XIIA	XIIB	XIIC	XIIIA	XIIIB	XIIIC
Optimum cure time t_{90} (min.)	7.2	7.4	7.5	7.1	7.3	7.4	6.9	7.1	7.2	6.7	6.8	6.9	6.4	6.5	6.6
Elastographic scorch time t_{10} (min.)	4.0	4.0	4.0	3.9	3.9	3.9	3.8	3.8	3.8	3.6	3.6	3.6	3.4	3.4	3.4
Cure rate index	31.25	29.41	28.57	31.25	29.41	28.57	32.26	30.30	29.41	32.26	31.25	30.30	33.33	32.26	31.25
Induction time (min.)	3.3	3.3	3.3	3.2	3.2	3.2	3.1	3.1	3.1	2.9	2.9	2.9	2.8	2.8	2.8

Table 5.9 Cure characteristics of mixes containing black ash with resin and black ash with carbon black (HAF) cured at 150°C

Cure characteristics	MIX NO.						
	XIVA	XIVB	XVA	XVB	XVC	XVD	XVE
Optimum cure time t_{90} (min.)	7.3	8.7	7.9	7.5	7.1	6.8	5.0
Elastographic scorch time t_{10} (min.)	4.2	2.0	3.7	2.9	2.7	2.5	2.2
Cure rate index	32.25	14.92	23.80	21.73	22.72	23.25	35.71
Induction time (min.)	3.6	1.4	3.0	2.1	2.0	1.8	1.1

Table 5.10 Characteristics of mixes containing carbon and silica separated from black ash (150°C)

Cure characteristics	MIX NO.			
	XVIA	XVIB	XVIIA	XVIIB
Optimum cure time t_{90} (min.)	6.5	6.4	5.1	4.9
Elastographic scorch time t_{10} (min.)	3.6	3.6	2.3	2.3
Cure rate index	34.48	35.71	35.71	38.46
Induction time (min.)	3.1	3.1	1.7	1.7

Table 5.11 Tensile properties of the vulcanizates containing husk as such and at different mesh size as a filler

Mix No.	Filler loading of husk (Phr)	Tensile strength (MPa)	Elongation at break (%)	Modulus at 200% elongation (MPa)
IA	25	6.69	543	1.61
IB	50	3.20	381	1.58
IC	100	1.74	223	1.62
IIA	25	9.53	601	1.88
IIB	50	6.40	541	1.87
IIC	100	3.20	319	1.90
IIIA	25	16.16	634	2.77
IIIB	50	8.73	475	3.04
IIIC	100	5.03	289	3.52
IVA	25	16.44	628	3.26
IVB	50	11.40	472	3.53
IVC	100	5.20	283	3.66
VA	50	9.78	509	3.01
VB	50	9.30	315	3.41

Table 5.12 Physical properties of the vulcanizates containing phenolic antioxidant from husk and styrenated phenol

Parameter		MIX No.					
		VIA	VIB	VIIA	VIIB	VIIIA	VIIIB
(1)		(2)	(3)	(4)	(5)	(6)	(7)
Tensile strength (MPa)	BA	23.01	22.94	26.88	26.85	24.65	24.68
	AA	13.51	14.30	19.63	19.67	19.30	20.16
Elongation at break (%)	BA	728	730	382	425	576	585
	AA	557	574	337	337	392	365
Modulus at 200% elongation (MPa)		2.24	1.93	8.76	8.55	4.35	4.35
Tear strength (N/mm)		34	35	127	129	74	75
Compression set (%)		30.34	29.98	36.47	36.55	50.00	50.00

BA - Before ageing, AA - After ageing.

Table 5.12 contd.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Hardness (Shore A)	40	40	65	65	67	67
Abrasion loss (cm^3/hr)	7.066	7.066	5.217	5.186	5.165	5.139
Resilience (%)	76.12	76.54	54.11	54.11	54.43	54.43
Crosslink density (m.mol/kg)	40.46	40.60	74.00	74.12	66.85	66.92

Table 5.13 Tensile properties of the vulcanizates containing black ash as such and at different particle size as a filler

Mix No.	Filler loading of ash (Phr)	Tensile strength (MPa)	Elongation at break (%)	Modulus at 200% elongation (MPa)
IXA	25	17.88	664	2.22
IXB	50	7.93	533	2.31
IXC	100	5.31	433	2.46
XA	25	17.42	666	2.03
XB	50	11.05	547	2.33
XC	100	7.33	484	2.62
XIA	25	18.06	674	2.18
XIB	50	13.06	592	2.42
XIC	100	7.93	492	3.07
XIIA	25	20.32	702	2.17
XIIB	50	15.76	590	2.62
XIIC	100	10.81	494	3.00
XIIIA	25	20.67	719	2.24
XIIIB	50	17.25	617	2.69
XIIIC	100	11.02	498	3.01

Table 5.14 Tensile properties of the vulcanizates containing black ash (100 mesh) with resin and black ash with carbon black as a filler

Mix No.	Filler loading (Phr)	Tensile strength (MPa)	Elongation at break (%)	Modulus at 200% elongation (MPa)
XIVA	50	13.06	592	2.42
XIVB	50	14.93	466	3.81
XVA	50	14.88	626	2.07
XVB	50	15.98	437	4.50
XVC	50	16.43	442	4.99
XVD	50	19.74	451	5.95
XVE	50	24.26	398	9.02

Table 5.15 Tensile and other physical properties of the vulcanizates containing carbon and silica (from black ash) as fillers

Parameter	MIX NO.			
	XVIA	XVIB	XVIIA	XVIIB
Tensile strength (MPa)	21.54	18.75	22.43	18.50
Elongation at break (%)	578	465	684	482
Modulus at 200% elongation (MPa)	3.40	4.43	3.02	4.17
Tear strength (N/mm)	71	-	82	-
Compression set (%)	26.70	-	25.68	-
Hardness (Shore A)	45	-	45	-
Abrasion loss (cm^3/hr)	7.776	-	7.388	-

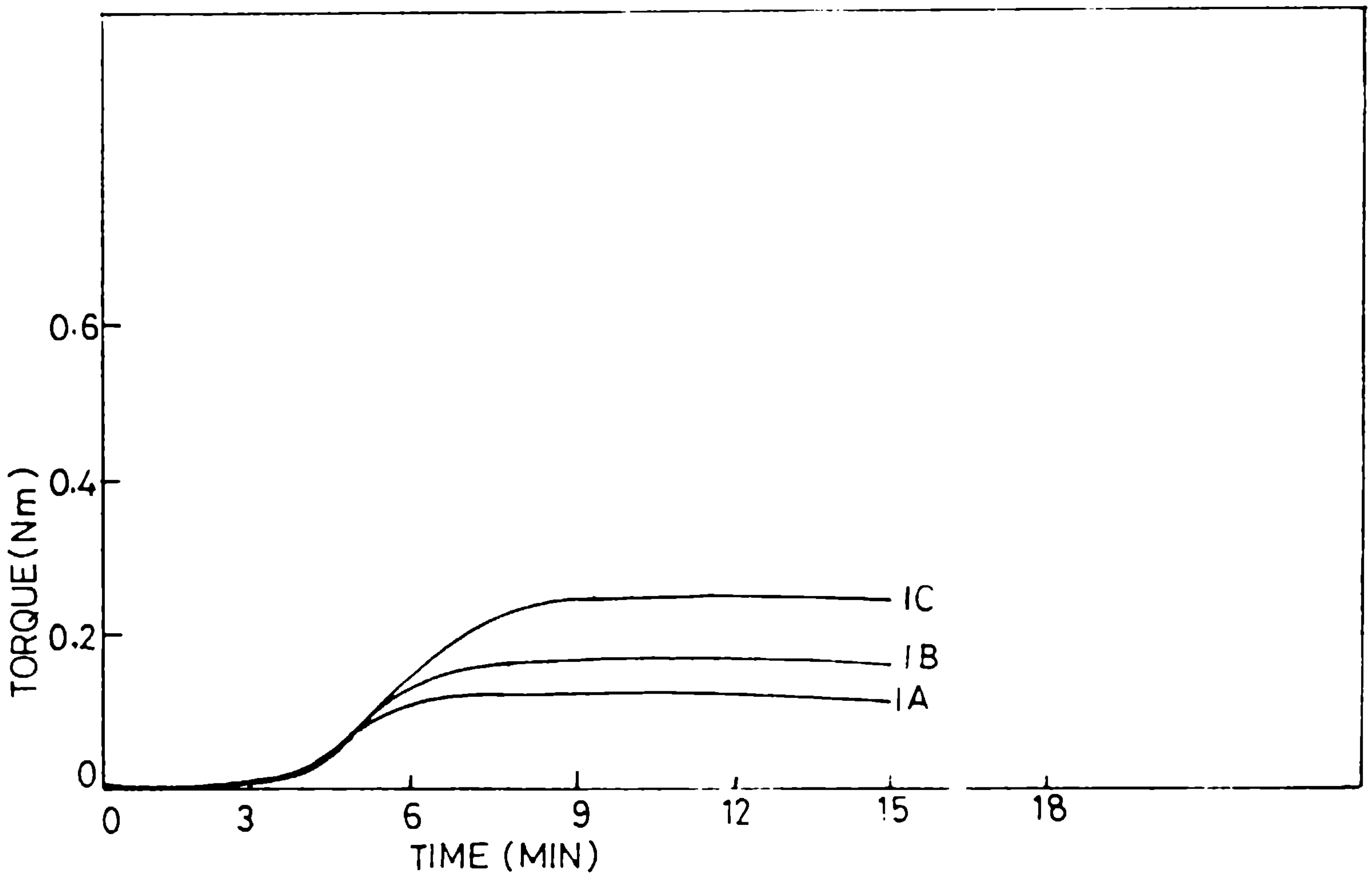

Fig.5.1 Cure curves of the mixes containing rice husk as such in natural rubber

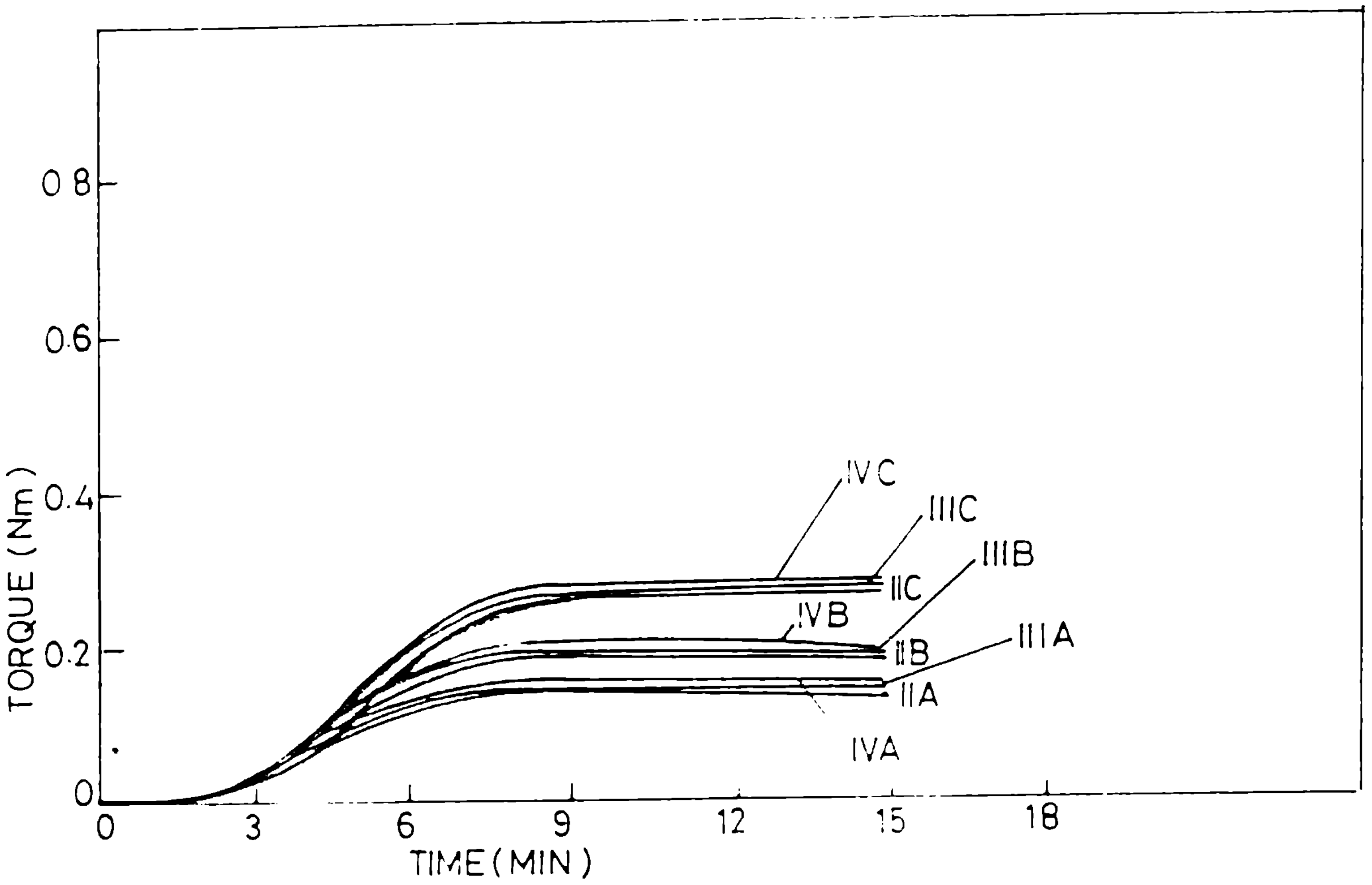

Fig.5.2 Cure curves of the mixes containing rice husk (50, 100 and 200 mesh) in natural rubber

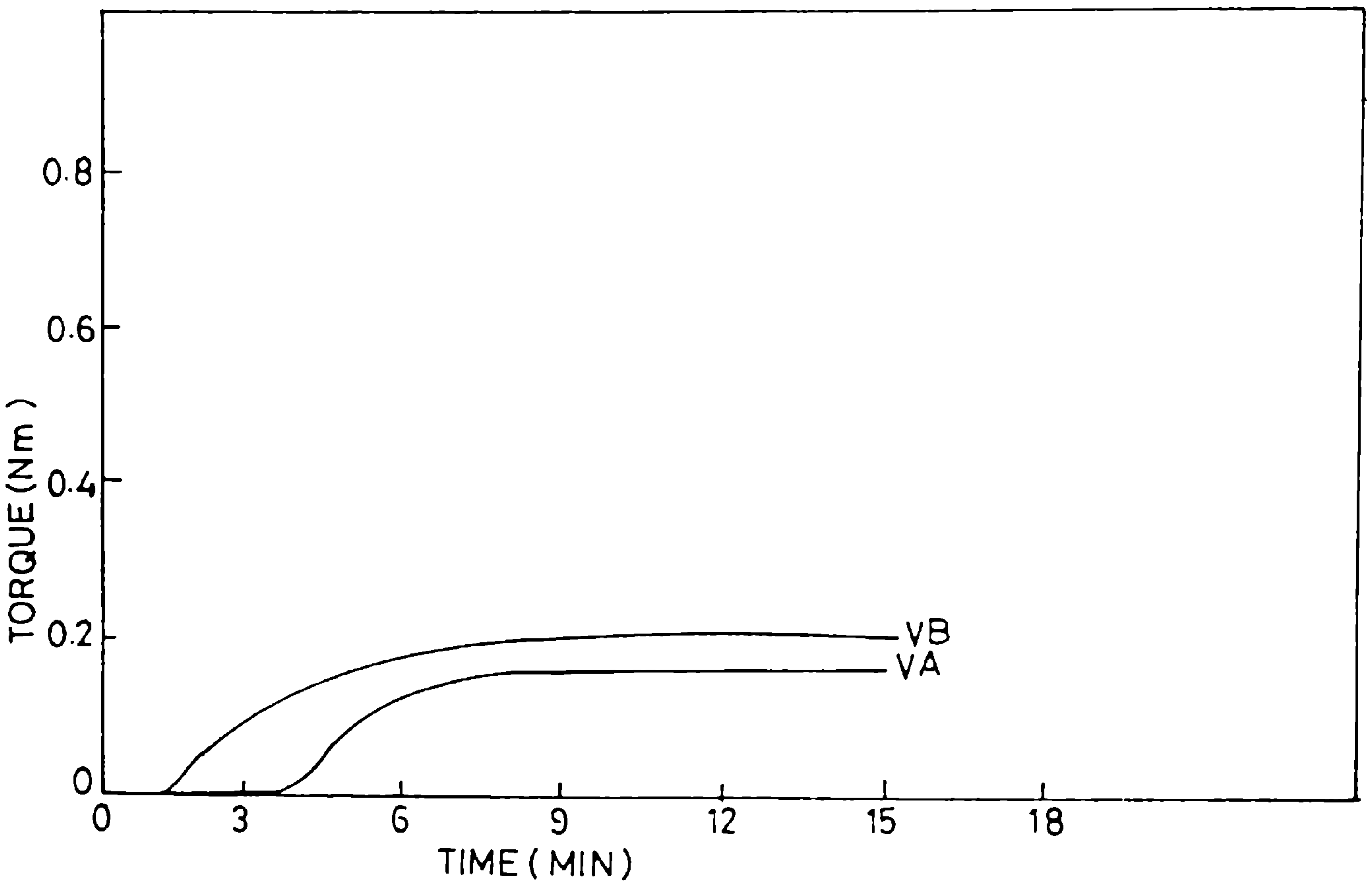

Fig.5.3 Cure curves of the mixes containing rice husk (100 mesh) with resins in natural rubber

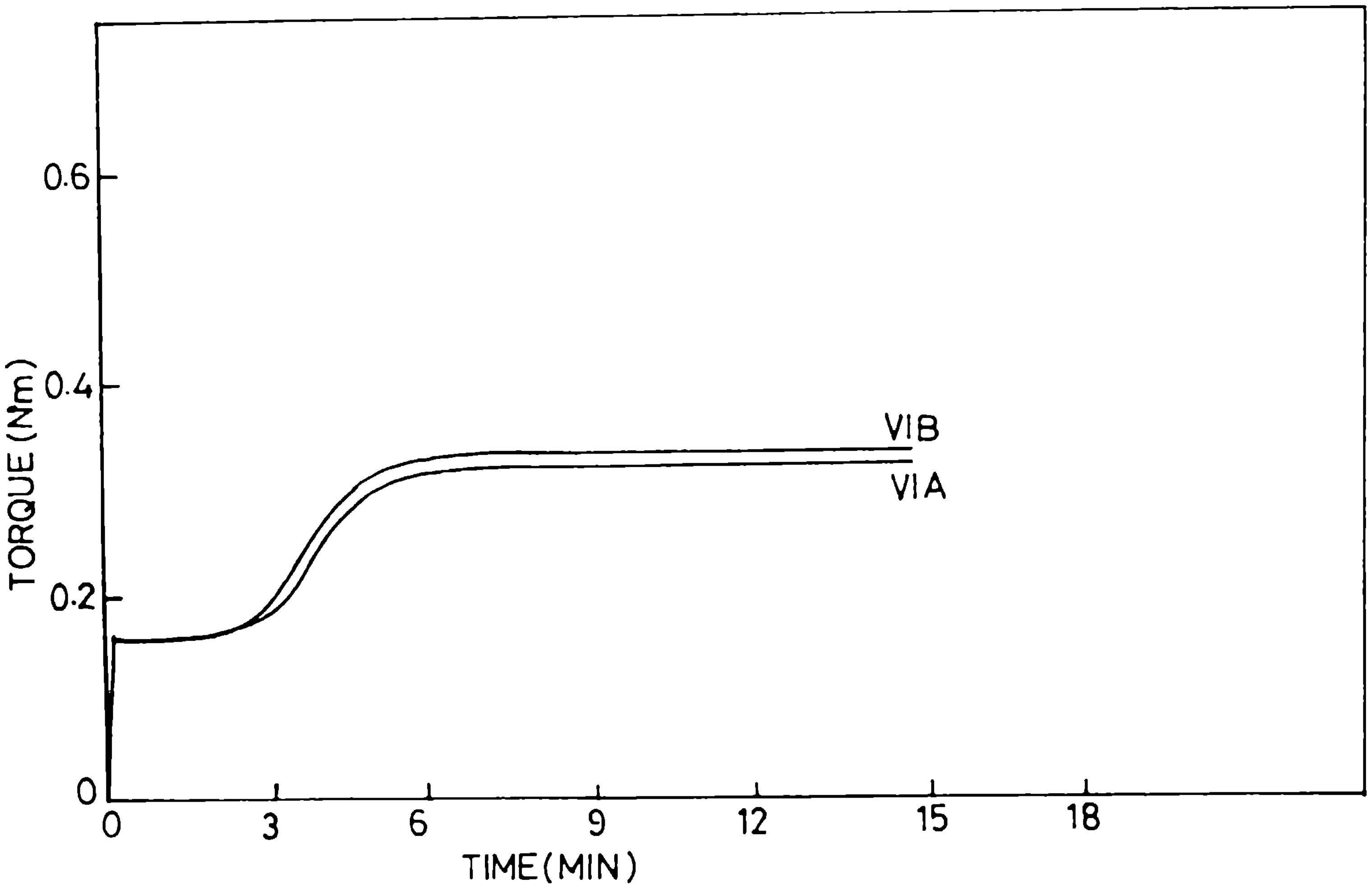

Fig.5.4 Cure curves of the mixes containing antioxidant from rice husk and styrenated phenol in NR gum compounds

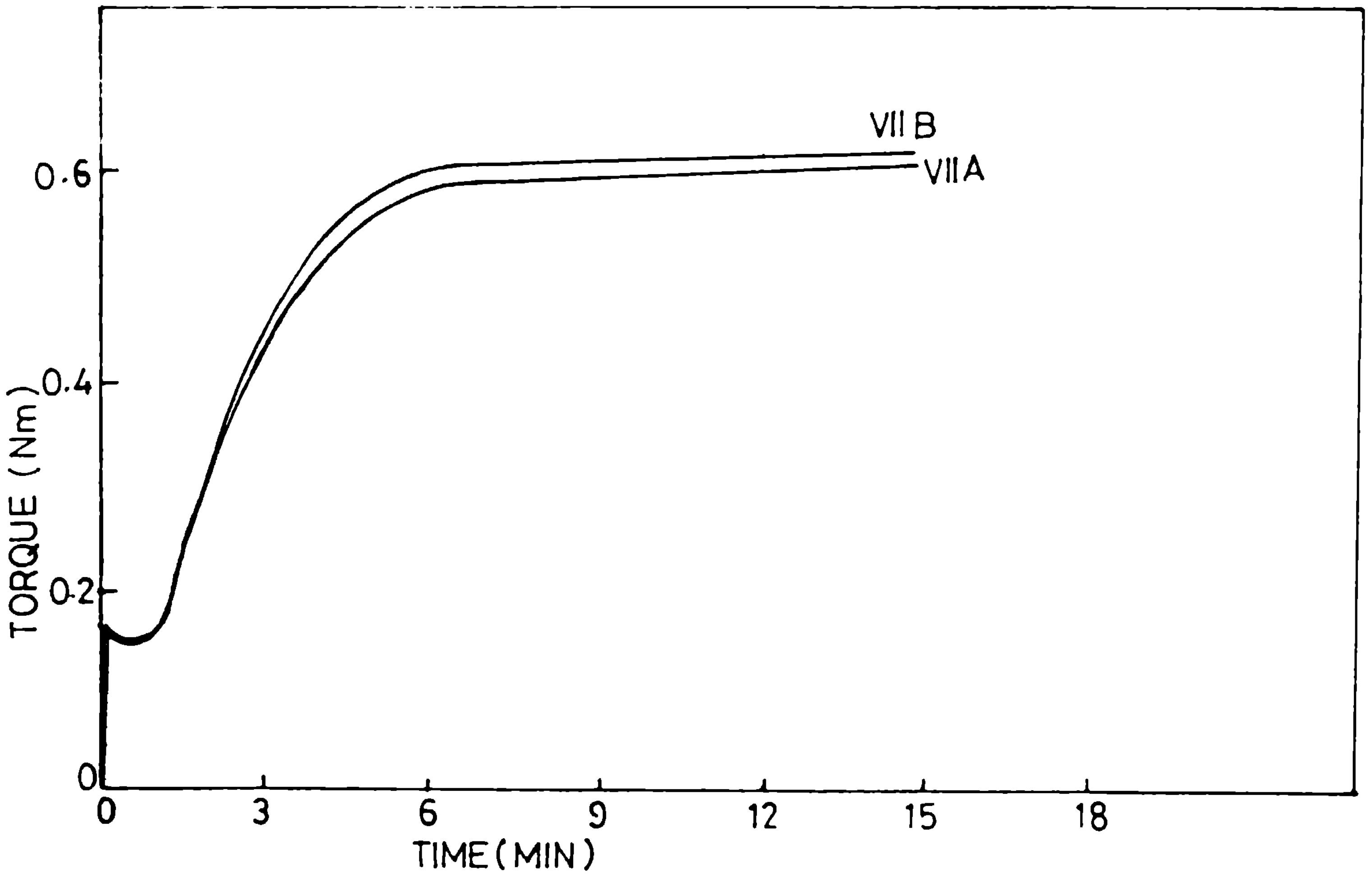

Fig.5.5 Cure curves of the mixes containing antioxidant from rice husk and styrenated phenol in NR carbon black filled compounds

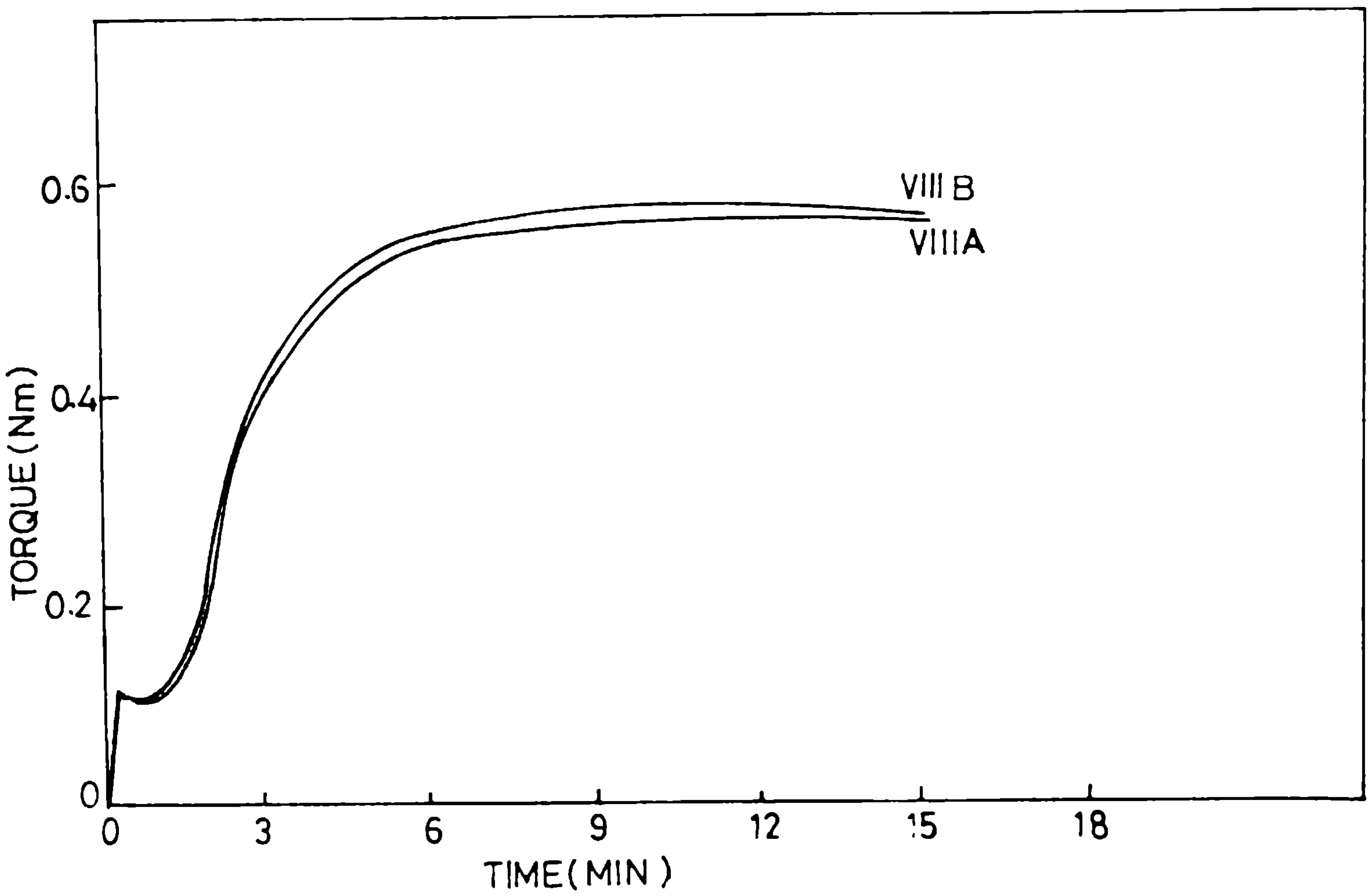

Fig. 5.6 Cure curves of the mixes containing antioxidant from rice husk and styrenated phenol in NR silica filled compounds

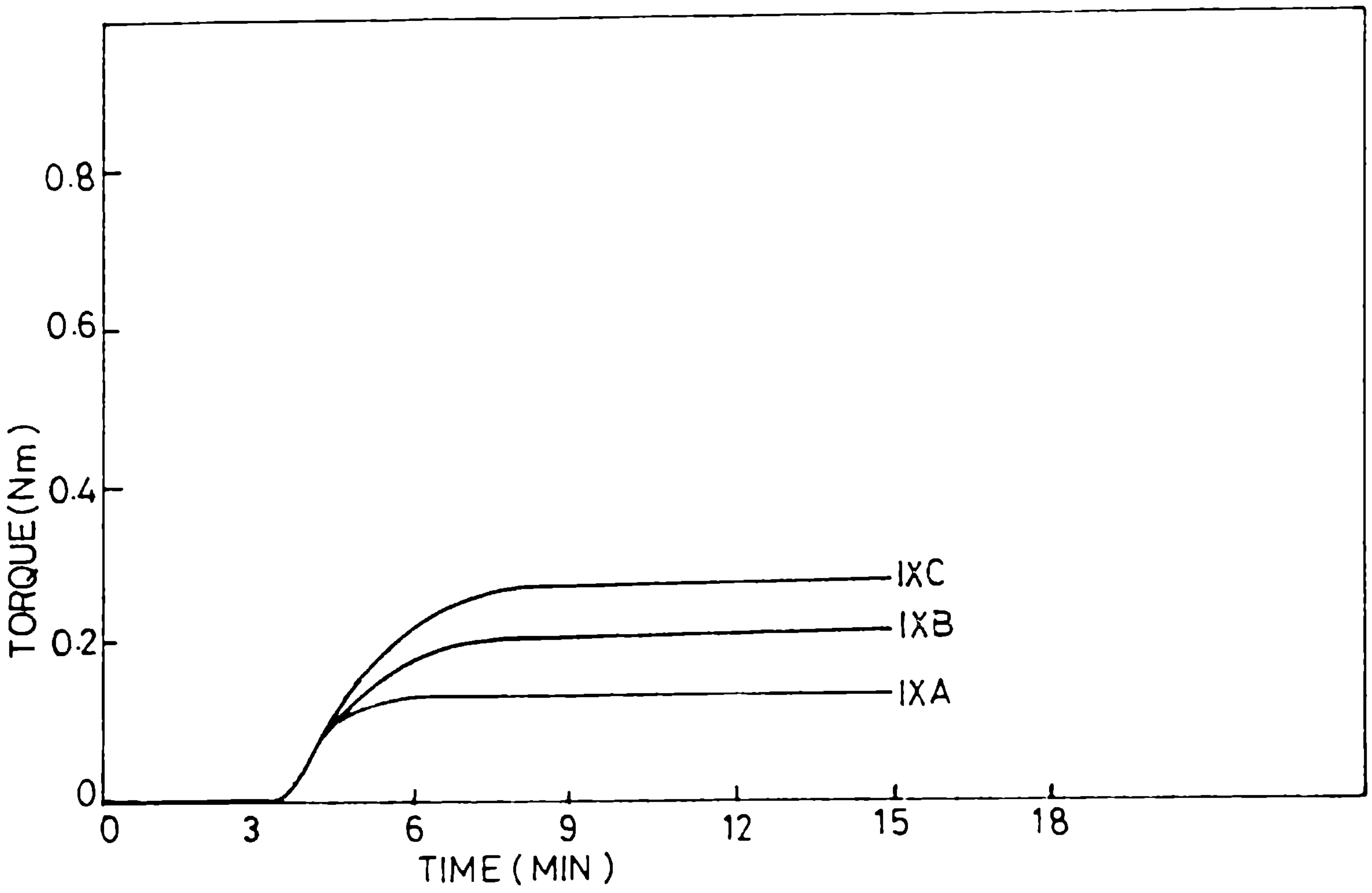

Fig.5.7 Cure curves of the mixes containing black ash as such in natural rubber

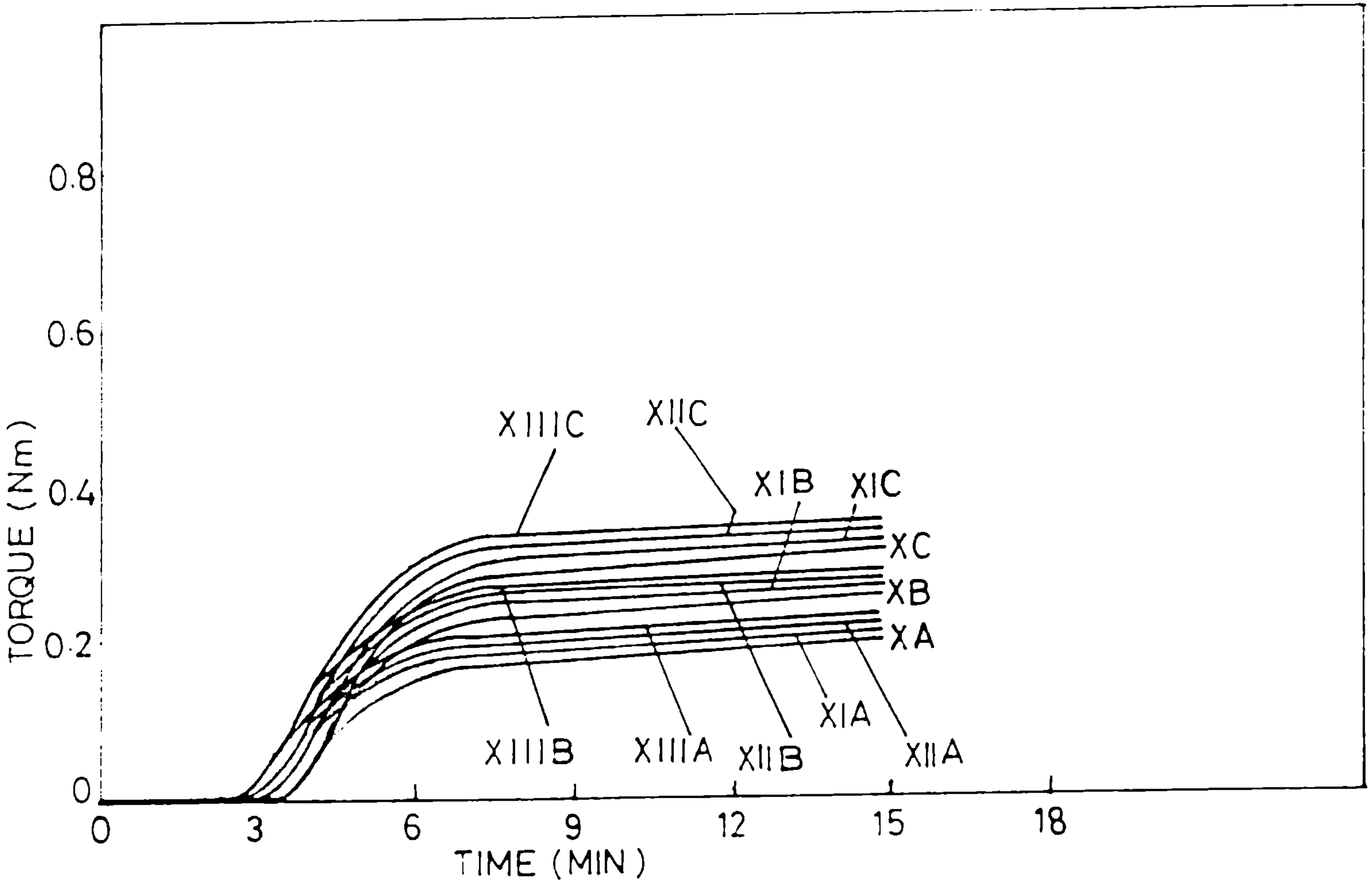

Fig.5.8 Cure curves of the mixes containing black ash (50, 100, 200 and 300 mesh) in natural rubber

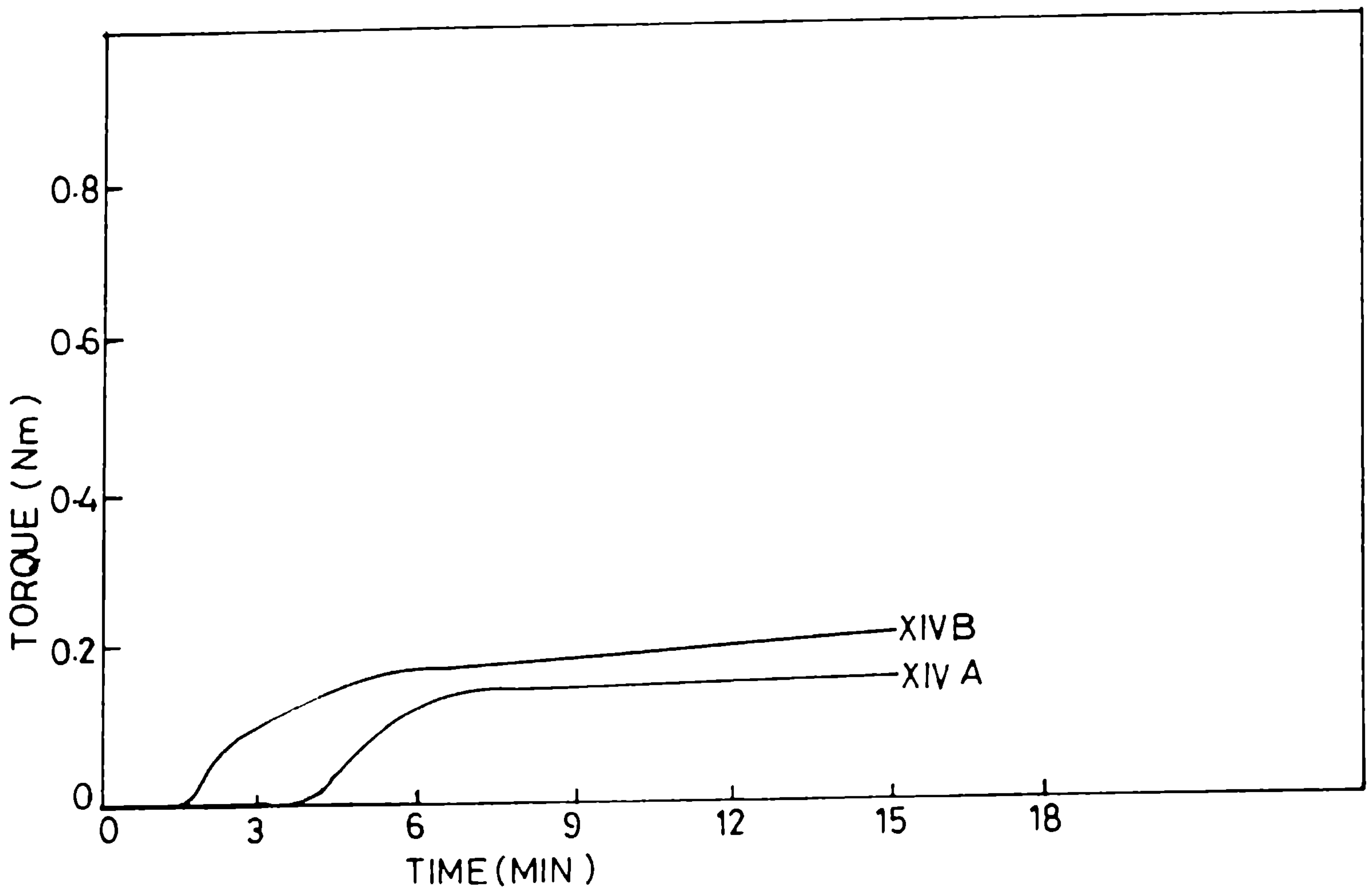

Fig.5.9 Cure curves of the mixes containing black ash (100 mesh) with resins in natural rubber

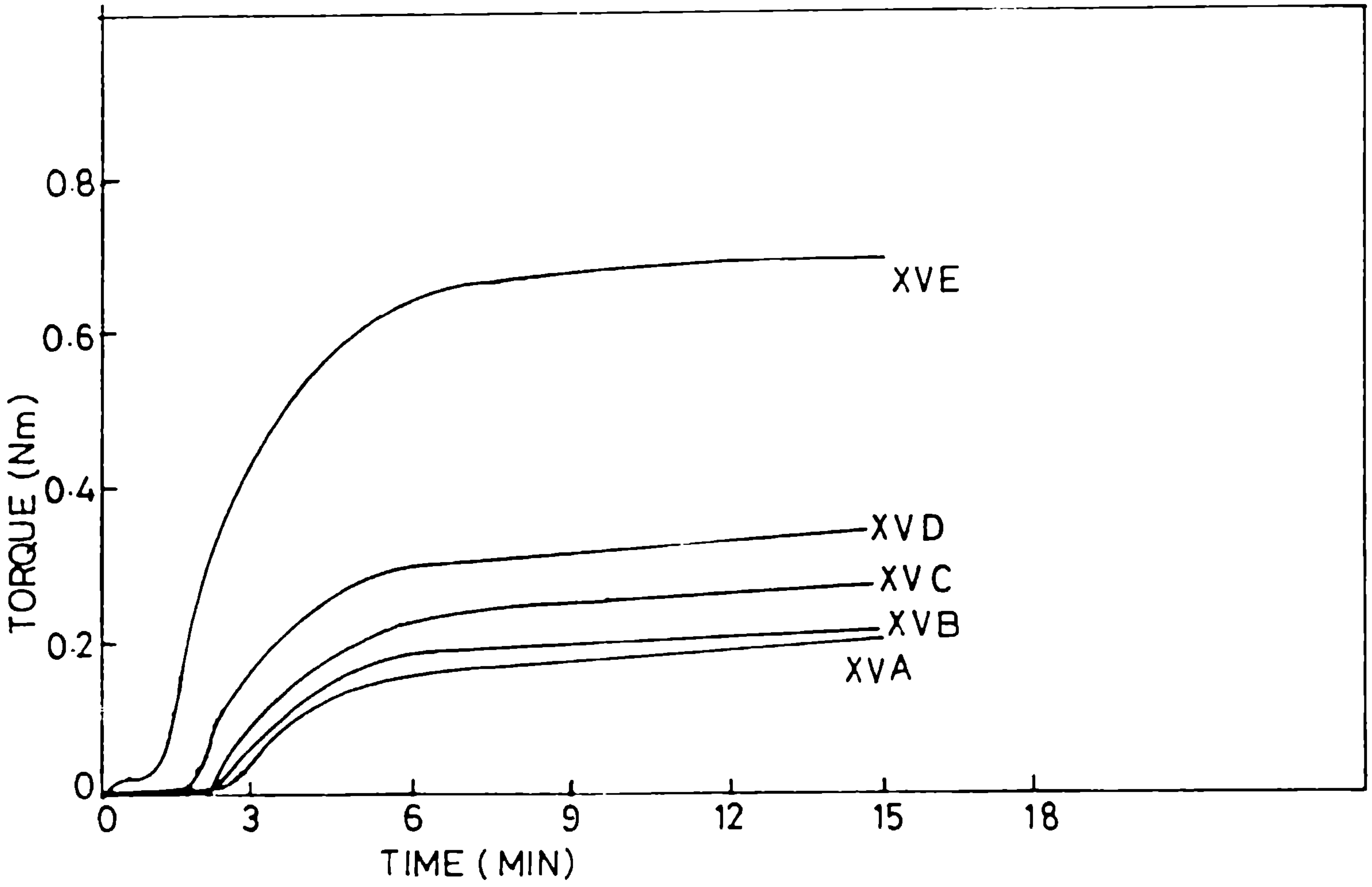

Fig.5.10 Cure curves of the mixes containing black ash (100 mesh) with carbon black (HAF) in natural rubber

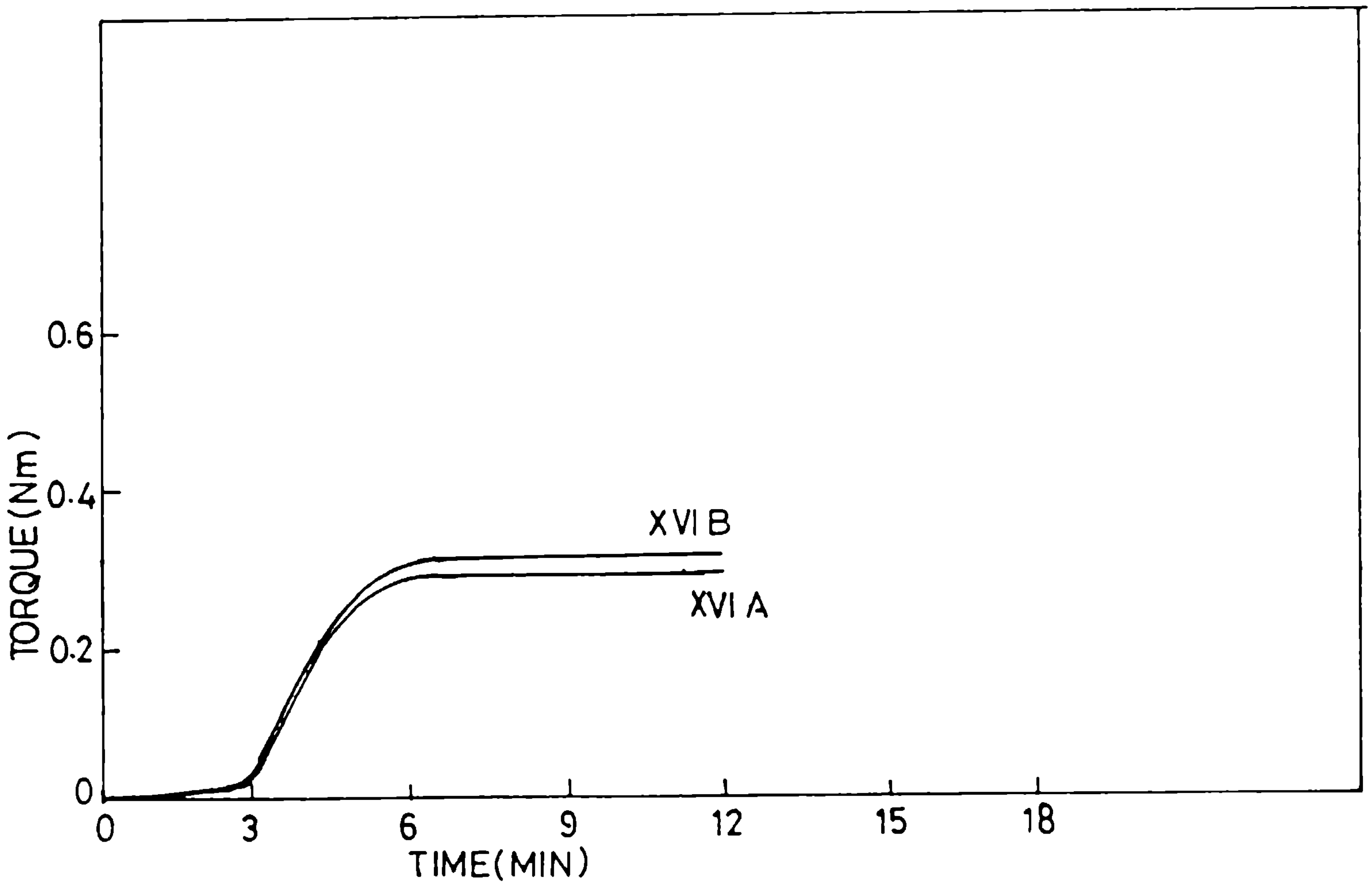

Fig.5.11 Cure curves of the mixes containing carbon (300 mesh) separated from black ash in natural rubber

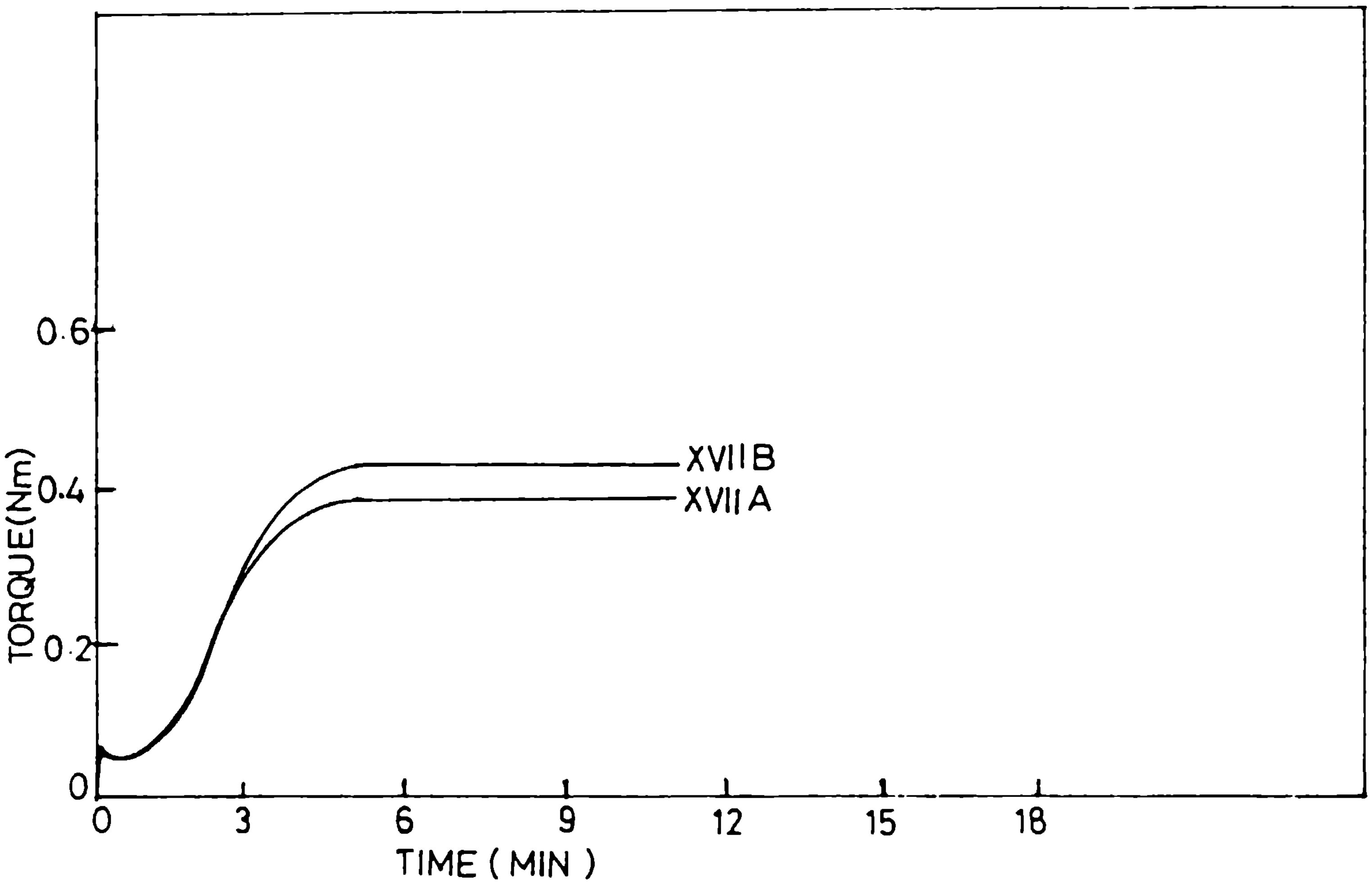

Fig.5.12 Cure curves of the mixes containing silica (300 mesh) separated from black ash in natural rubber

Chapter 6

COMPOUNDING AND VULCANIZATION STUDIES ON SBR USING RICE HUSK AND ITS BY-PRODUCTS

In the previous chapter the results obtained on a study on the utilization of rice husk and rice husk ash as fillers and the phenols extracted from rice husk as an antioxidant in natural rubber has been described. This chapter deals with a similar systematic study in a synthetic rubber viz., styrene butadiene rubber. This investigation is undertaken mainly because a lot of differences are encountered in the compounding and vulcanization of a synthetic rubber compared to natural rubber. For example, gum vulcanizates of synthetic rubbers have much lower tensile strength and resistance to tear propagation than those with natural rubber. However, the reinforcing fillers give the same level of mechanical properties for SR as for NR, but the degree of reinforcement by the fillers is higher in the former. Further, the reinforcing effect of an active filler as well as the dosage required can be quite different for different elastomers. The activity of a filler in synthetic rubber is often quite more pronounced because of their chemical structure and lack of strain crystallisation than in NR. The variation in the filler effectiveness of NR and SR can be explained with the theory of over stressed molecules. During stressing of NR a partial parallel orientation of the molecules occur, whereas those which are more orientated than others form stress induced crystals. NR compounds therefore require considerably less filler than synthetic rubbers.

The vulcanizates obtained by the use of gum compounds have some basic characteristic properties given by the elastomer used, e.g., good dynamic properties when natural rubber is used, resistance to swelling when nitrile rubber is used, resistance to ozone when ethylene-propylene rubber is used, resistance to elevated temperature in the case of silicone rubber and high resistance to gas permeation in the case of butyl rubber. The properties of gum compounds can be improved within limits by suitable choice of the vulcanization system which, however, do not suffice for its technical utilization. The gum vulcanizates prepared from crystallizing rubbers have technically limited uses, whereas those made from non-crystallizing elastomers have such mechanical properties that they cannot be utilized for most technical purposes. The unfilled compounds are also processed with difficulty and they would be too expensive for most uses. Therefore, the gum compounds must be suitably modified to the requirements put on them during use which is achieved by the addition of fillers. Generally, almost all properties of rubber are changed by filler loading. By incorporation of a filler, the processability of the rubber compound is improved and the cost of the product is reduced. Its density, modulus, hardness, tensile strength, wear resistance, dynamic properties, etc. etc. are all modified. Properties like modulus, hardness and hysteresis increase continuously with increasing amount of filler whereas the rebound resilience decreases. Other properties like tensile strength first improve upto a maximum and then, on addition of further filler, deteriorates. Fillers that improve some technically important properties - such as tensile strength, tear strength and wear resistance are called active or reinforcing fillers. Other fillers are termed inactive, inert or extenders. Their main effect is to cheapen the product.

The classification of fillers into reinforcing and inert types is only a convention and is inaccurate and inadequate in the strict sense. Actually no filler exists that is completely inert, because the vulcanizate properties always change by filler loading, and it depends on the viewpoint from which such a change is judged. The improvement in some properties is usually accompanied by a deterioration in others. Generally, every filler may be considered to be active that adjusts a given property to the required value, e.g., the hardness of the product. Use of fillers in rubber involves a lot of compromises. For example, if 30% of a filler is added to a compound and the deterioration of the observed property is only about 20% or if the property deteriorates by the full 30%, but the price decreases by more than 30%, it may be considered as an improving effect. The addition of a reinforcing filler is also known to increase the energy necessary for the rupture of the rubber and this value may be considered as a single criterion of the reinforcement. The measure of the energy necessary for breaking is available from the area under the stress-strain curve. According to the general definition by Kraus, the reinforcement of rubber may be considered as a modification of the viscoelastic and failure properties of the rubber by means of fillers, aimed at improving one or several properties without reducing the reversibility of deformations. From the practical point of view we may distinguish fillers into non-black and black types also.

The differences in the effects of the fillers are not given by the chemical composition of the filler alone but by the size of its particles and their shape and surface activity.

Like other materials, rubbers also suffer changes in its mechanical and other properties with time and their overall effect is called ageing. On ageing a number of properties important in service life change irreversibly. Therefore, additives such as antioxidants, the purpose of which is to retard oxidative degradation of the rubber is added so that the product retains its useful properties conferred by the composition of the compound. Antioxidants do not impart any distinct properties by themselves. The main factor in ageing of rubber is oxygen, which take part in different chemical reactions weakening the rubber chain. The nature and rate of changes are affected by other factors also such as heat, light, mechanical energy and other atmospheric effects. The effects of temperature and mechanical fatigue and the effect of some proxidant metals (Cu, Mn) will manifest themselves sooner or later in the service of the product. In practice, a single unfavourable effect seldom prevails; the effects are combined randomly, so that it is difficult to evaluate the ageing by a single laboratory test.

The actual course of ageing of rubbers is a function of the elastomer used, the vulcanization system and components of the compound. The reactivity of polymer with oxygen is determined by their chemical structure and therefore various rubbers show difference in resistance to ageing. From the point of view of mechanical properties, it is important how the original structure of the vulcanizate is changed by chemical reactions during ageing. The main structural changes are:

1. Scission of the crosslinks leading to a decrease in the network density resulting in a decrease in modulus and tensile strength and an increase in elongation and the deterioration of dynamic properties.

2. Formation of additional crosslinks (on reaction with oxygen) with an increase in network density, resulting in an increase in modulus and hardness and subsequently a decrease in the tensile strength and the crack growth resistance.

3. Random scission of the network chains on reaction with oxygen (mainly in unsaturated rubbers). This brings about a decrease in modulus, hardness and tensile strength and deteriorates dynamic properties.

4. Chemical modification of the polymeric chains, eg., cis-trans isomerization.

5. Changes in the crosslink character; For eg., the conversion of the thermally less stable polysulphide crosslinks in to more stable mono and disulphide links.

The structural changes described may take place simultaneously, but individual changes take place to different extents. The after-effects of antioxidant protection in natural rubber is seen to be different from those of synthetic rubbers. In NR for example, chain scission predominates during ageing, and the vulcanizate softens or even becomes sticky. In SBR, crosslinking dominates over scission, the vulcanizates harden on ageing and the elongation at break decreases. The reaction of rubber with oxygen is of a chain character with an autocatalytic course. In order to retard or even suppress its course, the free radicals formed should be bound, or the peroxides and hydroperoxides formed decomposed to innocuous products; this is the role of the antioxidant added.

Most active antioxidants cause staining of vulcanizates in light. The socalled non-staining antioxidants required for white compounds usually do not match the effect of staining antioxidants in all respects. Antioxidants migrate easily, i.e. they pass into materials with which they are in direct contact. Those materials which are in contact with rubber containing staining antioxidant then become dark in light.

Chemically, most antioxidants can be divided into two groups: amines, which are very effective but become coloured in light, and phenols, which constitute non-staining antioxidants. Amines suppress the degrading effect of oxygen during storage and also during application, and provide good protection against degradation at elevated temperatures. Many of them (derivatives of diphenylamine and p-phenylenediamine) are also effective against flexing fatigue and the effects of ozone. Phenols have a lower protective effect than amines, but their oxidation products are less coloured and therefore they do not stain white vulcanizates. Generally, phenols provide satisfactory protection against oxidation during storage and service at elevated temperatures. But in their effect against flexing fatigue they cannot match amines.

In SBR also, to improve the oxidative stability, one uses the conventional antioxidants based on either amine or phenolic type. Generally, the amount used is of the order of 1-2 phr. In many instances a combination of antioxidants are used to take advantage of their synergistic effect.

In recent years, rice husk has been found to be utilized as a fuel in husk fired furnaces for heating air and generating steam but these efforts have been mainly in areas where parboiling process is in vogue.[1] However, there are many parts of the country where raw milling is common and rice millers are generally disposing it off by heaping the husk and burning it into ash. Even when rice husk is used as a fuel in a furnace, the end product, the rice husk ash (black ash) is virtually a waste and its proper utilization has also been a problem in the rice mills. It is also difficult to produce white ash in industrial furnaces. In these furnaces, temperature during combustion goes above 900°C as a result of which silica particles present in inner and outermost surfaces of husk start sintering and fusing and envelop the carbon particles which prevent carbon, oxygen reaction thereby resulting in black ash production. Since black ash contains approximately 50 per cent silica, it can be used for the preparation of industrial chemical like sodium silicate[2] and also for various ceramic articles like potteries, electrical porcelains, sanitary wares etc.[3] Refractory bricks and light weight concrete can also be prepared from husk ash.[4] Activated carbon can also be obtained from husk ash. It can be used as an oil absorbent and because of this, it is useful as a sweeping compound in gasoline service stations, machine shops etc. Phenols present in the husk is mainly responsible for the protection of paddy during its storage period.

The use of specially prepared rice husk ash and begasse ash has been reported in compounding of SBR. This specially prepared rice husk ash composed essentially of 85-90% amorphous silica and 10-15% free carbon, was used as a filler at a loading of 60 phr in SBR compounding.[5] Rice husk ash has been compared with two other fillers viz., MT black and finely ground silica. The effect of the addition of 10 phr hydrocarbon resin was also studied. They have reported that the addition of resin increases the tensile strength from 8 MPa to 16 MPa and also hardness from 56 to 59. Tear strength was maintained in the same level while slight decrease in elongation value was noticed. Compression set and rebound values decreased due to the addition of the resin. The results of the study indicated that the ash was superior to mineral silica and was essentially equivalent in reinforcement to MT black. As rice husk ash is essentially amorphous silica, it was expected that silane coupling agent could be used to increase adhesion between rice husk ash and rubber. SBR compounds containing rice husk ash were prepared using r-mercapto propyl trimethoxy silane and showed that the rice husk ash responded very well to this coupling agent even at low concentrations. The addition of 1 phr of coupling agent increased the tensile strength from 14.5 MPa to 17 MPa whereas there was not much change in other physical properties. Ageing studies are also reported. It was observed that the addition of ash did not adversely affect the ageing characteristics.

Rai and co-workers also studied the use of rice husk white ash and begasse ash as fillers in SBR compounding.[6] It was found that rice husk ash was better as a reinforcing filler compared to begasse ash at any filler loading presumably due to the higher content of silica and lower content of iron and aluminium in the former. Rice husk ash and hydrated silica from the ash were used as fillers in SBR and the dielectric properties of the vulcanizates were investigated.[7]

Eventhough few reports are there in the literature on the use of specially prepared rice husk ash in the compounding of styrene butadiene rubber as a filler, the use of phenols extracted from husk has not been tried in rubber compounding. The present study aims at a systematic study on the use of the following materials in the vulcanization (sulphur accelerated system) of styrene butadiene rubber. (1) Rice husk as such and at different particle size (2) black ash (commercial grade) as such and of different mesh size, (3) carbon and silica separated from black ash as fillers and (4) phenols extracted from rice husk as antioxidant. It is important to note that the conventional antioxidant viz., amines and phenols used in rubber are known to exhibit toxicity while natural antioxidants extracted from rice husk have no toxic effects.

EXPERIMENTAL

Styrene butadiene rubber (synaprene 1502) having the specifications mentioned in chapter 2 was used for this study. The other compounding ingredients added alongwith SBR to prepare the mixes are given in Tables 6.1, 6.2, 6.3, 6.4 and 6.5. The specifications for activator, co-activator, accelerators, antioxidant, fillers, vulcanizing agent etc. are as given in chapter 2. Methyl alcohol, chloroform, n-hexane, CI resin, resorcinol and hexamine used are of analytical grade. The mixture of phenols extracted from husk, black ash obtained from husk and carbon and silica separated from black ash are used for the study. The details for extracting phenols from husk and also separation of carbon and silica from black ash have been given earlier.

Rice husk as such and sieved rice husk of different particle size at different levels of loading were tried (Table 6.1). The mixture of phenols extracted from rice husk was used as antioxidant in both gum and filled vulcanizates (Table 6.2). Black ash also was used at different particle size at different levels of loading (Table 6.3). Black ash (100 mesh) at 50 phr level was tried alongwith coumarone indene resin and with resorcinol and hexamine (Table 6.4). The above black ash was also tried with different proportions of conventional carbon black (HAF) (Table 6.4). The carbon and silica (300 mesh) separated from black ash were also tried as fillers at 25 and 50 phr levels (Table 6.5). The cure characteristics of all the above mixes and tensile and other physical properties of the vulcanizates evaluated are given in subsequent sections. For all the mixes containing silica, silane coupling agent (Si 69) was also used at 2 phr levels.

The high sulphur vulcanization system is used in this study. The method of preparation of mixes and determination of cure properties are as per the procedures detailed in chapter 2. The compounds were cured at 160°C to 90% of the cure time as obtained in the Goettfert elastograph (Model No.67.85) (ASTM D 1646 (1981)). Sheets for test samples were moulded in an electrically heated hydraulic press of 18"x18" platens maintained at 160°C and at a pressure of 11.764 MPa. Determination of the different tensile properties and other physical properties like compression set, resilience, hardness etc. were carried out as per the relevant ASTM procedures described earlier. Ageing studies were carried out in an air oven for 72 hr at 100°C (ASTM D-573-88).

RESULTS AND DISCUSSION

The cure curves of the mixes containing 25, 50 and 100 phr of rice husk used as such as a filler are given in Fig.6.1. Similarly the cure curves of the mixes containing powdered rice husk at 50, 100 and 200 mesh and at 25, 50 and 100 phr of loading are given in Fig.6.2. The different cure characteristics of the above mixes are given in Table 6.6. The torque developed is found to be minimum for the mixes containing 25 phr of rice husk and is maximum for the mixes containing 100 phr. It is also seen that slight increase of torque is noticed in mixes where smaller particle size of the husk is used. A reduction in cure time is observed whenever the particle size is reduced. The cure curves of the mixes containing 50 phr of rice husk (100 mesh) with coumarone indene resin (CI) and also with resorcinol and hexamine are given in Fig.6.3. The CI resin has no influence both on the torque and on the optimum cure time whereas resorcinol and hexamine had reduced the cure time with slight increase in torque values. The various cure characteristics of these mixes are given in Table 6.6. Slight variations in the induction time, scorch time and optimum cure time of the mixes are noticed depending upon the particle size and filler loading of the husk and the type of the resin used.

The cure curves of the different gum, carbon black and silica systems containing phenols from husk and styrenated phenol (control) are given in Figs.6.4, 6.5 and 6.6. Optimum cure time, cure rate index, scorch etc. are given in Table 6.7. There is not much variation in the induction time, scorch time and optimum cure time among the mixes containing antioxidant from husk and those of control. It is evident that the phenols extracted from husk do not have any advance effect on the cure characteristics of the mixes.

The cure curves of the mixes containing black ash as such at 25, 50 and 100 phr filler levels are given in Fig.6.7 and the cure curves of the mixes containing black ash (50, 100, 200 and 300 mesh) at 25, 50 and 100 phr filler loading are given in Fig.6.8. Cure characteristics of the above mixes are given in Table 6.8. The particle size of the black ash has a positive role in reducing the cure time of the mixes. The torque developed was higher for the mixes containing higher amounts of filler irrespective of the particle size of the black ash used. The cure curves of the mixes containing 50 phr of black ash (100 mesh) with CI resin and with resorcinol and hexamine are given in Fig.6.9. Addition of resorcinol and hexamine reduced the cure time to some extent. Torque value of this mix is also slightly higher. Different cure properties of these mixes are given in Table 6.9.

The cure curves of the mixes containing black ash (100 mesh) with carbon black (HAF) mixed in different proportions and at a filler loading of 50 phr are given in Fig.6.10. Addition of carbon black increases the torque value considerably. Cure time was maximum for the mix containing black ash and minimum for the one with carbon black. The results are reported in Table 6.9. The cure curves of the mixes containing carbon (prepared from black ash) at 25 and 50 phr filler levels are given in Fig.6.11. The cure curves of the mixes containing silica from black ash at similar filler levels are given in Fig.6.12. Corresponding cure properties are given in Table 6.10. The torque was higher at 50 phr filler loading in both carbon and silica systems.

The crosslink density values for the vulcanizates containing antioxidant from husk and those with styrenated phenol are given in Table 6.12. From the results, it is seen that the crosslink density value was highest for carbon black filled compounds followed by silica filled and then gum compounds. A slightly higher crosslink density was noticed for the mixes containing antioxidant from husk compared to the reference mixes. These differences in crosslink density values are reflected in the mechanical properties described in the following sections.

The tensile properties of the vulcanizates containing husk as a filler are given in Table 6.11. From the table, it is seen that tensile strength decreases with the increase of husk loading irrespective of the particle size used. As far as modulus is concerned, it increases with increase in filler loading. The results obtained with the mixes containing resins are given in Table 6.11. Slight increase in tensile strength is observed in the case of vulcanizates containing CI resin and also the ones with resorcinol and hexamine. Corresponding variations is noticed in the values of elongation at break and modulus.

In the second part of the experiments, mixture of phenols extracted from rice husk was used as antioxidant in SBR gum, SBR-carbon black and SBR-silica systems. Styrenated phenol is used as control in the other set of mixes. The tensile and other physical properties obtained for these various mixes are given in Table 6.12. From the results, it is seen that in the case of SBR gum compounds, the initial tensile strength and elongation was more or less same for the mixes containing styrenated phenol and also antioxidant from husk. Modulus is slightly higher for the mixes containing antioxidant from husk compared to the reference mixes. The retention of tensile properties on heat ageing was also more or less same in the different mixes. In the case of carbon black filled compounds, the initial tensile strength was higher for the mixes containing antioxidant from husk compared to control mixes. Elongation at break was more or less same for both the systems while modulus was higher for the control. In the silica filled vulcanizates also the initial tensile strength was more or less same for the different mixes. The elongation was higher and modulus was lower for the control mixes. It is seen that the retention of tensile properties on ageing is better for the mixes containing antioxidant from husk compared to the mixes containing styrenated phenol in both carbon black and silica filled vulcanizates. The results of this study indicate that the phenols extracted from rice husk provide antioxidant protection comparable to styrenated phenol in SBR-gum, SBR-carbon black and SBR-silica compounds without adversely affecting the cure characteristics of the mixes or the tensile properties of the vulcanizates.

The other physical properties of the above vulcanizates studied are tear strength, compression set, hardness, resilience and abrasion resistance. There is not much variation in tear strength among the different mixes except in carbon black vulcanizates. In the case of carbon black filled compounds, the tear strength was more for the mixes containing antioxidant from husk. Compression set was more or less same for the control and experimental mixes in all the systems. The same trend is seen in the case of resilience hardness and abrasion loss values also.

The tensile properties of the vulcanizates containing black ash as such, black ash with resins and black ash with carbon black (HAF) were also evaluated. The results obtained are given in Table 6.13. It is clear that when black ash is used as such no reinforcement is obtained for the filler eventhough cure properties are not adversely affected. When smaller particle size is used, there is a tendency for reinforcing the compound. The results of the experiments in which resins are used and in which HAF black is used along with black ash are given in Table 6.14. The results indicate that the addition of the resins has a positive effect on increasing the tensile strength. The results also indicate that the increase of tensile strength is directly proportional to the amount of carbon black used.

The results obtained on the tensile properties of the vulcanizates when carbon and silica separated from black ash is used are given in Table 6.15. The results suggest that if this carbon and silica are used without any further chemical treatment, only slight reinforcement of the vulcanizate can be obtained. At the same time as they do not show any adverse effect on the processing or curing characteristics of the mixes they may be used in products of medium or low tensile strength. Other physical properties like tear strength, abrasion loss, hardness etc. are also estimated (for 25 phr filler loadings) and are reported in Table 6.15.

CONCLUSIONS

The results of this study indicate that the rice husk and rice husk ash has not provided much reinforcement to the vulcanizates when they are used as such as filler in the sulphur vulcanization of styrene butadiene rubber. However some reinforcement effect is noticed when they are used in smaller particle size. The incorporation of CI resin or resorcinol with hexamine in the compounds can effect further reinforcement. Reasonable reinforcement can be obtained in the vulcanizates if black ash is used alongwith conventional carbon black in different proportions. The addition of these rice by-products does not exhibit adverse effects on processability or on the cure characteristics. Trials with carbon and silica separated from black ash as fillers also gave more or less similar results. Probably further chemical treatment is required for this carbon and silica to exhibit further reinforcing properties. This study also evaluates the phenols extracted from rice husk as antioxidant in different formulations with SBR and the results obtained are encouraging. This phenolic mixture gives sufficient antioxidant protection to the SBR systems under review. No adverse effect is shown by these phenols on the cure characteristics of the mixes or tensile properties of the vulcanizates.

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Table 6.1 Formulation of mixes containing husk of different particle size

M I X	IA	IB	IC	IIA	IIB	IIC	IIIA	IIIB	IIIC	IVA	IVB	IVC	VA	VB
Styrene butadiene rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Styrenated phenol	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mercaptobenzothiazyl disulphide	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Tetramethyl thiuram disulphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Husk (As such)	25	50	100	--	--	--	--	--	--	--	--	--	--	--
Husk (50 mesh)	--	--	--	25	50	100	--	--	--	--	--	--	--	--
Husk (100 mesh)	--	--	--	--	--	--	25	50	100	--	--	--	--	--
Husk (200 mesh)	--	--	--	--	--	--	--	--	--	25	50	100	--	--
Husk with CI resin	--	--	--	--	--	--	--	--	--	--	--	--	50	--
Husk with resorcinol and hexamine	--	--	--	--	--	--	--	--	--	--	--	--	--	50
Aromatic oil	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0	15.0	5.0
Sulphur	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

Table 6.2 Use of phenols extracted from husk as antioxidant in filled and unfilled vulcanizates of SBR

MIX	VIA	VIB	VIIA	VIIB	VIIIA	VIIIB
Styrene butadiene rubber	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
Mercaptobenzothiazyl disulphide	1.5	1.5	1.5	1.5	1.5	1.5
Tetramethyl thiuram disulphide	0.2	0.2	0.2	0.2	0.2	0.2
Styrenated phenol	1.0	--	1.0	--	1.0	--
Phenols from husk	--	1.0	--	1.0	--	1.0
Carbon black (HAF 330)	--	--	50	50	--	--
Precipitated silica (Vulkasil)	--	--	--	--	50	50
Aromatic oil	--	--	5	5	--	--
Naphthenic oil	--	--	--	--	5	5
Diethylene glycol	--	--	--	--	2	2
Silane coupling agent	--	--	--	--	2	2
Sulphur	2.0	2.0	2.0	2.0	2.0	2.0

Table 6.3 Formulation of mixes containing black ash of different particle size

MIX	IXA	IXB	IXC	XA	XB	XC	XIA	XIB	XIC	XIIA	XIIB	XIIC	XIIIA	XIIIB	XIIIC
Styrene butadiene rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Styrenated phenol	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mercaptobenzothiazyl disulphide	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Tetramethyl thiuram disulphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Black ash (As such)	25	50	100	—	--	--	--	--	--	--	--	--	--	--	--
Black ash (50 mesh)	--	--	--	25	50	100	--	--	--	--	--	--	--	--	--
Black ash (100 mesh)	--	--	--	--	--	--	25	50	100	--	--	--	--	--	--
Black ash (200 mesh)	--	--	--	--	--	--	--	--	--	25	50	100	--	--	--
Black ash (300 mesh)	--	--	--	--	--	--	--	--	--	--	--	--	25	50	100
Aromatic oil	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0
Sulphur	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

Table 6.4 Formulation of mixes containing black ash with resins and black ash with conventional black (HAF)

Mix	XIV A	XIV B	XV A	XV B	XV C	XV D	XV E
Styrene butadiene rubber	100	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Styrenated phenol	1	1	1	1	1	1	1
Mercaptobenzothiazyl disulphide	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Tetramethyl thiuram sulphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Black ash (-100 mesh) with CI resin	50	-	-	-	-	-	-
Black ash (-100 mesh) with resorcinol and hexamine	-	50	-	-	-	-	-
Black ash (-100 mesh)	-	-	50	-	-	-	-
Black ash with carbon black (75:25)	-	-	-	50	-	-	-
Black ash with carbon black (50:50)	-	-	-	-	50	-	-
Black ash with carbon black (25:75)	-	-	-	-	-	50	-
Carbon black	-	-	-	-	-	-	50
Aromatic oil	5	5	5	5	5	5	5
Sulphur	2	2	2	2	2	2	2

Table 6.5 Formulation of mixes containing carbon and silica from black ash

Mix	XVIA	XVIB	XVIIA	XVIIB
Styrene butadiene rubber	100	100	100	100
Zinc oxide	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5
Styrenated phenol	1	1	1	1
Mercaptobenzothiazyl disulphide	1.5	1.5	1.5	1.5
Tetramethyl thiuram disulphide	0.2	0.2	0.2	0.2
Carbon (-300 mesh)	25	50	-	-
Silica (-300 mesh)	-	-	25	50
Aromatic oil	2.5	5.0	-	-
Naphthenic oil	-	-	2.5	5.0
Diethylene glycol	-	-	2	2
Silane coupling agent	-	-	2	2
Sulphur	2	2	2	2

Table 6.6 Cure characteristics of mixes containing husk of different particle size (160°C)

Cure characteristics	MIX No.													
	IA	IB	IC	IIA	IIB	IIC	IIIA	IIIB	IIIC	IVA	IVB	IVC	VA	VB
Optimum cure time t_{90} (min.)	10.3	10.2	10.0	10.1	10.0	9.7	9.8	9.7	9.5	9.6	9.4	9.2	10.7	6.2
Elastographic scorch time t_{10} (min.)	4.8	4.8	4.8	4.3	4.3	4.3	4.0	4.0	4.0	3.8	3.8	3.8	4.8	2.5
Cure rate index	18.18	18.51	19.23	17.24	17.54	18.51	17.24	17.54	18.18	17.24	17.85	18.51	16.95	27.02
Induction time (min.)	4.2	4.2	4.2	3.7	3.7	3.7	3.3	3.3	3.3	3.0	3.0	3.0	4.0	1.7

Table 6.7 Cure characteristics of mixes containing phenolic antioxidants from husk

Cure characteristics	MIX NO.					
	VIA	VIB	VIIA	VIIB	VIIIA	VIIIB
Optimum cure time t_{90} (min.)	12.2	12.0	7.7	7.6	7.5	7.4
Elastographic scorch time t_{10} (min.)	5.6	5.4	2.3	2.3	2.0	2.0
Cure rate index	15.15	15.15	18.51	18.86	18.18	18.51
Induction time (min.)	4.8	4.6	1.5	1.5	1.2	1.2

Table 6.8 Cure characteristics of mixes containing black ash of different particle size (160°C)

Cure Characteristics	Mix No.														
	IXA	IXB	IXC	XA	XB	XC	XIA	XIB	XIC	XIIA	XIIB	XIIC	XIIIA	XIIIB	XIIIC
Optimum cure time t_{90} (min.)	10.1	10.0	9.9	9.8	9.7	9.5	9.6	9.5	9.4	9.5	9.3	9.2	9.3	9.1	9.0
Elastographic scorch time t_{10} (min.)	5.2	5.2	5.2	5.0	5.0	5.0	4.8	4.8	4.8	4.6	4.6	4.6	4.3	4.3	4.3
Cure rate index	20.40	20.83	21.27	20.83	21.27	22.22	20.83	21.27	21.73	20.40	21.27	21.73	20.00	20.83	21.27
Induction time (min.)	4.5	4.5	4.5	4.3	4.3	4.3	4.0	4.0	4.0	3.7		3.7	3.5	3.5	3.5

Table 6.9 Cure characteristics of mixes containing black ash with resin and black ash with HAF black (160°C)

Cure characteristics	Mix No.						
	XIVA	XIVB	XVA	XVB	XVC	XVD	XVE
Optimum cure time t_{90} (min.)	9.9	6.3	10.5	9.0	8.2	7.0	6.2
Elastographic scorch time t_{10} (min.)	4.4	2.4	4.2	3.4	2.8	2.6	2.1
Cure rate index	18.18	25.64	15.87	17.85	18.51	22.72	24.39
Induction time (min.)	3.7	1.9	3.6	2.9	2.2	2.1	1.5

Table 6.10 Cure characteristics of mixes containing carbon and silica from black ash (160°C)

Cure characteristics	MIX NO.			
	XVIA	XVIB	XVIIA	XVIIB
Optimum cure time t_{90} (min)	8.4	8.2	7.7	7.5
Elastographic scorch time t_{10} (min)	3.8	3.8	2.0	2.0
Cure rate index	21.73	22.72	17.54	18.18
Induction time (min)	3.0	3.0	1.1	1.1

Table 6.11 Tensile properties of the vulcanizates containing husk as such and at different mesh size

Mix No.	Filler loading of husk (phr)	Tensile strength (MPa)	Elongation at break (%)	Modulus at 200% elongation (MPa)
IA	25	1.56	117	1.55
IB	50	1.52	119	1.67
IC	100	1.50	120	1.83
IIA	25	1.69	126	1.58
IIB	50	1.62	130	1.70
IIC	100	1.59	142	1.86
IIIA	25	1.94	208	1.64
IIIB	50	1.90	224	1.74
IIIC	100	1.82	263	1.88
IVA	25	2.37	220	2.76
IVB	50	2.22	232	1.85
IVC	100	2.01	285	1.92
VA	50	2.23	181	1.86
VB	50	2.00	153	1.97

Table 6.12 Physical properties of the vulcanizates containing phenolic antioxidant from husk and control

Parameter		MIX NO.					
		VIA	VIB	VIIA	VIIB	VIIIA	VIIIB
Tensile strength (MPa)	BA	2.42	2.47	24.59	24.62	23.76	23.79
	AA	2.31	2.41	20.56	22.02	12.63	14.61
Elongation at break (%)	BA	261	264	386	390	557	540
	AA	135	144	210	215	156	159
Modulus at 200% (MPa)		1.86	1.93	9.37	9.12	6.79	6.81
Tear strength (N/nm)		14	14	51	64	60	61
Compression set (%)		26.25	25.60	22.90	22.80	37.50	37.64
Hardness (Shore A)		40	40	62	62	65	66
Abrasion loss (cm^3/hr)		5.580	5.548	4.484	4.536	4.500	4.475
Resilience (%)		63.13	63.40	53.14	53.14	51.87	51.56
Crosslink density (M.mol/kg)		74.20	74.35	82.65	82.23	80.27	80.62

Table 6.13 Tensile properties of the vulcanizates containing black ash as such and at different particle size

Mix No.	Filler loading (phr)	Tensile strength (MPa)	Elongation at break (%)	Modulus at 200% elongation (MPa)
IXA	25	1.58	202	1.54
IXB	50	1.53	226	1.57
IXC	100	1.47	264	1.65
XA	25	1.71	223	1.56
XB	50	1.58	245	1.62
XC	100	1.49	272	1.81
XIA	25	2.20	247	1.68
XIB	50	2.51	270	1.77
XIC	100	2.71	304	1.98
XIIA	25	2.34	263	1.84
XIIB	50	2.41	284	2.02
XIIC	100	2.84	312	2.20
XIIIA	25	2.44	268	1.92
XIIIB	50	2.80	290	2.04
XIIIC	100	3.49	324	2.21

Table 6.14 Tensile properties of the vulcanizates containing black ash (100 mesh) with resins and black ash along with HAF black as a filler

Mix No.	Filler loading (phr)	Tensile strength (MPa)	Elongation at break (%)	Modulus at 200% elongation (MPa)
XIVA	50	3.13	341	2.02
XIVB	50	2.82	253	2.33
XVA	50	2.82	283	2.33
XVB	50	6.14	354	3.10
XVC	50	14.16	407	5.32
XVD	50	18.20	401	7.15
XVE	50	24.59	336	9.37

Table 6.15 Tensile and other physical properties of the vulcanizates containing carbon and silica (from black ash) as fillers

Parameter	MIX NO.			
	XVIA	XVIB	XVIIA	XVIIB
Tensile strength (MPa)	4.06	3.44	4.25	5.01
Elongation at break (%)	314	220	224	171
Modulus at 200% elongation (MPa)	3.10	2.98	3.24	3.08
Tear strength (N/nm)	38	-	36	-
Compression set (%)	26.14	-	29.64	-
Hardness (Shore A)	46	-	45	-
Abrasion loss (cm^3/hr)	7.420	-	7.242	-

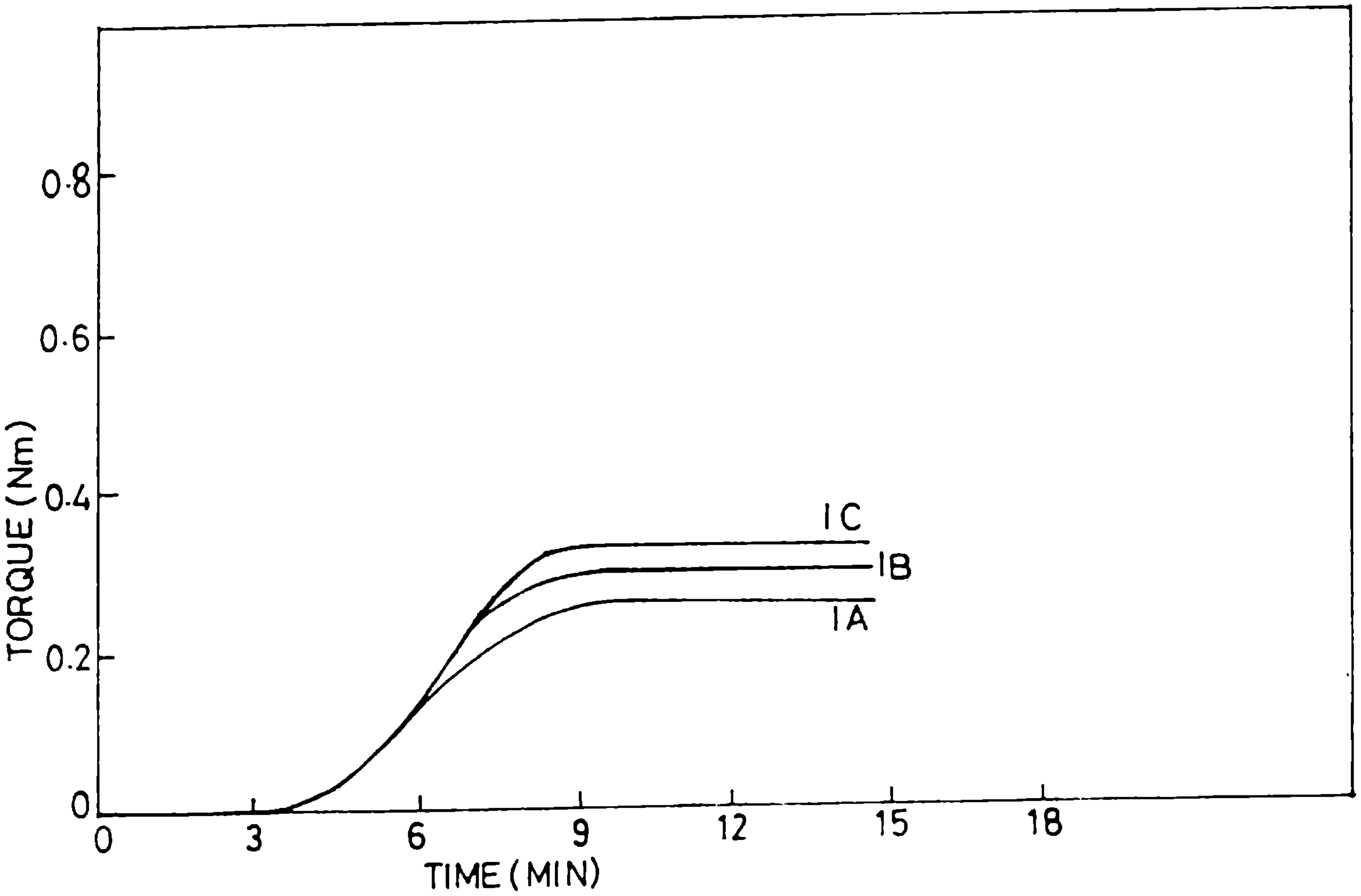

Fig.6.1 Cure variation of the SBR mixes containing rice husk as such.

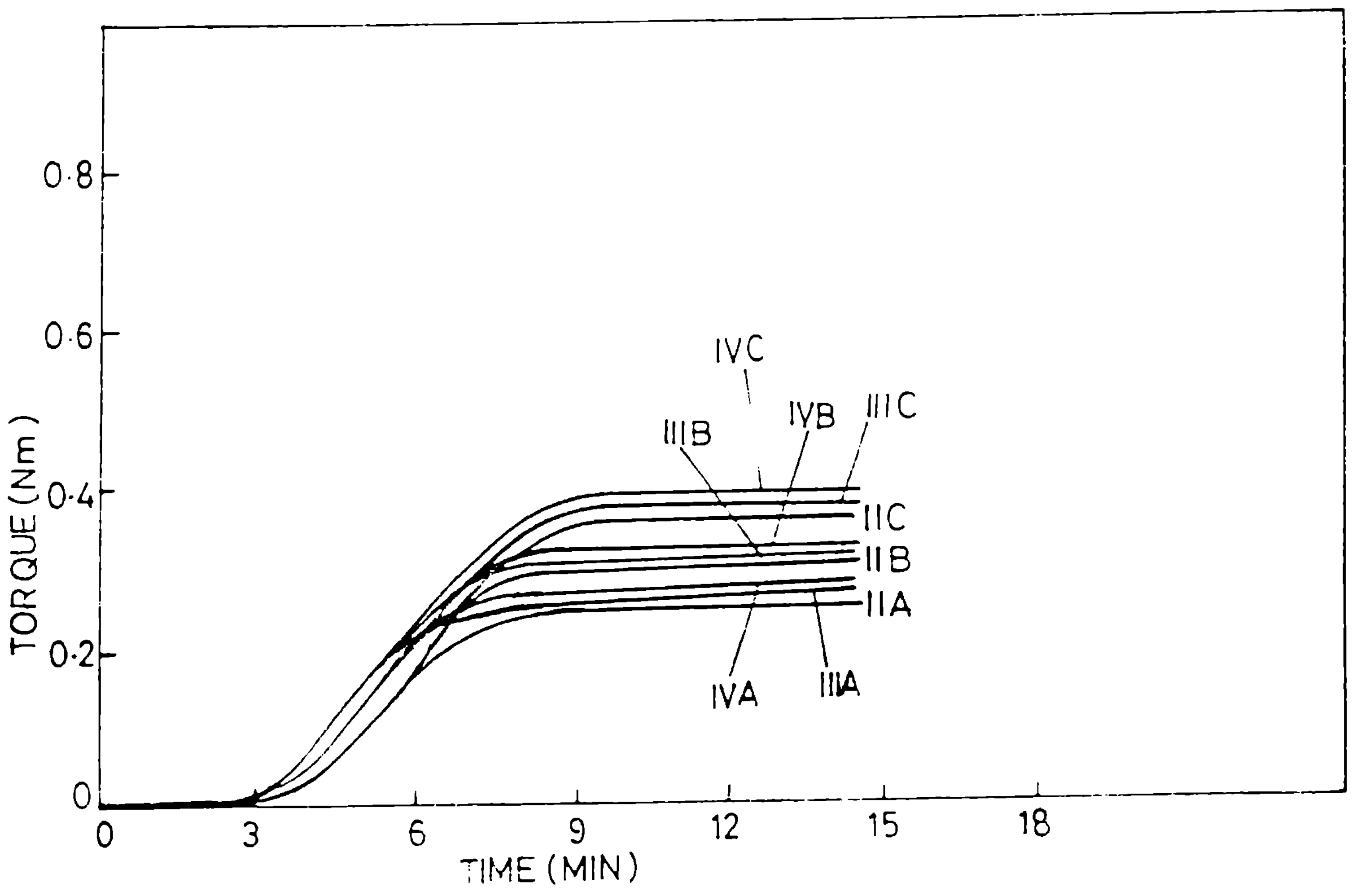

Fig.6.2 Cure variation of the SBR mixes containing rice husk (50, 100 and 200 mesh).

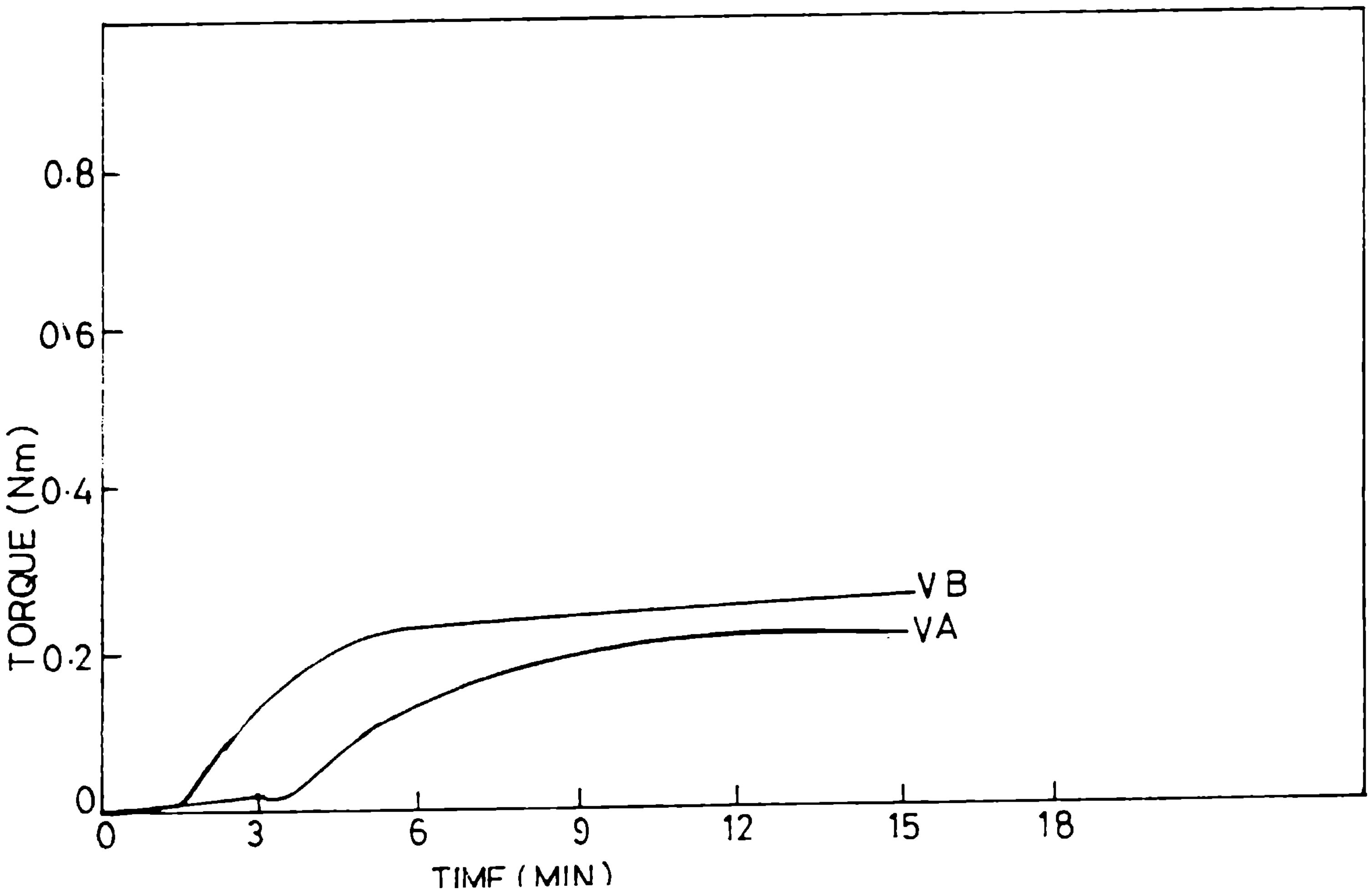

Fig.6.3 Cure variation of SBR compounds containing rice husk (100 mesh) with resins.

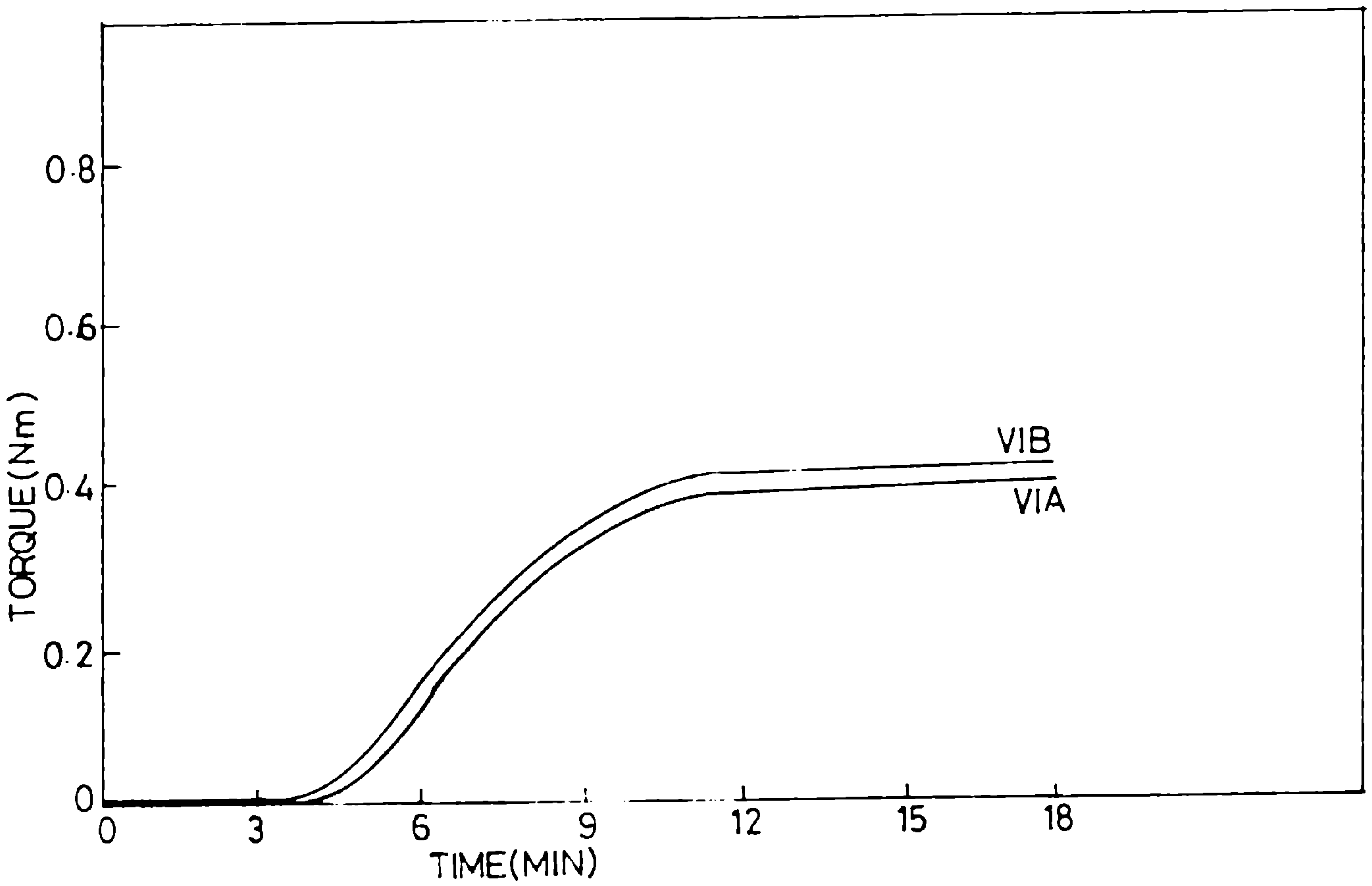

Fig.6.4 Cure variation of SBR gum compounds containing antioxidant from rice husk and styrenated phenol.

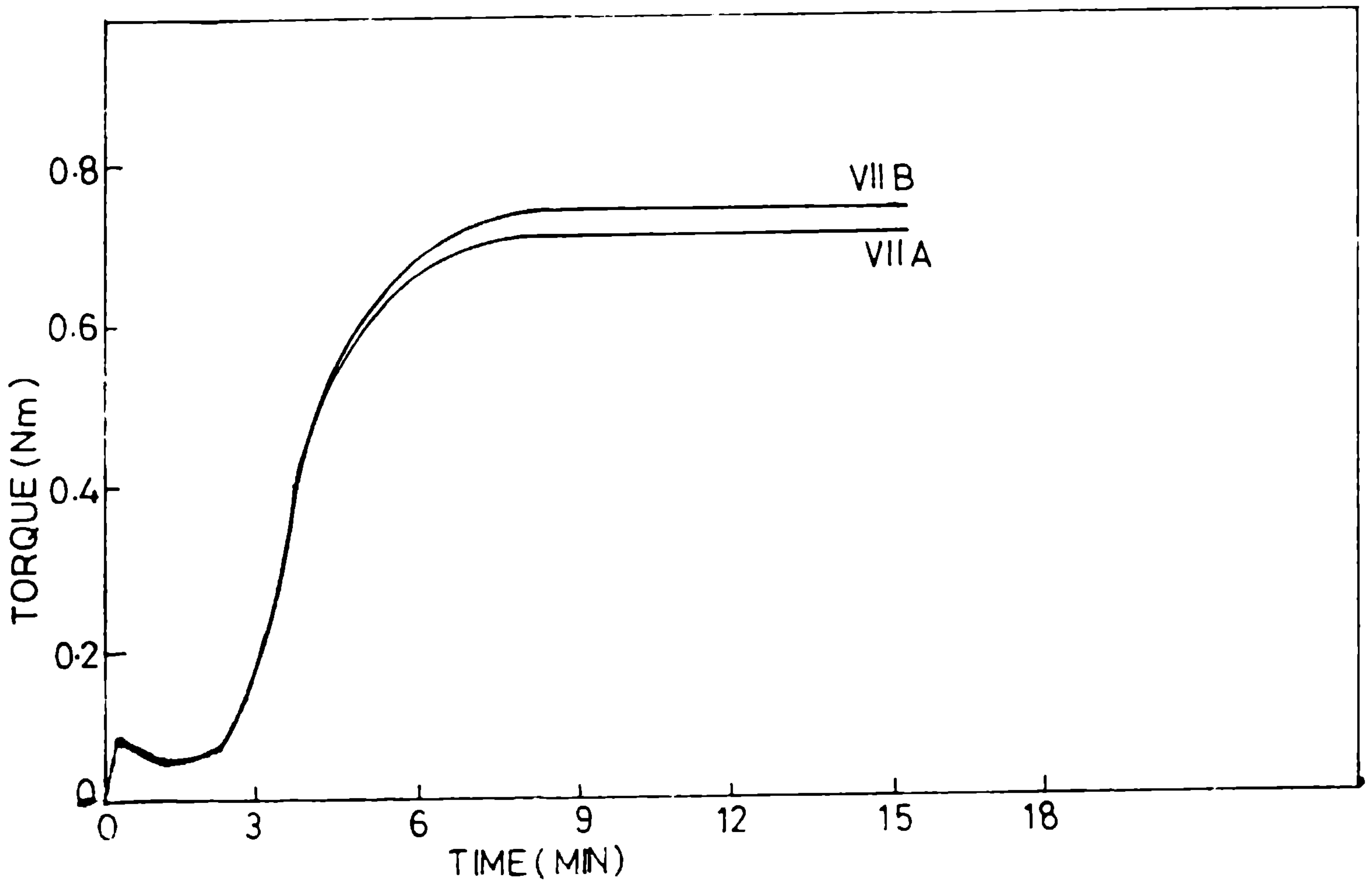

Fig.6.5 Cure variation of SBR carbon black filled compounds containing antioxidant from rice husk and styrenated phenol.

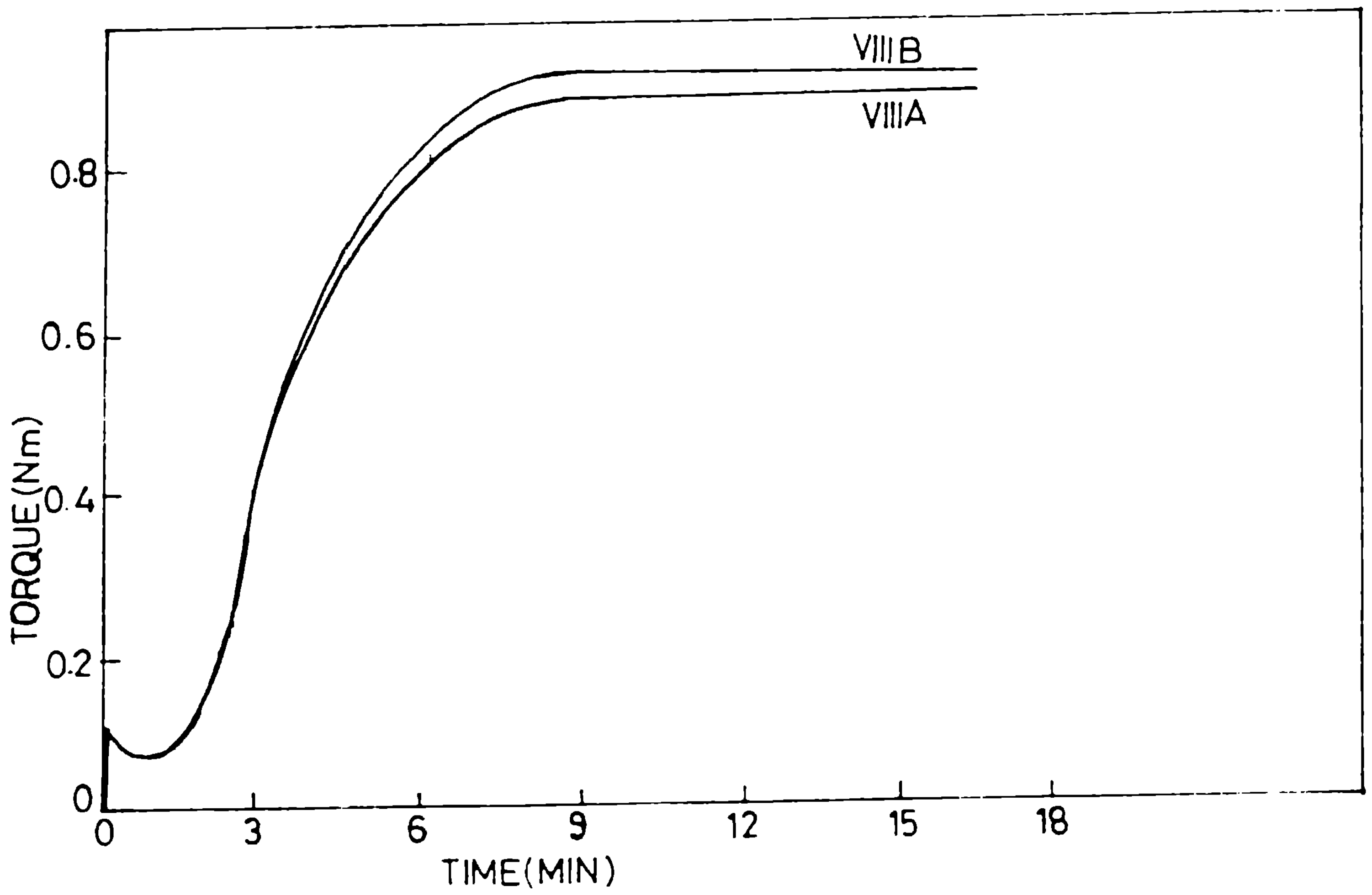

Fig.6.6 Cure variation of SBR silica filled compounds containing antioxidant from husk and styrenated phenol.

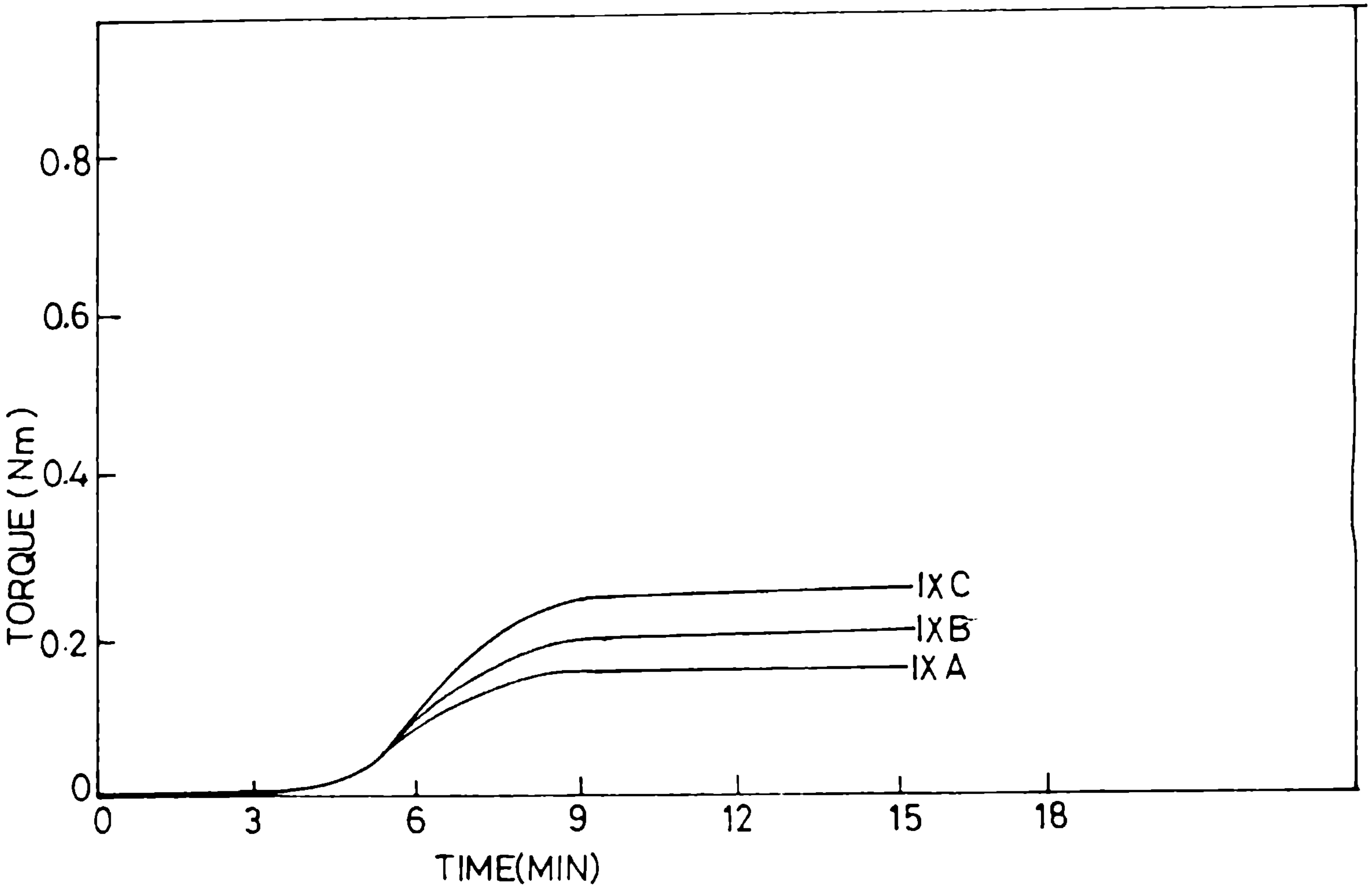

Fig.6.7 Cure variation of the SBR mixes containing black ash as such.

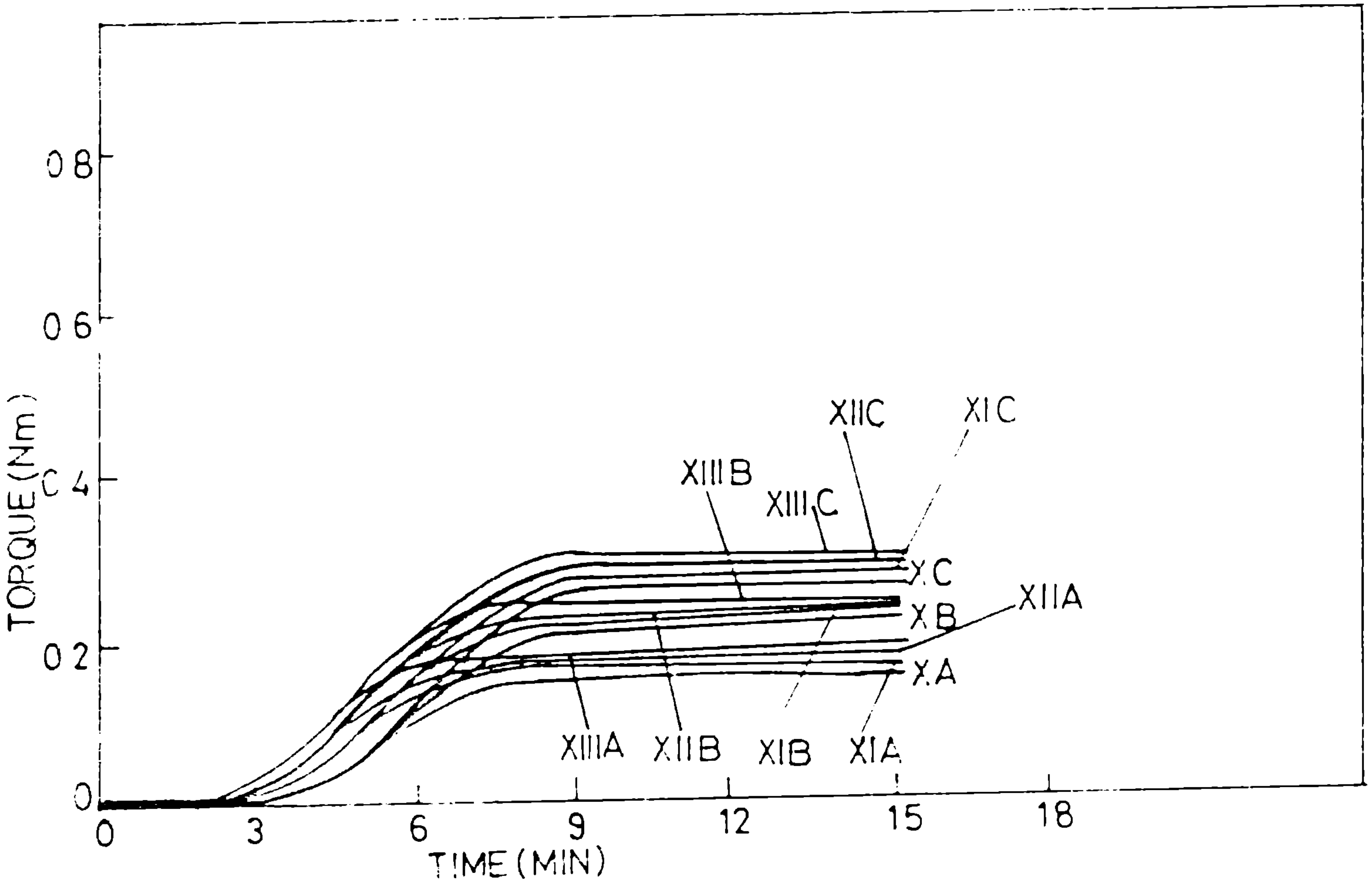

Fig.6.8 Cure variation of the SBR mixes containing black ash (50, 100, 200 and 300 mesh).

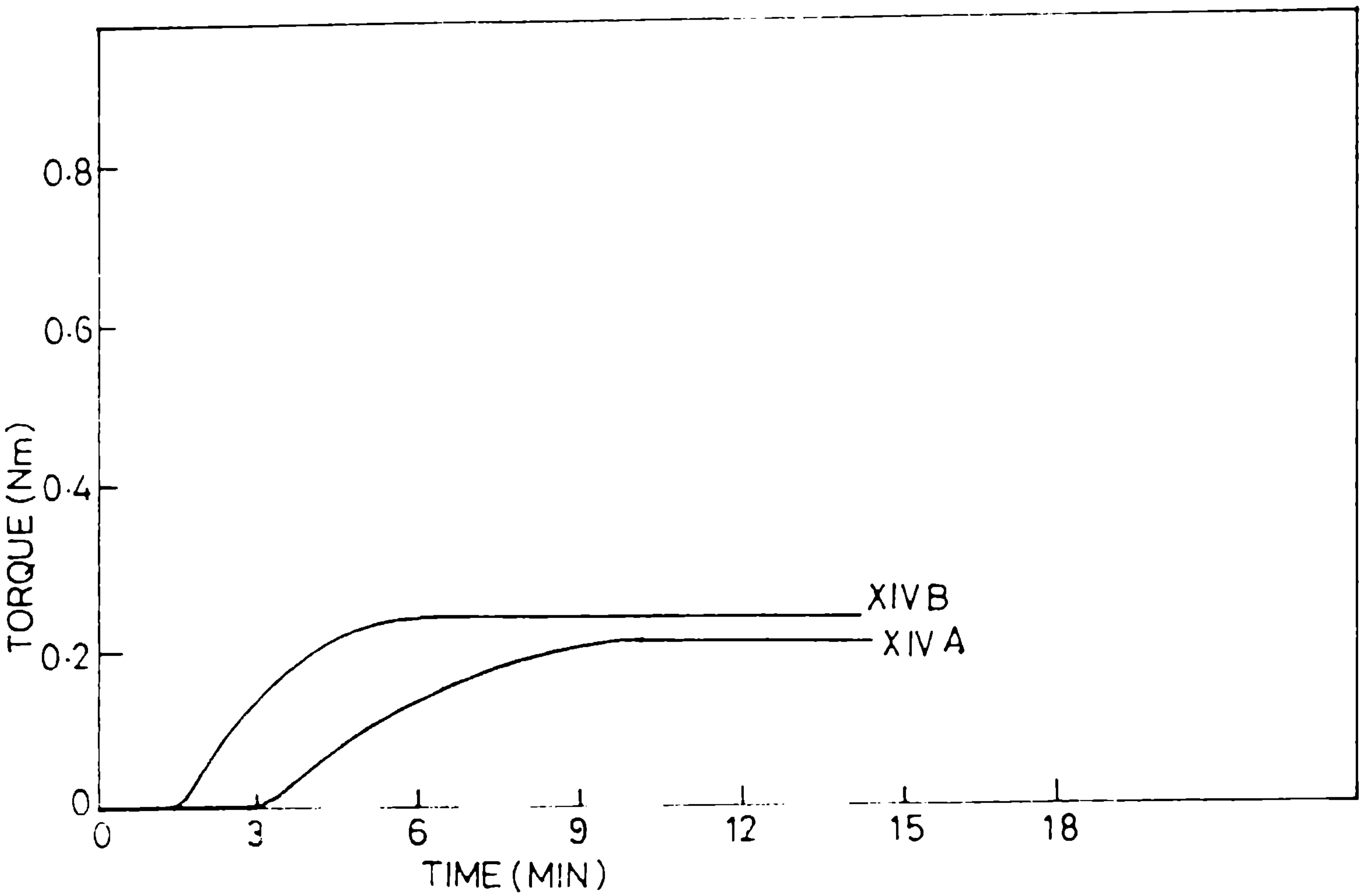

Fig.6.9 Cure variation of SBR compounds containing black ash with resins.

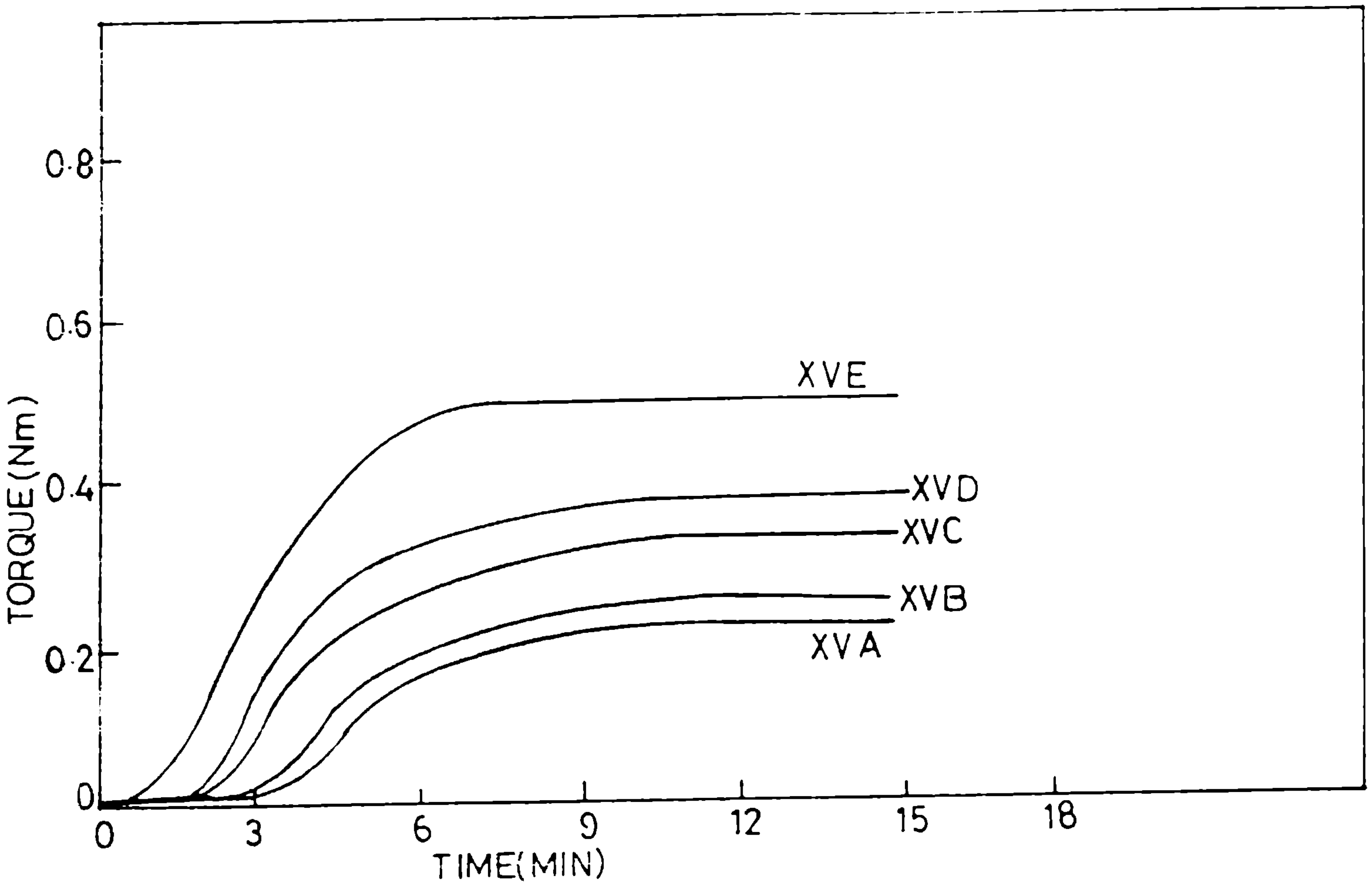

Fig.6.10 Cure variation of the SBR mixes containing black ash (100 mesh) with carbon black (HAF).

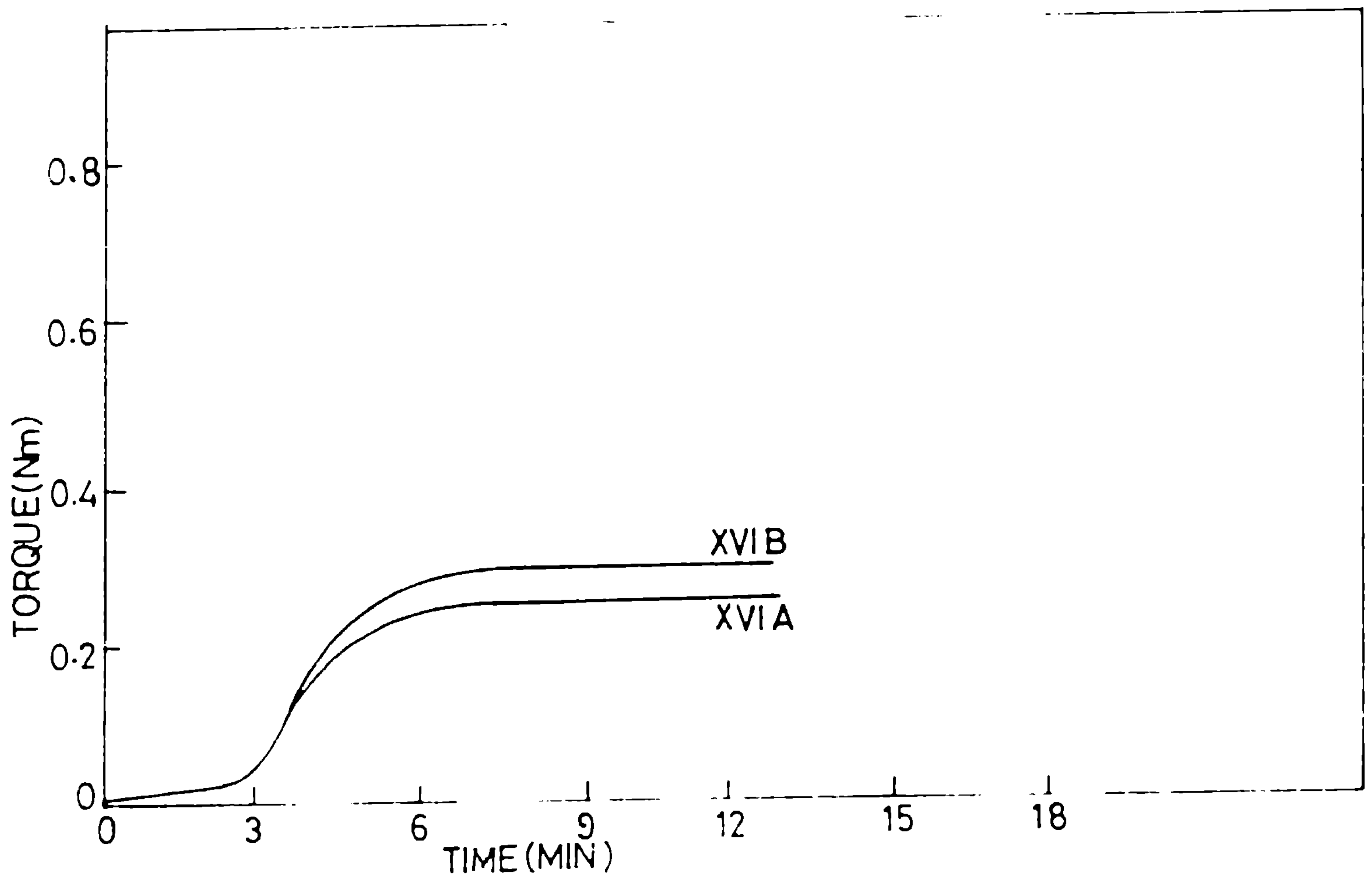

Fig.6.11 Cure variation of the SBR compounds containing carbon (300 mesh) from black ash.

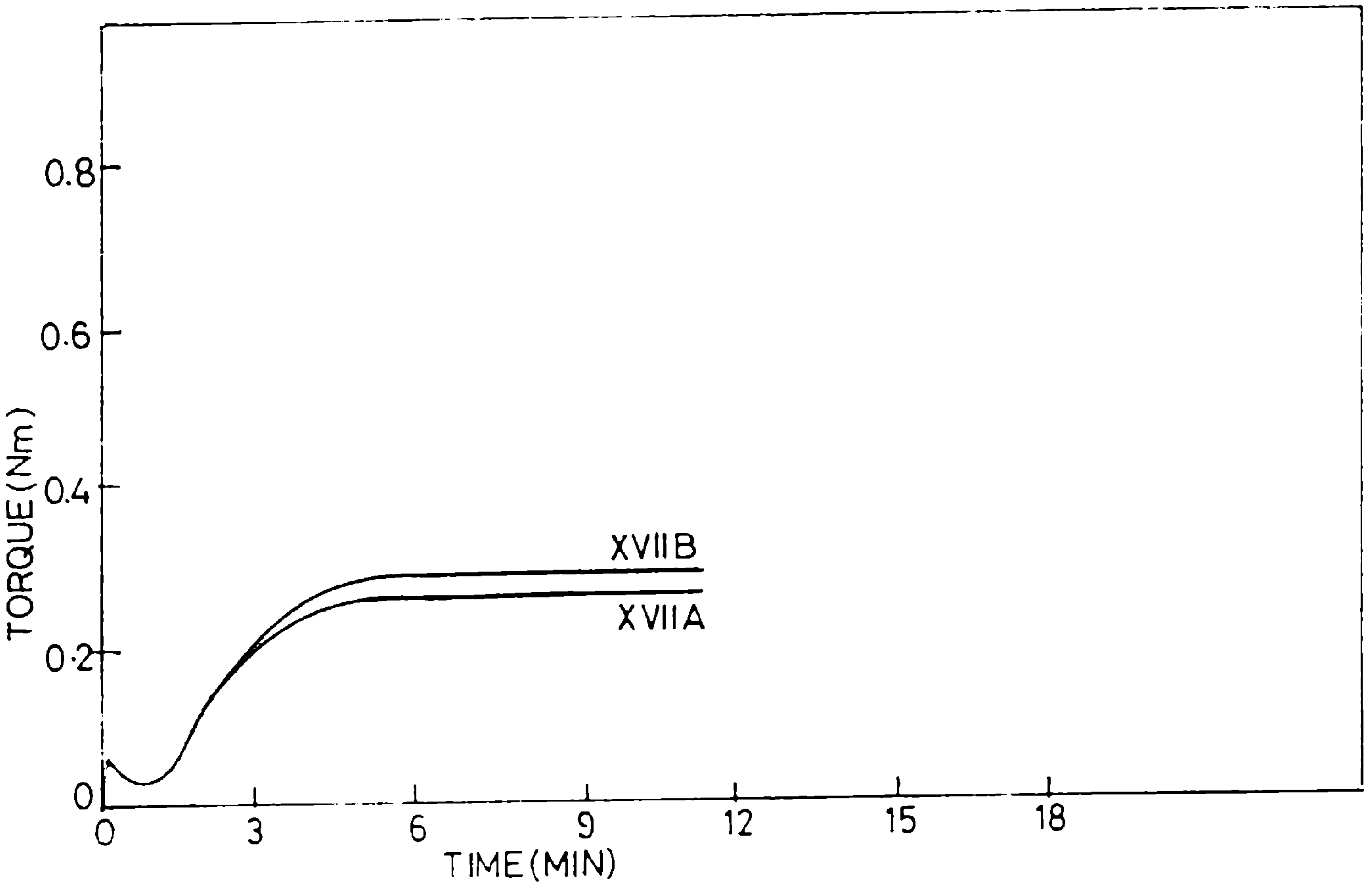

Fig.6.12 Cure variation of SBR compounds containing silica (300 mesh) from black ash.

Chapter 7

SUMMARY AND CONCLUSIONS

The thesis consists of seven chapters. The first chapter is a general introduction on rice by-products, their composition and utilization at present. The different milling processes adopted in paddy and the major by-products obtained from these processes viz. rice husk, rice bran, rice bran oil and rice husk ash are described. The physical properties and chemical composition of the rice husk and its general uses are given in detail. The chemical composition of the rice bran and its separation from paddy is also included. The details of solvent extraction process used for obtaining rice bran oil and also its chemical constitution is discussed in this chapter. Also described is the preparation and the different uses of rice husk ash. A literature survey is also done on the utilization of rice by-products in rubber and plastics as on today. The scope and objectives of the present study is also included at the end of this chapter.

In the second chapter, the materials used for this study, their specifications and different experimental procedures adopted are given. Processability studies using a Brabender plasticorder is explained. Procedures adopted is described in sufficient detail for the preparation of different rubber mixes using two roll mixing mill and also for determination of cure characteristics using Goettfert Elastograph (model 67.85). Vulcanization was carried out in an electrically heated hydraulic press of 18"x18" platens maintained at 150/160°C and at a pressure of 11.764 MPa. The tensile properties of the vulcanizates were determined using Zwick Universal Testing Machine (model 1474). Hardness was measured using shore durometer as per ASTM D 2240. The abrasion testing was done with DIN abrader and rebound resilience with Dunlop tripsometer. Compression set was determined by ASTM method D 395. Ageing studies was carriedout in an ageing oven as per ASTM D 573. Determination of total crosslink concentration by the swelling method has been detailed. Chemical test methods like extraction of phenols from rice husk, separation of carbon and silica from black ash, estimation of higher fatty acids in rice bran oil etc. also form part of this chapter.

Chapter 3 deals with the use of rice bran oil in place of co-activator (stearic acid), antioxidant and processing aid (aromatic/naphthenic oil) in carbon black and silica filled systems of natural rubber compounding. Rice bran oil contains fatty acids like oleic acid and phenols like tocopherol and oryzanol. It was presumed that these fatty acids will act as co-activator, and tocopherol and oryzanol will impart antioxidant property. Rice bran oil will serve as the processing aid also. The processing behaviour of rice bran oil was compared with conventional processing aids like aromatic/naphthenic oil and the quantity of oil required in each case was optimised with the help of Brabender Plasticorder. The mixes obtained from different formulations were evaluated for the various cure characteristics like induction time, scorch time and optimum cure time. The results showed that these cure characteristics were not adversely affected by introduction of rice bran oil instead of aromatic/naphthenic oil in both carbon black and silica filled systems. Mechanical properties like tensile strength, elongation at break and modulus were more or less same for both control as well as experimental mixes. Other physical properties like hardness, compression set, resilience, tear strength and abrasion resistance were also comparable. The estimation of total chemical crosslink density indicate that the systems containing carbon black and rice bran oil showed higher crosslink density values than those with aromatic oil. But in the case of silica systems the crosslink density values did not show much variation among the different mixes. It was also observed that the vulcanizates containing rice bran oil and the control mixes containing conventional antioxidant retained more or less same level of tensile properties on heat ageing.

The results of this study indicate that high FFA raw rice bran oil which is at present used in the soap industry can be used in natural rubber compounding where a sulphur accelerated system is used. It is seen that this oil can replace the processing oil, fatty acid and antioxidant in a natural rubber compound without much affecting the cure characteristics of the mixes and the physical properties of the vulcanizates. This is all the more important because the mineral oils based on petroleum resources used at present as processing aids in rubber are becoming prohibitively costly in India. At the same time rice bran oil (non-edible) is available at much cheaper rates. The results also suggest that phenolic antioxidants used for rubber compounding which are somewhat toxic in nature can also be replaced with rice bran oil by virtue of the presence of phenols in it.

The fourth chapter describes the use of rice bran oil in place of stearic acid, styrenated phenol and aromatic/naphthenic oil in carbon black and silica filled systems in a synthetic rubber viz. styrene butadiene rubber (SBR 1502). This study was undertaken mainly because of the fact that a lot of differences are encountered in the compounding and vulcanization of natural rubber vis-a-vis a synthetic rubber. The optimization of processing characteristics in this rubber using aromatic/naphthenic oil and rice bran oil was carried out in Brabender Plasticorder. The different cure characteristics of the mixes from relevant formulations were evaluated and it was found that the cure values are comparable with the reference mixes where conventional ingredients are used. Tensile and other physical properties evaluated for the vulcanizates containing rice bran oil/aromatic oil in carbon black filled and rice bran oil/naphthenic oil in silica filled systems indicate only marginal differences between experimental mixes and control formulations. In the case of chemical crosslink density, the mixes containing rice bran oil exhibit slighty higher crosslink density values compared with those containing aromatic/naphthenic oil. Tensile properties of the former vulcanizates were also slightly higher. Ageing resistance of the vulcanizates containing rice bran oil was also found to be comparable with the reference mixes containing styrenated phenol.

From the results obtained in this study it is clear that raw rice bran oil can be advantageously used in the sulphur vulcanization of styrene butadiene rubber also. This oil can very well replace the conventional processing oils, fatty acid and antioxidant in the SBR compounds under review. Evaluation of cure characteristics of the mixes containing rice bran oil and those containing conventional processing aids such as aromatic oil in carbon black filled systems indicate that rice bran oil does not have any adverse effect on the cure properties of the mixes. A similar trend is also seen in silica systems where rice bran oil was used in place of naphthenic oil. A study of the physical properties of the vulcanizates (before and after ageing) also points to more or less similar conclusions. Studies on the processing characteristics also suggest that SBR compounds can be processed with rice bran oil similar to other conventional processing aids. This oil also exhibits co-activator and antioxidant properties by virtue of the presence in it of higher fatty acids and phenols respectively.

The fifth chapter deals with the use of rice husk and rice husk by-products in NR compounds. In this study, we used rice husk as such and also after powdering and sieving into different mesh size (50, 100 and 200) as filler in different NR formulations at different levels of loading. Trials were also made using husk as a filler alongwith CI resin and with hexamine and resorcinol. The mixture of phenols extracted from husk was used as antioxidant in NR gum and filled compounds and results compared with the mixes containing styrenated phenol as control. Black ash was also used as such and at different mesh size (50, 100, 200 and 300) at different phr levels. Here also resins like CI and hexamine with resorcinol were incorporated. Carbon and silica were separated from black ash and tried separately as fillers in different natural rubber formulations. Trials were also made using black ash alongwith conventional filler viz., HAF black at different proportions. The results of the cure characteristics of the mixes containing rice husk indicate that the torque value of the mixes increased as the filler loading increased irrespective of the particle size of the husk used. Also a slight reduction in cure time was observed whenever the particle size used was smaller. In the case of mixes containing resins, the CI resin did not have influence on the torque developed as well as on cure time where as resorcinol and hexamine prolonged the cure with some increase in torque. The cure curves of the mixes containing antioxidant from husk and those with styrenated phenol indicate that the torque developed is slightly higher for the former systems. In the case of rice husk ash also,finer the particle size, lesser was the cure time. As expected, the torque value of the mixes increased as the filler loading increased. The effect of resins in rice husk ash also was more or less same as in the case of rice husk. In the case of mixes containing conventional carbon black alongwith black ash, the torque developed was minimum for the mix containing black ash alone and maximum for the mix containing conventional carbon black alone.

The crosslink density values for the compounds containing antioxidant from husk and for those with styrenated phenol show that these values are higher for the former mixes. Regarding the tensile properties of the vulcanizates containing husk, it is noticed that not much improvements in these properties are effected by the addition of husk. Among the different mixes, tensile strength was better for the compounds containing finer particles of husk compared to those containing coarser ones. Modulus values also showed more or less similar pattern. In the case of mixes where resins are added, the tensile strength of the vulcanizates are seen to increase to some extent with the addition of these resins. The tensile and other physical properties of the various mixes containing phenols from husk and those with styrenated phenol indicats that the tensile properties of the vulcanizates are not adversely affected by incorporation of these phenols. The retention of tensile properties on heat ageing is also quite comparable when styrenated phenol is replaced with phenols from the husk.

The evaluation of tensile properties of the vulcanizates containing black ash indicate that significant reinforcement is not obtained when ash is used as such as filler. But the tensile strength and modulus is slightly higher for the compounds containing finer particles of ash. The addition of resins to black ash increased the tensile strength of the vulcanizates to some extent. In the case of mixes where conventional carbon black is added along with black ash, the increase of tensile strength and modulus are directly proportional to the amount of carbon black added. Evaluation of the tensile properties of the vulcanizates containing carbon and silica (separated from black ash) also suggest that these fillers when used as such do not impart much reinforcement character to the compounds. At the same time as processing or curing properties of the mixes are not adversely affected, this carbon and silica (untreated) can be used in NR compounding for products of medium or low tensile strength.

The sixth chapter deals with the use of rice husk, rice husk ash and carbon and silica separated from husk ash as fillers and phenols extracted from husk as antioixdant respectively in the compounding and vulcanization studies on styrene butadiene rubber. The phenols extracted from husk was tried as antioxidant in gum and filled vulcanizates. The different fillers were used at different particle size and in different filler loadings.

With regard to the different cure properties, reduction in cure time was observed whenever the particle size of the filler used was lesser. This was true for both rice husk and rice husk ash. The addition of CI resin had no effect on cure properties both in rice husk and rice husk ash whereas resorcinol and hexamine reduced the cure time with some increase of torque. The incorporation of HAF black to black ash increased the torque value considerably. With regard to the mixes containing different antioxidants, torque was slightly higher for the mixes containing phenols from husk compared to control mixes containing styrenated phenol.

With regard to the evaluation of different vulcanizate properties, increase in tensile strength was observed in the case of vulcanizates containing CI resin and also the ones with resorcinol and hexamine. Concerning the ageing properties, the retention of tensile properties on heat ageing was better for the mixes containing phenols from husk compared to the reference vulcanizates. The addition of resins has a positive effect in increasing the tensile strength. The addition of carbon black to black ash also had the effect of substantially increasing the tensile strength. In the case of carbon and silica (separated from black ash), when they are used as such, reinforcement obtained is minimal.

Eventhough rice husk and rice husk ash cannot provide much reinforcement to the vulcanizates when they are used as such in the sulphur vulcanization of styrene butadiene rubber, some reinforcement effect is noticed when they are used in smaller particle size. The incorporation of resorcinol with hexamine in the compound also effected some improvement in tensile properties. Reasonable reinforcement can be obtained further in the vulcanizate if black ash is used alongwith HAF black in different proportions. The addition of these rice by-products however do not exhibit much adverse effect on processability or on the cure characteristics of the different mixes under review. The results obtained on the use of the phenols extracted from husk as antioxidant in different formulations with SBR are encouraging. This phenolic mixture gives sufficient antioxidant protection to the different SBR systems and is comparable in properties to styrenated phenol. No adverse effect is shown by these phenols on the cure characteristics or on the tensile properties of the vulcanizates.

The research publications based on the work reported in the thesis is included at the end.

LIST OF PUBLICATIONS BASED ON THIS WORK REPORTED IN THE THESIS

1. Rice bran oil as a novel compounding ingredient in sulphur vulcanization of natural rubber, A.P.Kuriakose and G.Rajendran, European Polymer Journal, Vol.31, No.6, pp.595-602, 1995.

2. Use of rice bran oil in the compounding of styrene butadiene rubber, A.P.Kuriakose and G.Rajendran, Journal of Material Science, Vol.30, pp.2257-2262, 1995.

3. Rice husk as filler and phenols extracted from rice husk as antioxidant in vulcanization studies of NR, A.P.Kuriakose and G.Rajendran, Journal of Polymer-Plastics Technology and Engineering (in press).

4. Use of black ash and carbon and silica separated from black ash as fillers in the compounding studies of NR, A.P.Kuriakose and G.Rajendran, Journal of Kautschuk Gummi Kunststoffe (Accepted for publication).

5. Rice husk and phenols extracted from it as filler and antioxidant respectively in the sulphur vulcanization of SBR 1502, A.P.Kuriakose and G.Rajendran, European Polymer Journal (Communicated).

6. Use of rice by-products as filler in the vulcanization studies of styrene butadiene rubber, A.P.Kuriakose and G.Rajendran, Journal of Material Science (Communicated).