CURING STUDIES OF ELASTOMER BLENDS
WITH SPECIAL REFERENCE TO NR/SBR AND NR/BR BLENDS

A thesis submitted by

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CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by Smt.Rani Joseph under my supervision and guidance in the Department of Polymer Science and Rubber Technology. No part of the 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 supervision of Dr.D.Joseph Francis, Professor and Head, Department of Polymer Science and Rubber Technology, Cochin University of Science & Technology, Cochin-682022, in the Department of Polymer Science and Rubber Technology. No part of this thesis has been presented for any other degree from any other institution.

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CONTENTS

LIST OF ABBREVIATIONS USED IN THIS THESIS

NR - Natural rubber
SBR - Styrene-butadiene rubber
BR - Polybutadiene (Butadiene rubber)
EPDM - Ethylene-propylene-diene-rubber
NBR - Acrylonitrile-butadiene rubber
CR - Polychloroprene (Chloroprene rubber)
IR - Synthetic polyisoprene (Isoprene rubber)
IIR - Butyl rubber
Cl IIR - Chloro butyl rubber
PPO - Poly (2,6-dimethyl 1-1,4-phenylene oxide)
PMMA - Poly (methyl methacrylate)
DCP - Dicumyl peroxide
CBS - N-cyclohexyl-2-benzthiazyl sulphenamide
TMTD - Tetramethyl thiuram disulphide
DPG - Diphenyl guanidine
MBT - Mercaptobenzthiazole
TBBS - N-tert-butyl-2-benzthiazyl-sulphenamide
DTDM - Bis-morpholine disulphide
HAF black - High abrasion furnace black
PBN - Phenyl-β-naphthylamine
EV - Efficient vulcanizing
T_g - Glass transition temperature
T_m - Melting temperature
$\bar{M}_W$ - Weight average molecular weight
V_r - Volume fraction of rubber network
V_{r_o} - Value of V_r for filled vulcanizates
M_c - Number average molecular weight of rubber chains between crosslinks
χ - Polymer-solvent interaction parameter

V_s - Molar volume of solvent

ρ_r - Density of rubber

ρ_s - Density of solvent

ϕ - Volume fraction of carbon black

c - Parameter for each type of carbon black

Phr - Parts per hundred rubber

$\frac{\text{m.mole}}{\text{Kg.RH}}$ - Millimole/kilogram of rubber hydrocarbon

rpm - Revolutions per minute

ML(1+4) at 100°C- Mooney viscosity determined using large rotor after a dwell time of one minute and rotor run of 4 minutes at 100°C

ASTM - American Society for Testing and Materials

BS - British Standards

Chapter 1

INTRODUCTION

INTRODUCTION

Rubber has such remarkable and desirable properties that it is being put to many engineering applications like bearings, springs and seals in addition to the manufacture of bulk products like tyres, tubes, belts, hoses etc. Loads could be safely supported and misalignments accommodated by its ready elastic deformability, shock and vibrations could be isolated by exploiting its energy absorbing properties and spring characteristics and the deformability and resilience of rubber could be used to advantage in the provision of efficient seals.

The base rubbers which almost all rubbery materials contain to a lesser or greater extent are classified into two broad groups, natural and synthetic. Synthetic rubbers are further classified into two categories namely, the general purpose types like styrene-butadiene rubber (SBR) and polybutadiene rubber (BR) which are intended for the manufacture of tyres and general mechanical products and the special purpose types which have special properties and are in consequence intended for specialized applications. However, one type of rubber may not possess all the physical properties desired in a finished product and so normally two or more rubbers are blended together.

Polymer blends

Investigations on industrial utilization of polymer blends were started just at the time when the first steps were taken to synthesize plastics and elastomers. The blending of commercially available polymers provides the manufacturer with an inexpensive route to product line expansion. The chemical and physical properties of constituents of blends are well-known, and blends can often be processed using existing equipments.

Two component polymer systems, in general, can be described by the following equations.[1,2]

$$P = P_1C_1 + P_2C_2 + IP_1P_2$$

where P is a certain property value for the blend, P_1 and P_2 are the values of that property for the isolated components, and C_1 and C_2 are the respective concentrations of the constituents in the blend. I is a number that, for the system, defines the level of synergism created by combining the two constituents. If I is positive then the property profile of the mixture exceeds that expected for a simple arithmetic averaging of the two components' properties. This is termed synergistic. If I is negative then the polymer has properties that are below the values predicted by an arithmetic averaging. This is termed nonsynergistic. Examples of synergistic behaviour are the improved ozone resistance of blends of styrene-butadiene rubber (SBR) and ethylene-propylene-diene-terpolymer (EPDM), increased electrical conductivity for blends of natural rubber (NR) and polychloroprene (CR) and improved tensile strength obtained for blends of polystyrene and poly(2,6-dimethyl-1, 4-phenylene oxide) (PPO).

Polymer systems for which I is equal to zero (or very close to zero) are called 'additive' blends; their properties are essentially arithmetic averages of the properties of their components. Fig.1.1 illustrates, for two component systems, the ideas of additive, synergistic and nonsynergistic properties. Alloys are synergistic polymer systems.

Polymer-polymer miscibility

From a thermodynamic point of view, every polymer has same solubility in every other polymer, but the magnitude in most cases is exceedingly low.[3] For example, if polystyrene is fluxed on a mill with poly(methyl methacrylate) (PMMA) a two-phase mixture results, no matter how long or intensive the mixing. On the other hand if one fluxes polystyrene on a mill with PPO as the second component, one phase results. It is thermodynamically stable because no matter how slowly the mixer

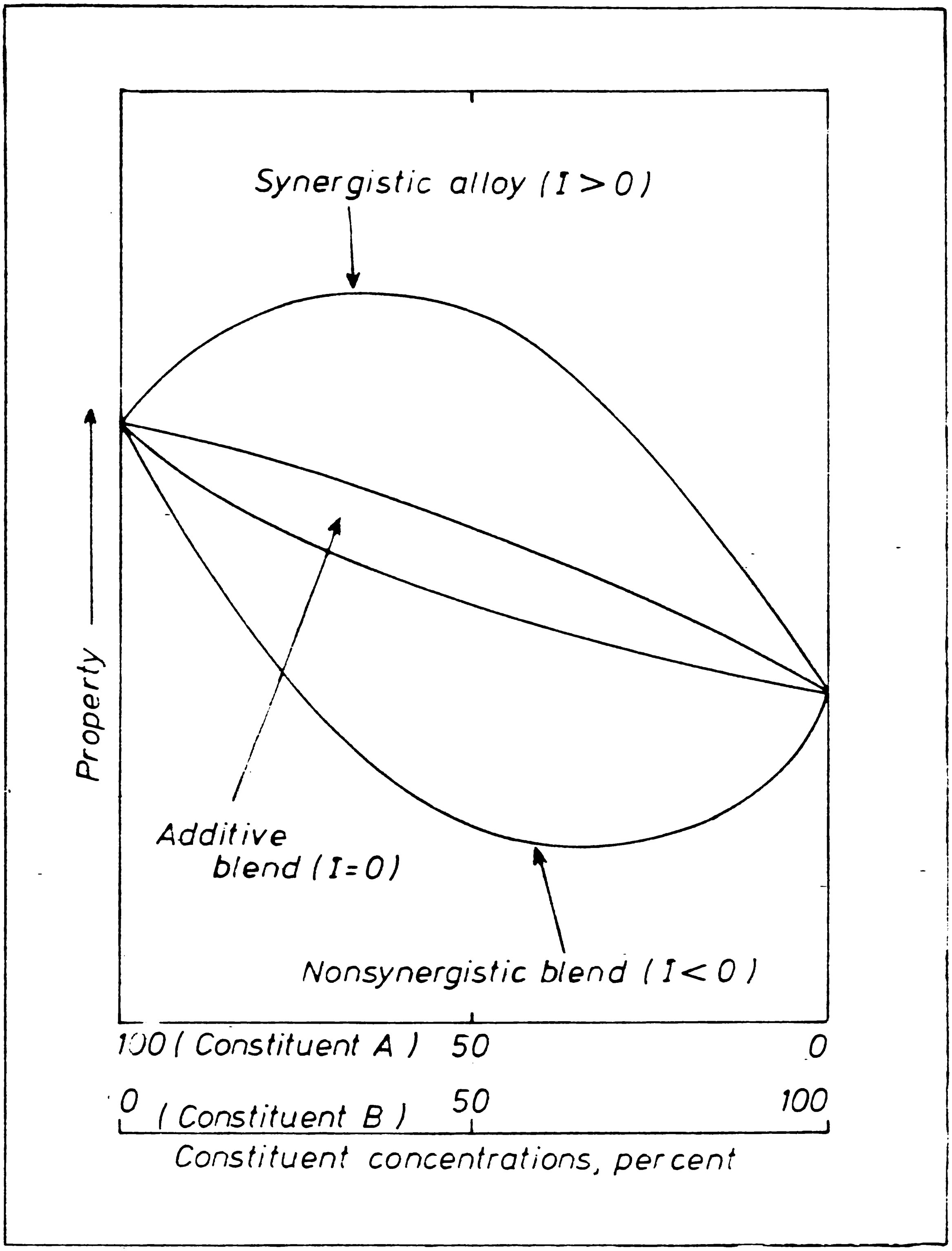

Fig.1.1 Properties of a binary polymer blend as a function of the composition.

turns or how long one waits there is still only one phase. The first represents an example of an immiscible blend, the second a miscible blend.

Homogeneous or miscible blends are characterized by one value of any physical parameter, whereas several values of the same parameters (corresponding to the number of components) are characteristic of immiscible or heterogeneous systems.[4] For example, polyblends of two incompatible materials show two or multiple glass-transition temperatures. At the same time a homogeneous polymer blend has one glass transition lying between those of the two polymers. Thus many of the current methods employed to determine polymer-polymer miscibility depend on the transitional behaviour of polymer blends.[5] In mechanical methods, the polymer blend is subjected to small amplitude cyclic deformations and the variations of elastic and viscoelastic properties at the transition yield necessary information. Data obtained over a broad temperature range can be used to ascertain the miscibility behaviour. In a highly phase-separated polymer blend, the transitional behaviour of the individual components will be unchanged. Likewise in a miscible blend a single and unique transition will appear. In dielectric methods the transition data is obtained from electrical measurements rather than dynamic mechanical testing. The advantage is the ease with which the frequency can be changed. However, determination of transitions of nonpolar polymers is difficult. The variation of dielectric constant at transition is measured in electrical methods. Dilatometric methods capitalize on the discontinuity in the rate of volume change with temperature in the region of the glass transition, while the calorimetric methods observe the change in specific heat of polymers when passing through the glass transition.

For the detailed characterization of the phase morphology in blends, microscopy is unmatched by any other technique.[6] Optical (visible light) contrast can arise from a number of sources such as colour, opacity, refractive index, orientation, absorption etc. With transmission electron microscope (TEM), electron scattering differences are the primary source of contrast. The scanning electron microscope (SEM) on the other hand, depends primarily on surface texture for contrast.

Scattering methods depend on the principle that a stable homogeneous mixture is transparent, whereas unstable nonhomogeneous mixture is turbid unless the components of the mixture have identical refractive indexes.[3] Probably the oldest and most used method of determining polymer-polymer miscibility is the mutual-solvent approach (ternary method).

It consists of dissolving and thoroughly mixing a 50/50 mixture of two polymers at low to medium concentrations in a mutual solvent. Miscibility is said to prevail if phase separation does not occur for a few days. Other methods like inverse gas chromatography, solution viscosity, melt rheology, melting point depression, sorption probes, spectroscopic techniques are also employed for the study of blends.[7]

Methods of successfully predicting miscibility of polymer blends need further development. One method showing limited promise was proposed by Shaw[8] based on a two-component solubility parameter approach. A match of the dispersive and polar solubility parameters for separate polymers was used as a basis of predicting miscibility. However, this method is of relevance to those systems without specific interactions only. Designing polymer systems with specific interactions has proven to be a successful method to achieve miscibility.[9,10]

The utility of polymer blends obviously does not require achieving miscibility. In fact most of the multi-component polymer systems commercially utilized are two phase blends. This is due to a consequence of the limited number of interesting miscible polymer blends. However, there are many cases where a two-phase system offers a specific advantage over that expected for a single phase blend of the same constituents. The primary utility of two-phase behaviour in polymer blends lies in the ability to improve the impact strength of brittle, glassy polymers.[11] An important example of a commercial two-phase blend is impact polystyrene. In block copolymers used as thermoplastic elastomers, two-phase behaviour is the key to elastomeric properties at normal use temperatures combined with thermoplastic characteristics at temperatures suitable for conventional thermoplastic fabrication. Addition of rubber in plastics has been shown to yield definite improvements in the environmental stress rupture resistance. There are a variety of similar examples where two phase blends are successfully used.[3]

For phase-separated systems, interfacial adhesion between the respective phases governs the ultimate mechanical properties. For polymeric constituents having limited affinity for each other, the interface represents a flaw yielding ultimate properties significantly lower than that expected from constituent values. If indeed polymers are miscible excellent adhesion is expected, providing sufficient temperature and pressure are employed to allow for molecular mixing.

The primary advantage realized with miscible polymer blends compared to the immiscible blend counterparts is the assurances of mechanical compatibility. The simplified average of ultimate mechanical properties is not always the observed or expected case, due to the importance of the position of the glass transition temperature (T_g) and of brittle-ductile behaviour. The blend can indeed attain a tensile strength higher than the constituents in the case of mixing a lower modulus ductile polymer with a high modulus brittle polymer as shown for PPO-polystyrene blends. In fabrication, miscible blends will also offer advantages over immiscible blends in regard to surface characteristics and weld-line strength. These processing variables are more commonly encountered in injection moulding (due to the higher shear rates) as opposed to extrusion or compression moulding. Lack of phase separation tendencies obviously is a great advantage during processing and service of miscible blends.[12]

Elastomer blends

All rubbers have shortcomings in one or more properties. There are therefore technical reasons for blending as it should be possible to obtain the right compromise in properties on blending two rubbers. The difficulties experienced in processing some rubbers also necessitate blending. There are also appreciable differences in price between rubbers emphasising economic reasons for blending. Two examples seem to illustrate these considerations.[13] (1) In tread compounds the high abrasion resistance under certain conditions conferred by the use of polybutadiene (BR) is desirable but the poor road holding and rib tearing properties are not, hence blends of BR with natural rubber (NR) and styrene-butadiene rubber (SBR) are usually employed. (2) The resistance of polychloroprene (CR) to ozone is outstandingly good but its price is high and accordingly blending of CR with cheaper rubbers is normally practised for applications in white sidewalls. Ethylene-propylene-diene-rubber (EPDM) is added to elastomer formulations for improved oil acceptance and ozone resistance, acrylonitrile-butadiene rubber (NBR) for improved oil resistance, polychloroprene (CR) for improved flame resistance, polybutadiene (BR) for improved low temperature flexibility, butyl rubber (IIR) for improved gas impermeability etc.[14]

Although elastomer blends have been employed commercially for many years a fundamental understanding of the rheological and physical properties of blends relating to the properties of constituents and morphology is still limited.[15] Physical properties of cured polymer blends are generally inferior to those predicted from the properties of the component polymers. This is especially true for the cured blends of dissimilar polymers having large differences in polarity and unsaturation such as EPDM and NBR which usually show inferior properties well below the values anticipated from the additivity. In polymer blends with similar polarity and similar unsaturation the cured blends frequently show additive properties, the so-called 'covulcanized' state is realized. A typical example of covulcanization would be in blends of SBR and BR.[16]

Factors affecting properties of elastomer blends

One of the most prominent reasons for the inferior properties of the cured elastomer blends is that the constituents are to a great or lesser extent incompatible on the molecular scale and exist in the form of two separate phases.[17] A heterogeneous blend usually results when two chemically dissimilar rubbers are mixed. Several investigators[18-21] have examined this morphology under electron microscopes but little scientific work has been done to establish the factors which are important in determining the mechanical properties of such blends. It is convenient to divide the variables of a blend system into two categories: direct and indirect variables[22] (Table 1.1). The direct variables can be further subdivided into those which are important because the pure component properties depend on them and those that are unique to the blend systems. The direct variables are the fundamental ones and can be controlled by the indirect or processing variables.

The first three fundamental variables are those that also affect the pure components. They are the glass transition temperature (T_g), the molecular weight and crosslink density

Table 1.1 Blend variables

A Direct variables (fundamental)

- 1 Glass transition temperature
- 2 Molecular weight
- 3 Crosslink density
- 4 Composition
- 5 Morphology
- 6 Interfacial adhesion
- 7 Relative stiffness

B Indirect variables (processing)

- 1 Mixing conditions (time, temperature, torque)
- 2 Annealing
- 3 Crosslinking agents

of the components. Among the rubbery materials a higher T_g or molecular weight generally increases toughness for a given crosslink density.[23] In addition, it is well known that the mechanical properties of elastomers depend very strongly on crosslink density.[24] Specifically, the energy required to rupture an elastomer in simple tension generally passes through a maximum as a function of crosslink density.

The remaining four direct variables are unique to blends. The properties obviously depend on the properties of each component in the blend. In addition, the morphology of the blend may be important. One rubber may form the continuous phase while the other is dispersed phase or a cocontinuous structure when both phases are continuous may exist. Also, various sizes and shapes of the dispersed particles are possible.

The interfacial adhesion between the two phases may determine the path that a growing crack takes in a deformed rubber blend and also determines the extent to which stresses can be transferred between the matrix and particle phases. If interfacial adhesion is sufficiently low, small cavities may be opened up between the dispersed domains and the matrix when the blend is stressed. Thus the interfacial adhesion plays a key role in determining the mechanical properties. The relative stiffness between the two phases is a function of the molecular weight, T_g, and rate of crosslinking (and scission if it occurs) of the two ~~rubber~~ phases. The micro-deformation of the blend particles will depend in part on this property. It is found in many composites that the relative stiffness also affects the mechanical properties.

Three processing variables are listed in Table 1.1. The morphology of a blend depends upon the conditions under which the ~~rubbers~~ components are mixed. Two methods have been used in literature. (1) Solutions of ~~rubbers~~ ~~Elastomer~~ polymers are stirred together, then dried or precipitated. (2) The bulk ~~rubbers~~ ~~Elastomer~~ polymers are ~~comasticated~~ mixed in a ~~Brabender~~ extruder or similar high shearing mixer. Most investigators have used the latter method. With this technique, the mixing time, temperature, and/or speed can be varied to obtain different morphologies. Another means of changing the morphology is by annealing after mixing. This can cause an increase in dispersed particle size or phase inversion. The effect of distribution of the crosslinking agents is discussed later.

Filler distribution

The foregoing discussion was mainly based on gum elastomer blends and when a solid particle (filler) is added to elastomer blends, an additional question is how the particles distribute in each polymer phase and how this distribution affects the compound properties.[25-28] In other words when dealing with multiphase polymer systems one of the most important aims is to optimize the physical-mechanical properties desired in the finished product (via) appropriate processing. This optimization is especially needed in the blends of two or more rubbers that are used for tyres, conveyor belts, hoses or other rubber goods.[29]

The effect of an appreciable volume loading of filler on the properties of cured elastomeric vulcanizates depends on whether the elastomer is stress crystallizing or not. Dinsmore[30] reported that the ratios of the tensile strengths of black filled to that of gum vulcanizates is 1 to 1.5 for NR vulcanizates and 5 to 10 for vulcanizates of SBR and similar elastomers. Thus appreciable improvements in strength properties may be obtained for non-stress-crystallizing rubbers by incorporation of carbon black. Further, certain elastomers have optimum filler loadings for particular properties such as wear and tear resistance.[31] As different rubbers have different responses to filler loadings for certain properties, control of filler distribution in elastomer blends could have corresponding specific effects.

When filler is added to a binary elastomer blend it goes to the less viscous polymer and when the viscosity becomes equal to that of the highly viscous polymer it would be taken up by both the polymers.[32] So often the low viscosity polymer gets highly loaded. Hess[29] demonstrated that carbon black normally locates preferentially in the BR component of a 50/50 NR/BR preblend and that this distribution results in optimum vulcanizate performance. The incorporation of carbon black into 50/50 elastomer preblends indicated that black affinity decreased in the order of BR, SBR, CR, NBR, NR, EPDM and IIR.[33] The factors that dominate the partitioning of carbon black are the degree of saturation of the polymers, their viscosities and their polarities and the method of mixing.[34]

The compounding of carbon black is greatly dependent on the method of mixing used.[35] The location of 40 phr GPF black in 50/50 NR/BR blends has been controlled by mixing separate black motherstocks and blending these. The normal mix is one in which the two rubbers are blended in a Banbury before adding the black and the rest of the compounding ingredients. Tensile and tear properties showed improvement as more black located in the BR phase. 50/50 blends of BR and a high styrene SBR containing 50 phr black overall were prepared by blending a 50/50 BR/HAF black masterbatch and SBR gum. The blends were found to exhibit higher abrasion resistance than identical compounds mixed conventionally. It would hence seem possible that by correct filler distribution in rubber blends, especially those involving BR, to enhance certain vulcanizate properties.

Curing aspects of elastomer blends

It is of paramount importance in a binary elastomer blend that both the constituents cure to an optimum level. Results of dynamic mechanical studies and thermal analysis suggest that a two phase system is liable to change to a more homogeneous one with curing. Blends of BR and SBR display two dynamic mechanical loss peaks in the uncured state characteristic of the individual rubbers. These peaks merge quickly to form an intermediate loss peak on vulcanization of the blends probably due to interphase crosslinking.[33-36] So in a binary elastomer blend, formation of interphase crosslinking when the two rubber phases undergo crosslinking is a necessary criterion for developing good mechanical properties.[37] Formation of interphase crosslinks is in competition with intraphase crosslinking. So interphase crosslinking is possible only when the cure rates in the two rubbers are comparable.[38] The different possibilities of crosslinking in a binary elastomer blend are shown in Fig.1.2.

The most prominent factor which leads to the mismatch of cure ratio in two rubbers is the nonproportional division of the curatives. It is very difficult to distribute

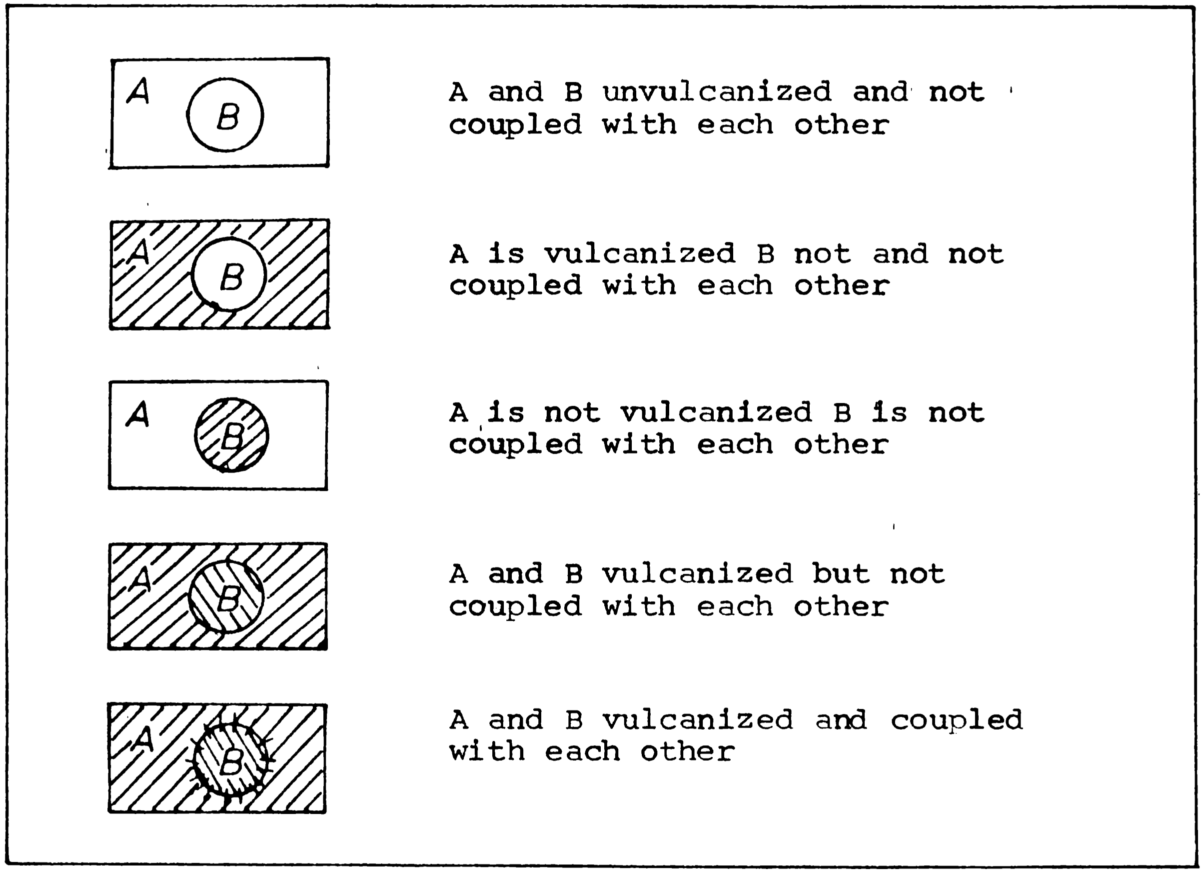

Fig.1.2 Various modes of crosslinking in a binary elastomer blend.

the curatives in the two rubbers as required by the compounder. This is especially so since the solubility of the compounding ingredients is different in the constituents of an elastomer blend. This leads to diffusion of compounding ingredients before, during and after vulcanization and this is recognised as an important factor in the overall properties of the rubber article.[39] In certain cases it can be of benefit since waxes and p-phenylene diamine rely heavily on diffusion to provide optimum protection against degradation by ozone.[40,41]

The diffusion of compounding ingredients such as oil, curatives and antidegradants may occur within a particular rubber stock.[42] The diffusion across the rubber to rubber interphase can be detrimental causing a change in the distribution of materials, which may result in a change in physical properties, a loss in adhesion or antidegradant protection and staining of light coloured compounds.[43]

Curative migration should be of particular concern in an uncured tire since it contains many interfaces between different rubber compounds with differing cure systems. It is widely established that several commonly used curatives such as sulphur, TBBS, CBS, TMTD, DPG and DTDM will diffuse quite readily across a rubber to rubber interphase.[42-45] As solubility of the curatives is greater in high unsaturation rubbers than in low unsaturation rubbers migration will occur to the former type. As the cure rate is also faster in the high unsaturation rubbers, the imbalance will be accentuated. In view of the associated under and over cure of the phases, the vulcanizate properties of blends of high and low unsaturation rubbers may not attain the desired levels. Attempts have been made, particularly with blends of EPDM and high unsaturation rubbers, to improve compatibility and co-crosslinking. These include grafting of accelerators on to EPDM,[46] conversion of EPDM into a macromolecular retarder by addition of certain N-chlorothioamides[47] etc. Similar attempts have been made successfully to make the crosslinking agent chemically bound to the elastomer in which it has lowest solubility and then blend it with another elastomer and also to use vulcanizing systems that perform independently of polymer unsaturation in elastomer combinations.[48]

Gardiner showed that the inferior properties of rubber blends result from the diffusion of the curative from the less polar to more polar elastomer phases.[49,50] This diffusion was shown to occur very quickly during both the mixing and the vulcanization phases of compound processing. Gardiner further noted that the very polar thiuram disulphide accelerators showed the greatest tendency to migrate because of their much greater solubility in the polar elastomer phase of a blend. Guillaumond determined the comparative solubilities of conventional curatives in several rubbers.[51] It was shown that sulphur is 1.5 times soluble in SBR as in BR or EPDM, MBT 4.5 times soluble in SBR as in EPDM and BR, TMTD 3 times soluble in SBR as in BR or EPDM etc. Several methods have been suggested for improving the covulcanization of elastomer blends. A lot of literature is available on the methods suggested for covulcanization of EPDM with other polar elastomers, such as halogenation of EPDM[52], use of certain higher alkyl substituted accelerators[53], lead oxide in place of zinc oxide[54] etc. It appears that the solubility of the compounding ingredients exercise a profound influence on the properties of the vulcanizates of elastomer blends especially when the constituents are incompatible.

Crosslink type and network structure of vulcanized elastomer blends

The single most important factor in determining the physical properties of rubber vulcanizates is the degree of crosslinking. In the case of sulphur vulcanization, the nature of the crosslinks and the presence of other rubber-bound side products of vulcanization may also influence physical properties. In the general case, diene rubbers form not only mono-, di- and polysulphidic crosslinks but pendent sulphide groups terminated by an accelerator residue, cyclo sulphides, conjugated diene and triene units, cis-trans isomerized olefin units and vicinal crosslinks[55-57] (Fig.1.3). Di- and especially polysulphidic crosslinks not only display poor thermal ageing resistance as a consequence of their high chemical reactivity but also affect other physical properties. Their enhancement of relaxation and swelling processes is almost certainly due to their reaction ability to undergo rapid interchange which allow crosslink breakage and reformation to occur.[58,59] The same mechanism has been put forward for the improvement of strength properties by polysulphidic crosslinks,[60,61] but this has been contested.[62,63] Nevertheless networks formed with high proportions of polysulphidic crosslinks display higher tensile strength and tear strength than networks prepared with monosulphidic or carbon-carbon crosslinks.[64-66] There is also some evidence that resilience and resistance to fatigue failure are enhanced.[64] The main chain modifications formed by side reactions also appear to affect some properties. Some of these are probably a consequence of an increase in polarity and/or an increase in the glass-transition temperature of the rubber. Others are a result of interruptions in the stereoregularity of the elastomeric backbone as a consequence of which the tendency to crystallize is reduced. Thus the physical properties of sulphur vulcanizates of diene rubbers depend on the network

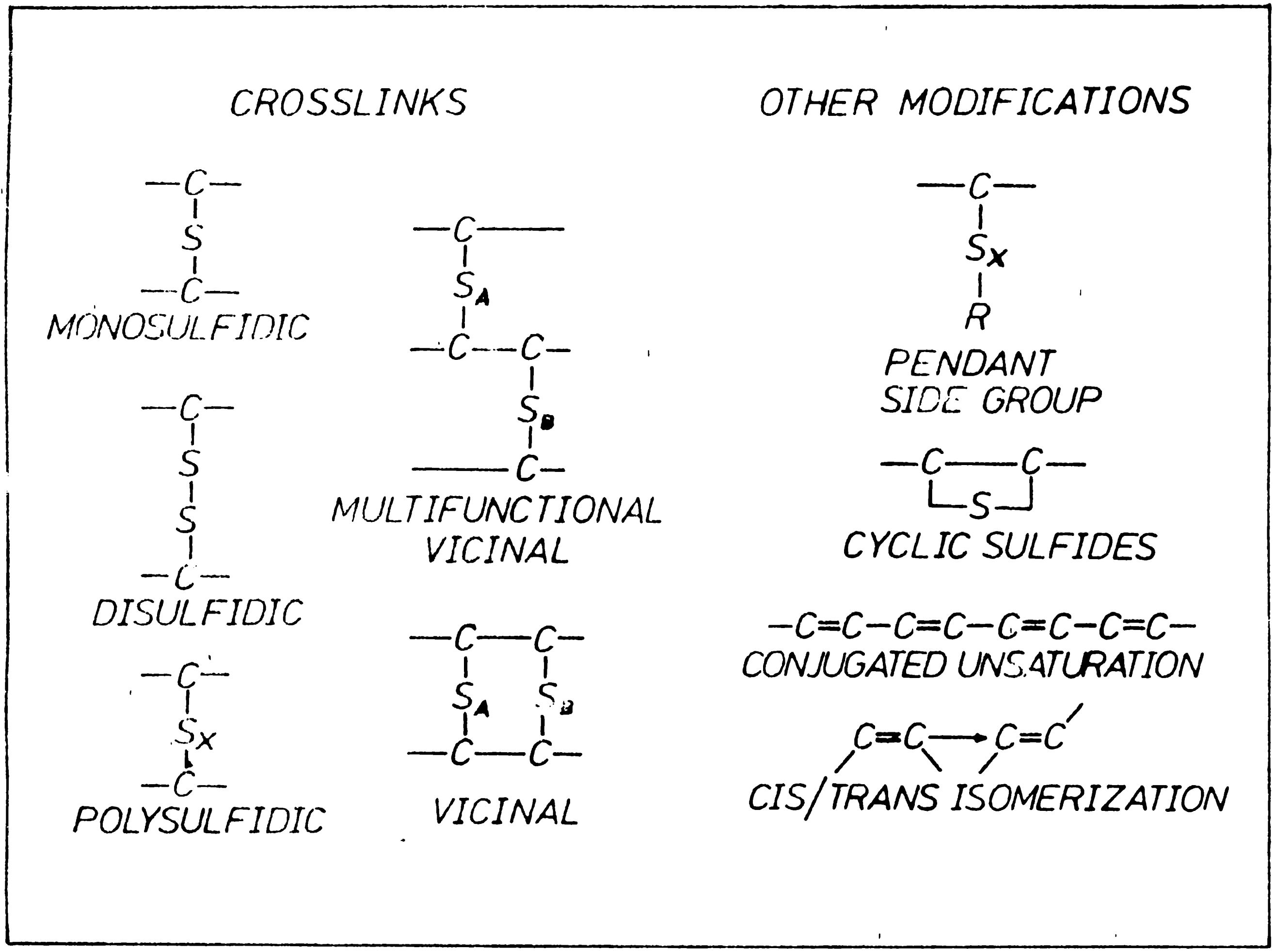

Fig.1.3 Structural features of sulphur vulcanized diene rubbers.

structure which is composed of the degree of crosslinking, crosslink structure and main-chain modifications. So the primary objective of the rubber compounder must be to select a mix composition and vulcanizing conditions to achieve an appropriate network structure which will give and maintain optimum physical properties. Achieving a desired network structure in vulcanizates of elastomer blends is far too difficult than in individual rubbers due to the unproportional division of the curatives between the constituents and the varied response of the rubbers towards them. However, arriving at optimum network structures in the constituent rubbers of an elastomer blend is important since almost every property of the blend vulcanizate depends upon the network structure.

One of the most important and fascinating aspect of current activities in vulcanization chemistry is the problem of determining the structure of rubber vulcanizates. Eventhough the crosslink density of a vulcanizate could be determined from several methods, the most straightforward determination is from swelling data. Crosslinked networks swell to equilibrium extents when immersed in suitable solvents. The fundamental equation relating the equilibrium degree of swelling defined by V_r, the volume fraction of rubber network in the swollen gel, to crosslink concentration ($1/2M_c$) where M_c is the number average molecular weight of the rubber chains between crosslinks is that due to Flory and Rehner,[67,68]

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

where ρ is the density of the rubber, χ an interaction constant characteristic of rubber and swelling liquid termed the rubber-solvent interaction parameter and V_s the molar volume of the swelling liquid. The particular difficulty in using the equation for elastomer blends is that χ must first be determined for the corresponding blends.

In the determination of crosslink density in the gum phase of filler reinforced networks Kraus has contributed significantly[69,70] by showing mathematically how the volumes of equilibrium swollen filled and unfilled networks should interrelate with the volume fraction of the filler. He found that V_r and V_{r_o} (the value V_r would have had in the absence of filler) are related by the expression,

$$\frac{V_{r_o}}{V_r} = 1 - \frac{m\phi}{1-\phi}$$

where $m = V_{r_o} - 1 + 3c(1 - V_{r_o}^{1/3})$

ϕ = volume fraction of filler in the rubber mixture,

and c = parameter characteristic of the filler (c = 1.20 for N 330 black).

The V_{r_o} values can then be translated via the Flory-Rehner equation into chemical crosslink concentrations for the rubber phase of the filled system, employing a filler such as reinforcing carbon black.

The concentration of crosslink types (monosulphidic, disulphidic and polysulphidic) could be estimated from determinations of chemical crosslink densities of vulcanizates before and after treatment with thiolamine chemical probes which specifically break particular crosslink types.[71,72] Treatment of vulcanizates with propane-2-thiol (0.4M) and piperidine (0.4M) in benzene at room temperature for 2 hours cleaves the polysulphidic crosslinks in the network. To cleave both di- and polysulphidic crosslinks, leaving monosulphidic crosslinks intact the vulcanizates could be treated with a solution of 1-hexane thiol (1M) in piperidine at room temperature for 48 hours. Assuming that carbon-carbon crosslinks are absent in the network concentration of mono-, di- and polysulphidic crosslinks can be arrived at. The amounts of free sulphur and sulphur existing as zinc sulphide also could be determined to get a feel of the combined sulphur and efficiency of crosslinking. The amount of combined sulphur in the vulcanizates may be taken as the amount of sulphur added according to formulation minus the amounts of free sulphur and zinc sulphide sulphur.

Objectives and scope of the present work

As stated in the beginning the history of blends in the rubber industry is long and a variety of rubber technology has been amassed. However, the systems are extremely complex and there are a great many points that require clarification.

There are a large number of commercial examples and property advantages of immiscible elastomer blends.[73] Blends of natural rubber (NR) and polybutadiene (BR) have shown various advantages including heat stability, improved elasticity and abrasion resistance. Ethylene-propylene-diene-rubber (EPDM) blended with styrene-butadiene rubber (SBR) has shown improvements in ozone and chemical resistance with better compression set properties. Blends of EPDM and nitrile rubber (NBR) have been cited as a compromise for obtaining moderate oil and ozone resistance with improved low temperature properties. Neoprene

(CR)/BR blends offer improved low temperature properties and abrasion resistance with better processing characteristics etc.

However, in many of the commercial two-phase elastomer blends, segregation of the crosslinking agents, carbon black or antioxidants preferentially into one phase can result in failure to attain optimum properties. Soluble and insoluble compounding ingredients are found to be preferentially concentrated in one phase. The balance of optimum curing of both phases therefore presents a difficult problem. It has been the aim of this study to improve the performance of commercially important elastomer blends such as natural rubber (NR)/styrene-butadiene rubber (SBR) and natural rubber/polybutadiene rubber (BR) by industrially viable procedures.

Two methods that could be directly employed in the industry for improving the performance of elastomer blends are

1. Select suitable blending techniques to slow down the migration of compounding ingredients from one phase to another.

2. Formulate the mixture in such a way as to take care of the possible migration of compounding ingredients from one phase to the other.

It is proposed to study the effect of different blending techniques on selected elastomer blends. However, employing suitable blending techniques to improve the performance of elastomer blends is more time and energy consuming than the second method and hence emphasis would be placed on the latter technique for studies on NR/SBR and NR/BR blends. 50/50 blends of NR/SBR and NR/BR would be selected for study. Different formulations would be employed for these blends and the curing behaviour and the vulcanizate properties would be evaluated. Since the properties of rubber vulcanizates are determined by their network structures, it is proposed to decipher the network structure of the vulcanizates by chemical probes so as to correlate it with the mechanical properties. The changes occurring in the network structure with heat ageing and the corresponding changes in the physical properties also would be evaluated.

For the chemical evaluation of the network structure of the NR/SBR and NR/BR vulcanizates it is required to know the polymer-solvent interaction parameters for these blends. It is proposed to calculate the interaction parameters for these blends from the Flory-Rehner equation by equating the network density of the same vulcanizate in two solvents.[74]

Scanning electron microscopy (SEM) is now widely employed to observe the micro structure of the fracture surfaces[75-77] and hence to study about the fracture mechanisms. Fracture surfaces of NR/SBR and NR/BR blends under tension and abrasion would be examined to correlate them with the strength and type of failure of these materials.

Since the properties of blends strongly depend on miscibility of the constituents an attempt would also be made to determine the relative miscibility of the blends from their curing behaviour.

This thesis is divided into the following chapters:

Chapter 1	Introduction
Chapter 2	Experimental techniques
Chapter 3	Curing studies of elastomer blends
Chapter 4	Studies on natural rubber/styrene-butadiene rubber blend
Chapter 5	Studies on natural rubber/butadiene rubber blend
Chapter 6	Polymer-solvent interaction parameter for elastomer blends
Chapter 7	Scanning electron microscopy examination of the fracture surface of elastomer blends
Chapter 8	Summary and conclusions.

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Chapter 2

EXPERIMENTAL TECHNIQUES

EXPERIMENTAL TECHNIQUES

The materials used and the details of the experimental procedures adopted are described in this chapter.

Materials

Elastomers

1. Natural rubber

Natural rubber (NR) used was solid block-rubber, ISNR-5 grade, obtained from Rubber Research Institute of India, Kottayam. The Mooney viscosity (ML(1+4) at 100°C) of the rubber was 85.3 and $\bar{M}_w$ 7.70x10^5.

2. Styrene-butadiene rubber

Styrene-butadiene rubber (SBR) was Synaprene 1500 grade obtained from Synthetics and Chemicals Ltd., Bareilly. The Mooney viscosity (ML(1+4) at 100°C) was 49.2.

3. Polybutadiene rubber

Polybutadiene rubber (BR) was obtained from Indian Petrochemicals Corporation Ltd., Baroda. The rubber was 97% 1,4 (cis) and had a Mooney viscosity (ML(1+4) at 100°C) of 48.

4. Acrylonitrile-butadiene rubber

Acrylonitrile-butadiene rubber (nitrile rubber) (NBR) was obtained from Synthetics and Chemicals Ltd., Bareilly. The rubber was medium acrylonitrile grade (33%) with a Mooney viscosity (ML(1+4) at 100°C) of 40.9.

5. Ethylene-propylene-diene- rubber

Ethylene-propylene-diene-rubber (EPDM) used had a diene content of 3% and a Mooney viscosity (ML(1+4) at 100°C) of 55.5.

Other ingredients

1. Carbon black (filler)

Carbon black used in this study was high abrasion furnace black (HAF, N 330) supplied by M/s.Carbon and Chemicals (India) Ltd., Cochin.

2. Zinc oxide (activator)

Zinc oxide was supplied by M/s.Meta Zinc Ltd., Bombay having the specifications given below.

Specific gravity : 5.570±0.08

Zinc oxide content : 98%

Acidity : 0.4% max.

Heat loss (2 hrs. at 100°C) : 0.5% max.

3. Stearic acid (activator)

Stearic acid was supplied by Godrej Soap (P) Ltd., Bombay, and had the following specifications.

Melting point	: 50-69°C
Acid No.	: 185-210
Iodine No.	: 9.5 max.
Specific gravity	: 0.85±0.01
Ash	: 0.1% max.

4. TMTD (accelerator)

Tetramethyl thiuram disulphide (TMTD) supplied by Vithoga Chemicals, Mudickal had the following specifications.

Melting point	: 138°C
Specific gravity	: 1.405±0.025
Ash	: 0.5% max.
Moisture	: 1% max.

5. CBS (accelerator)

N-cyclo hexyl-2-benzthiazyl sulphenamide (CBS) used in the study was Santocure CBS supplied by Polyolefins Industries, Bombay, having the following specifications.

Ash	: 0.5% max.
Moisture	: 0.5% max.
Specific gravity	: 1.27

6. Sulphur (crosslinking agent)

Sulphur was supplied by Standard Chemical Company Pvt.Ltd., Madras and had the following specifications.

Specific gravity : 2.05
Acidity : 0.01% max.
Ash : 0.10% max.
Solubility in CS_2 : 98% max.

7. Di cumyl peroxide (crosslinking agent)

Di cumyl peroxide (DCP) used in the study was commercial grade 40% active powder.

8. Aromatic oil (process oil)

Aromatic oil was supplied by Hindustan Petroleum Corporation. It had the following specifications.

Specific gravity : 0.95-0.98
Viscosity gravity constant (VGC) : 0.907
Aniline point : 25°C
Flash point : 245°C

9. PBN (antioxidant)

Phenyl-β-naphthylamine (PBN) was commercial grade supplied by Indian Explosives Ltd., Rishra.

10. Reagents for network structure elucidation

Propane 2-thiol, 1-hexane thiol and piperidine were analytical grade reagents supplied by Fluka, Germany.

11. Solvents

Benzene, toluene, and iso-octane were of analytical grade.

Experimental procedure

1. Mixing and homogenization

A. Using the mixing mill

Mixing and homogenization of elastomers and compounding ingredients were done on a laboratory size (15 cm x 33 cm) two roll mill at a friction ratio of 1:1.2. The elastomer was given one pass through the nip (0.002x100)". Then it was given 2 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 70±5°C during the mastication. After the nerve has disappeared, the compounding ingredients were added as per ASTM D 3184 (1980) and D 3182 (1982) in the order activators, fillers, accelerators and curing agents. 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 a nip gap of 3 mm. For the preparation of compounds of elastomer blends, the elastomer blend was prepared initially by giving sufficient time for proper mixing at controlled mixing temperatures and then the other additives were added as described above unless otherwise specified.

B. Using the Brabender Plasticorder

A Brabender Plasticorder (torque rheometer) model PL3S was used in this study. The heart of the torque rheometer is a jacketed mixing chamber whose volume is approximately 40 cc. Mixing or shearing of the material in the mixing chamber is done by two horizontal rotors with nigs or protrusions. The torque developed during mixing is made visible with the help of a dynamometer balance. The temperature of the mixing chamber is controlled by circulating hot oil. The temperature could be set at any value upto 300°C. The actual temperature in the mixing chamber is measured and indicated. Different types of rotors could be employed depending upon the nature of the polymers. Since mixing conditions (rotor type, rpm and temperature) can be specifically fixed, proper control of mixing with repeatable results is possible on the torque rheometer. Since lateral mixing which has to be done manually on a mixing mill, is taken care of in the torque rheometer by the specially shaped rotors, manual work is also much less. The sequence of addition of the ingredients was done in the same way as done for the mixing on the mixing mill. In the case of compounds based on elastomer blends, the elastomers were blended initially and then the other ingredients were added unless otherwise specified.

2. Determination of cure characteristics of rubber compounds

A. Using Goettfert Elastograph

The Goettfert Elastograph used in the study for determination of curing behaviour of rubber compounds was model 67.85. This is a rotorless curemeter and the torque-time curve (vulcanization curve) is generated by the oscillation of the lower half of the cavity in which the polymer mix is charged. The reaction chamber is biconical in shape, so that the shear angle remains constant throughout the specimen. Further, by using a specimen of a defined size obtained by means of a special stamping press, the chamber can be filled completely restricting oxidative breakdown as well as ensuring greater reproducibility.

The upper platen is brought to the lower by means of a ram actuated by compressed air. The relevant data that could be taken from the torque-time curve are

1. Minimum torque: This is the torque attained by the mix after homogenizing at the test temperature before the onset of cure.

2. Maximum torque: This is the torque recorded after the curing of the mix is completed.

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

4. Scorch time: This is the time taken for 2 units (0.2 Nm) rise above the minimum torque (about 10% vulcanization).

The elastograph computer evaluates the vulcanization curve and prints out these data after each measurement. It is also capable of generating many other data such as the cure rate curve.

B. Using Monsanto Rheometer

The Monsanto Rheometer used in the study for determining the curing behaviour of rubber compounds was model R 100. In this instrument the rubber compound is contained in a cylindrical cavity 50 mm x 10 mm and has embedded in it a biconical rotor of diameter 37 mm which is oscillated sinusoidally through a small arc amplitude (1 to 3 degree). The cavity and specimen are maintained to within ±0.5°C and the force required to oscillate the disc is measured. The torque-time curve (vulcanization curve) of the Rheometer is similar to that of the Elastograph and all the relevant data could be taken accordingly.

3. Mooney viscosity measurement

The Mooney viscosities of the raw rubbers were measured on the Mooney viscometer which is designed for measuring the shearing viscosity of rubber and rubber like materials by a disc rotating (2 rev/min.) in a cylindrical cavity set at 100°C and filled with rubber under test. In running a viscosity test the sample was allowed to warm up for one minute after the platens were closed and the motor was then started. Reading taken after 4 minutes was reported as the Mooney viscosity of rubber (ML(1+4) at 100°C). The procedure given in ASTM D 1646 (1981) was followed.

4. Moulding of test sheets

The test sheets for determining the physical properties were prepared in standard moulds by compression moulding on a single day light electrically heated press having 30 cm x 30 cm platens at a pressure of 45 kg/cm^2 on the mould. The rubber compounds were vulcanized upto their respective optimum cure times at 150°C unless otherwise specified. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold 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.

5. Physical test methods

A. Tensile strength, elongation at break and modulus

These tests were carried out according to ASTM D 412 (1980) using dumb-bell specimens on a Zwick universal testing machine model 1445. The instrument was kept in an AC room and the average temperature of testing was 25±2°C. Samples were punched from compression moulded sheets parallel to the mill grain direction using a dumb-bell die (C-type). The thickness of the narrow portion was measured by bench thickness gauge. The sample was held tight by the two grips, the upper grip of which was fixed. The rate of separation of the power actuated lower grip was 500 mm/minute.

The computer attached to the machine calculates the tensile strength, elongation at break and modulus (stress at a given elongation) and prints out these data after each testing.

B. Hardness

The hardness (Shore A) of the moulded samples was tested using Zwick 3114 hardness tester in accordance with ASTM D 2240 (1981). The tests were performed on mechanically unstressed samples of 300 mm diameter and minimum 6 mm thickness. A load of 12.5 N was applied and the readings were taken after 10 seconds of the identation after firm contact had been established with the specimens.

C. Compression set

The samples (1.25 cm thick and 2.8 cm 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.

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

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

D. 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 a Zwick universal testing machine. The speed of extension was 500 mm/minute and the test temperature 25±2°C.

E. Ageing studies

Dumb-bell samples for evaluation of physical properties were prepared and kept in an air oven at predetermined temperatures for specified periods. Physical properties like tensile strength, elongation at break, modulus etc., were measured before and after ageing and the percentage retention of these properties was evaluated for assessing the effect of ageing. The procedure given in ASTM D 573 was followed.

6. Scanning electron microscopy observation

Scanning electron microscope (SEM) was first introduced in 1965 and it has since become a very useful tool in polymer research for studying morphology.[1-3] In this technique an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors and magnified. An image of the investigated microscopic region of the specimen is thus photographed.

If the specimen under investigation is not a good conductor, it should be coated with a thin layer of conducting material like platinum or gold. This is done by placing the specimen in a high vacuum evaporator and vaporizing the conducting material held in a tungsten basket (vacuum dispersion).

The SEM observations reported in the present investigation were made on the fracture surface of tensile test specimen and abraded surface of the abrasion test specimen. The fractured and abraded surfaces of the samples were carefully cut out without disturbing the surface. These surfaces were then sputter coated with gold within 24 hours of testing. The SEM observations were made within one week after gold coating. The gold coated samples were kept in desiccators before the SEM observations were made. The shapes of the tensile test specimens, direction of the applied force and portions from where the surfaces have been cut out for SEM observations are shown in Fig. 2.1.

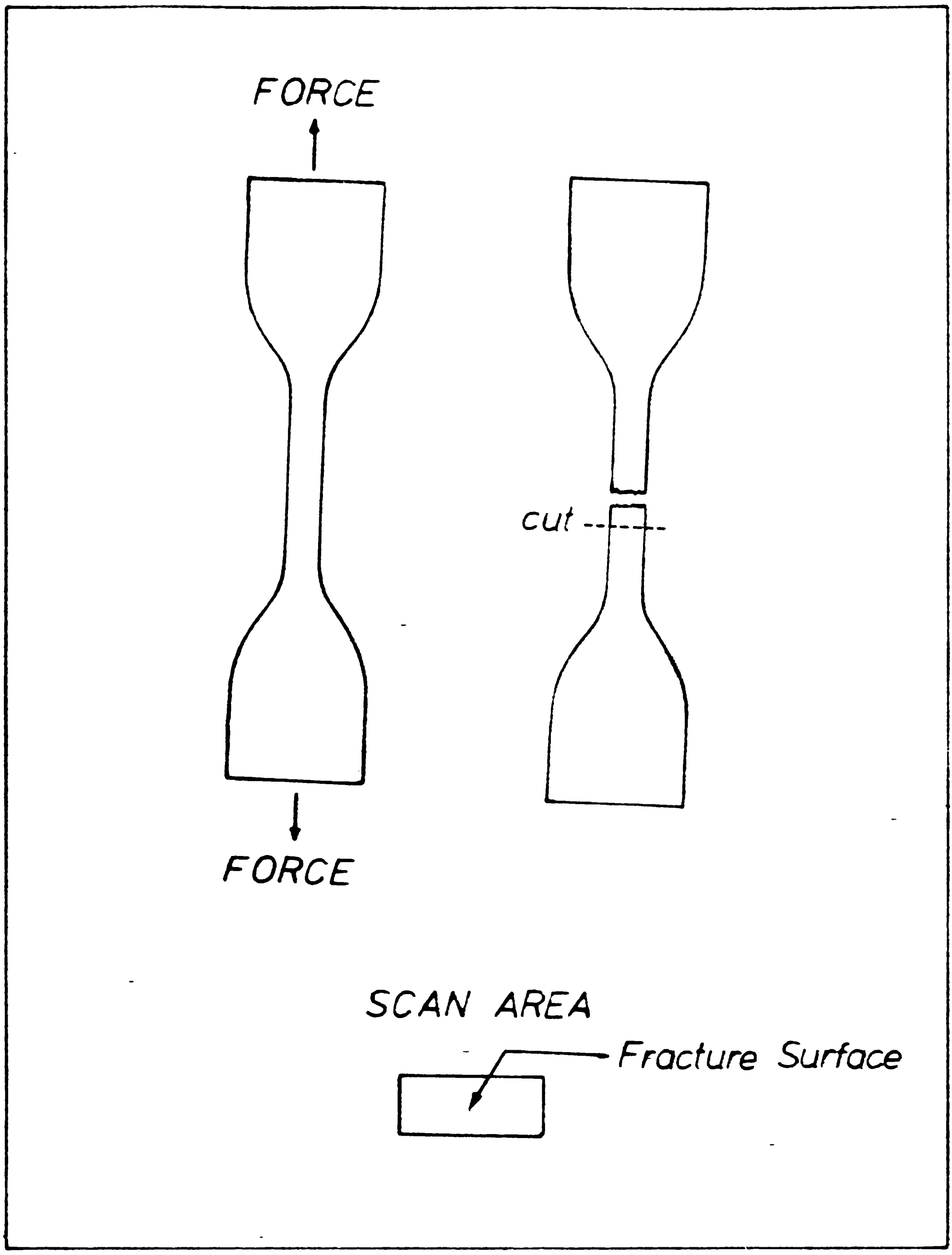

Fig.2.1 SEM scan area of the tensile fracture surface.

7. Chemical test methods

A. Free sulphur estimation

Free sulphur was determined in the cured samples before and after ageing, according to ASTM D 297-72 A.

The principle of this method is based on the reaction of free sulphur with sodium sulphite to give sodium thiosulphate which is finally titrated against standard iodine solution.

$$S + Na_2SO_3 \longrightarrow Na_2S_2O_3$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

Two grams of finely divided or grained sample were digested gently with 100 ml of aqueous sodium sulphite solution (50 gm/litre) for 16 hrs. in presence of 5 ml of sodium stearate suspension in water (1 gm/litre) to assist wetting and approximately one gm of paraffin wax to avoid aerial oxidation. 100 ml of strontium chloride (5 gm/litre) solution was added to precipitate fatty acids and 10 ml of cadmium acetate solution (30 gm/litre) to remove accelerators. For the vulcanizates containing higher proportions of accelerators additional

10 ml of cadmium acetate solution was added to ensure complete precipitation of the accelerators. Rubber and the precipitate were separated by filtration. It was then washed twice with 75 ml portions of cadmium acetate wash solution (1.2 gm/litre). To the filtrate 10 ml of 40% formaldehyde solution was added with vigorous stirring and subsequently acidified with glacial acetic acid (10 ml). The solution was cooled below 10°C by adding enough crushed ice and titrated with 0.05 N iodine solution using starch as indicator.

A blank run was taken without sample and this value was subtracted from the titre values of the sample.

$$\text{Free sulphur \%} = \frac{(x-y) \times N \times 0.032 \times 100}{W}$$

where x is the volume of iodine solution required for the titration of the sample in cc, y the volume of iodine solution required for the titration of the blank in cc, N the normality of iodine solution and W the weight of sample taken.

B. Zinc sulphide estimation

The procedure is based on the following reaction.

$$ZnS + 2HCl \rightarrow ZnCl_2 + H_2S$$

$$H_2S + CdCl_2 \rightarrow CdS + 2HCl$$

$$CdS + 2H^+ + I_2 \rightarrow Cd^{++} + 2HI + S$$

The finely divided sample (2 gm) along with 25 ml of freshly distilled peroxide free ether was placed in the digestion flask of the apparatus adopted by Adam and Johnson.[4] The reaction flask was immersed in a constant temperature bath maintained at 37°C. 100 ml of absorbing solution (5 gm of $CdCl_2$, 25 gm of sodium acetate, and 25 ml of glacial acetic acid per litre of the solution) was used for absorbing the gas generated during digestion. After the sample had become swollen in ether (1 hr.) 25 ml of conc. HCl was added to the digestion flask and nitrogen gas was bubbled through the reaction mixture for a period of 1 hr. The amount of H_2S liberated from the sample by HCl - ether digestion, which is the measure of ZnS sulphur, was absorbed as CdS in the absorbing solution. A measured excess of 0.05 N iodine solution was added and the excess iodine was back titrated against 0.05 N sodium thiosulphate solution using starch as indicator. A blank titration was also conducted. From the two titre values the volume of iodine reacted with cadmium sulphide was noted. The amount of zinc sulphide sulphur was calculated, as follows.

$$\text{Zinc sulphide sulphur \%} = \frac{V x N x 0.016 x 100}{W}$$

where V is the volume of iodine reacted with cadmium sulphide, N the normality of iodine solution and W the weight of sample taken. The procedure given in BS 902 Pt. 1310 (1958) was followed.

C. Determination of concentration of crosslinks of the vulcanizates

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

Samples of approximately 1 cm diameter, 0.20 cm thickness and 0.20 gm weight were punched out from the central portion of the vulcanizate and allowed to swell in solvent (benzene or toluene) containing 0.1% phenyl-β-naphthylamine (PBN). After 24 hours the solvent containing PBN was replaced by pure solvent and after another two hours, swelling was stopped. The swollen sample was weighed, solvent removed in vacuum and the sample weighed again.

The volume fraction of rubber (V_r) in the swollen network was then calculated by the method reported by Ellis and Welding[5] from the following equation.

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

where

T = Weight of the test specimen

D = Deswollen weight of the test specimen

F = Weight fraction of insoluble components

A_o = Weight of the absorbed solvent corrected for the swelling increment

ρ_r = Density of rubber

ρ_s = Density of solvent.

The value of ρ_r and ρ_s taken were

ρ_r (NR) = 0.92 g/cm^3 ρ_s (benzene) = 0.875 g/cm^3

ρ_r (SBR) = 0.94 g/cm^3 ρ_s (toluene) = 0.886 g/cm^3

ρ_r (BR) = 0.93 g/cm^3

The crosslink density ($1/2M_c$) was then determined from V_r using the Flory-Rehner equation,[6,7]

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

where

V_s = molar volume of solvent

V_s (benzene) = 90 cc/mole

V_s (toluene) = 104 cc/mole

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

Values of parameter χ taken for calculations[8,9] were the following.

For NR - Benzene $\chi = 0.40$

NR - Toluene $\chi = 0.42$

SBR- Benzene $\chi = 0.31$

SBR- Toluene $\chi = 0.32$

BR - Benzene $\chi = 0.314$

BR - Toluene $\chi = 0.34$

For NR/SBR and NR/BR blends, χ was found to very linearly with composition (Chap.6). Hence the average value of χ was taken for 50/50 blends of these polymers.

In the case of carbon black filled vulcanizates the value of V_r was converted into V_{r_o} (the value V_r would have had in the absence of black) by means of the Kraus' equation[10]

$$V_{r_o} = V_r \left[1-m\phi/(1-\phi)\right]$$

where $m = V_{r_o}-1+3c\left[1-(V_{r_o})^{1/3}\right]$

ϕ = Volume of fraction of carbon black in the rubber compound c = Parameter for carbon black (in the case of N 330, c = 1.20).

V_{r_o} was then substituted in the Flory-Rehner equation in place of V_r to obtain the crosslink density.

D. Determination of concentration of different types of crosslinks[11-13]

1. Concentration of polysulphidic crosslinks

The concentration of polysulphidic crosslinks was estimated from the change in the crosslink density of the vulcanizates before and after treatment with propane-2-thiol and piperidine which cleaves the polysulphidic crosslinks in the network. Vulcanizate sample weighing about 0.2-0.3 gm was allowed to stand in excess of solvent (benzene/toluene) containing 0.1% PBN for 24 hours at room temperature. Then the solvent was replaced by a solution (100 ml) of 0.4M propane-2-thiol and piperidine in the solvent containing 0.5% PBN for two hours. On completion of reaction the sample was removed from the reagent solution, washed with petroleum ether (40°C-60°C) four times, surface dried on filter paper as quickly as possible and dried in vacuum to constant weight at room temperature. The specimen was then kept in excess of the solvent with 0.1% PBN for 24 hours and finally extracted for 2 hours in pure solvent.

The swollen sample was weighed, solvent removed in vacuum and the sample weighed again. The volume fraction of rubber (V_r) was then determined as before and the crosslink density was determined.

2. Concentration disulphidic and monosulphidic crosslinks

Both polysulphidic and disulphidic crosslinks in the vulcanizates could be cleaved by treatment with 1-hexane thiol in piperidine. The determination of crosslink density before and after this treatment gives the concentration of monosulphide linkages, assuming carbon-carbon linkages to be negligible. Since the concentration of polysulphidic linkage was determined before, the concentration of disulphidic linkages also could be estimated.

Vulcanizate sample weighing about 0.2-0.3 gm was allowed to stand in 100 ml of 1-hexane thiol in piperidine (1M solution) containing 0.5% PBN for 48 hours at room temperature. The mixture was agitated occasionally. On completion of reaction the sample was removed from the reagent solution, washed with petroleum ether (40°C-60°C), four times, surface dried on filter paper as quickly as possible and dried in vacuum to constant weight at room temperature. Then the specimen was kept in excess solvent (benzene or toluene) containing 0.1% PBN for 24 hours. Finally the specimen was kept in pure solvent for 2 hours and weighed. Then the solvent was removed in vacuum and the deswollen sample was weighed. The volume fraction of rubber in the swollen network (V_r) was then determined as before and the crosslink density was calculated.

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Chapter 3

CURING STUDIES OF ELASTOMER BLENDS

CURING STUDIES OF ELASTOMER BLENDS

I. Effect of blending techniques on the curing of elastomer blends

The single most important factor in determining the physical properties of rubber vulcanizates is the degree of crosslinking.[1] In a binary elastomer blend the degree of crosslinking in both the rubbers should be optimum to develop the best possible physical properties. In addition to the two phases having optimum crosslink densities, there should occur some interphase crosslinking.[2] Such an ideal situation is called the covulcanized state of an elastomer blend.[3] Formation of interphase crosslinks is in competition with intraphase crosslinking and hence a significant amount of interphase crosslinks are formed only when the cure rates in the two rubbers are comparable.[4] Hence, achieving a covulcanized state is usually difficult due to the differences in cure rates, solubility of curatives and diffusion characteristics of fillers and other compounding ingredients etc. between the elastomers. The solubility of conventional curatives is higher in the rubbers which have higher polarity and higher unsaturation than in low unsaturation and low polarity rubbers. This explains why use of chlorobutyl in place of butyl rubber for blending with diene elastomers gives better general physical properties and why variation of the termonomer in blends of EPDM with dienes influences physical properties.[5]

Due to the differences in solubility one component grabs a major share of the curatives during the compounding stage. This is followed by migration of the curatives from the less soluble to the more soluble phase.[6] Migration was observed to commence in a very short time (e.g., 3 sec. at 307°F) indicating that a diffusion gradient may be produced between dissimilar elastomers considerably before significant vulcanization occurs. Such migration will be accentuated by higher curative reaction rates in the higher diene elastomers, causing excess material to be drawn from adjacent phases. Thus in a two-phase elastomer blend, the optimum curing of both phases presents a difficult problem. In this study an attempt is made to observe whether different blending techniques at the compounding stage could alleviate this problem at least partly. Three typical binary elastomer blends are selected and the effect of blending techniques on the curing behaviour of these blends is reported.

The rubber blends selected for the study were[7,8]

A. A compatible blend from non-polar constituents with similar unsaturation (polybutadiene rubber (BR)/styrene-butadiene rubber (SBR).

B. An incompatible blend from non-polar constituents with large difference in unsaturation (natural rubber (NR)/ ethylene-propylene-diene rubber (EPDM)).

C. An incompatible blend with similar unsaturation but large difference in polarity (natural rubber (NR)/acrylonitrile-butadiene rubber (NBR)).

Experimental

The formulations selected for the individual rubbers are shown in Table 3.1. The formulations were selected such that if the curatives got distributed in the two rubbers according to them, optimum cure could occur in the two constituents of the rubber blends at about the same time. For each of the rubber blends, BR/SBR, NR/EPDM and NR/NBR the following blending techniques were employed.

1. The rubbers were blended together. The total amount of the additives for both the rubbers was then added to the rubber blend.

2. The compound for each constituent of the blend was prepared separately. Then these compounds were blended together.

3. The total amount of the additives was added to the slower curing rubber (SBR, EPDM or NBR). Then the other rubber was blended with this compound.

Table 3.1 Formulations for individual rubbers

Rubber	NR 100	SBR 100	BR 100	NBR 100	EPDM 100
ZnO	5	5	5	5	5
Stearic acid	2	2	2	2	2
CBS	0.6	1.0	0.8	1.5	2.5
TMTD	--	0.8	0.2	0.8	3.0
Sulphur	2.5	2.25	2.4	1.5	1.5

The compositions of the BR/SBR blends selected for studying the curing behaviour were 85 BR/15 SBR, 70 BR/30 SBR and 55 BR/45 SBR. Each of the above compositions was prepared by all the three blending techniques described before. The same compositions of NR/EPDM and NR/NBR blends were also selected for study. The compounds were prepared on a Brabendar Plasticorder model PL 3S at about 50°C using a rotor speed of 30 rpm according to ASTM D 3182 (1982). The cure characteristics of the compounds were determined on a Goettfert Elastograph model 67.85 at 150°C. 50/50 blends of BR/SBR, NR/EPDM and NR/NBR were selected for determining the tensile properties (by employing the same formulations given in Table 3.1). The blends were prepared by the three blending methods on a laboratory mixing mill. The cure curves of the compounds were taken on the Elastograph and then the compounds were vulcanized upto their optimum cure times on an electrically heated laboratory hydraulic press. Dumb-bell samples for tensile tests were punched out along the mill grain direction from the vulcanized sheets of 15x15x0.2 cm size. Tensile properties of the vulcanizates were determined at 25°C as per ASTM D 412 (1980) test method on a Zwick universal testing machine model 1445 at a crosshead speed of 500 mm/minute.

Results and Discussion

Curing behaviour of blends

Figure 3.1 shows the curing behaviour of BR and SBR.

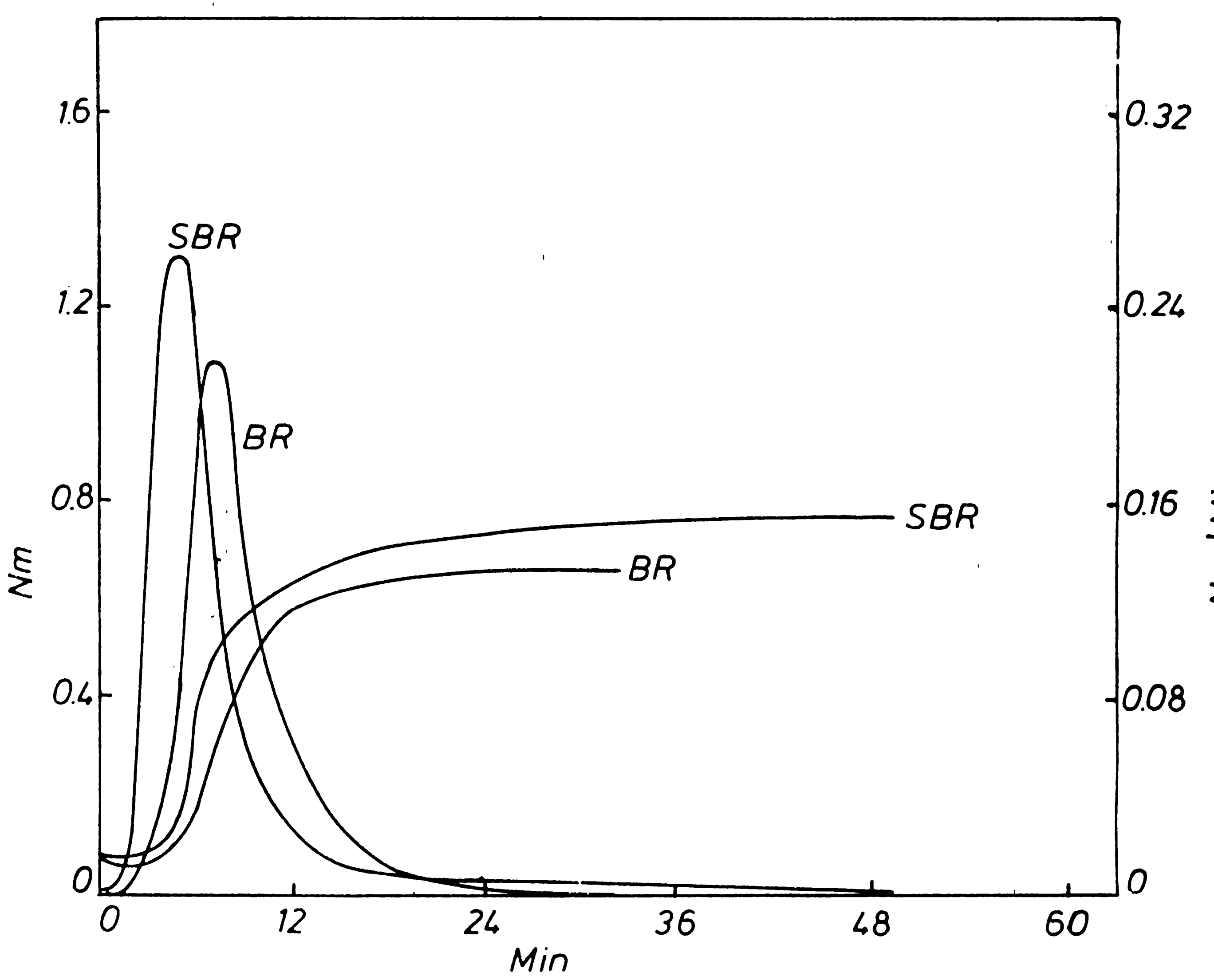

Fig.3.1 Cure curves and cure rate curves of SBR and BR (Ref. Table 3.1).

The scorch times and cure times of BR and SBR calculated from the cure curves are shown in Table 3.2 For the compounds selected, BR has slightly better scorch safety than SBR and also cures faster than SBR. Table 3.2 also shows the cure characteristics of the different combinations of BR/SBR blends prepared by the three different blending techniques. It is interesting to note that the different blending techniques do not produce much variations in the curing behaviour of BR/SBR blends. This may be due to good compatibility of the rubbers resulting in an almost single phase behaviour.[9,10] The blends, depending upon their composition display an intermediate behaviour between those of SBR and BR. The 85 BR/15 SBR blend shows more or less the behaviour of BR alone but when the amount of SBR increases the cure characteristics settle at an intermediate value between those of BR and SBR. This variation is due to the change in the total amounts of curatives added to accommodate the different combinations. Figure 3.2 shows the cure curves of 50/50 blends of BR and SBR prepared by the three blending methods. It may be observed that all the three curves show a combined behaviour of BR and SBR without much variations as expected.

Figure 3.3 shows the cure curves of NR and EPDM and the cure characteristics calculated from the cure curves are shown in Table 3.2. As expected, NR has less scorch safety

Table 3.2 Cure characteristics of elastomers and elastomer blends

	SBR	BR	85 BR/15 SBR			70 BR/30 SBR			55 BR/45 SBR		
			1	2	3	1	2	3	1	2	3
Scorch time, min.	4.0	5.0	4.8	4.8	4.8	4.6	4.6	4.6	4.4	4.4	4.4
Cure time, min.	11.0	9.0	9.8	9.8	9.9	10.2	10.2	10.2	10.0	10.0	10.0

	NR	EPDM	85 NR/15 EPDM			70 NR/30 EPDM			55 NR/45 EPDM		
			1	2	3	1	2	3	1	2	3
Scorch time, min.	4.0	5.5	3.0	3.5	3.5	2.5	3.0	3.0	2.0	2.5	2.5
Cure time, min.	10.0	15.0	7.5	8.0	8.5	6.5	7.0	7.5	5.5	6.2	7.0

	NR	NBR	85 NR/15 NBR			70 NR/30 NBR			55 NR/45 NBR		
			1	2	3	1	2	3	1	2	3
Scorch time, min.	4.0	3.0	3.5	3.8	3.8	3.5	3.5	3.5	3.0	3.0	3.0
Cure time, min.	10.0	9.5	9.5	9.8	9.3	9.0	9.3	9.0	8.5	9.0	8.0

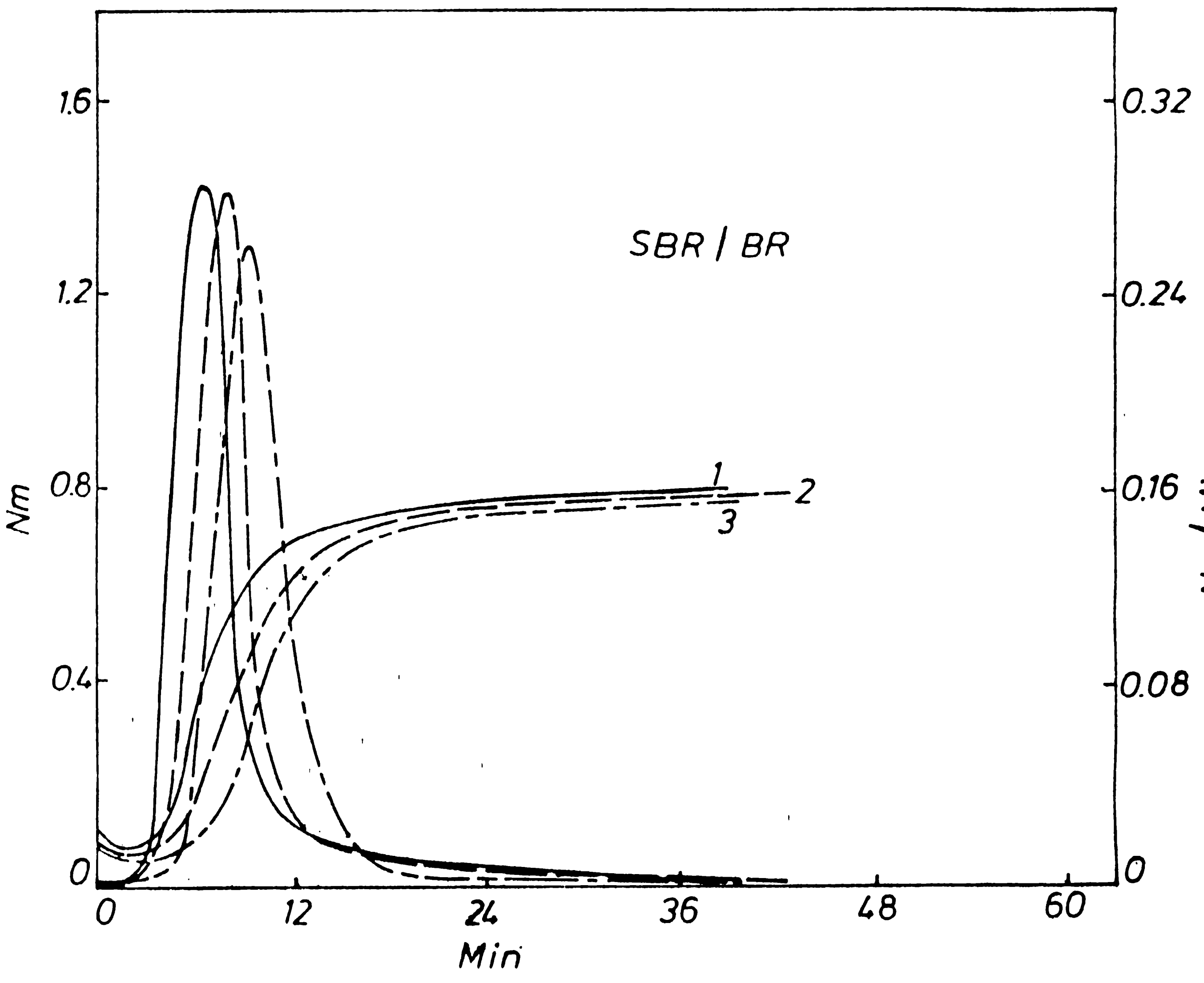

Fig.3.2 Effect of blending techniques on the curing behaviour of 50/50 SBR/BR blend.

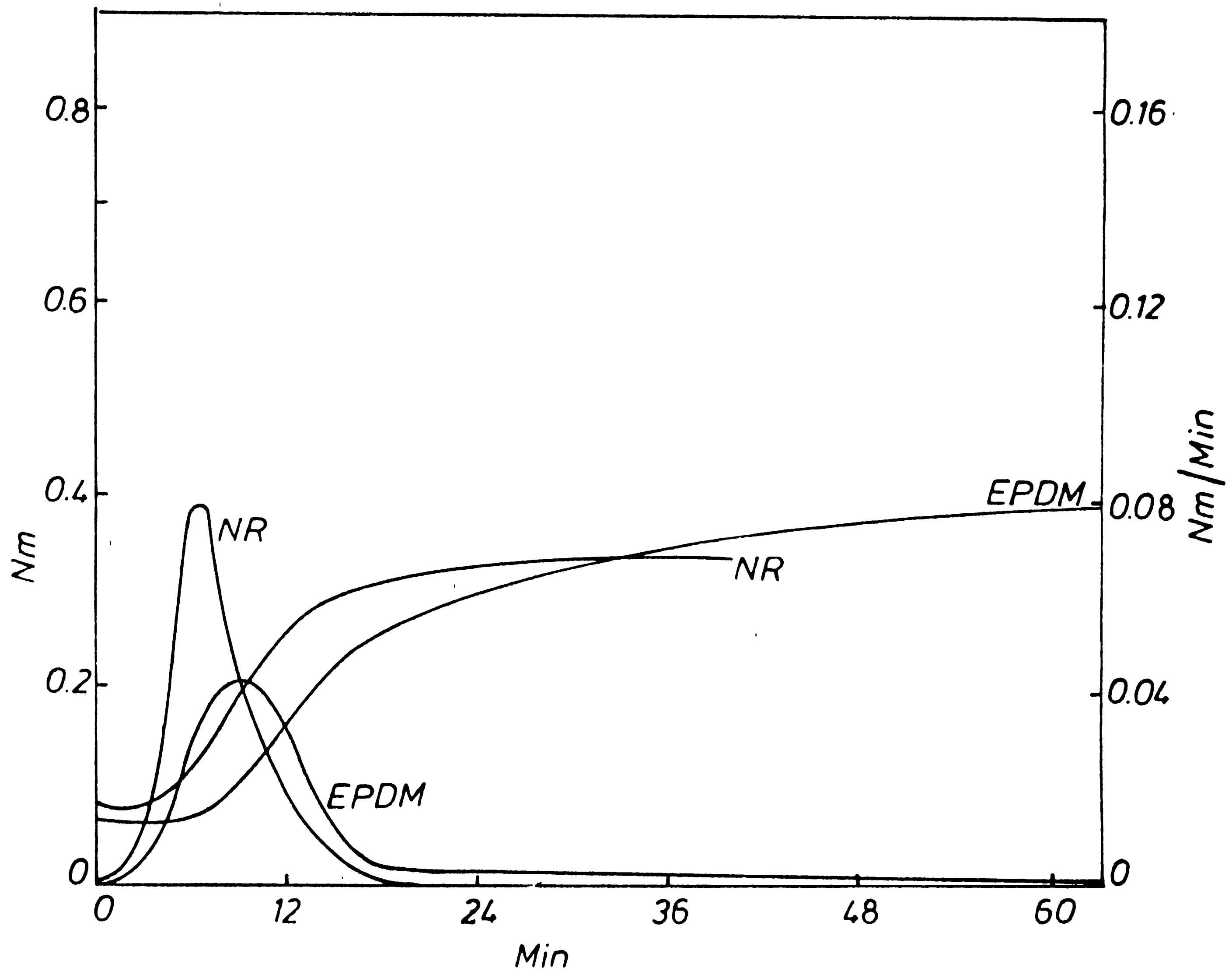

Fig.3.3 Cure curves and cure rate curves of NR and EPDM (Ref. Table 3.1).

and cures faster compared to EPDM. The cure characteristics of the different combinations of NR/EPDM blends are also given in Table 3.2. Since the scorch times and cure times of NR and EPDM are not very close, there should be some effect on the curing behaviour of NR even when EPDM is added to it in small amounts. However, instead of an expected increase in the scorch and cure times, the scorch safety decreases and the curing becomes faster in the case of the 85 NR/15 EPDM blend. Also, all the three types of blends of this composition show only marginal differences. This suggests that NR phase takes a larger share of the curatives due to preferential migration. This might have resulted due to the incompatibility of the rubbers and larger unsaturation of the NR phase which results in higher solubilities of the curatives.[11,12] The EPDM phase which is deprived of its share of curatives might be undercured. Of the three types of blends type 1 blend shows the least scorch safety and the fastest cure rate since NR can easily grab the maximum amount of curatives in this case. When higher percentages of EPDM are added the scorch safety further decreases and curing rate further increases. This is obviously the behaviour of NR alone with the additional amounts of CBS and TMTD. Figure 3.4 shows the cure curves of 50/50 blends of NR and EPDM. Clearly all the blends follow an NR behaviour with the type 1 blends showing fastest cure rate and least scorch safety.

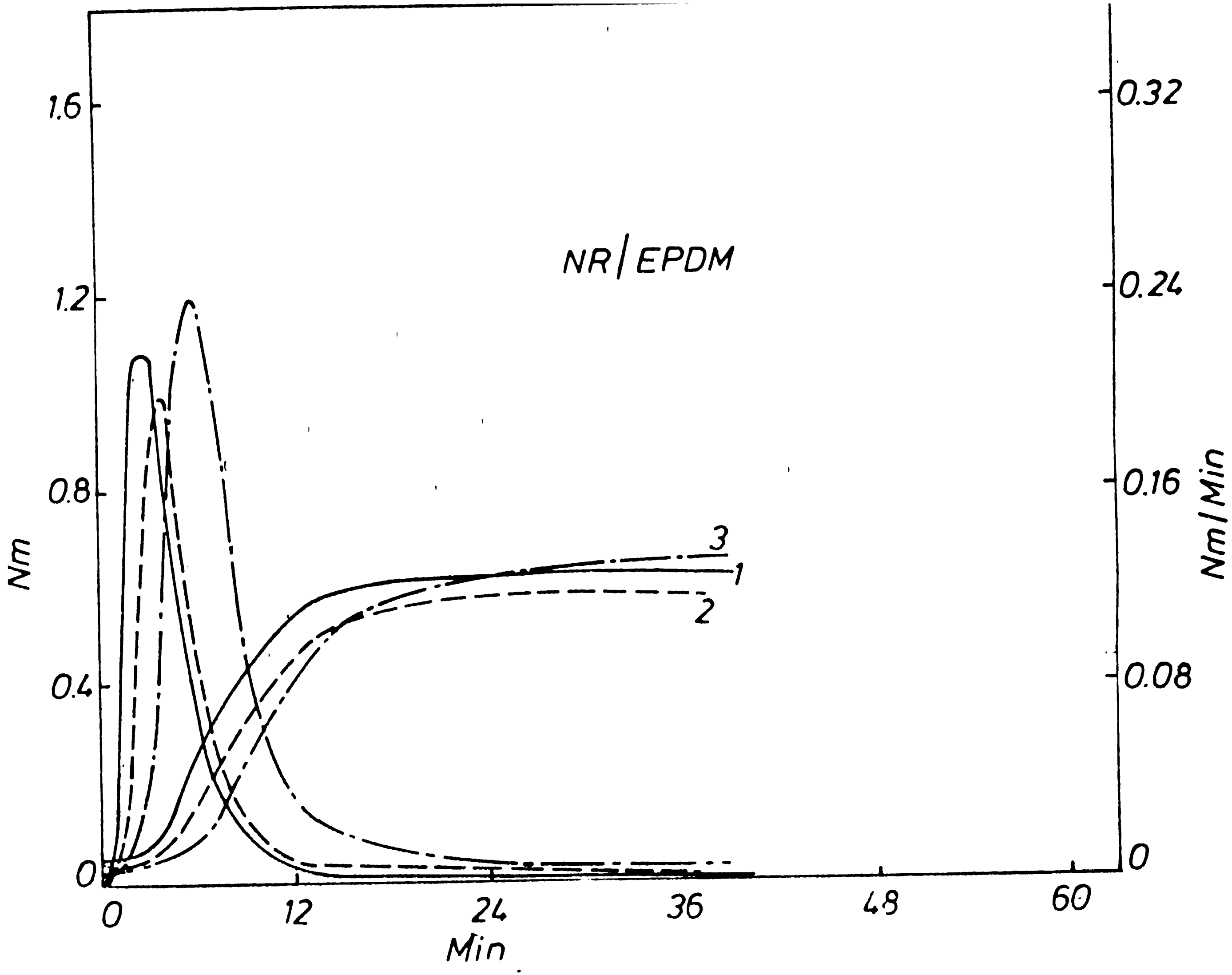

Fig.3.4 Effect of blending techniques on the curing behaviour of 50/50 NR/EPDM blend.

Figure 3·5 shows the cure curves of NR and NBR and the scorch times and cure times calculated from the cure curves are shown in Table 3.2. For the compounds selected for study NR has slightly better scorch safety and slightly higher cure time. The curing behaviour of the NR/NBR blends is interesting (Table 3.2). Eventhough NR and NBR are incompatible, they show a combined curing behaviour. In the case of 85 NR/15 NBR blend, the behaviour is more or less that of NR alone obviously due to the low concentration of NBR. However, type 1 blend shows slightly faster cure rate compared to that of NR alone as shown by the reduction in the scorch and cure times. This might be due to the presence of a small amount of TMTD in the NR phase which was intended for NBR. Since chances of such migration of TMTD are less in type 2 and 3 blends, their curing behaviour is similar to that of NR alone. For the 55 NR/45 NBR blend, the amount of NBR is sufficient to influence the curing behaviour of the blend. Type 1 blend obviously gets a good amount of TMTD in the NR phase and the blend shows NR behaviour at an enhanced rate. Blend 2 shows a combined behaviour of NR and NBR. This shows that there is no preferential migration of the curatives to any one phase. This might be because the tendencies for migration of the curatives to either NR or NBR are fairly balanced. The tendency for diffusion of the curatives to the NBR phase might be due to the polarity of NBR whereas that to the NR phase due to the comparatively

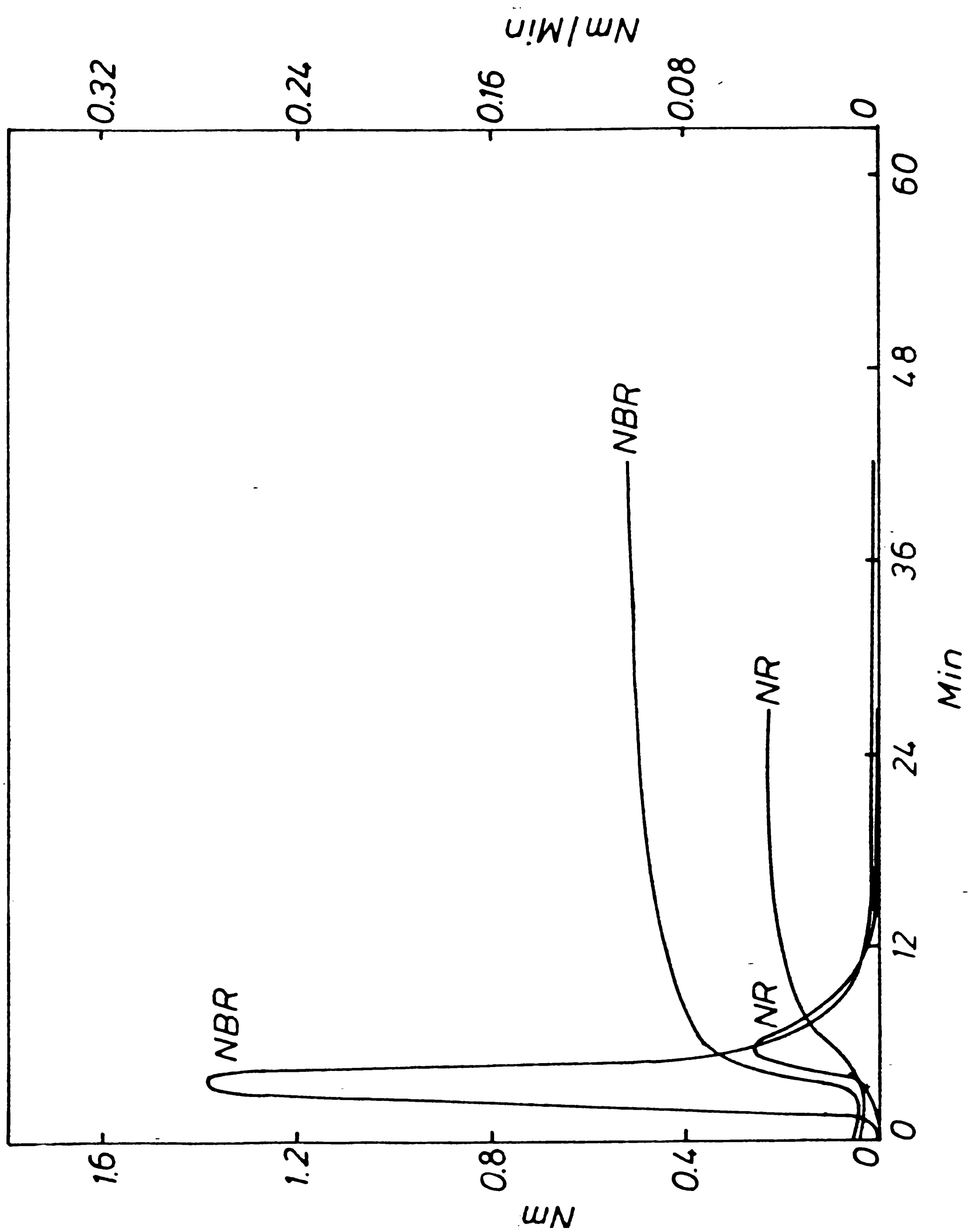

Fig.3.5 Cure curves and cure rate curves of NR and NBR (Ref. Table 3.1).

higher unsaturation of NR.[11-13] If the migration of the curatives to the two phases is thus delicately balanced the different blending methods can shift the distribution of curatives in the two phases and hence the blending methods are likely to produce the maximum possible effects in this blend. Type 3 blend shows an NBR behaviour which shows that NR is not able to get a good share of the curatives in this case. The 70 NR/30 NBR blend shows similar behaviour with less pronounced effects due to the low composition of NBR. Fig . 3.6 shows the cure curves of 50/50 blends of NR and NBR. The curing behaviour is similar to that of the 55 NR/45 NBR blend.

Tensile properties

The tensile strength and elongation at break of the vulcanizates of the rubbers and rubber blends are shown in Table 3.3. As expected, the SBR/BR blend might be existing in a covulcanized state.[14] The tensile strengths of the blends are close to the additive value of the individual rubbers. The elongation at break is also close to the arithmetic average.

In the case of NR/EPDM blends, EPDM might be forming the continuous phase due to its lower density.[15] In a two phase blend such as this where the rate of vulcanization in

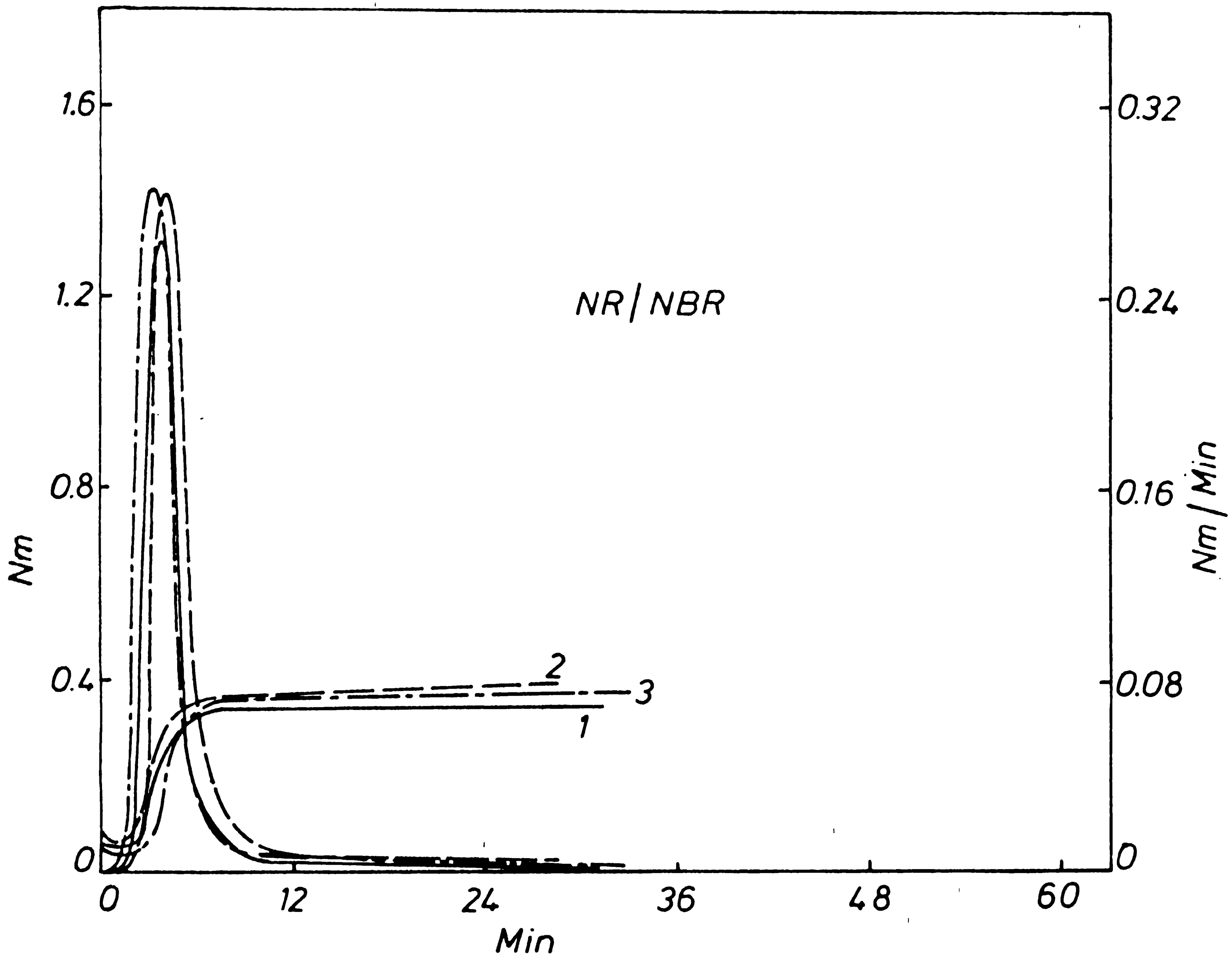

Fig.3.6 Effect of blending techniques on the curing behaviour of 50/50 NR/NBR blend.

Table 3.3 Tensile properties of the vulcanizates

Rubber/ Rubber blend	Tensile strength (MPa)	Elongation at break (%)
SBR	2.20	200
BR	1.50	150
<u>SBR/BR</u>		
1	1.80	160
2	1.82	170
3	1.82	172
NR	16.0	700
EPDM	1.50	150
<u>NR/EPDM</u>		
1	3.02	168
2	2.98	162
3	2.85	156
NR	16.0	700
NBR	1.50	150
<u>NR/NBR</u>		
1	12.10	653
2	11.0	673
3	10.0	693

one of the two phases (NR) is much higher than that of the other phase (EPDM), significant amount of interphase crosslinking also might be absent.[16] Hence the tensile properties are more likely to be affected by the EPDM phase and this might be the reason for the low value of the strength. The improvement in tensile strength over that of EPDM is only little and this seems to be largely influenced by the degree of crosslinking in the NR phase. The elongation at break is also similar to that of the EPDM phase which forms the continuous phase.

In the case of the NR/NBR blends, the tensile strengths observed are more than the arithmetic average of the constituents eventhough this is also likely to form a two-phase blend. The high values of strength suggest that NR forms the continuous phase or that both phases exist in the continuous state. Also, the rate of vulcanization in the two phases might be comparable which permits the formation of a significant amount of interphase crosslinks.[17] The exact value of the strength seems to be affected more by the degree of crosslinking in the NR phase which has a higher strength. The amount of curatives in the NR phase might be maximum in blend 1 which shows maximum strength and least in blend 3 which shows least strength. The elongation at break is again found to be more influenced by the continuous phase.

Conclusions

1. The distribution of curing agents largely depends on the nature of the rubbers. The curing agents tend to migrate preferentially to the rubber with higher unsaturation, or higher polarity.

2. Compatible blends are not affected much by the distribution of curatives. During vulcanization they are likely to attain a covulcanized state and hence their properties are nearly equal to the arithmetic average of the properties of the constituents.

3. If for a given binary rubber blend the tendency of the curatives for migration to the two rubbers is nearly same, the blending parameters can influence to a great extent the distribution of the curatives in the two rubbers and hence the mechanical properties of the blend.

4. The mechanical properties of the vulcanizates of elastomer blends seem to be most affected by the degree of cross-linking in the two rubbers and the rubber which forms the continuous phase.

II. Cure characteristics as an index of rubber-rubber miscibility

When the properties of rubber blends are examined the problem of compatibility invariably arises since the desirable properties of the constituent blend polymers are frequently lost on mixing which is usually ascribed to the lack of compatibility.[17] The various methods available for characterizing the compatibility of polymers include microscopy, thermal analysis, X-ray, dynamic mechanical properties etc. Only a few polymer blends are truly miscible on the molecular level which can be expected to appear and behave like single component polymers. Blends exhibiting partial miscibility are the most common. A given blend composition is sometimes labelled as either compatible or incompatible depending upon the experimental methods used for measuring the compatibility. For instance,observing a single T_g in dilatometric measurement, Bartenev[18] classified NR/BR blends as compatible, while NR/SBR blend was considered incompatible, by Dannis[19] since with DTA measurements he observed the retention of the individual transition peaks. Microscopic investigation of Walters and Keyte[20] showed that even NR/SBR, NR/BR and SBR/BR blends are heterogeneous mixtures. It may be inferred that the blends NR/SBR, NR/BR and SBR/BR, though practically miscible, are not miscible on the molecular level. However, it is worth knowing the relative miscibility of rubbers since the mechanical, thermal, rheological and other properties of a polymer blend depend strongly on its state of miscibility.

Conversion of raw rubber (blend) to a usable product is basically a three step process. Crosslinking agents, filler and other compounding ingredients are added, the compounded stock is shaped into the desired form and this form is heated (cured) to introduce crosslinks (covalent bonds) between the polymer chains to produce a three dimensional network with vastly improved properties. Before the actual curing, it is necessary to find the cure characteristics of the compound in conventional eqipments like Monsanto Rheometer, Goettfert Elastograph etc. An attempt has been made in this study to determine whether the state of miscibility of an elastomer blend could be predicted from the cure characteristics of the blend itself. The blends selected were the following.

SBR/BR NR/SBR NR/BR	Representing miscible systems[7,8]
NR/EPDM NR/NBR	Representing immiscible systems[7,8]

Only gum formulations based on the above rubber blends were selected to avoid the influence of filler distribution.

1. Variation of sulphur and accelerator on particular elastomer blends

Experimental

In this study 50/50 blends of SBR/BR and NR/EPDM were selected to represent the miscible and immiscible systems respectively. The amounts of sulphur and accelerator were varied, keeping the levels of the other ingredients constant to see whether any pattern could be observed in their cure characteristics. The formulations employed for the study are shown in Tables 3.4 and 3.5. The compounds were prepared on a Brabender Plasticorder model PL 3S at about 50°C, using roller type rotors at a speed of 30 rpm. The elastomer blends were prepared initially and then the other ingredients were added as per the ASTM D 3182 (1983). The compounds were then sheeted out on a laboratory mixing mill and the cure curves were taken on a Goettfert Elastograph model 67.85 at 150°C.

Results and Discussion

The cure characteristics of the mixes are also shown in Tables 3.4 and 3.5. The curing becomes faster with increase in either sulphur or accelerator as seen from the reduction in the optimum cure times both for the SBR/BR and NR/EPDM blends. The scorch safety also decreases with

Table 3.4 Formulations and cure characteristics of compounds (variation of concentration of curatives)

Formulation	A	B	C	D	E	F	G	H
SBR	50	50	50	50	50	50	50	50
BR	50	50	50	50	50	50	50	50
ZnO	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
CBS	0.8	0.8	0.8	0.8	0.6	0.8	1.0	1.2
Sulphur	1.75	2.0	2.5	2.75	2.25	2.25	2.25	2.25
<u>Cure characteristics</u>								
Scorch time, min.	11.5	11	10.5	10	11.5	11	10.5	10
Cure time, min.	25.5	24	22.5	21	27	24.5	22.5	19
Maximum torque, Nm	0.42	0.50	0.58	0.64	0.55	0.57	0.60	0.625

Table 3.5 Formulations and cure characteristics of compounds (Variation of concentration of curatives)

Formulation	A	B	C	D	E	F	G	H
NR	50	50	50	50	50	50	50	50
EPDM	50	50	50	50	50	50	50	50
ZnO	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
CBS	1	1	1	1	0.8	1.2	1.4	1.6
Sulphur	1.75	2.0	2.25	2.5	2.25	2.25	2.25	2.25
<u>Cure characteristics</u>								
Scorch time, min.	6	5.5	5.0	4.5	6	5.5	5.0	4.5
Cure time, min.	14	12	11	9	14	12	11.5	8.5
Maximum torque, Nm	0.15	0.16	0.17	0.18	0.17	0.19	0.225	0.25

increase in sulphur or accelerator as expected for both the blends. The maximum torque, a measure of the crosslink density increases steadily with increase in either sulphur or accelerator. Since almost similar behaviour is exhibited by both the blends of SBR/BR and NR/EPDM, this type of study may not be much useful in deciphering the compatibility of constituent elastomers. SBR/BR blends being compatible the state of cure in the two rubbers might be comparable. Since a miscible system behaves almost similar to that of a single component, a smooth variation in the cure characteristics of the blend with variation in sulphur or accelerator is expected. In the NR/EPDM blend the state of cure in the two phases might not have reached optimum levels. Vulcanization will eventually leave one phase overcured and the other undercured. The incompatibility of the constituents and the large difference in polarity of the rubbers might be contributing to this effect. The study shows that the imbalance in the distribution of the curatives and curing of the two phases is more or less steadily maintained when the amounts of sulphur and accelerator are varied.

2. Variation of the polymer composition of elastomer blends at constant curatives level

Experimental

In this study also the SBR/BR system was selected to represent a miscible blend and the NR/EPDM system to represent an immiscible blend. The polymer composition in the blends was varied keeping the levels of sulphur and accelerator same to study its effect on the cure characteristics. The formulations employed for the study are shown in Table 3.6. The compounds were prepared and the cure characteristics were determined as described in section 1.

Results and Discussion

The cure characteristics of the mixes are also shown in Table 3.6. Addition of BR to SBR or SBR to BR produces smooth variations in the cure characteristics. BR shows better scorch safety than SBR but has slightly lower cure time. Hence addition of BR to SBR increases the scorch time but reduces the cure time. Similarly addition of SBR to BR reduces the scorch safety but increases the cure time. Thus over the whole range of composition of SBR/BR blends we have a smooth variation of the curing behaviour with the behaviour of SBR at one end and that of BR at the other. It may be inferred that addition of a compatible elastomer will produce smooth variations in the cure characteristics of a given elastomer. This could be used as an index in measuring compatibility.

In the case of NR and EPDM, the cure characteristics are widely apart when the same composition of curatives is

Table 3.6 Formulations and cure characteristics of compounds (Variation of polymer composition)

	SBR/BR blend						NR/EPDM blend				
Formulation	A	B	C	D	E		F	G	H	I	J
SBR	100	75	50	25	0	NR	100	75	50	25	0
BR	0	25	50	75	100	EPDM	0	25	50	75	100
ZnO	4	4	4	4	4	ZnO	4	4	4	4	4
Stearic acid	2	2	2	2	2	Stearic acid	2	2	2	2	2
CBS	1	1	1	1	1	CBS	1.2	1.2	1.2	1.2	1.2
Sulphur	2.25	2.25	2.25	2.25	2.25	Sulphur	2.25	2.25	2.25	2.25	2.25
Cure characteristics											
Scorch time, min.	10	10.5	11.0	12.0	13.5		5.0	4.5	5.5	12.5	--
Cure time, min.	25	24.7	24.5	24.3	24.0		7.5	7.0	12.0	21.5	--

employed for both of them. In fact the EPDM phase does not show any appreciable curing. The cure characteristics of the blends are surprising in that the 75 NR/25 EPDM blend shows a higher curing rate than that of NR alone as indicated by the lower scorch time and cure time. This is obviously the curing of the NR phase alone since this phase might be getting a larger share of curatives (more than 75% of the curatives) this time than when it was alone. The crosslinking in the EPDM phase might not have reached optimum level since it is deprived of even its share of curatives. However, the curing of 50 NR/50 EPDM blends is slower than that of NR alone. This shows that NR is not getting its original share when it was all by itself. This might be because the EPDM phase forms the continuous phase in this matrix due to its lower density and hence the discrete NR phase fails to get a good share of the curatives. It may be observed that there is no regular pattern in the curing behaviour of the blend with progressive addition of one of the components. This may be taken as a general rule of incompatible blends and hence the effect of varying polymer composition on the curing behaviour of elastomer blends might be a useful way of predicting the comparative miscibility between the constituent elastomers.

3. Cure characteristics as an index of the compatibility between elastomers

The following elastomer blends were used in this study:

NR/SBR	Representing miscible
NR/BR	systems
NR/EPDM	Representing immiscible
NR/NBR	systems

Experimental

Two blends were prepared with each of the synthetic rubbers (SBR, BR, EPDM and NBR) and NR by keeping the amount of the synthetic rubbers at 20% and 40% of the total elastomer weight. An efficient vulcanizing (EV) compound and a semi-efficient vulcanizing (semi-EV) compound were prepared with each of the elastomer combinations. The formulations used are shown in Tables 3.7 and 3.8. Blends were prepared on the Brabender Plasticorder as described under section 1. The cure curves of the compounds were taken on a Monsanto Rheometer model R 100 at 150°C.

Table 3.7 Formulations and cure characteristics of compounds (Semi-EV system)

Formulation	A	B	C	D	E	F	G	H	I
NR	100	80	80	80	60	80	60	80	60
SBR	--	20	40	--	--	--	--	--	--
BR	--	--	--	20	40	--	--	--	--
EPDM	--	--	--	--	--	20	40	--	--
NBR	--	--	--	--	--	--	--	20	40
ZnO	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CBS	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
TMTD	0.25	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
Cure characteristics									
Scorch time, min.	3.5	5.0	6.0	4.5	5.0	3.5	4.0	2.4	4.5
Cure time, min.	6.5	7.0	8.5	6.5	7.0	5.5	6.0	4.5	6.5

Table 3.8 Formulations and cure characteristics of compounds (EV system)

Formulation	A	B	C	D	E	F	G	H	I
NR	100	80	80	80	80	80	80	80	80
SBR	--	20	40	--	--	--	--	--	--
BR	--	--	--	20	40	--	--	--	--
EPDM	--	--	--	--	--	20	40	--	--
NBR	--	--	--	--	--	--	--	20	40
ZnO	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
Stearic acid	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
TMTD	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50
Sulphur	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Cure characteristics									
Scorch time, min.	2.2	2.50	2.50	2.50	2.50	2.20	2.50	2.50	2.50
Cure time, min.	7.0	8.0	8.0	8.0	8.0	6.2	8.5	8.5	7.0

Results and Discussion

The cure curves of the compounds are shown in Figs.3.7-3.10. and the cure characteristics of the compounds calculated from the cure curves are shown in Tables 3.7 and 3.8.

Semi-EV system

A comparison of the cure curves of NR with those of NR/SBR blends (Figs.3.7 and 3.8) show that the curing becomes slower with increase in the SBR content. This is expected since SBR vulcanizes more slowly than NR, and it requires higher acceleration.[21] A regular pattern is visible in the cure characteristics (Table 3.7) when the amount of SBR is increased. This can be expected to be due to the compatibility of the elastomers. The addition of BR also shows the same pattern of change but with less pronounced effects. This is also expected since BR is also fairly compatible with NR and the cure characteristics of BR are similar to those of SBR but the sulphur and accelerator requirements are intermediate between those of NR and SBR.[21] The NR/EPDM blends are found to cure faster than NR (Figs.3.7 and 3.8 and Table 3.7). This behaviour seems to be abnormal since EPDM has a much slower cure rate than NR.[22] This might indicate that the NR phase grabs a major

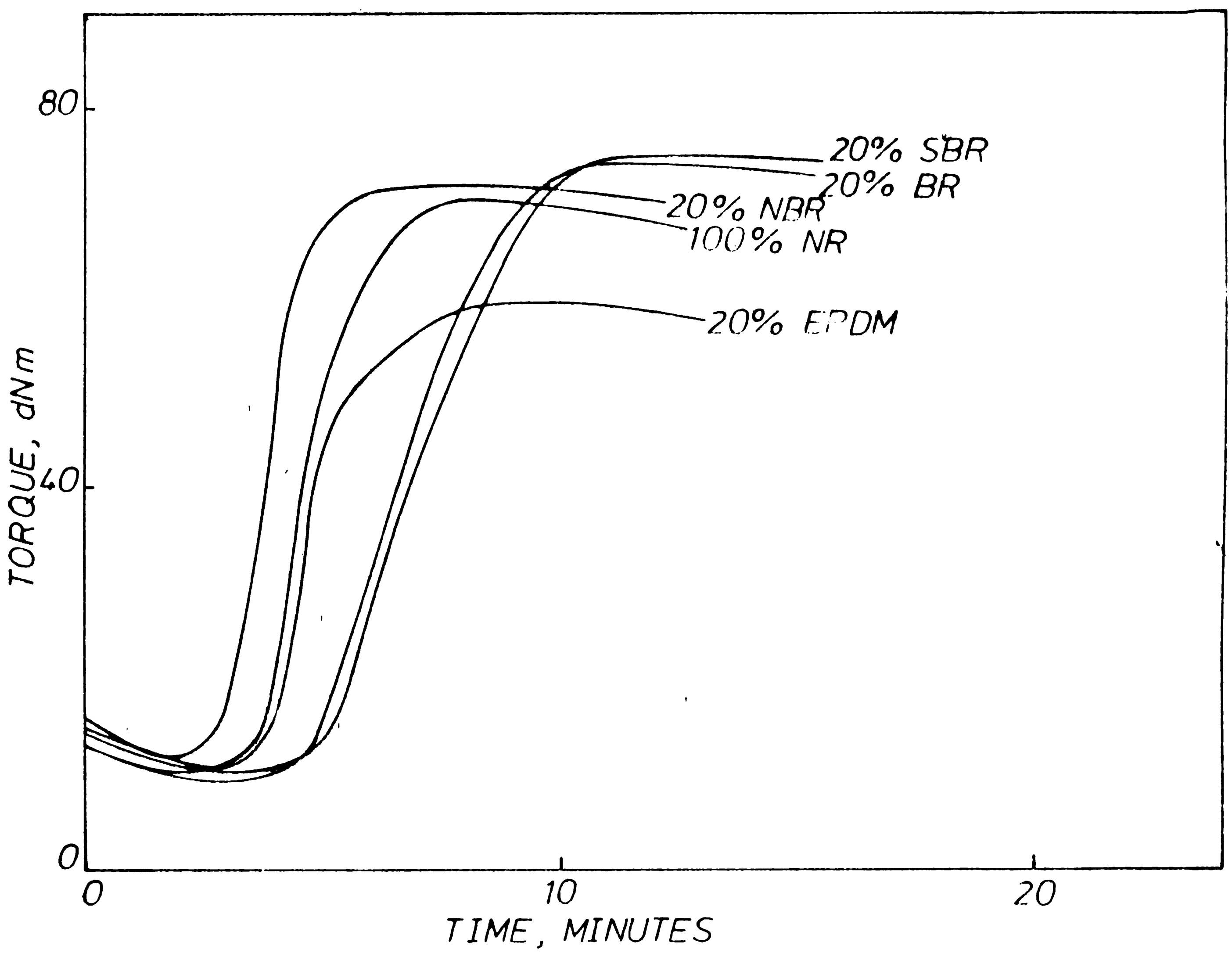

Fig.3.7 Cure curves of NR and blends of NR with 20% synthetic rubbers (Semi EV system).

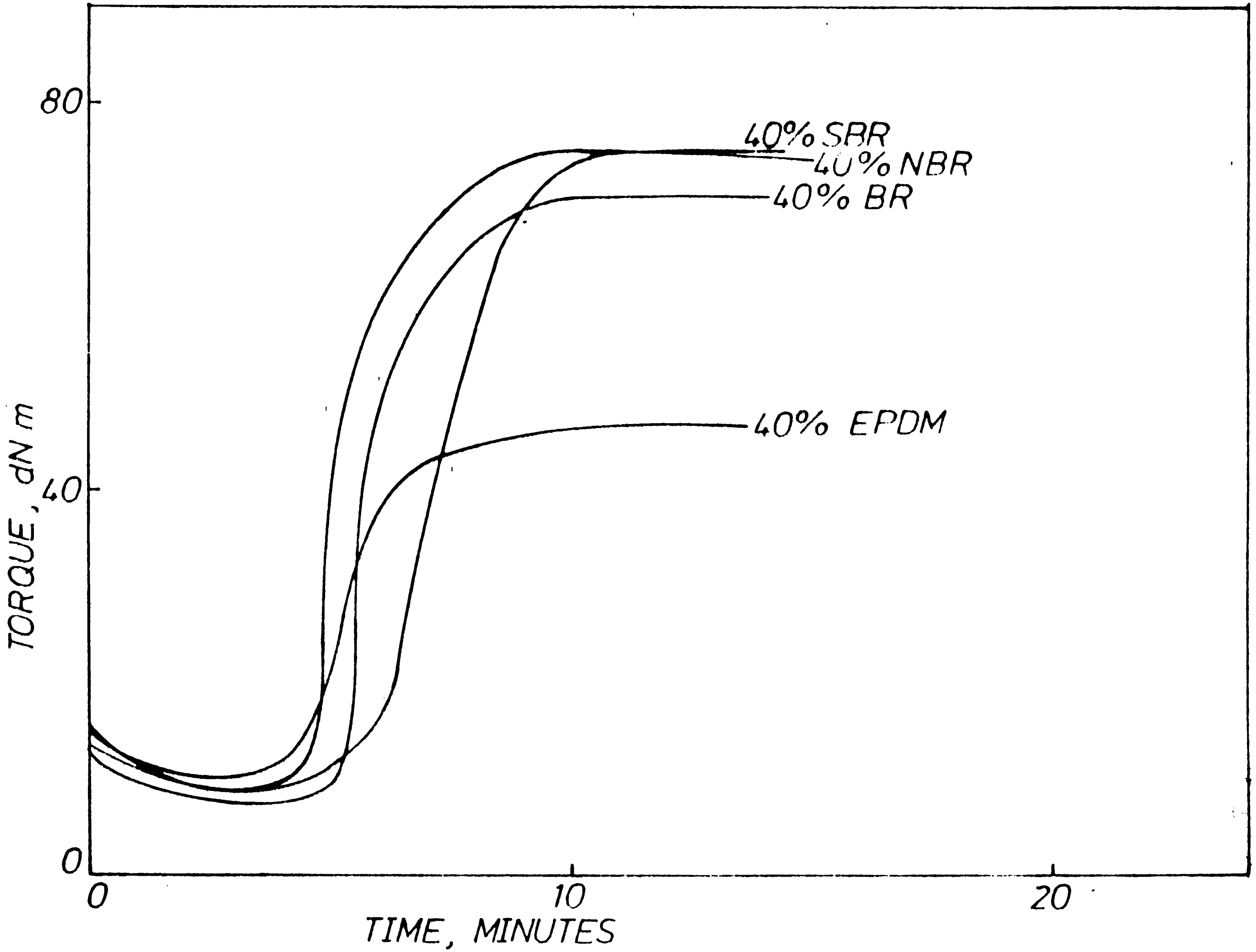

Fig.3.8 Cure curves of blends of NR with 40% synthetic rubbers (Semi EV system).

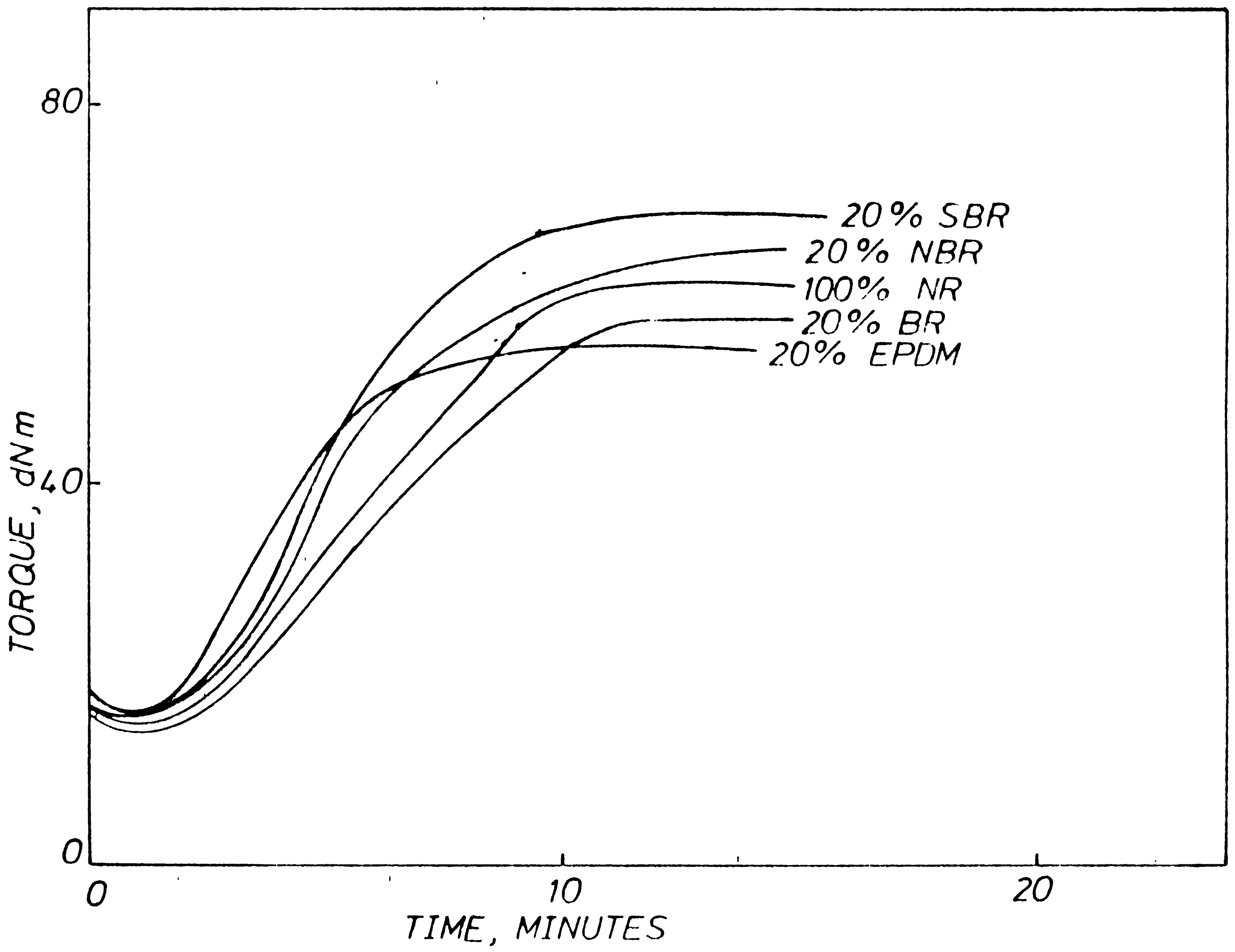

Fig.3.9 Cure curves of NR and blends of NR with 20% synthetic rubbers (EV system).

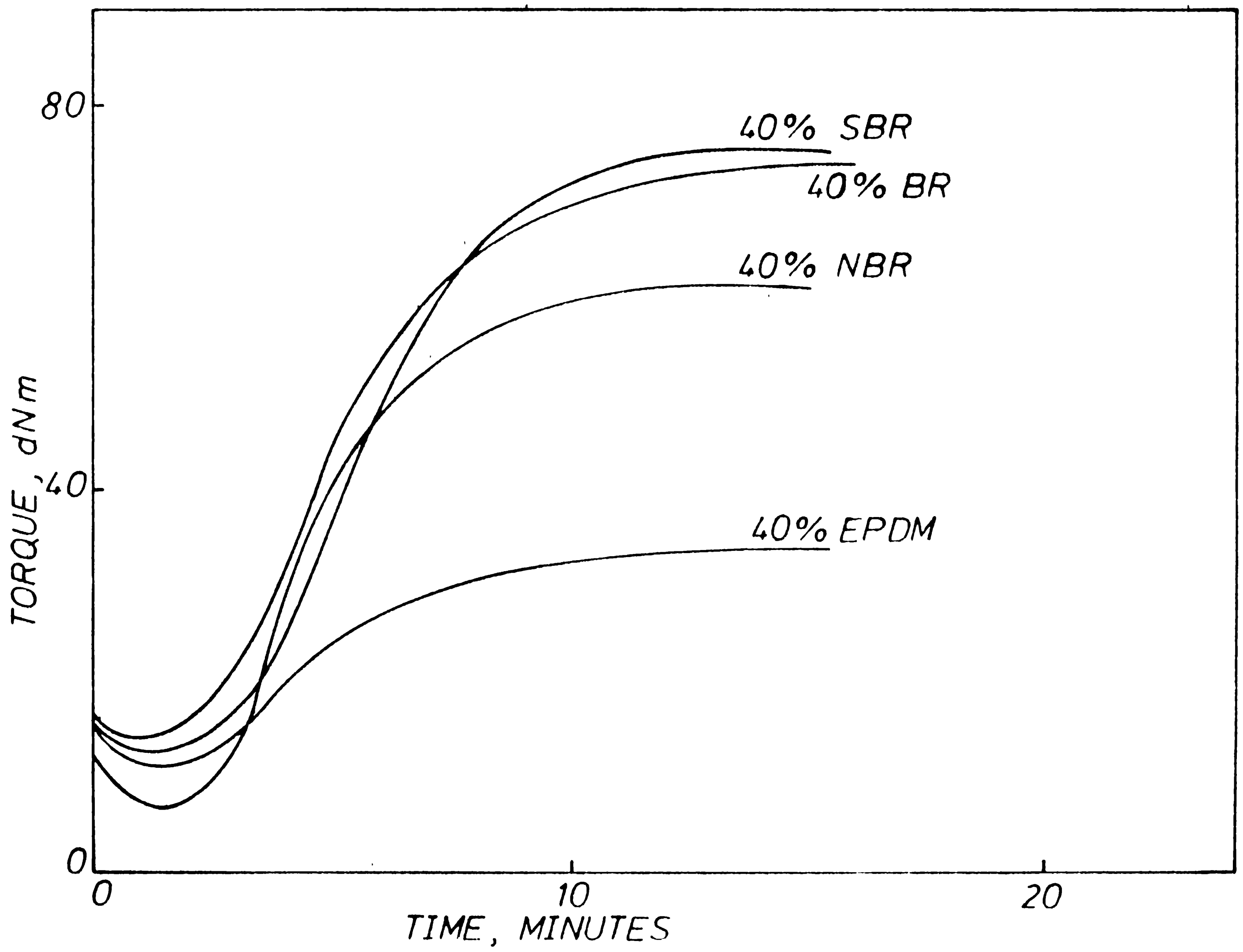

Fig.3.10 Cure curves of blends of NR with 40% synthetic rubbers (EV system).

share of curatives and hence is getting cured faster. This also can be expected to result from the incompatible nature of the rubbers and the large differences in unsaturation between them. Also, a definite pattern of change in the cure characteristics with varying amounts of EPDM is also not visible. The curing behaviour of NBR is similar to that of SBR, but requires less sulphur and more accelerator.[23] However, the curing behaviour of the NR/NBR blend also does not belong to a set pattern. Curing of NR becomes faster with addition of 20% NBR (Figs.3.7 and 3.8). This behaviour is similar to that of the NR/EPDM blend and might be due to the larger share of curatives taken by the NR phase in turn due to the incompatibility of the rubbers and the large difference in polarity between them.

EV system

The behaviour of the different blends is more or less similar to that of the semi-EV system (Figs.3.9 and 3.10). NR/SBR and NR/BR blends show a clear pattern of increase in scorch and cure times of NR with addition of SBR or BR (Table 3.8). However, the variations between SBR and BR are less pronounced in this case. The cure characteristics of NR/EPDM and NR/NBR blends again display an irregular behaviour since there is no pattern when increasing amounts of EPDM or NBR are added to NR.

Conclusions

The study shows that the curing behaviour of elastomer blends could be employed as an index of measuring the relative miscibility between the constituent elastomers. If the compatibility between two elastomers A and B is to be determined, small amounts of B may be added to A (or vice-versa) keeping the amount of curatives constant and the cure characteristics (scorch times and optimum cure times) of the blends may be compared with those of A. If there is a regular pattern in the curing behaviour of the blends (either decrease or increase in cure rates) compared to that of A and if the cure characteristics of the blends are in between those of the individual characteristics of A and B then the elastomers may be considered to be fairly compatible. The amount of B added to A may be kept low since phase inversion behaviour of the blends might produce unpredictable behaviour.

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Chapter 4

STUDIES ON NATURAL RUBBER/STYRENE-BUTADIENE RUBBER BLEND

STUDIES ON NATURAL RUBBER/STYRENE-BUTADIENE RUBBER BLEND

A common composite article such as a tyre is a mixture of wire (metal), textile cord (organic fibre) and rubber compounds. The rubber compound itself is a mixture of elastomer, filler and curatives. Moreover, the elastomer part may be a mixture of two or more rubbers. Fig.4.1 shows the properties of 4 different types of rubber related to tyre properties, expressed in terms of their glass transition temperature (T_g).[1] It may be seen that cis-polybutadiene (BR) has the lowest wet grip and air impermeability but has the best low temperature and heat build up performance. Chlorobutyl (Cl IIR), however, has very good wet grip and air impermeability properties but poor (high) heat build up and poor low temperature performance.

Natural rubber (NR) and styrene-butadiene rubber (SBR) are the world's leading general purpose rubbers and about two-thirds of their total output goes into tyres but they also find widespread use in many other areas of rubber goods production such as belting, flooring and mats, hose, shoe soles and heels and many other industrial and domestic applications. In India, a larger amount of NR is used than SBR because NR is readily available while in countries like USA a larger amount of SBR is used. While passenger car tyres may be made entirely from SBR, in commercial vehicle tyres NR/SBR blends are used and

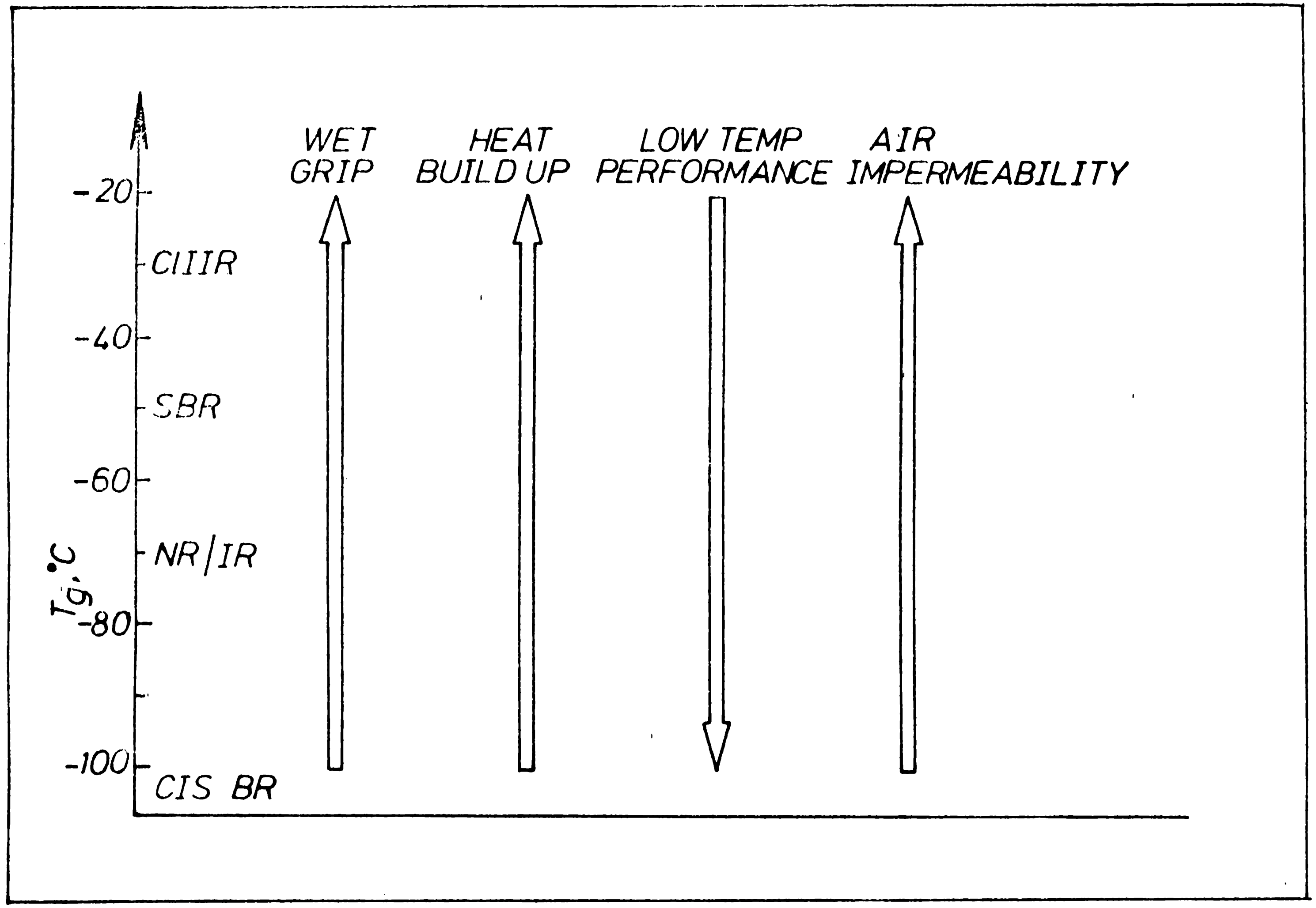

Fig.4.1 Some important tyre properties of rubbers Vs. glass transition temperature (T_g).

the natural rubber content generally increases with the size of the tyre. In these applications the requirements of maximum wear resistance, good resistance to tread groove cracking and rib tearing plus minimum heat generation can be met only by natural rubber.[2] The tread wear and wet skid resistance of SBR elastomers and blends is dealt with by Kienle.[3] Information on the practical aspects of NR/SBR blends were reported by Springer,[4] including flex cracking, processing and vulcanizing. Fatigue characteristics of mixtures of SBR and NR have been investigated by Fugimoto.[5] Because of their allround importance this study was undertaken on NR/SBR blends.

Like NR, SBR is an unsaturated hydrocarbon polymer. Hence unvulcanized compounds will dissolve in most hydrocarbon solvents and other liquids of similar solubility parameters while cured stocks will swell extensively.[6] Both materials will undergo many olefinic type reactions such as oxidation, ozone attack, halogenation, hydrohalogenation and so on, although the activity and detailed reactions differ because of the presence of the adjacent methyl group in the natural rubber molecule. Both rubbers may be reinforced by carbon black and neither can be classed as a heat-resistant rubber.

Compared with natural rubber, raw SBR is more uniform in many cases. It is more uniform in quality and compounds are more consistent in both processing and product properties. It is more uniform in the sense it usually contains fewer undesired contaminants. SBR does not breakdown to any great extent on mastication. The synthetic material is usually supplied at a viscosity considered to provide the best balance between 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. However, mill mixing of NR is usually easier and the synthetic rubber lacks tack and green strength and this is of consequence in tyre building, particularly with radial tyres.

While natural rubber is crystalline with a T_m of about 50°C, SBR is amorphous. Although crystallinity in natural rubber is reduced by the presence of crosslinks and fillers and other additives, it still crystallizes on extension giving a rubber of good tensile strength, even with gum stocks. On the other hand gum vulcanizates of the amorphous SBR are weak and it is essential to use reinforcing fillers such as fine carbon blacks to obtain products of high strength. Black-reinforced SBR vulcanizates do, however, exhibit very good abrasion resistance, generally being superior or comparable to natural rubber compounds above 14°C. On the other hand they have lower resilience and resistance to tearing and cut growth. The ageing behaviour of SBR is quite different from that of natural rubber: the synthetic material tends to crosslink rather than exhibit chain scission on oxidation.[7]

In the 1960s, considerable work was undertaken by the Malaysian Rubber Producers Research Association to study the nature of sulphur crosslinks in natural rubber vulcanizates. It was found that whereas conventional accelerator-sulphur systems led to substantial amounts of disulphidic and polysulphidic linkages, there were very few monosulphidic crosslinks. On the other hand, if the sulphur content was reduced and the accelerator content boosted, the vulcanizates had a much higher proportion of monosulphidic crosslinks. In the case of natural rubber, the higher monosulphidic content led to a distinct improvement in resistance to thermal and oxidative ageing but at the expense of a much reduced flex life.[8] Such higher accelerator-low sulphur systems are frequently referred to as efficient vulcanization systems (EV systems). Subsequent studies using SBR[9] have shown several interesting features which may briefly be summarised as follows.

1. Conventional SBR vulcanizates have a monosulphidic crosslink content similar to that of an EV natural rubber system.

2. The replacement of a conventional cure by an EV curing system also increases the monosulphidic content with SBR, in this case to a value about twice that for a natural EV system.

3. Whereas the crosslink density of conventionally cured SBR vulcanizates increases on ageing at elevated temperatures (e.g. 110°C) the EV-cured material has a stable crosslink density at the same temperature.

4. The reduction in fatigue life shown with natural rubber EV systems is not duplicated with SBR. Indeed EV SBR compounds after ageing show much better fatigue resistance than conventional compounds after ageing.

In general it would appear that use of EV systems in SBR leads to a lower aged modulus and hardness, better retention of elongation at break and a general overall improvement in compression set and heat build-up. In practice, because of the high cost of accelerators, true EV systems are not often used with SBR. Semi-EVs (that is of intermediate accelerator-sulphur ratios) that provide a useful compromise between cost and performance are commonly employed.

From the foregoing discussion it is clear that the network structure of vulcanizates formed and its effect on the physical properties varies considerably with the nature of elastomers.[10] While some amount of literature is available on the influence of network structure on the physical properties of NR vulcanizates, similar information on synthetic rubber vulcanizates is meagre. Thus in designing suitable formulations for blends of elastomers like NR and SBR, careful consideration has to be given to prepare optimum network structures suitable for particular applications. However, no definite rules are available for designing compounds of NR/SBR blends for achieving a set of vulcanizate properties. SBR is slower curing than NR and higher accelerator levels are necessary in order to obtain equivalent cure times.[11,12] Based on this simple statement, compounds for NR/SBR blends are now designed by giving sulphur and accelerators at intermediate levels between those required for NR and SBR. This is far from satisfactory since the curatives may be unproportionally distributed between NR and SBR and the network structures formed in the two elastomers may be different. In this study different formulations are employed for a 50/50 NR/SBR blend by varying the amounts of sulphur and accelerator and the cure characteristics and physical properties of the vulcanizates are compared. The network structure of the vulcanizates is also deciphered by chemical probes. During service the degree of crosslinking may increase or decrease depending upon the elastomer, temperature and other factors with a possible rearrangement in the nature of crosslinks.[10] To understand the behaviour of NR/SBR blends in service the vulcanizates were subjected to accelerated thermal ageing for a specified period of time and then the physical properties again evaluated. The network structure was further examined by chemical probes to observe the changes occurring during ageing.

I. Studies on 50/50 blends of NR and SBR without fillers

Experimental

In this study fillers were not used to avoid the effect of filler distribution between the two rubbers. Both conventional and semi-EV curing systems were employed for study. The formulations used are shown in Tables 4.1 and 4.2. The compounds were prepared on a laboratory mixing mill. The cure curves of the mixes were taken at 150°C on a Monsanto Rheometer model R 100.

The compounds were vulcanized upto the respective optimum cure times on a steam heated laboratory hydraulic press. The tensile properties of the vulcanizates were determined according to ASTM D 412 (1980) on a Zwick universal testing machine. The compression set and hardness of the vulcanizates were determined according to ASTM D 395 (1969) and ASTM D 2240 (1968) respectively. The ageing resistance

Table 4.1 Formulations and cure characteristics of gum NR/SBR compounds (conventional system)

Formulation	A	B	C	D	E	F	G	H
NR	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
SBR	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
CBS	0.8	0.8	0.8	0.8	0.6	1.0	1.2	1.4
Sulphur	1.8	2.0	2.5	3.0	2.0	2.0	2.0	2.0
<u>Cure characteristics</u>								
Scorch time, min.	11.0	10.5	10.5	10.5	12.5	12.0	12.0	11.5
Optimum cure time, min.	21.0	20.0	19.5	19.5	24.5	18.5	18.0	16.5
Maximum torque, d.Nm	59.0	63.0	72.0	79.0	60.0	67.0	71.0	74.0
Reversion, number of units dropped in 5 min.	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

Table 4.2 Formulations and cure characteristics of gum NR/SBR compounds (Semi EV system)

Formulation	I	J	K	L	M	N	O	P
NR	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
SBR	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
CBS	1.2	1.2	1.2	1.2	1.0	1.25	1.5	2.0
Sulphur	1.2	1.5	1.8	2.1	1.6	1.6	1.6	1.6
<u>Cure characteristics</u>								
Scorch time, min.	9.5	12.0	12.5	11.0	14.5	14.0	13.5	12.0
Optimum cure time, min.	19.5	19.5	18.5	17.5	25.0	21.0	20.5	18.5
Maximum torque, d.Nm	55.0	66.0	68.0	77.0	61.0	67.0	69.0	73.0
Reversion, number of units dropped in 5 min.	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

of the vulcanizates was determined by keeping them at 100°C for 48 hours in an air oven and then measuring the retention in physical properties.

The total crosslink density and the percentage of polysulphidic, disulphidic and monosulphidic linkages were determined as per the procedures outlined in Chapter 2 from the swelling data of the vulcanizates in benzene. Free sulphur was determined iodometrically by converting it to sodium thiosulphate according to ASTM D 297-72A. Zinc sulphide sulphur was determined iodometrically from the formation of cadmium sulphide as described in BS 902, pt 1310 (1958).

Results and Discussion

The cure curves of the compounds are shown in Figs.4.2-4.5. The cure characteristics calculated from the cure curves are also shown in Tables 4.1 and 4.2. Increasing the amount of CBS at constant sulphur level reduces the scorch safety and speeds up vulcanization both in the conventional and semi-EV systems as expected. Variation of sulphur at constant accelerator level also produces similar behaviour but with less pronounced effects. The maximum torque, a measure of the crosslink density, increases steadily with increase in sulphur or CBS both in the conventional and

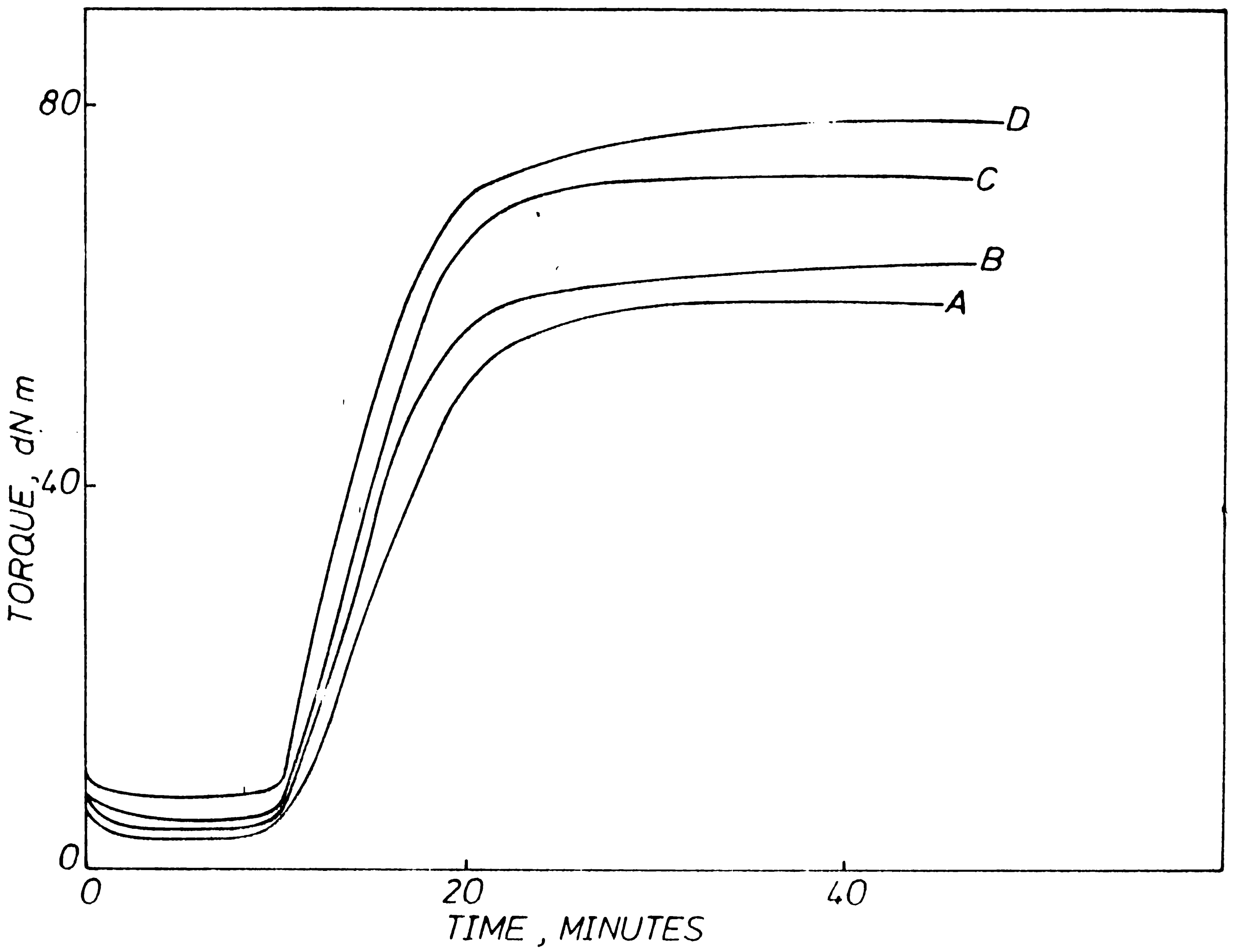

Fig.4.2 Effect of sulphur variation on the curing behaviour of 50/50 NR/SBR blend - Conventional system (Ref.Table 4.1).

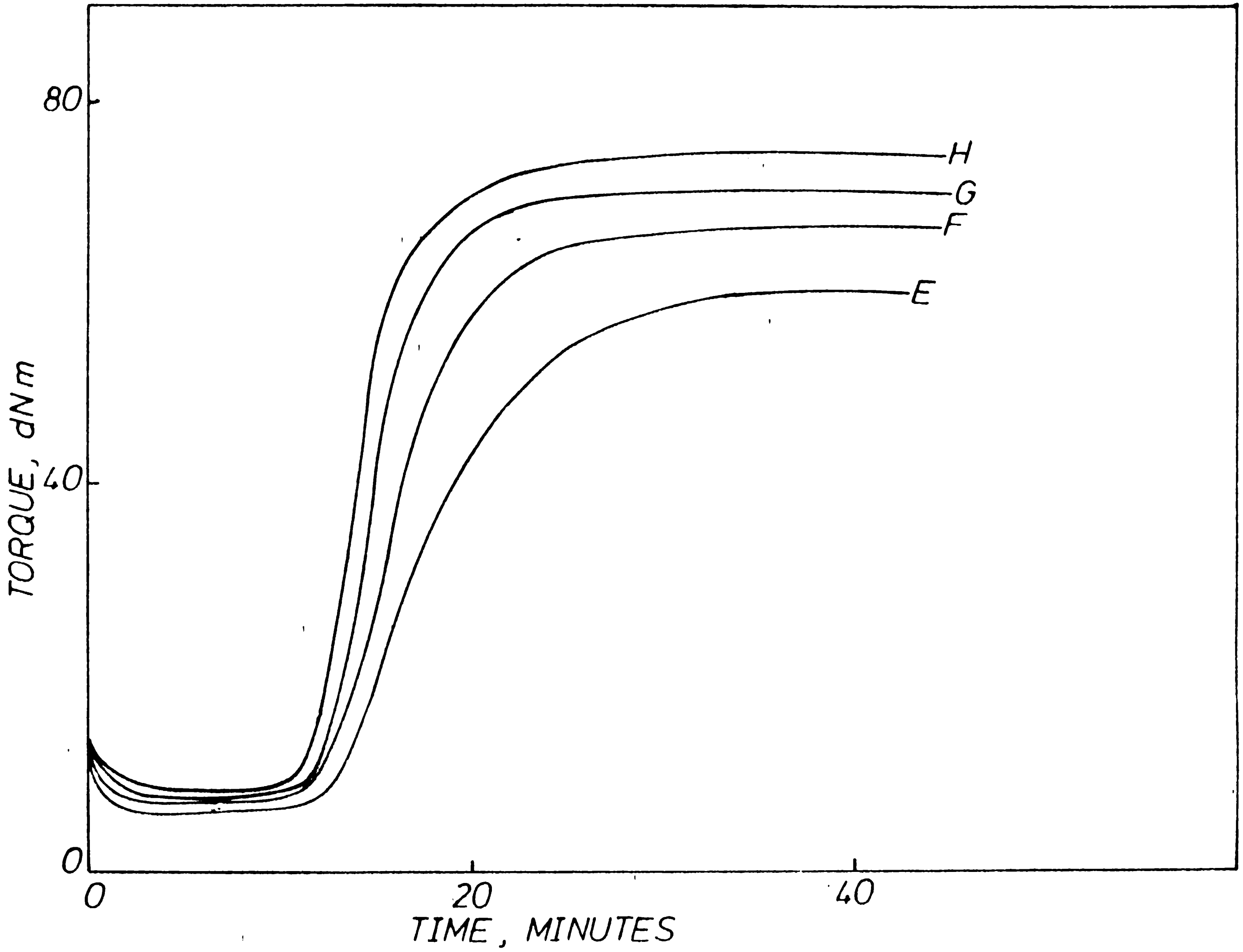

Fig.4.3 Effect of accelerator variation on the curing behaviour of 50/50 NR/SBR blend - Conventional system (Ref.Table 4.1).

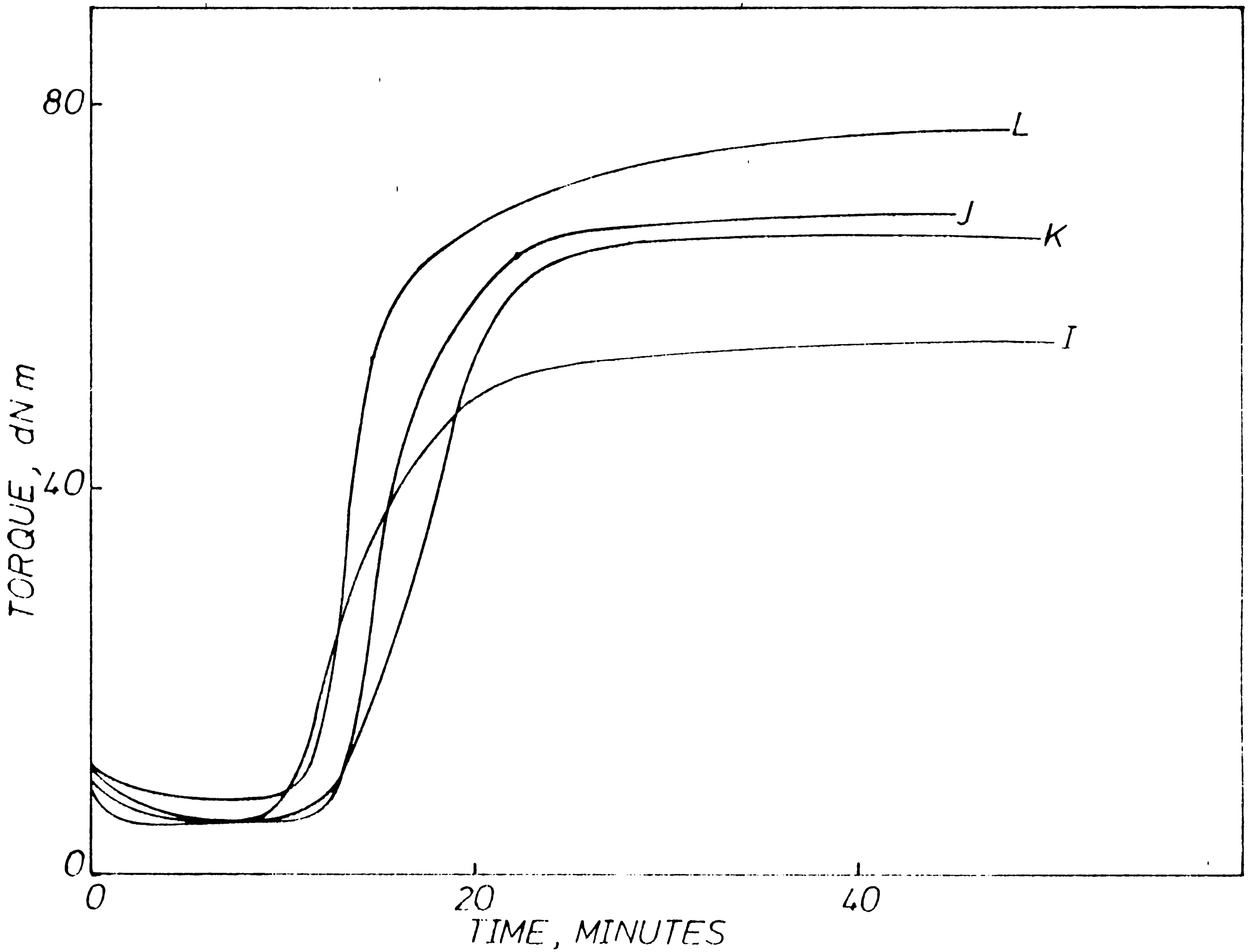

Fig.4.4 Effect of sulphur variation on the curing behaviour of 50/50 NR/SBR blend - Semi EV system (Ref.Table 4.2).

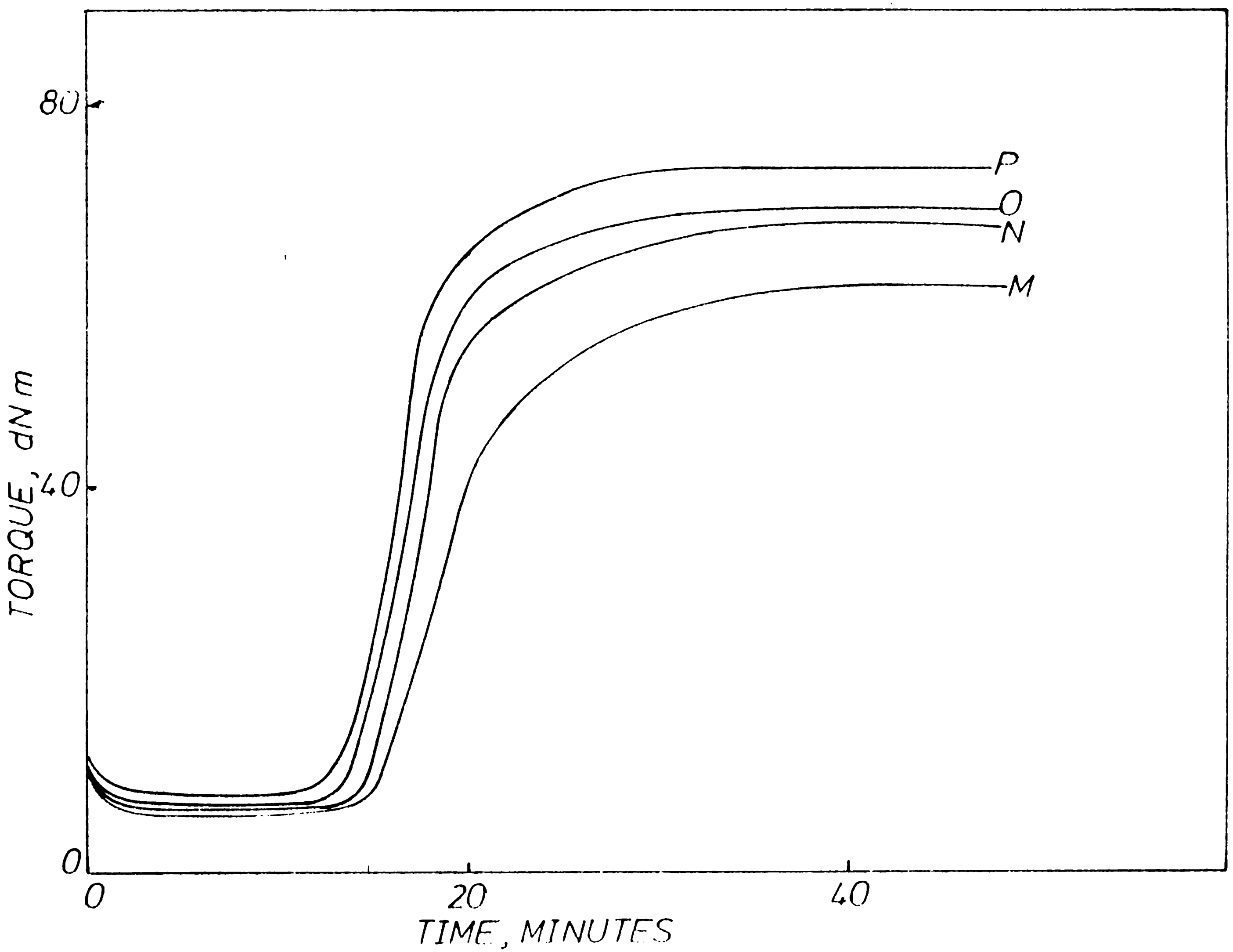

Fig.4.5 Effect of accelerator variation on the curing behaviour of 50/50 NR/SBR blend - Semi EV system (Ref.Table 4.2).

semi-EV systems. The curing behaviour of the blend is thus similar to that of a single elastomer. Unlike the curing of NR no compound shows any tendency for reversion. However, the curing behaviour of the blends seems to be more tilted towards an NR behaviour. This might be because of a slightly larger share of curatives going to the NR phase. This preferential migration might leave the NR phase slightly over crosslinked and the SBR phase slightly under crosslinked.

Table 4.3 shows the results of the chemical characterisation of the vulcanizates employing conventional systems. The crosslink density is found to increase with addition of sulphur or CBS as expected. It is found that polysulphidic crosslinks constitute the major part of crosslinks in this case. The concentration of monosulphidic and disulphidic crosslinks before ageing could not be estimated since the vulcanizate sample partly dissolved in benzene after the cleavage of poly-and disulphidic linkages, obviously due to the very low concentration of monosulphidic linkages. However, it is observed that there is a significant conversion of polysulphidic linkages to di- and monosulphidic linkages during ageing. The overall crosslink density is also found to increase with ageing. This behaviour could be explained based on the outline reaction scheme originally proposed for vulcanization of NR. In the transformation of the initial

Table 4.3 Chemical characterisation of gum NR/SBR vulcanizates (Conventional system)

Vulcanizate	A	B	C	D	E	F	G	H
Total crosslink density (m.mole/kg RH)	45.55	50.07	59.85	69.05	46.94	55.35	58.85	65.22
Polysulphidic crosslinks (%)	71.70	74.12	77.62	81.26	74.49	72.40	70.08	67.15
Free sulphur concentration (m.mole/kg RH)	60.66	71.86	76.83	84.39	74.27	60.83	48.47	30.39
Zinc sulphide sulphur concentration (m.mole/kg RH)	41.08	45.82	50.16	54.93	47.62	46.74	44.32	40.98
<u>After ageing</u>								
Total crosslink density (m.mole/kg RH)	49.23	56.64	65.35	75.65	54.55	62.42	65.82	70.20
Polysulphidic crosslinks (%)	52.96	54.32	57.12	58.75	54.94	52.57	49.26	46.87
Disulphidic crosslinks (%)	30.20	28.62	25.16	21.38	28.36	30.82	31.25	35.34
Free sulphur concentration (m.mole/kg RH)	9.37	10.12	11.83	11.85	12.53	9.17	8.75	8.43

polysulphidic networks into the final network in NR two principal reactions were identified.[13-16] The first reaction is desulphuration giving rise to crosslink shortening and leading eventually to monosulphidic crosslinks. The second reaction is thermal decomposition forming cyclic mono- and disulphides and conjugated dienes and trienes in the rubber backbone and zinc sulphide. It appears that the first reaction is more important in NR/SBR blends under moderate temperatures. This might be the reason for the improved reversion resistance of the blends too.

Free sulphur content and the amount of sulphur existing as zinc sulphide increase with higher concentrations of sulphur but decrease with higher concentrations of CBS as expected. While a part of the free sulphur gets used up in further reactions,probably additional crosslinking,the amount of zinc sulphide sulphur remains more or less the same during thermal ageing. This further shows that thermal decomposition of polysulphidic network via the second route mentioned earlier is not significant.

Table 4.4 shows the results of the chemical characterisation of the vulcanizates of the semi-EV system. As in the case of the conventional system, the crosslink density increases with increase in the amount of sulphur of CBS.

Table 4.4 Chemical characterisation of gum NR/SBR vulcanizates (Semi EV system)

Vulcanizate	I	J	K	L	M	N	O	P
Total crosslink density (m.mole/kg RH)	36.06	43.76	52.43	62.18	41.44	48.27	55.86	64.59
Polysulphidic crosslinks (%)	61.15	62.06	63.20	68.23	63.23	62.96	60.06	58.89
Free sulphur concentration (m.mole/kg RH)	16.49	24.71	30.82	48.68	38.45	29.46	22.29	19.05
Zinc sulphide sulphur concentration (m.mole/kg RH)	23.59	31.46	39.16	45.40	42.17	36.95	28.39	19.24
After ageing								
Total crosslink density (m.mole/kg RH)	44.80	52.82	60.12	69.92	45.20	52.92	60.87	69.70
Polysulphidic crosslinks (%)	29.17	30.34	32.14	33.53	34.38	30.82	26.76	22.42
Disulphidic crosslinks (%)	40.50	39.13	38.64	37.15	39.68	39.72	41.26	42.86
Free sulphur concentration (m.mole/kg RH)	5.55	6.29	8.18	10.02	12.26	9.74	7.36	6.59

However, the amount of polysulphidic linkages is much less in this case compared to the conventional system. The concentration of monosulphidic linkages was found to be higher but its exact determination was found to be difficult as before. As in the case of the conventional system there is a significant conversion of polysulphidic linkages to di- and monosulphidic linkages at the time of ageing. The variation of free sulphur and zinc sulphide sulphur is found to be similar to that of the conventional system. It appears that the changes in the network structure occurring during ageing in this case are similar to those of the conventional system.

The physical properties of the vulcanizates are shown in Figs.4.6-4.15. Tensile strength of the vulcanizates (Figs.4.6 and 4.7) is found to improve steadily when the amount of sulphur or CBS is increased both in the conventional and semi-EV systems which might be due to a higher degree of crosslinking induced by them. Vulcanizates of the conventional system are generally found to display higher strength. This might be due to a higher concentration of polysulphidic crosslinks[17-19] in the conventional vulcanizates than that of the semi-EV vulcanizates. The deterioration in tensile strength of the vulcanizates with ageing may be principally due to main chain scission.[20-23] The chain shortening of a large fraction of polysulphidic crosslinks may also be

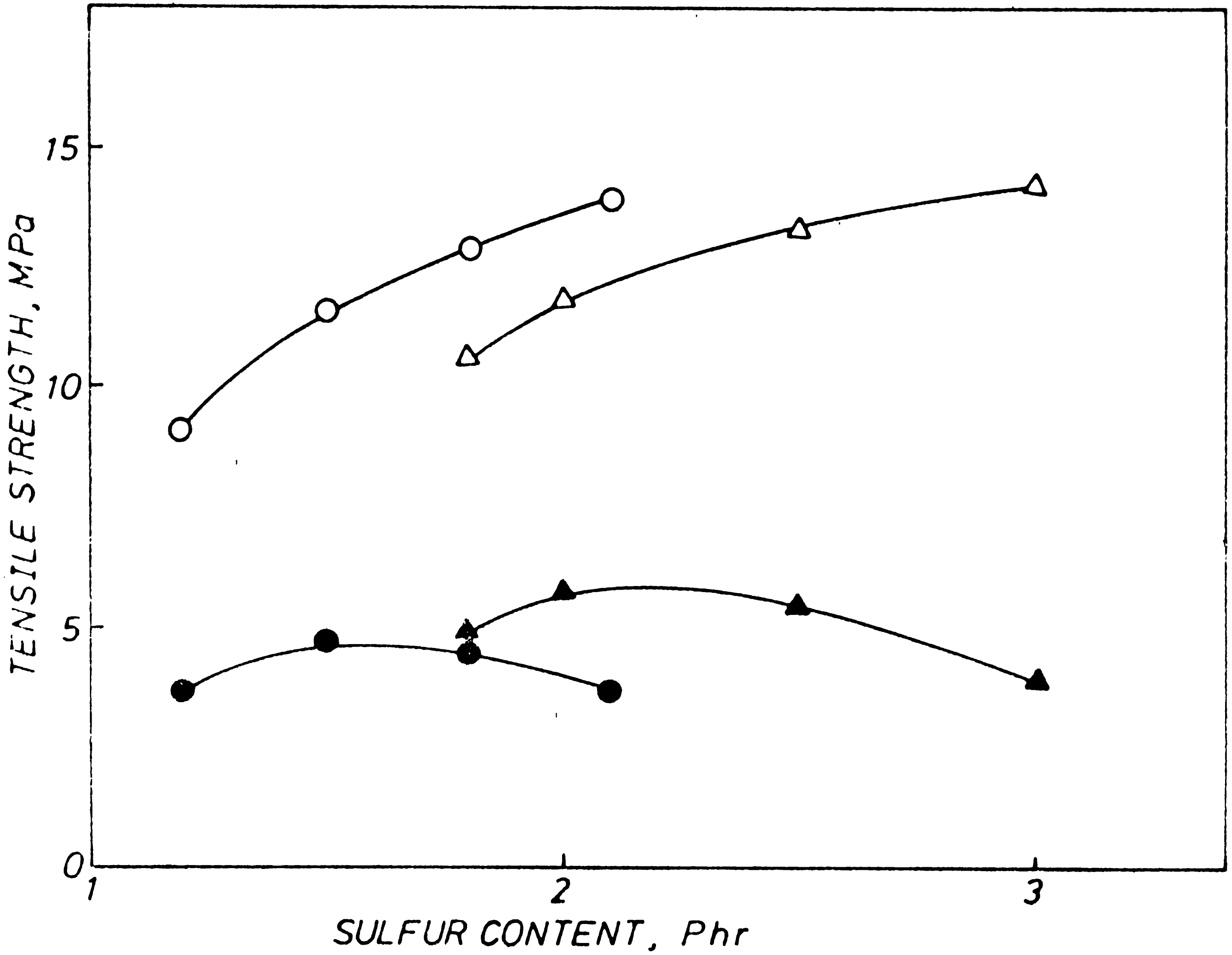

Fig.4.6 Variation of tensile strength of gum 50/50 NR/SBR vulcanizate with sulfur content: (△) Conventional system before ageing; (▲) Conventional system after ageing; (○) Semi-EV system before ageing; (●) Semi-EV system after ageing.

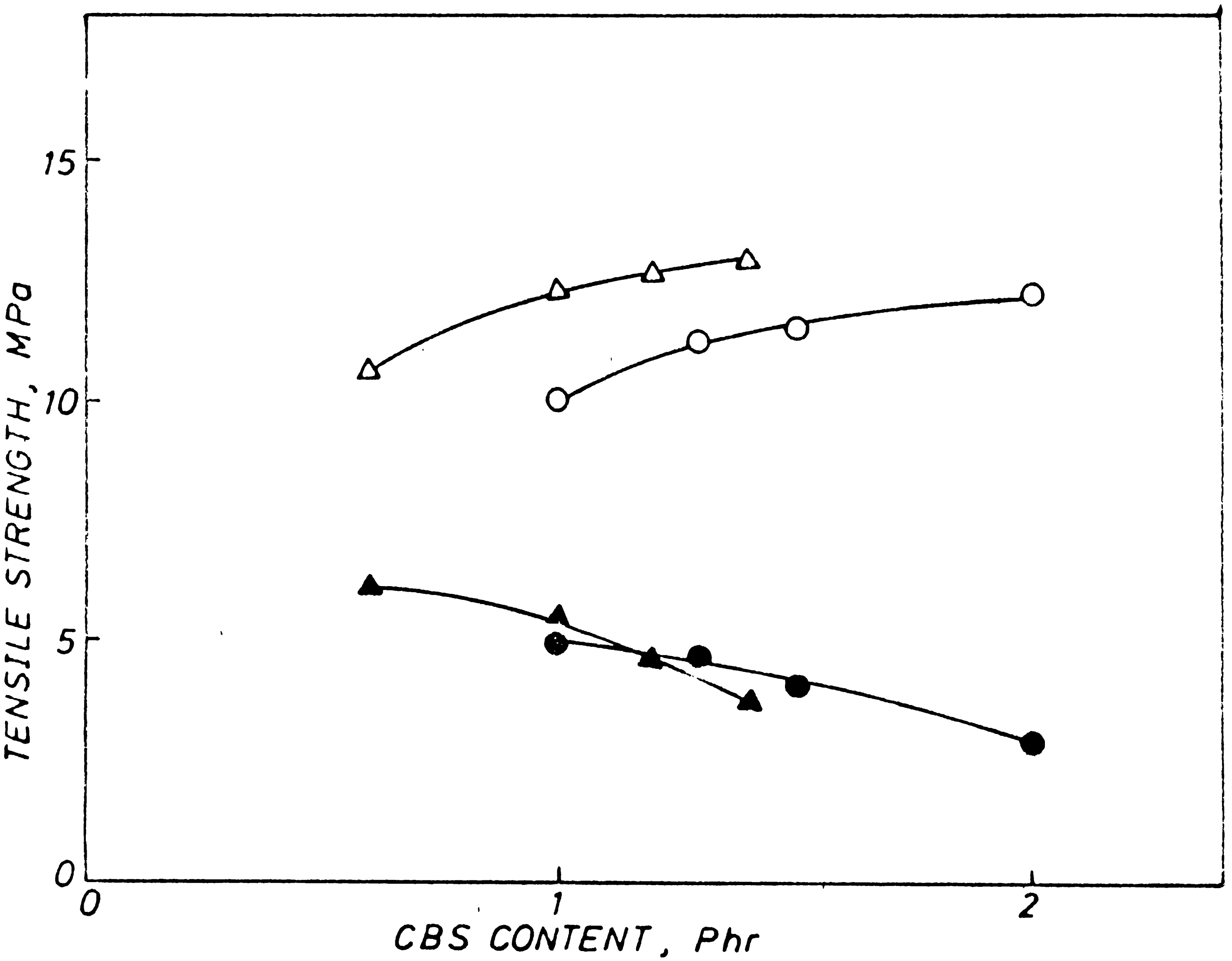

Fig.4.7 Variation of tensile strength of gum 50/50 NR/SBR vulcanizate with CBS content: (△) Conventional system before ageing; (▲) Conventional system after ageing; (○) Semi-EV system before ageing; (●) Semi-EV system after ageing.

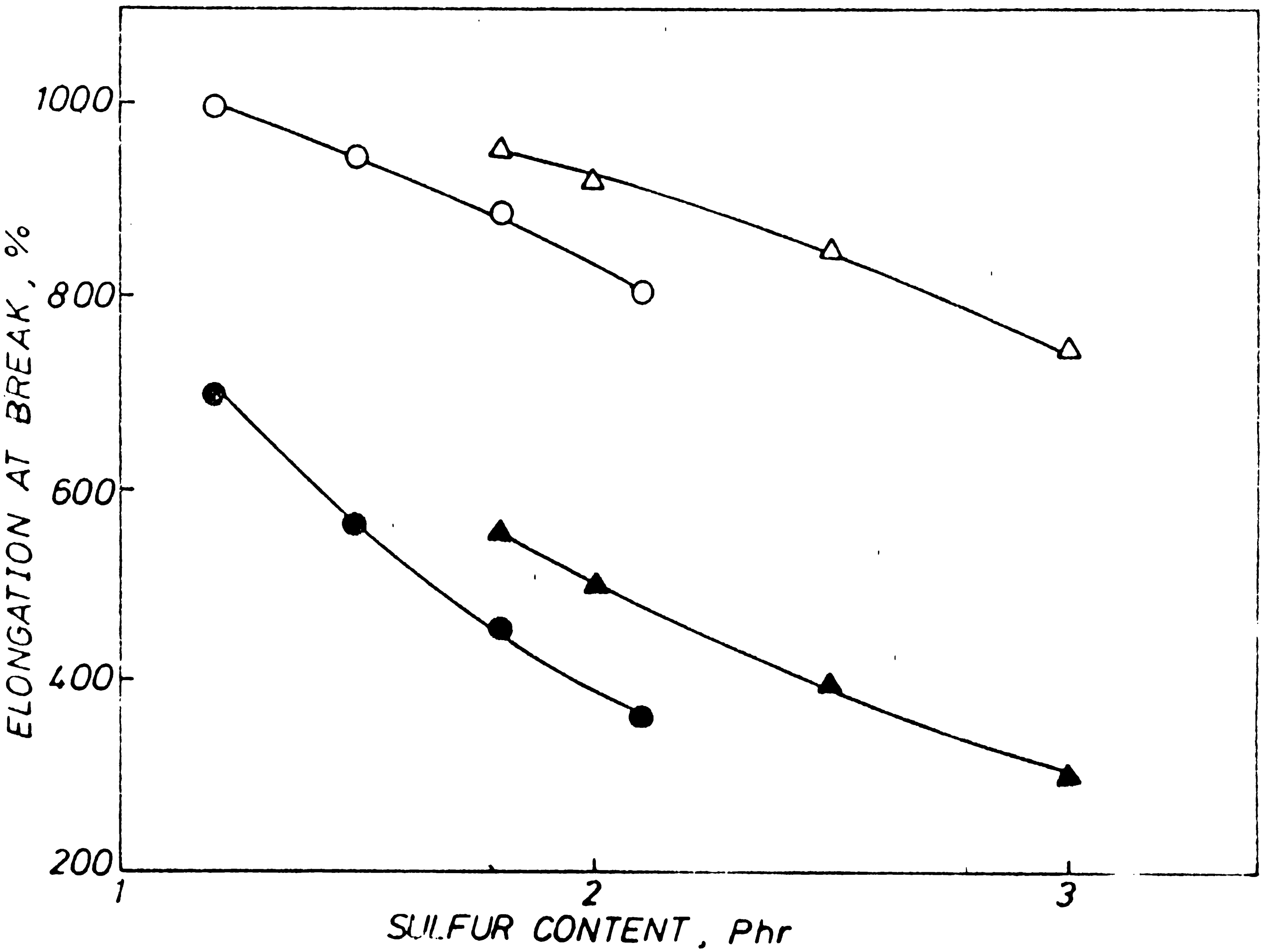

Fig.4.8 Variation of elongation at break of gum 50/50 NR/SBR vulcanizate with sulfur content: (△) Conventional system before ageing; (▲) Conventional system after ageing; (○) Semi-EV system before ageing; (●) Semi-EV system after ageing.

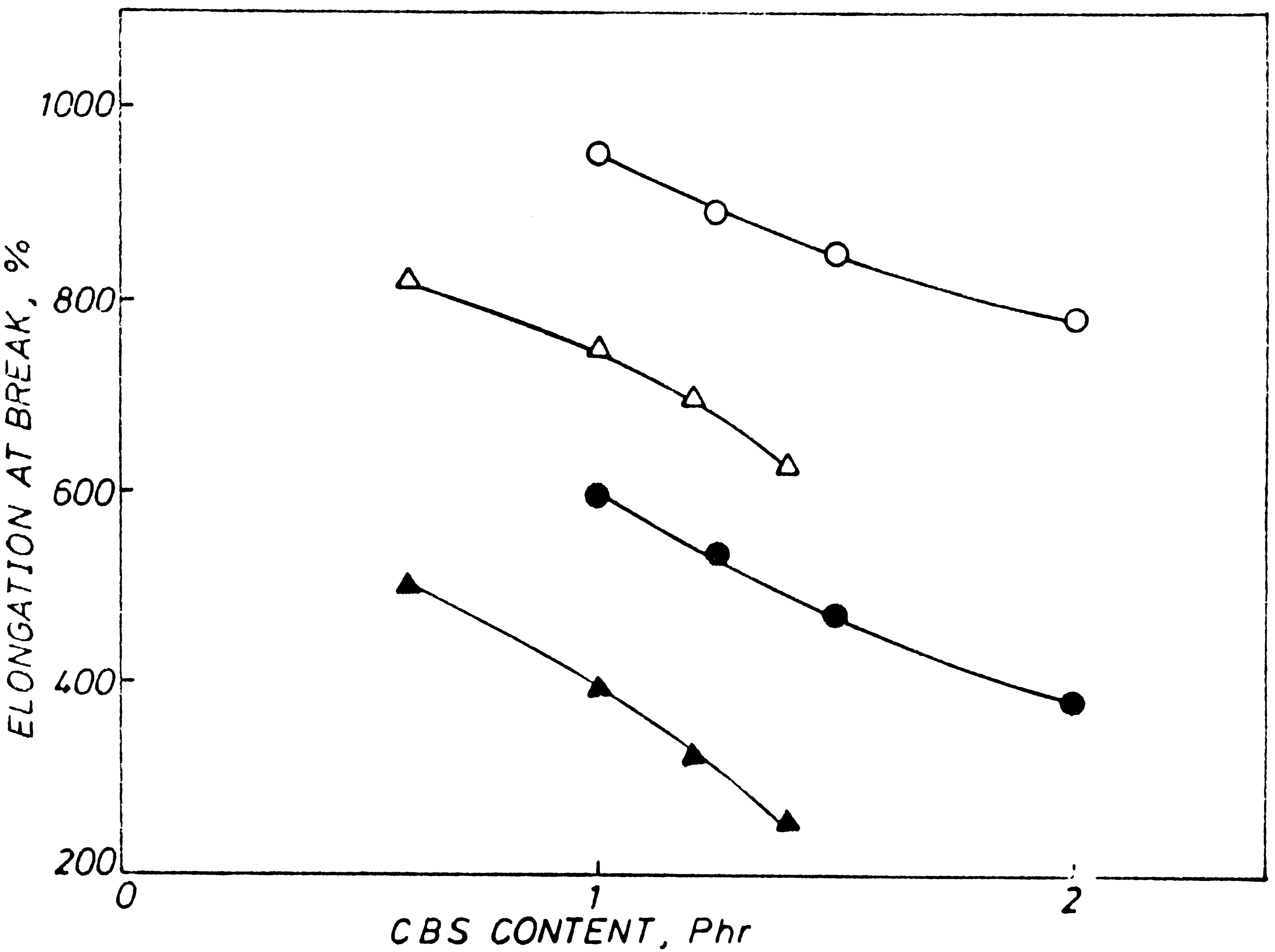

Fig.4.9 Variation of elongation at break of gum 50/50 NR/SBR vulcanizate with CBS content: (△) Conventional system before ageing; (▲) Conventional system after ageing; (○) Semi-EV system before ageing; (●) Semi-EV system after ageing.

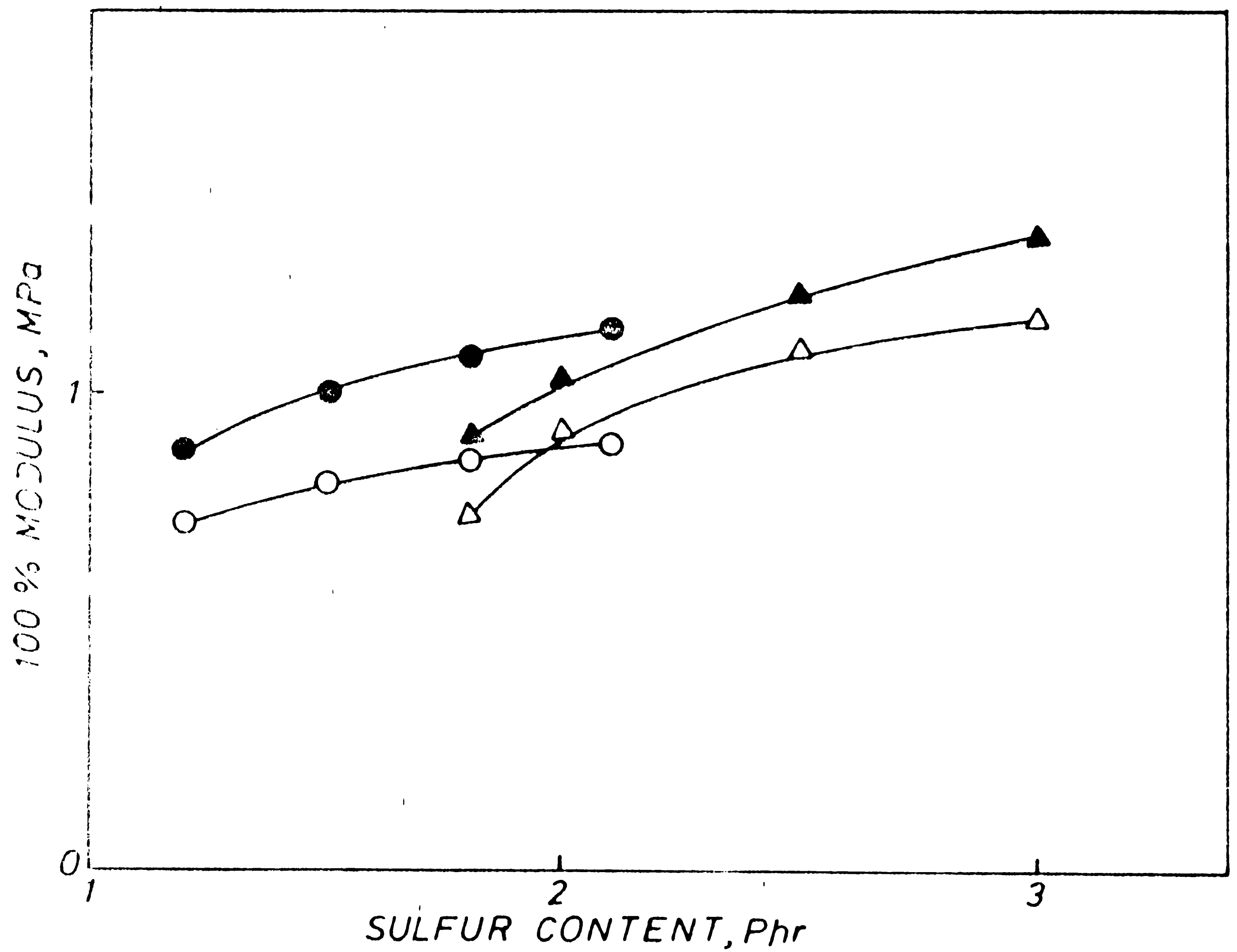

Fig.4.10 Variation of modulus of gum 50/50 NR/SBR vulcanizate with sulfur content: (△) Conventional system before ageing; (▲) Conventional system after ageing; (○) Semi-EV system before ageing; (●) Semi-EV system after ageing.

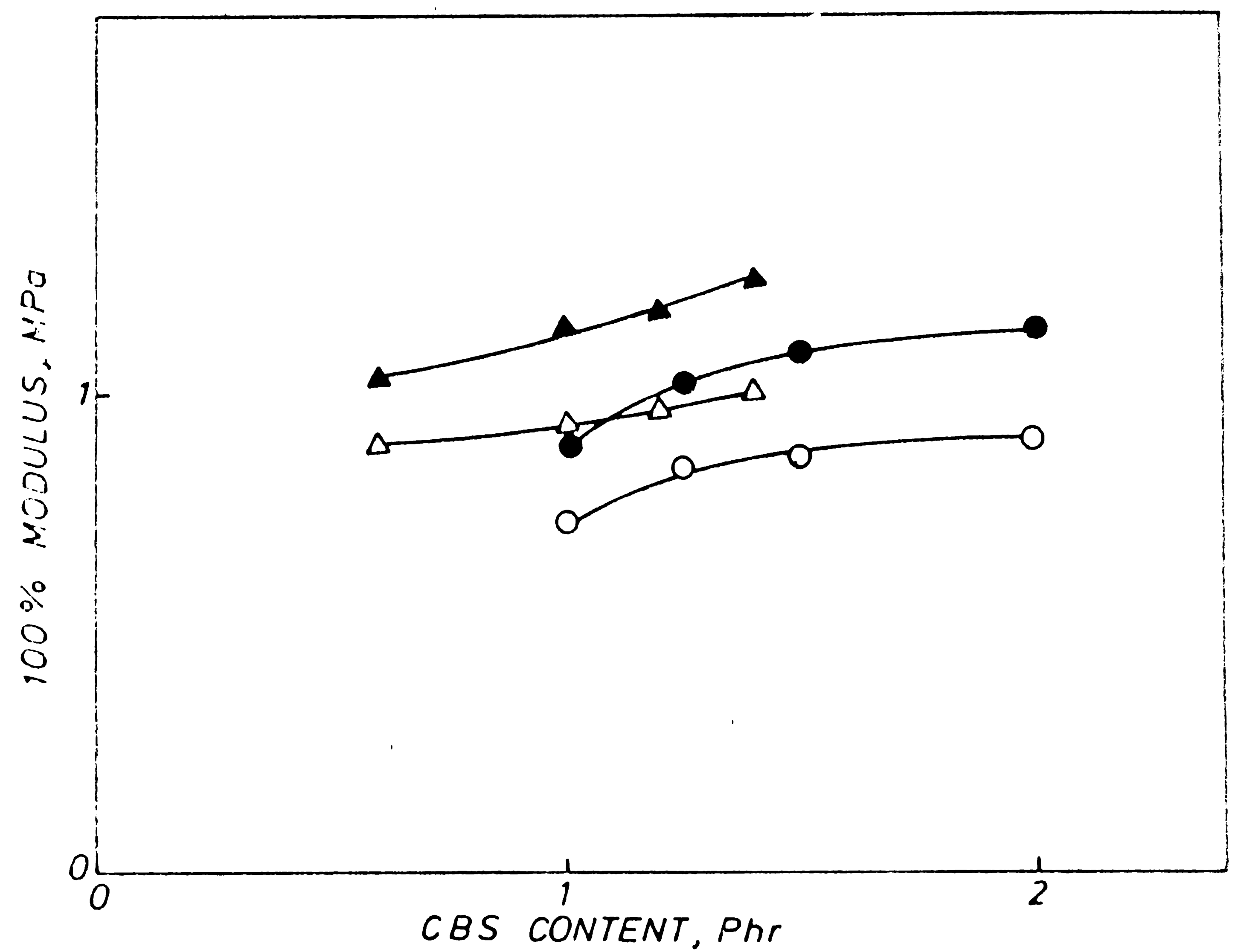

Fig.4.11 Variation of modulus of gum 50/50 NR/SBR vulcanizate with CBS content: (△) Conventional system before ageing; (▲) Conventional system after ageing; (○) Semi-EV system before ageing; (●) Semi-EV system after ageing.

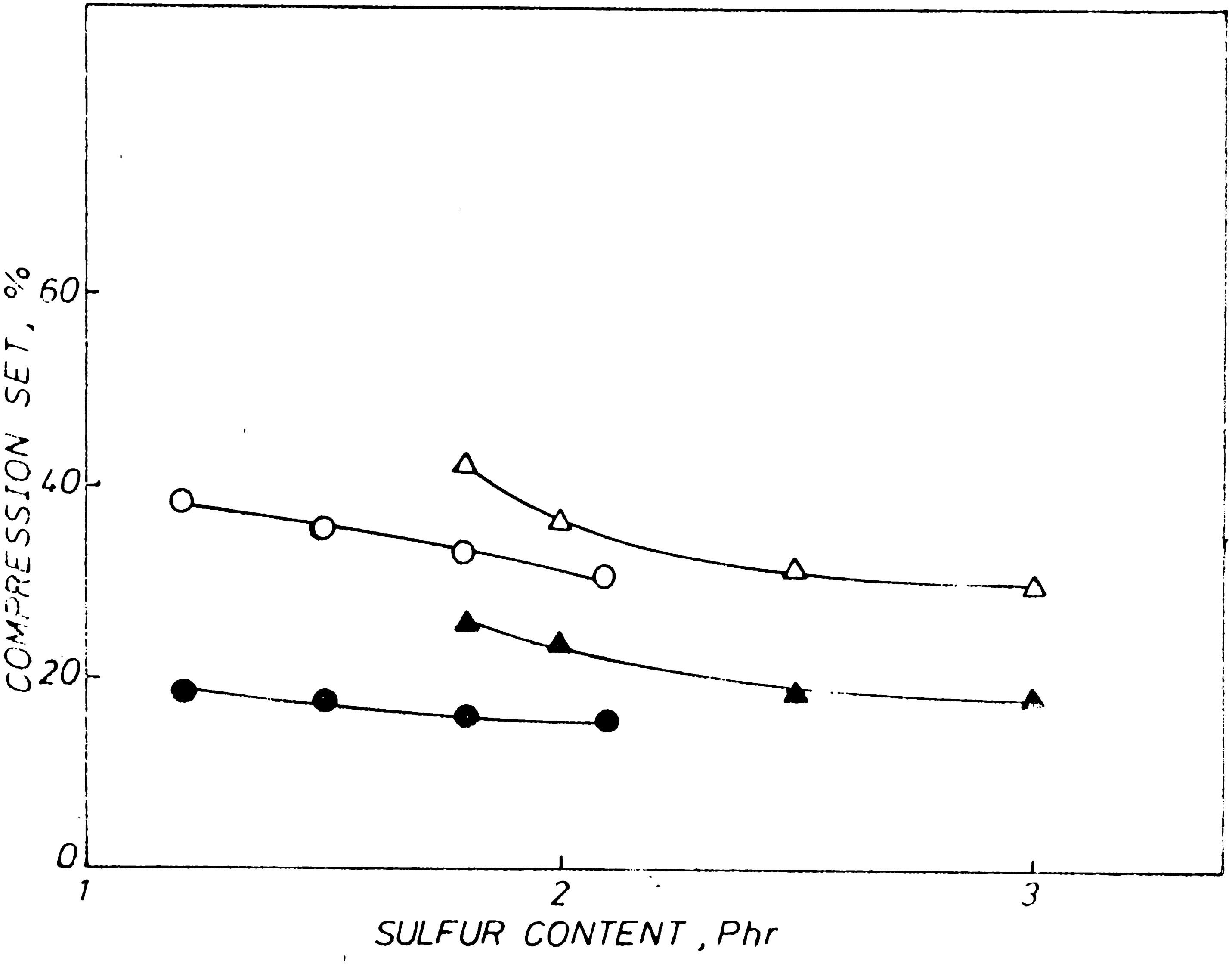

Fig.4.12 Variation of compression set of gum 50/50 NR/SBR vulcanizate with sulfur content: (△) Conventional system before ageing; (▲) Conventional system after ageing; (○) Semi-EV system before ageing; (●) Semi-EV system after ageing.

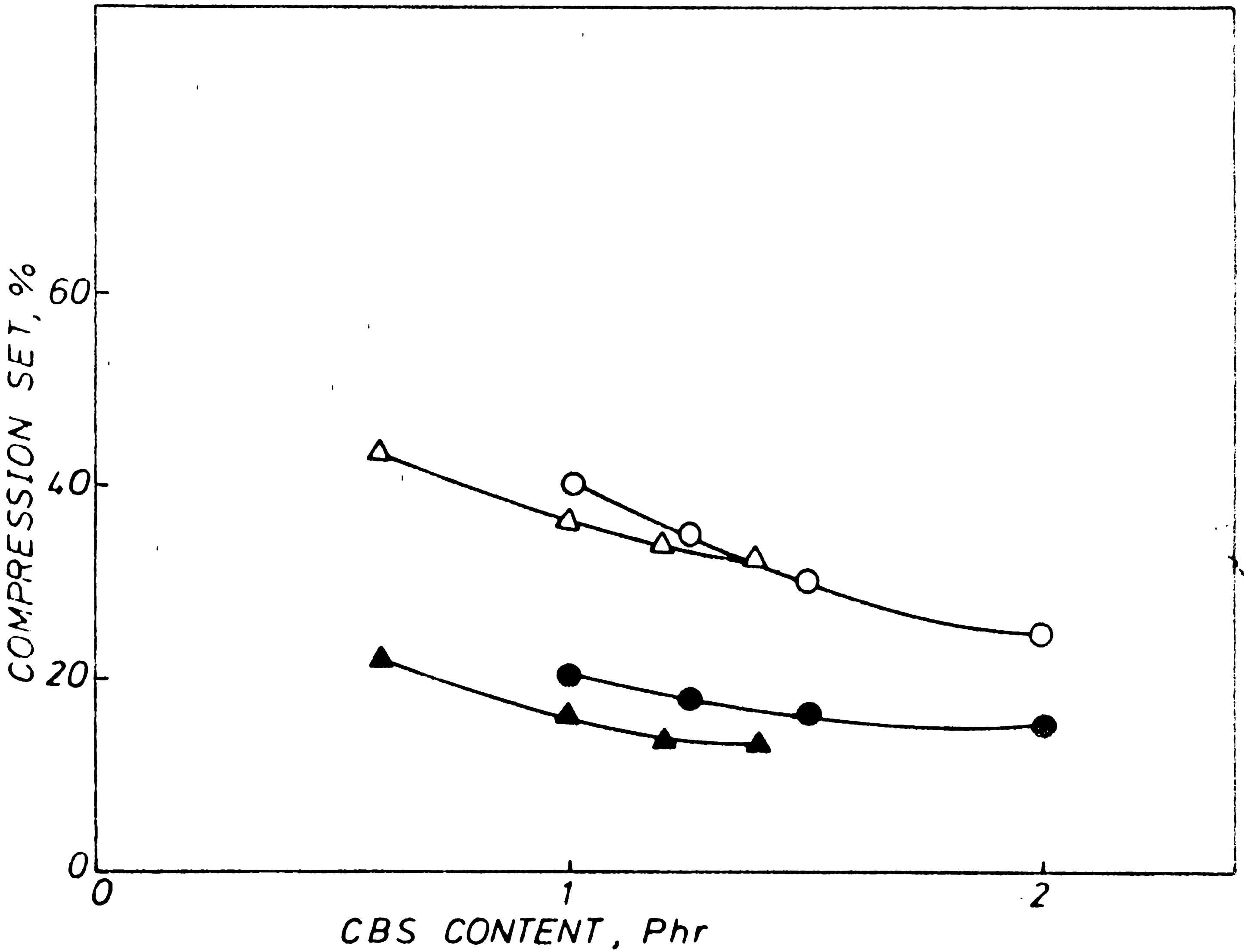

Fig.4.13 Variation of compression set of gum 50/50 NR/SBR vulcanizate with CBS content: (△) Conventional system before ageing; (▲) Conventional system after ageing; (○) Semi-EV system before ageing; (●) Semi-EV system after ageing.

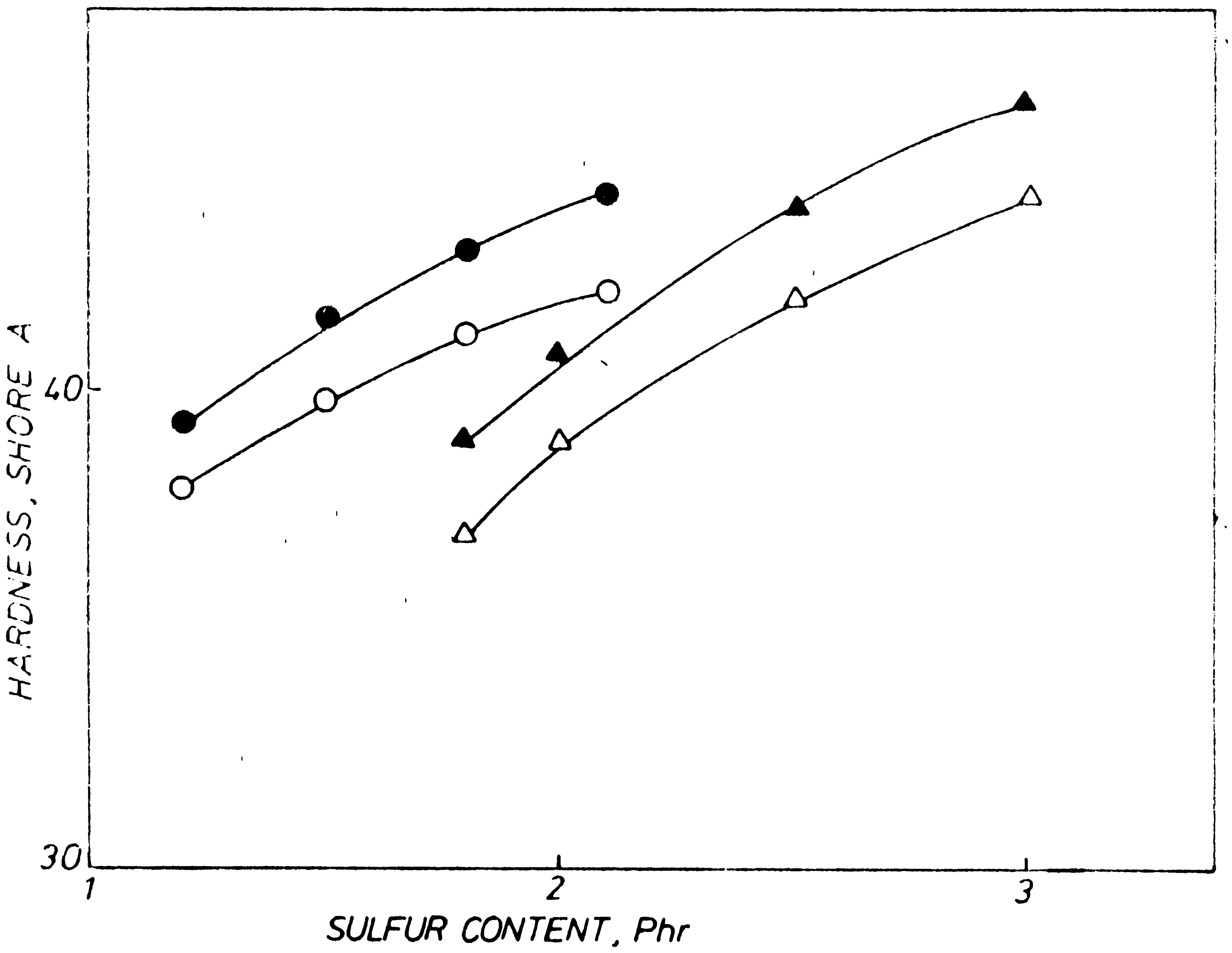

Fig.4.14 Variation of hardness of gum 50/50 NR/SBR vulcanizate with sulfur content: (△) Conventional system before ageing; (▲) Conventional system after ageing; (○) Semi-EV system before ageing; (●) Semi-EV system after ageing.

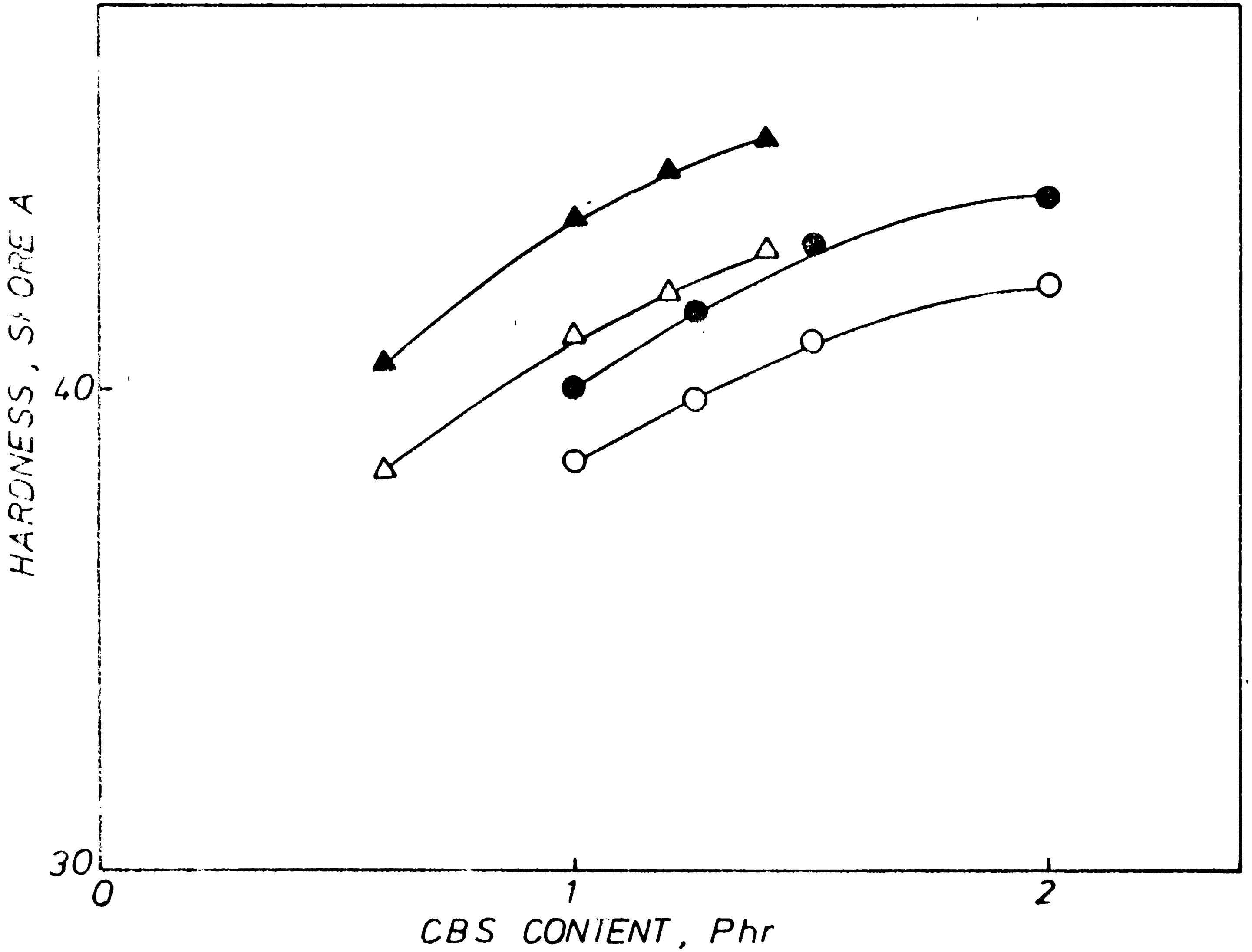

Fig.4.15 Variation of hardness of gum 50/50 NR/SBR vulcanizate with CBS content: (△) Conventional system before ageing; (▲) Conventional system after ageing; (○) Semi-EV system before ageing; (●) Semi-EV system after ageing.

contributing to this effect. There seems to be an optimum network structure which gives maximum retention in tensile strength. Other mechanical properties like elongation at break (Figs.4.8 and 4.9), modulus (Figs.4.10 and 4.11), compression set (Figs.4.12 and 4.13) and hardness (Figs. 4.14 and 4.15) are found to depend more directly on the degree of crosslinking and less on the nature of crosslinks. Elongation at break decreases with increase in the degree of crosslinking whereas modulus, compression set and hardness improve with higher degree of crosslinking. The variation in these properties with thermal ageing also follows the variation of crosslink density. The elongation at break decreases with ageing, whereas modulus, compression set and hardness improve both in the conventional and semi-EV systems.

II. Studies on filled 50/50 blends of NR and SBR

Experimental

Since all industrially important NR/SBR blends contain fillers, this study was done on filled 50/50 blends of NR and SBR. The formulations employed for study are given in Table 4.5. The compounds were prepared on a laboratory mixing mill. The cure curves of the mixes were then taken at 150°C on a Monsanto Rheometer model R 100.

Table 4.5 Formulations and the cure characteristics of filled NR/SBR compounds

Formulation	A	B	C	D	E	F	G	H
NR	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
SBR	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
ZnO	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
PBN	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
HAF (black (N 330)	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Aromatic oil	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
CBS	0.8	0.8	0.8	0.8	0.6	1.0	1.2	1.4
Sulphur	1.8	2.0	2.5	3.0	2.0	2.0	2.0	2.0
<u>Cure characteristics</u>								
Scorch time, min.	6.5	6.5	6.0	6.0	6.0	6.0	6.0	6.0
Optimum cure time, min.	17.5	17.0	16.5	16.0	20.0	15.0	13.0	12.0
Maximum torque, d.Nm	74.0	82.0	92.0	100.0	72.0	84.0	90.0	94.0
Reversion, number of units dropped in 5 min.	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

The compounds were then vulcanized upto their optimum cure times at 150°C on a steam heated laboratory hydraulic press. The tensile properties of the vulcanizates were determined as per ASTM D 412 (1980) on a Zwick universal testing machine. The hardness of the vulcanizates was determined according to ASTM 2240 (1968) and expressed in shore A units. The ageing resistance of the vulcanizates was determined by keeping the sample at 100°C for 48 hours in an air oven and then measuring the retention in these properties.

The overall crosslink density and the percentage of polysulphidic, disulphidic and monosulphidic linkages of the vulcanizates before and after ageing were determined from the swelling data in benzene by the procedures outlined in Chapter 2. The amount of free sulphur was determined iodometrically by converting it to sodium thiosulphate according to ASTM D 297-72 A. Zinc sulphide sulphur was determined iodometrically from the formation of cadmium sulphide as described in BS 902 pt. 1310 (1958).

Results and Discussion

The cure characteristics of the compounds calculated from the cure curves are shown in Table 4.5. When the amount of CBS is increased at constant sulphur level, the vulcanization becomes faster as evidenced by the decrease in the cure times. Increasing the amount of sulphur, keeping the amount of CBS constant also speeds up vulcanization. However, the increase in cure rate in this case is not as pronounced as in the previous case. The maximum torque, a measure of the crosslink density, increases steadily with increase in sulphur and/or CBS. The curing of the blends shows more of an NR behaviour than that of SBR. This might be because the conventioanl curatives used in this study are more soluble in the NR phase and hence a larger share of the curatives is going to the NR phase. This means that the state of cure in the SBR phase is not optimum. However, the presence of SBR seems to give very good reversion resistance to the blend since none of the mixes shows any tendency for reversion. This is in conformity with the behaviour of the gum compounds.

Table 4.6 shows the results of the swelling studies done to examine the network structure of the vulcanizates. The total crosslink density increases with increase in sulphur and/or accelerator. Vulcanizates with comparatively higher amount of sulphur and lower amounts of accelerator are found to have a larger percentage of polysulphidic crosslinks. The total crosslink density is found to be slightly higher than that of the corresponding gum compound employed in

Table 4.6 Chemical characterisation of filled NR/SBR vulcanizates

Vulcanizate	A	B	C	D	E	F	G	H
Total crosslink density (m.mole/kg RH)	42.03	46.32	56.81	70.01	40.65	47.15	52.12	58.52
Polysulphidic crosslinks (%)	62.00	66.32	72.73	78.57	66.02	64.33	63.21	62.32
Monosulphidic crosslinks (%)	b	b	b	b	b	b	b	b
Free sulphur concentration (m.mole/kg RH)	21.25	26.58	39.67	48.69	28.82	22.81	20.42	18.77
Zinc sulphide sulphur concentration (m.mole/kg RH)	34.35	35.66	42.28	50.02	35.90	33.80	30.50	28.29
<u>After ageing</u>								
Total crosslink density (m.mole/kg RH)	58.85	62.63	74.83	90.51	57.42	66.72	72.32	85.78
Polysulphidic crosslinks (%)	54.83	55.12	56.25	58.16	55.21	52.34	51.18	48.32
Monosulphidic crosslinks (%)	18.62	19.12	19.84	20.34	16.32	17.21	18.85	21.25
Free sulphur concentration (m.mole/kg RH)	8.90	11.40	17.45	21.91	9.49	6.84	5.54	4.78

section I. This might be due to the mild accelerator action of carbon black. The slightly lower percentage of polysulphidic crosslinks in the vulcanizates also confirm this reasoning. However, the percentage of disulphidic and monosulphidic linkages could not be estimated in the vulcanizates before ageing as in the case of the gum vulcanizates since the samples got dissolved in the solvent partly after treatment with the reagent to cleave polysulphidic and disulphidic linkages, obviously due to the low concentration of monosulphidic linkages. The crosslink density of the vulcanizates is found to increase with ageing. An examination of the percentage of poly-, di- and monosulphidic linkage of the vulcanizates before and after ageing indicates that the increase in crosslink density might be due to a fraction of the polysulphidic linkages getting shortened with additional crosslinking. This is also similar to the behaviour of the corresponding gum vulcanizates. The variation in the crosslink density with ageing increases with higher amounts of sulphur or accelerator in the original mix. This might be due to a larger proportion of polysulphidic crosslinks being available for shortening in the former case, whereas in the latter case it might be due to a higher amount of accelerator.[10]

It is observed that the amounts of free sulphur and zinc sulphide sulphur increase with increasing amounts of sulphur but decrease with increasing amounts of accelerator in the original mix. Whereas the amount of zinc sulphide sulphur remains more or less constant with ageing, part of free sulphur gets used up in further crosslinking at the time of ageing. This is again the behaviour shown by the gum compounds.

Except tensile strength (Figs.4.16 and 4.17) other physical properties show a definite relationship with crosslink density. Elongation at break (Figs.4.18 and 4.19) decreases with increase in crosslink density whereas modulus (Figs.4.20 and 4.21) and hardness (Figs.4.22 and 4.23) show a direct proportionality with crosslink density as expected. The variation of elongation at break, modulus and hardness with ageing also could be explained by the increase in crosslink density with ageing.

The tensile strengths of the vulcanizates are found to depend on the proportions of poly-, di- and monosulphidic linkages in addition to the crosslink density. A higher percentage of polysulphidic crosslinks is found to result in higher tensile strength as expected. The tensile strengths of the vulcanizates are found to decrease with ageing. This might be due to the decrease in the concentration of polysulphidic crosslinks and due to other factors such as main chain scission occurring during ageing. The

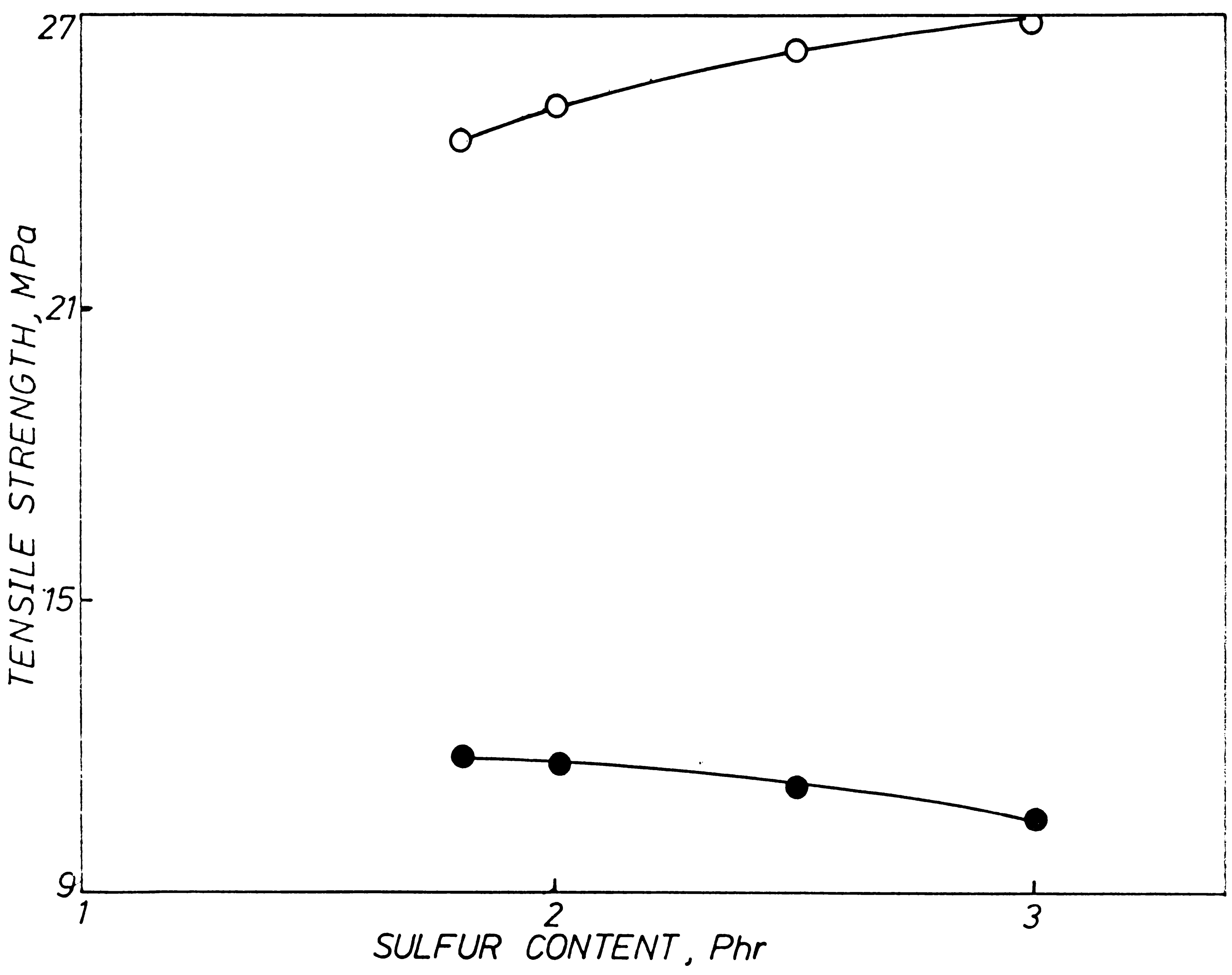

Fig.4.16 Variation of tensile strength of filled 50/50 NR/SBR vulcanizate with sulfur content: (○) before ageing; (●) after ageing.

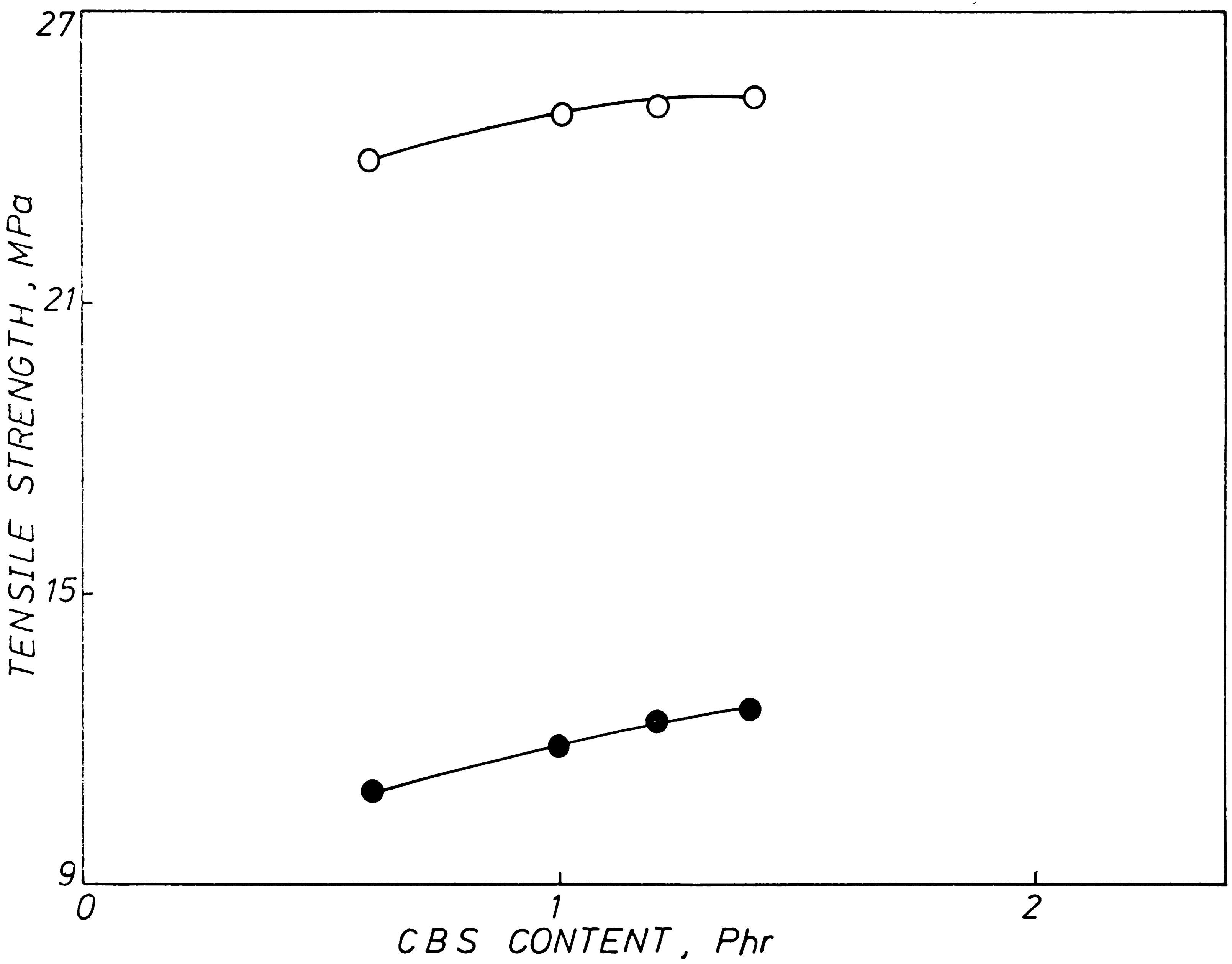

Fig.4.17 Variation of tensile strength of filled 50/50 NR/SBR vulcanizate with CBS content: (○) before ageing; (●) after ageing.

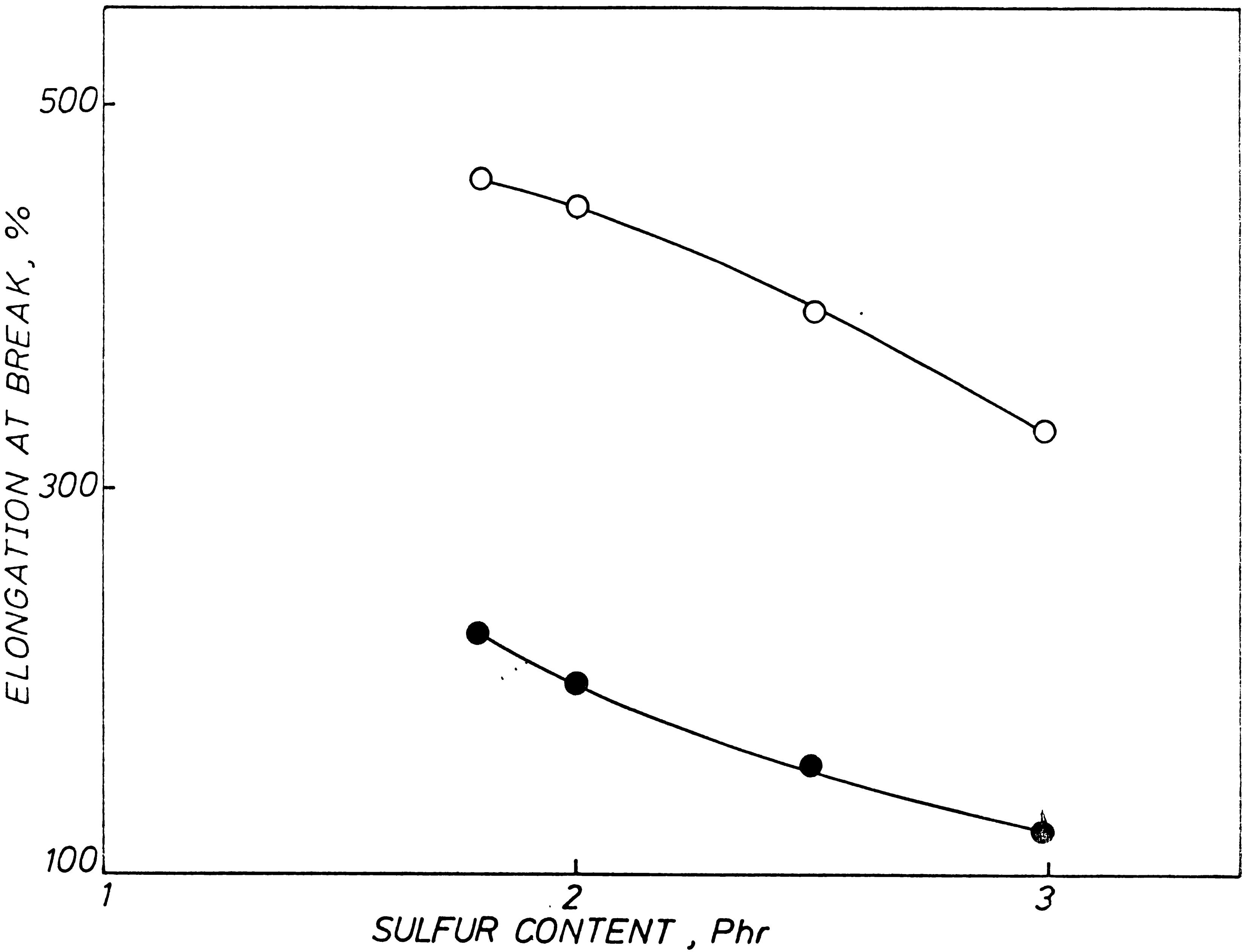

Fig.4.18 Variation of elongation at break of filled 50/50 NR/SBR vulcanizate with sulfur content: (○) before ageing; (●) after ageing.

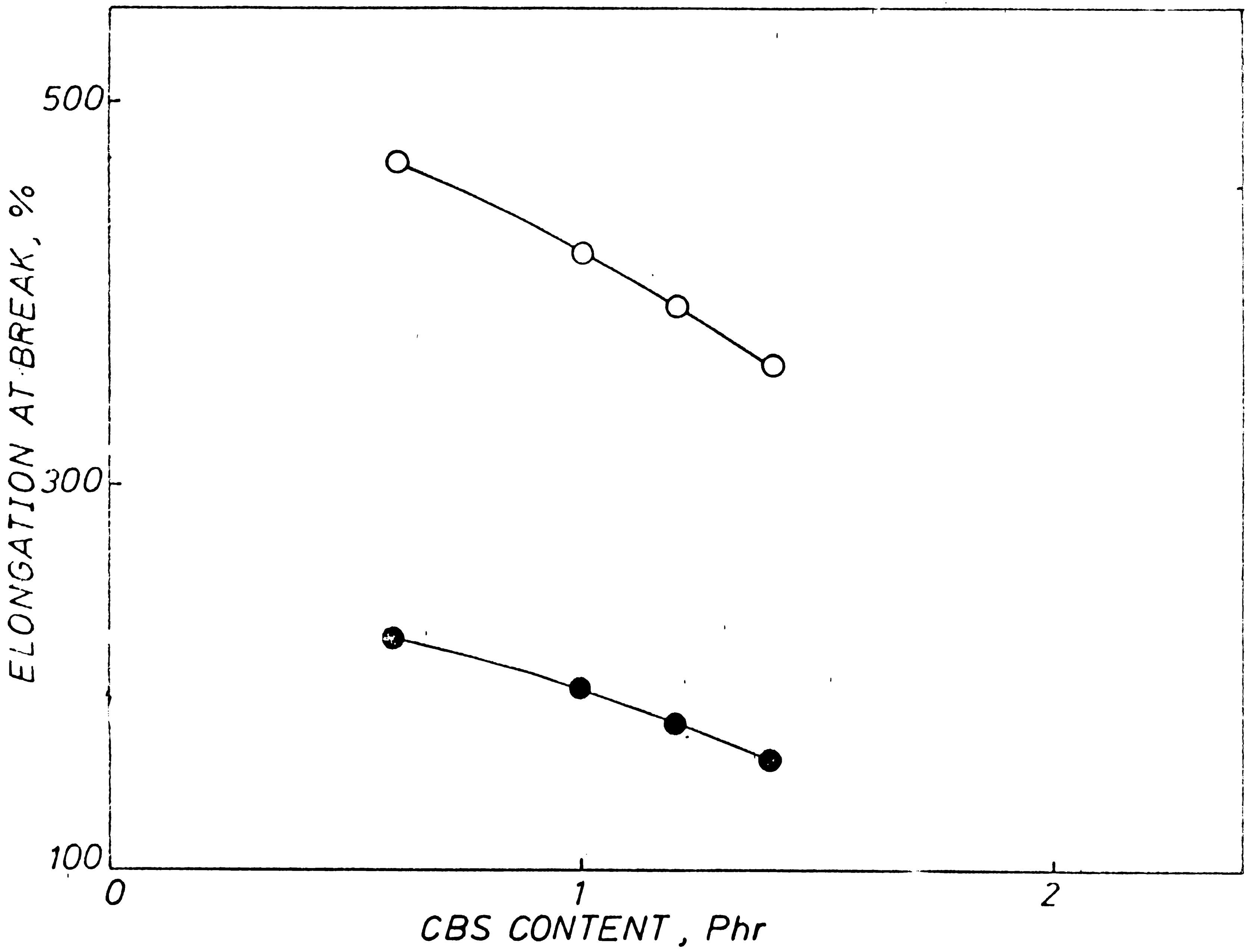

Fig.4.19 Variation of elongation at break of filled 50/50 NR/SBR vulcanizate with CBS content: (○) before ageing; (●) after ageing.

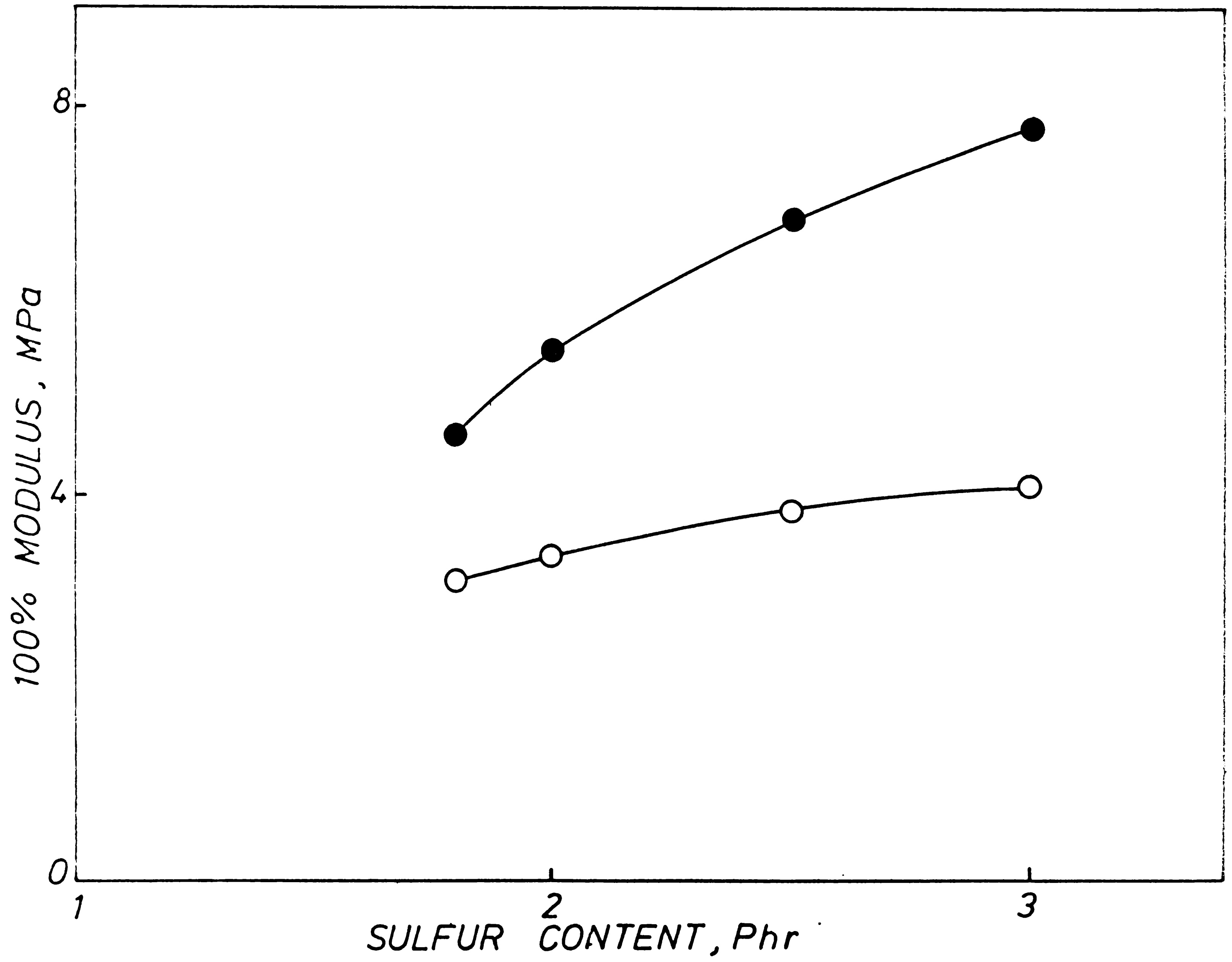

Fig.4.20 Variation of modulus of filled 50/50 NR/SBR vulcanizate with sulfur content: (○) before ageing; (●) after ageing.

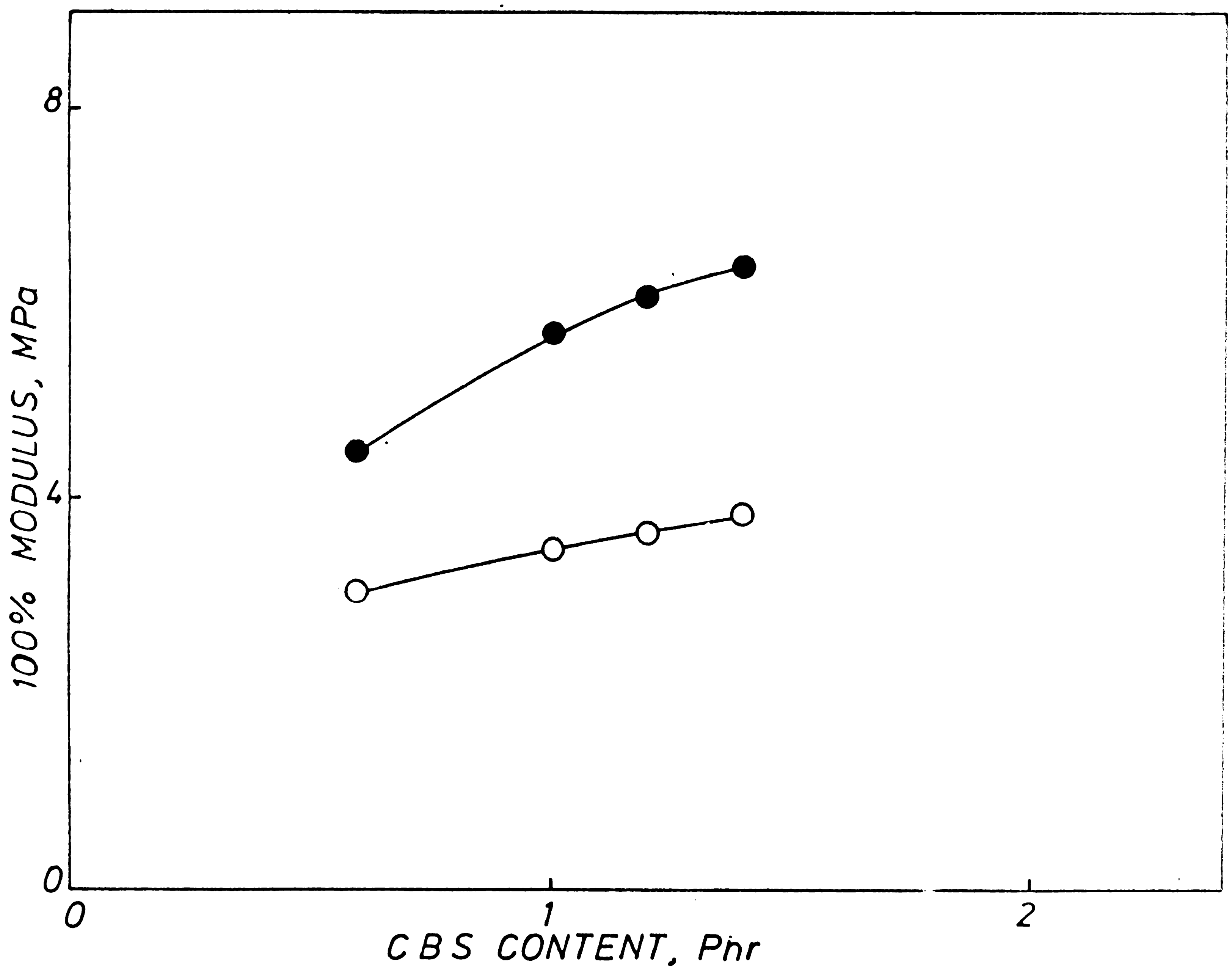

Fig.4.21 Variation of modulus of filled 50/50 NR/SBR vulcanizate with CBS content: (○) before ageing; (●) after ageing.

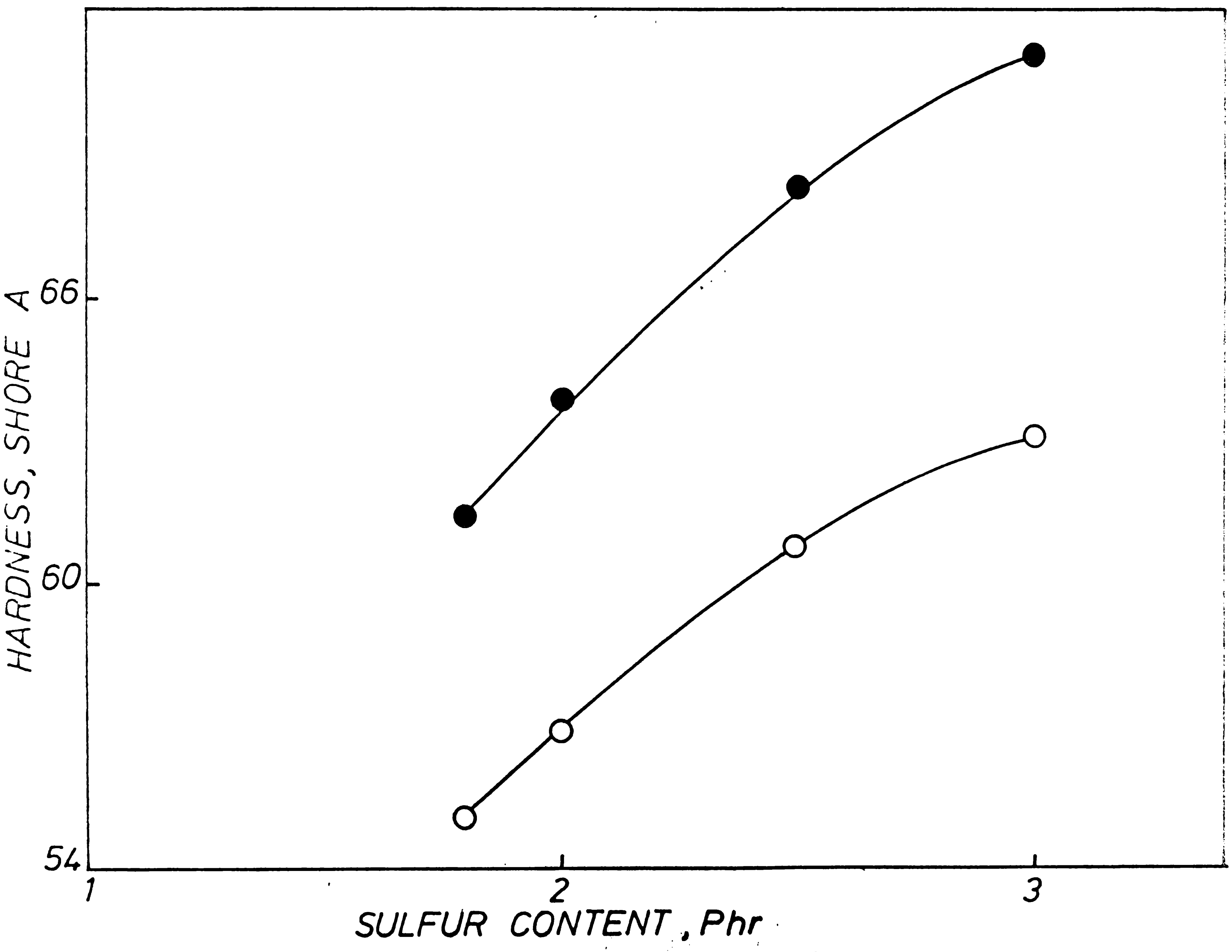

Fig.4.22 Variation of hardness of filled 50/50 NR/SBR vulcanizate with sulfur content: (○) before ageing; (●) after ageing.

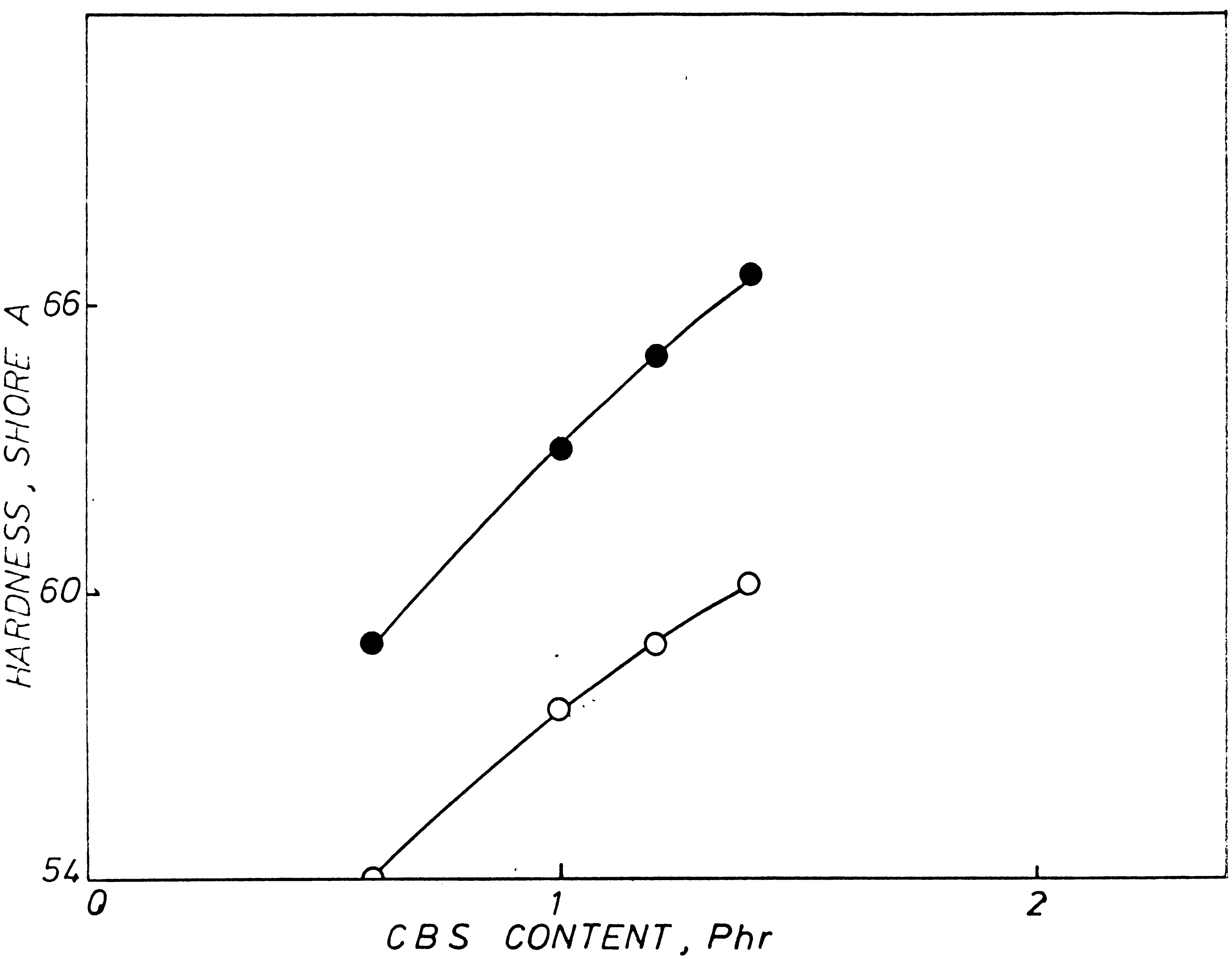

Fig.4.23 Variation of hardness of filled 50/50 NR/SBR vulcanizate with CBS content: (○) before ageing; (●) after ageing.

vulcanizates with less amount of sulphur and more accelerator are generally found to display higher ageing resistance which indicates that monosulphidic linkages are more resistant to ageing than polysulphidic linkages as expected.[24]

Conclusions

The study helps to draw the following conclusions about the cure characteristics and vulcanizate properties of 50/50 NR/SBR blend.

1. The total crosslink density and the proportions of mono-, di-, and polysulphidic linkages in both filled and gum vulcanizates could be estimated by the simplified chemical probes described in Chapter 2.

2. Formulations employing conventional and semi-EV curing systems show good resistance to reversion. There are only marginal improvements in thermal ageing resistance of the vulcanizates employing a semi-EV system.

3. The NR phase takes a larger share of the curatives leaving the SBR phase slightly under-crosslinked. However, this does not seem to affect the physical properties much. The distribution of carbon black between the rubbers also does not lead to serious problems in this blend.

4. The overall crosslink density increases at the time of thermal ageing accompanied by chain shortening of the polysulphidic linkages with additional crosslinking.

5. The dependence of physical properties on the network structure is more or less similar to that observed for SBR.

6. The amount of combined sulphur in the vulcanizate slightly decreases with increase in sulphur and/or decrease in accelerator contents as seen from the amounts of free sulphur and zinc sulphide sulphur in the vulcanizates. Part of the free sulphur is found to take part in additional crosslinking at the time of ageing whereas the amount of zinc sulphide sulphur remains more or less the same.

7. Varying the amounts of sulphur and accelerator produces smooth variations in the curing behaviour and vulcanizate properties. Hence designing suitable formulations to achieve specific vulcanizate properties is not difficult.

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Chapter 5

STUDIES ON NATURAL RUBBER/BUTADIENE RUBBER BLEND

STUDIES ON NATURAL RUBBER/BUTADIENE RUBBER BLEND

The introduction of cis-1,4-polybutadiene (butadiene rubber) (BR) during the late 1950's is probably the single most important development relating to the use of elastomer blends in tyres. In blends with NR, BR has enabled significantly improved tread wear and groove cracking resistance without reduction in resilience.[1] Better oil extension and higher black loadings are additional benefits made possible by the development of BR, along with less dependence on the availability of NR.[2,3]

Sorbach and co-workers[4,5] reported a 20% higher tread wear index for 50/50 NR/BR over straight NR and 46% higher wear for 50/50 SBR/BR over an all SBR tread. Brown and co-workers[6] showed similar results and also reported that a finer carbon black (N 220) was needed to maximize the BR tread wear advantage. In addition to improved tread wear resistance, lower running temperatures and improved cold weather performance for BR compounds were also reported. Evstratov[7] and co-workers evaluated the tread wear performance of NR/BR and SBR/BR blends under different road conditions.

Under test conditions with considerable breaking and turning, the wear advantage of treads containing BR was found to increase.

From the foregoing discussion it is clear that the most important advantage of adding BR to NR is the improved abrasion resistance. However, the improvement in elasticity and abrasion resistance is at the expense of the tensile strength and modulus of NR. On the other hand, addition of NR to BR improves the poor processing properties of BR. As in the case of NR/SBR blends, there is no definite rule for designing compounds based on NR/BR blends for specific applications. The sulphur and accelerator requirements of BR are intermediate between those of natural rubber and those of styrene-butadiene rubbers. As compared with natural rubber, rather less sulphur and more accelerator are required.[8] It is based on this rule of thumb that now formulations are designed for NR/BR blends. Some studies are reported on the effect of different formulations on the vulcanizate properties of NR/BR blends. It has been pointed out that if sulphur content of 50/50 NR/BR blends is decreased, accelerator content must be increased to maintain modulus but although scorch, ageing resistance and compression set are improved, strength as well as resistance to tearing, flex cracking and cut growth are reduced.[9] However, no systematic study has been undertaken to determine the influence of different formulations on the network structure of NR/BR vulcanizates and how the network structure affects the mechanical properties of vulcanizates. In this study carbon black filled 50/50 NR/BR blends were vulcanized using several conventional curing systems designed by varying the amounts of sulphur and accelerator and the cure characteristics, network structure and vulcanizate properties were compared. The changes occurring in the network structure upon thermal ageing of the vulcanizates and their influence on the physical properties of the vulcanizates were also determined.

Experimental

The formulations of the mixes employed for the study are given in Table 5.1. The compounds were prepared on a laboratory mixing mill. The cure curves of the mixes were taken at 150°C on a Monsanto Rheometer model R 100. The compounds were then vulcanized upto the respective optimum cure times on a steam heated laboratory hydraulic press. The total crosslink density and the percentage of poly-, di- and monosulphidic linkages of the vulcanizates were determined from the swelling data in toluene as per the procedures outlined

Table 5.1 Formulations of NR/BR compounds

Formulation	A	B	C	D	E	F	G	H
NR	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
BR	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
ZnO	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
PBN	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
HAF black (N 330)	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Aromatic oil	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
CBS	0.7	0.7	0.7	0.7	0.6	0.8	1.0	1.2
Sulphur	1.8	2.2	2.6	3.0	2.2	2.2	2.2	2.2

in Chapter 2. Free sulphur in the vulcanizates was determined iodometrically by converting it to sodium thiosulphate according to ASTM D 297-72 A. Zinc sulphide sulphur was determined iodometrically from the formation of cadmium sulphide as described in BS 902, Pt.1310 (1958).

The tensile properties of the vulcanizates were determined as per ASTM D 412 (1980) using dumb-bell specimens at 25°C at a crosshead speed of 500 mm/min on a Zwick universal testing machine. The hardness of the vulcanizate was determined according to ASTM 2240 (1968) and expressed in shore A units. The ageing resistance of the vulcanizates was determined by keeping them at 100°C for 48 hours in an air oven and then measuring the retention in the tensile properties.

Results and Discussion

The cure curves of the compounds are shown in Figs.5.1 and 5.2. Increasing the amount of CBS at constant sulphur level (Fig.5.2) speeds up vulcanization as evidenced by the decrease in cure time and scorch time as expected. When the amount of sulphur is varied keeping the amount of CBS constant, (Fig.5.1) the same pattern is again observed, however with less pronounced effects. The maximum torque, a

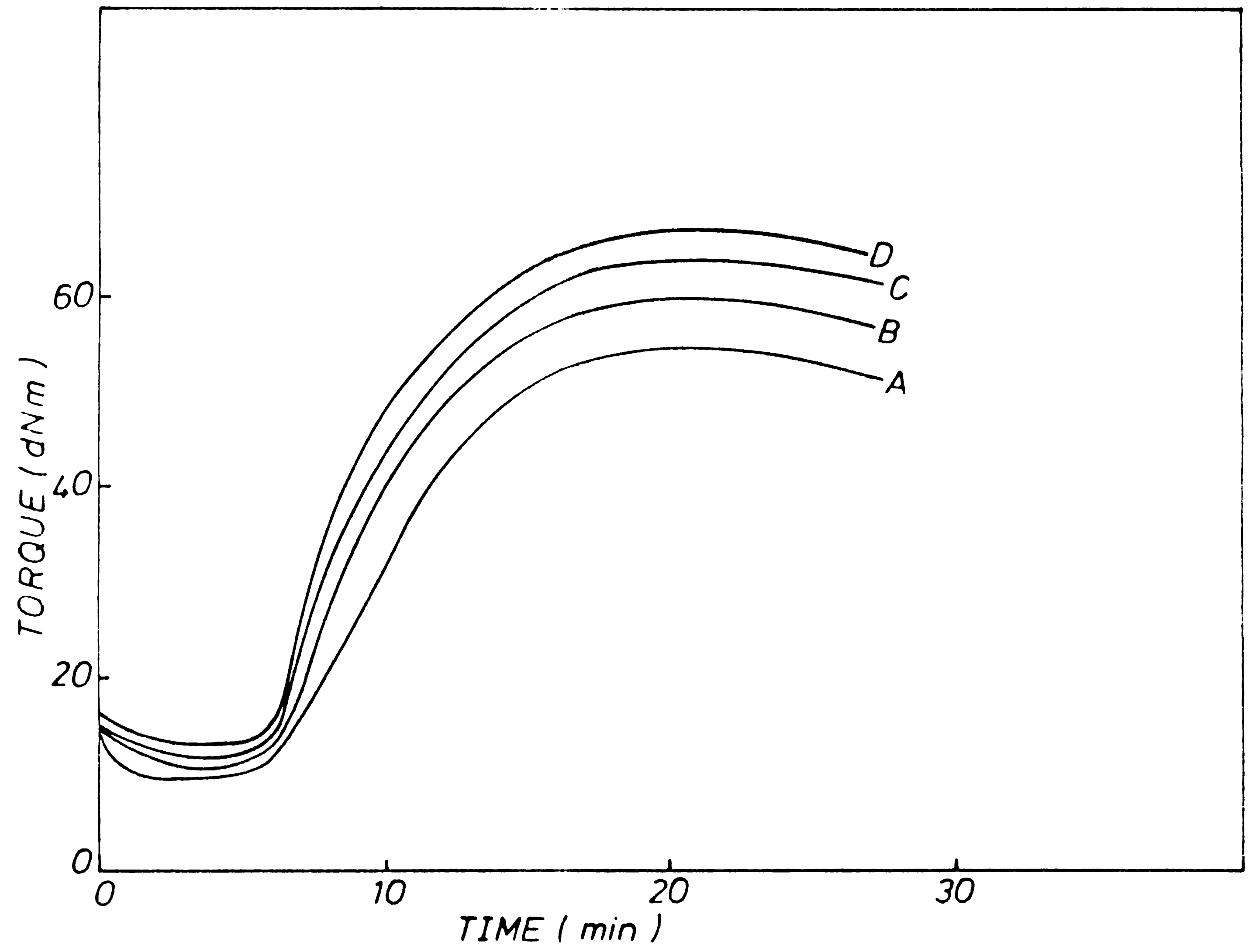

Fig.5.1 Effect of sulphur variation on the curing behaviour of 50/50 NR/BR blend.

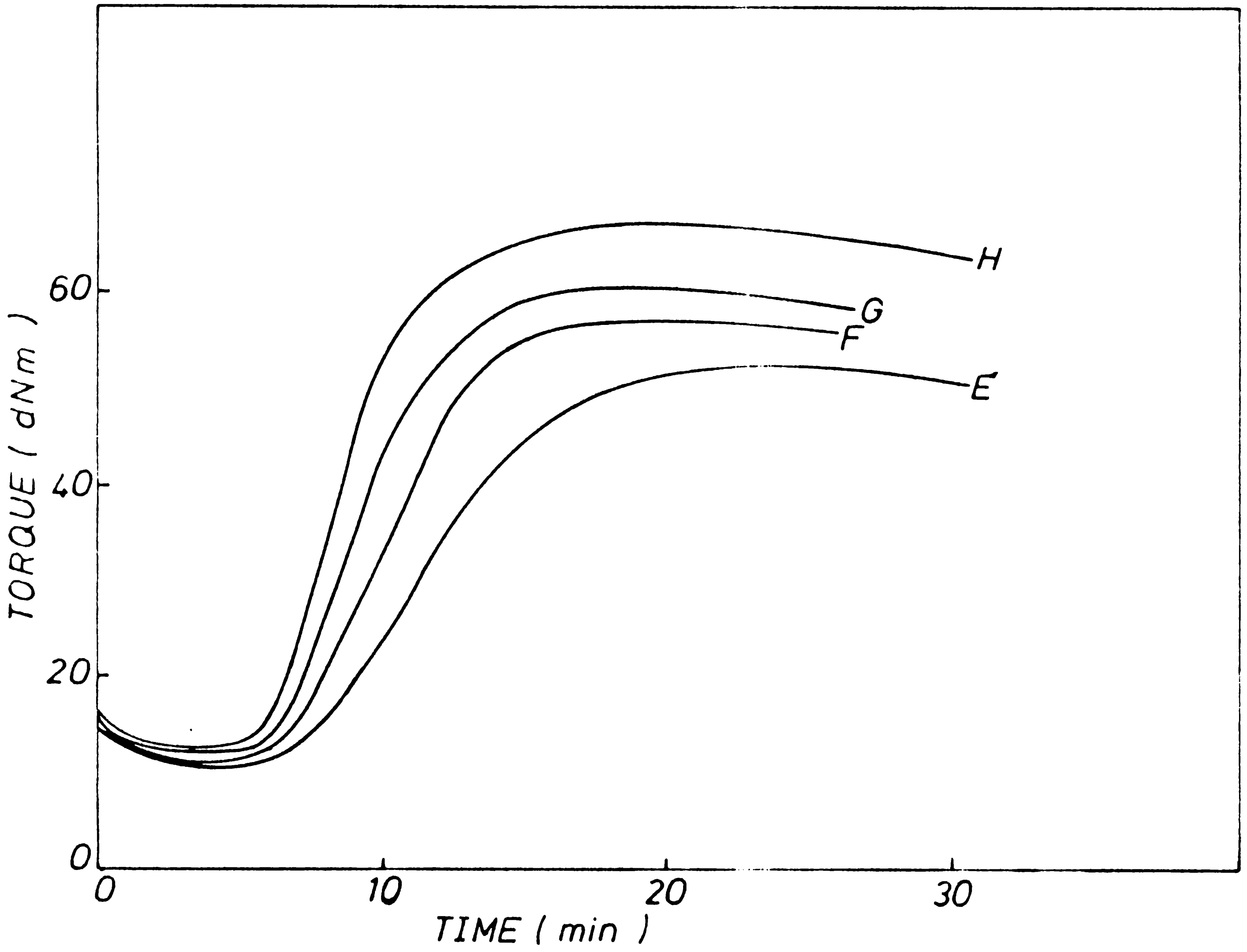

Fig.5.2 Effect of accelerator variation on the curing behaviour of 50/50 NR/BR blend.

measure of the crosslink density, increases steadily with increase in sulphur or CBS. The curing behaviour of the blend indicates that formulations for NR/BR blends could be designed as in the case of single elastomers since variation of the curatives produces smooth variations in the curing behaviour. The reverting behaviour of the blends is not as pronounced as in the case of NR alone. This shows that BR offers some improvement to the thermal reversion of NR as expected.[10] However this blend is not as resistant to reversion as that of 50/50 NR/SBR blends since all the mixes selected for this study show slight tendency for reversion.

Table 5.2 shows the results of the chemical characterization of the vulcanizates. The total crosslink density increases with increase in either sulphur or accelerator as expected. The variation of crosslink density with ageing is interesting. In 50/50 NR/SBR blend the crosslink density increases with ageing mainly due to the shortening of the polysulphidic crosslinks with additional crosslinking (Chapter 4) which shows that the ageing behaviour of the blend is like that of SBR.[11] However, in 50/50 NR/BR blend, the crosslink density decreases with ageing. This might mean that the effect of additional crosslinking induced by the chain shortening effect of the polysulphidic crosslinks is offset by the scission in the main chain. This shows that the ageing

Table 5.2 Chemical characterisation of NR/BR vulcanizates

Vulcanizate	A	B	C	D	E	F	G	H
Total crosslink density (m.mole/kg RH)	34.13	38.12	44.52	58.26	34.05	37.42	44.68	58.82
Free sulphur concentration (m.mole/kg RH)	52.53	57.32	65.62	73.34	58.83	46.82	37.23	29.61
Zinc sulphide sulphur concentration (m.mole/kg RH)	21.22	28.33	35.82	44.32	31.77	28.33	24.23	20.82
After ageing								
Total crosslink density (m.mole/kg RH)	28.54	32.68	38.12	44.62	27.71	30.23	34.68	38.82
Polysulphidic crosslinks (%)	51.36	53.12	56.81	59.76	56.32	51.64	48.26	45.79
Free sulphur concentration (m.mole/kg RH)	12.85	15.23	18.42	20.52	12.82	10.32	8.24	6.20

behaviour of 50/50 NR/BR blend is more inclined towards that of NR. The difference in crosslink density before and after ageing decreases with increase in sulphur content of the compound. This might be due to an increase in the percentage of polysulphidic crosslinks in the original vulcanizate with increase in the amount of sulphur which might have given rise to more crosslinking via chain shortening. Likewise, the increase in the difference in crosslink density with increase in CBS content might be due to decrease in the percentage of polysulphidic crosslinks in the original vulcanizates with increase in CBS content.

The cleavage of polysulphidic linkages in the vulcanizates before ageing led to the breakdown of the vulcanizates indicating that the majority of the crosslinks are polysulphidic in nature. This shows that the amount of polysulphidic linkages in the matrix is higher than that of 50/50 NR/SBR blend (Chapter 4). This further shows that the network structure of 50/50 NR/BR blend is more similar to that of NR. The concentration of monosulphidic linkages in the vulcanizates was found to be low even after ageing since the vulcanizates broke down after the cleavage of polysulphidic and disulphidic linkages. This is obviously due to the very low concentration of monosulphidic linkages in the original vulcanizates. The percentage of polysulphidic linkages after ageing increases with increase in sulphur content of the formulation and decreases with increase in CBS content. This might be reflecting the variation of the percentage of polysulphidic linkages in the original vulcanizates. However, the differences between the values might have come down due to the conversion of a fraction of polysulphidic linkages to shorter linkages.

The amount of combined sulphur in the vulcanizate may be taken as the amount of sulphur added according to the formulation less the amount of free sulphur and sulphur existing as zinc sulphide. It is observed that the amounts of free sulphur and zinc sulphide sulphur increase with increasing sulphur but decrease with increasing accelerator in the mix. The amounts of zinc sulphide sulphur remains more or less constant with ageing, but part of free sulphur seems to get used up in further crosslinking during ageing. This behaviour is similar to that of the NR/SBR blend (Chapter 4).

The tensile strength of the vulcanizates improves with increase in the sulphur content or CBS content (Figs.5.3 and 5.4) obviously due to the increase in crosslink density. This behaviour is in conformity with the observation that if sulphur content of 50/50 NR/BR blends is decreased, accelerator content must be increased to maintain modulus.[12] However, there might be slight reduction in strength in formulations

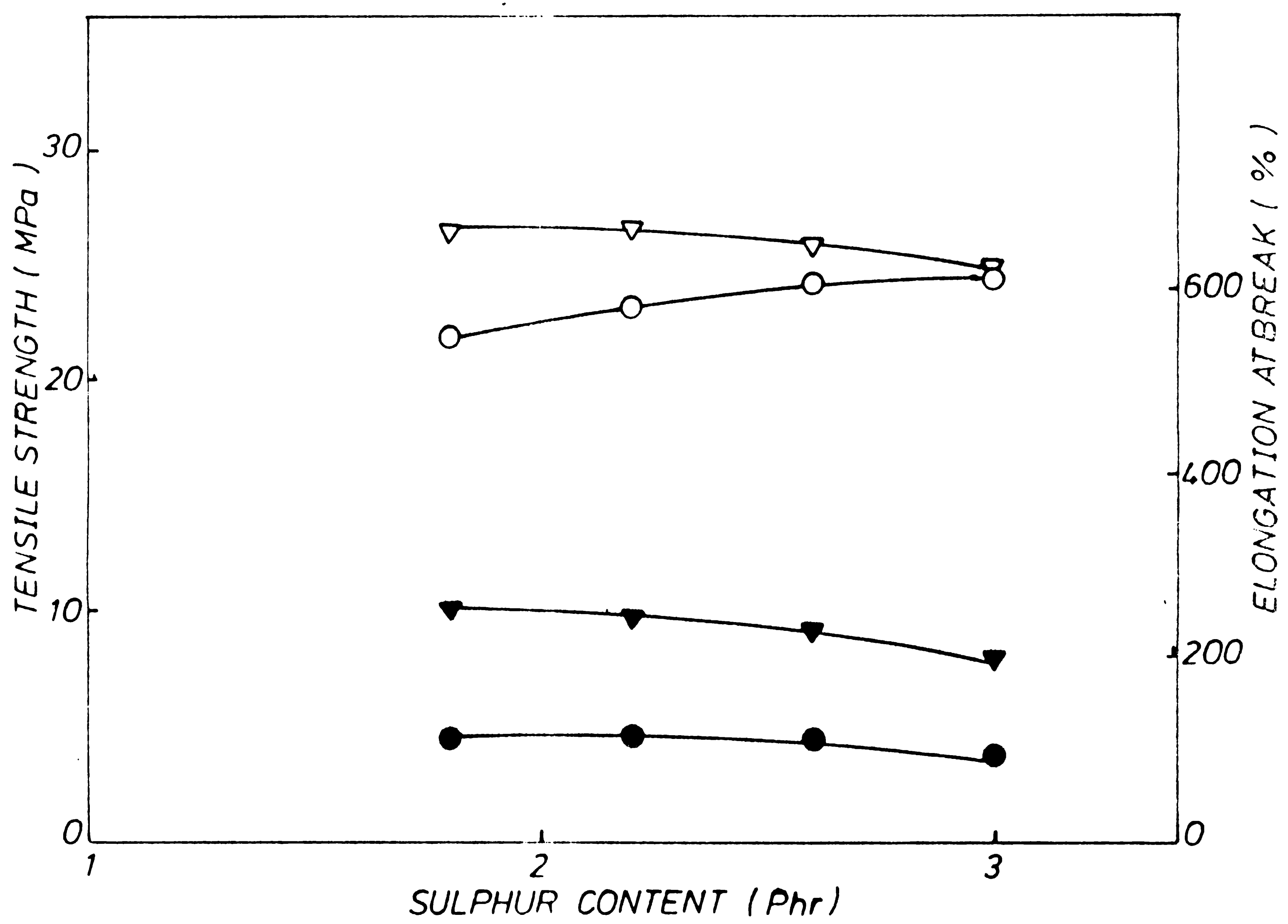

Fig.5.3 Variation of tensile strength (○) and elongation at break (△) of 50/50 NR/BR vulcanizates with sulphur content: (○, △) before ageing; (●, ▲) after ageing.

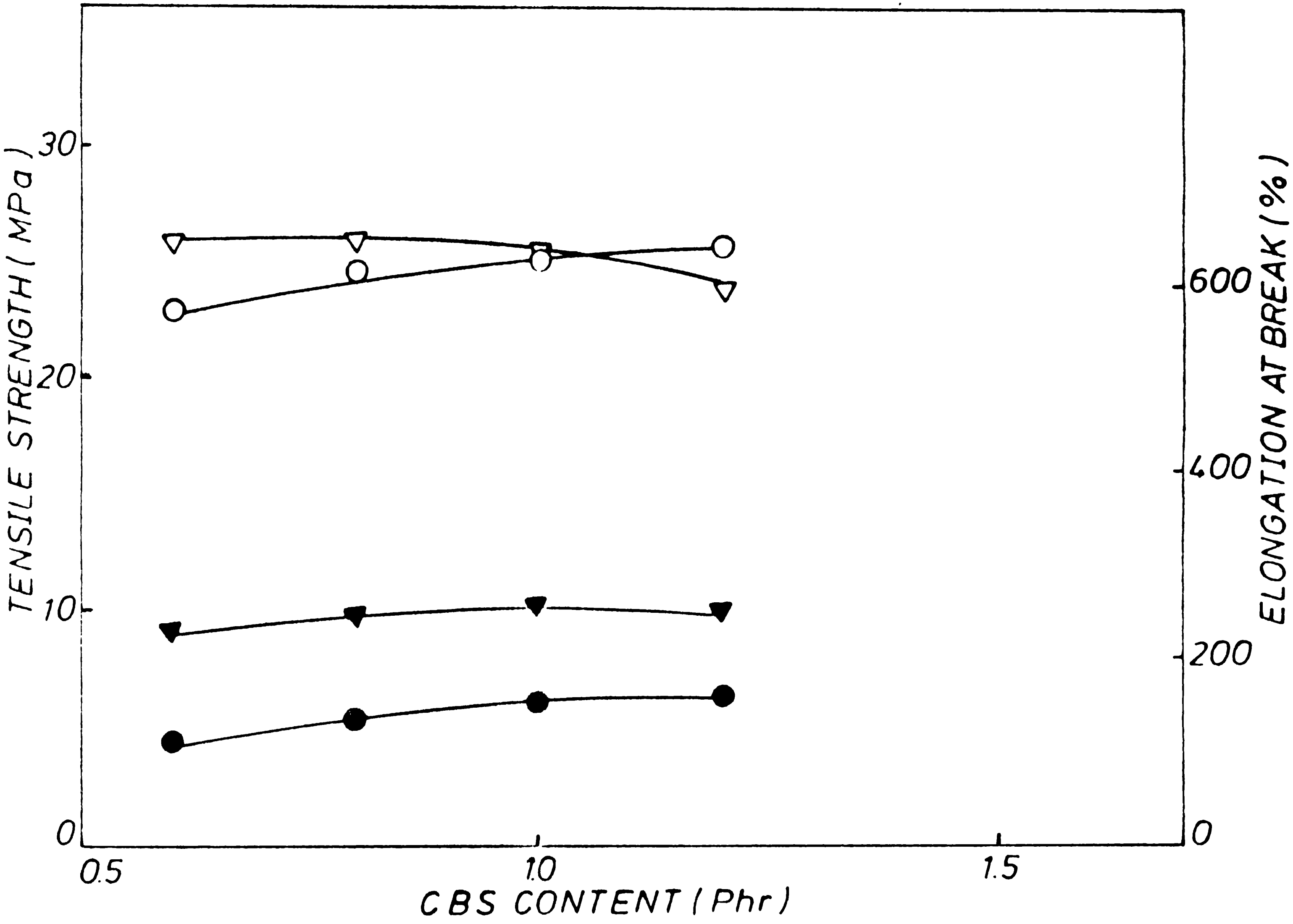

Fig.5.4 Variation of tensile strength (○) and elongation at break (△) of 50/50 NR/BR vulcanizates with CBS content: (○, △) before ageing; (●, ▲) after ageing.

containing low sulphur and high accelerator due to low concentration of polysulphidic crosslinks. The overall behaviour shows that varying the amounts of sulphur and accelerator in 50/50 NR/BR blends produces smooth variations in the curing behaviour and vulcanizate properties as in the case of single rubbers. The elongation at break decreases with increase in sulphur content or CBS content as expected (Figs.5.3 and 5.4). Both tensile strength and elongation at break severely deteriorate with ageing which might be due to the extensive main chain scission. The 50/50 NR/BR blend seems to be less resistant to ageing than the 50/50 NR/SBR blend (Chapter 4). The destruction of network in the case of this blend seems to the more similar to that of NR. The retention in tensile strength and elongation at break are slightly better in the formulations with higher accelerator to sulphur ratio. This shows that the vulcanizates in these cases have more stable network structures, due to higher concentration of monosulphidic crosslinks.

Hardness and modulus which are direct measures of the crosslink density improve with increase in sulphur and/or accelerator (Figs.5.5 and 5.6). Whereas these properties improve with ageing for 50/50 NR/SBR blend (Chapter 4), these decrease in this case. This behaviour is expected since the total crosslink density decreases in the case of the 50/50 NR/BR blend with ageing. The retention in these properties

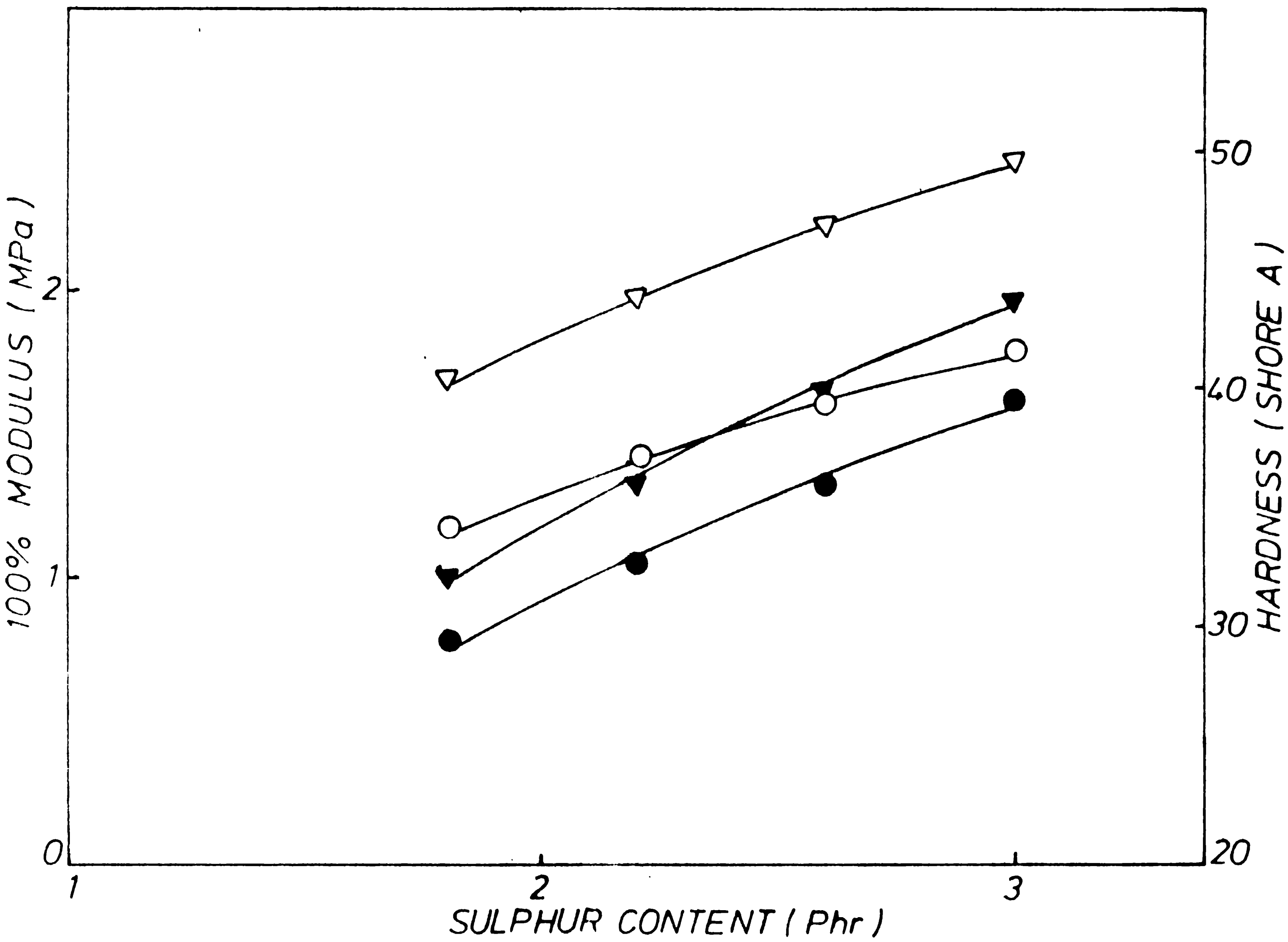

Fig.5.5 Variation of modulus (○) and hardness (△) of 50/50 NR/BR vulcanizate with sulphur content: (○,△) before ageing; (●,▲) after ageing.

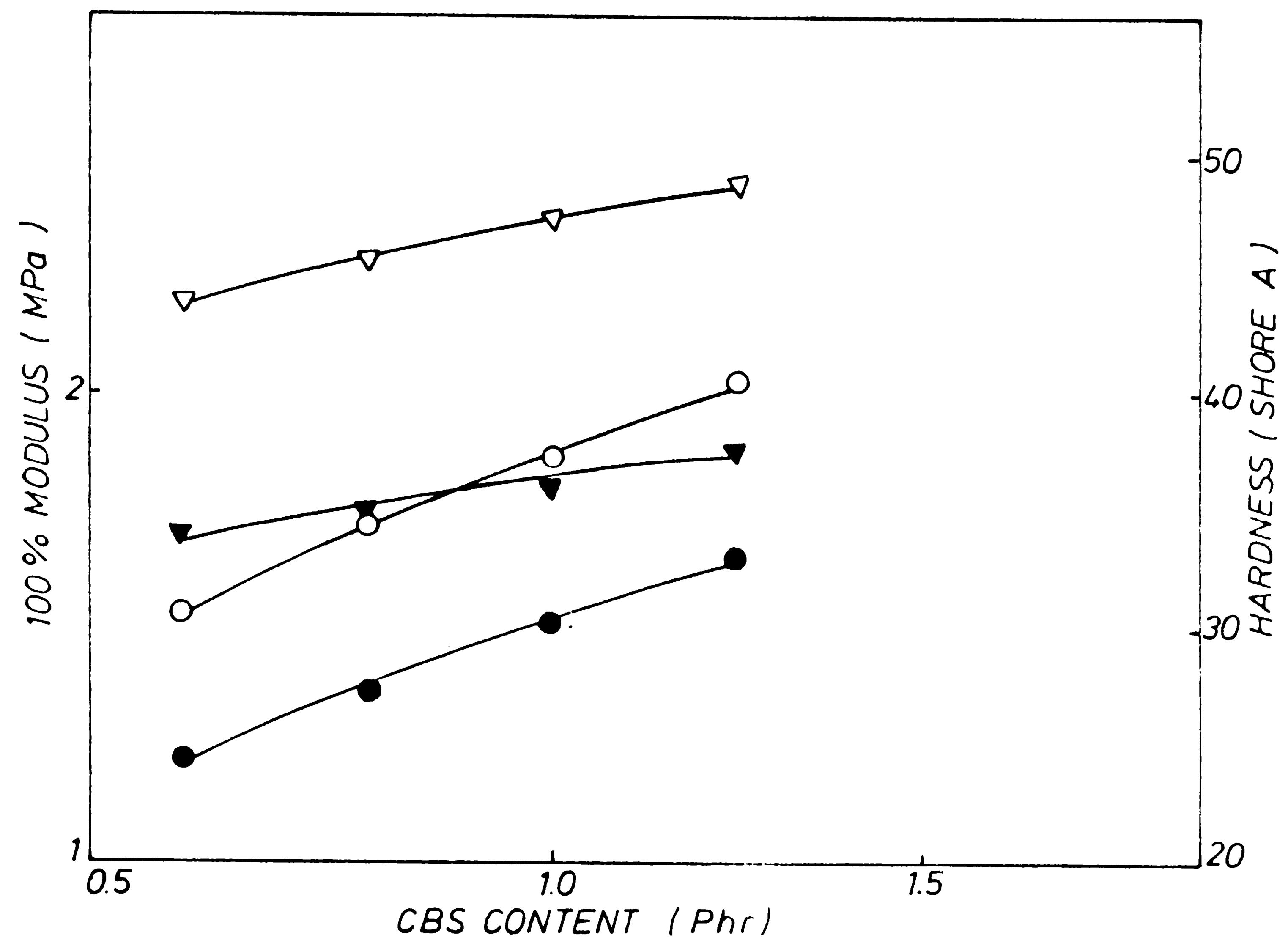

Fig.5.6 Variation of modulus (○) and hardness (△) of 50/50 NR/BR vulcanizates with CBS content: (○,△) before ageing; (●,▲) after ageing.

improves with increase in sulphur content in the compound. This is because a larger percentage of polysulphidic linkages is available in these cases for chain shortening and the resulting additional crosslinking leads to only a slight reduction in the overall crosslink density.

Some special characteristics of 50/50 NR/BR blend require mention. Mill mixing of 50/50 NR/BR blend was found to be much easier than that of BR alone. This behaviour agrees with the common observation that difficulties in the processing of polybutadienes could be overcome by blending with natural rubber.[13] The properties of 50/50 NR/BR blends were much dependent upon the blending parameters. This behaviour might be related to the distribution of carbon black in the two rubbers. As demonstrated by Hess[13] if the black locates preferentially in the BR component, optimum vulcanizate properties will result. While carbon black could be located in the BR·phase by special blending techniques, only normal blending method (preparing the rubber blend initially and then adding the other ingredients in the usual order) was tried in this study. Hence the filler distribution might be dependent mostly on the affinity of carbon black to the two rubbers [14] and the initial viscosity levels of the rubber phases.[15] While BR is very resistant to breakdown during mastication, there is a significant change in the viscosity of NR with mastication. This means that if a higher mastication time is given for NR it can result in the accumulation of a larger amount of black in that phase. Another reason for the dependence of the properties of this blend upon the blending parameters can be the phase inversion phenomenon observed in 50/50 NR/BR blend.[16] The blending parameters could shift the phase morphology of the blend resulting in widely differing properties for the blend.

Conclusions

The following conclusions could be drawn about the cure characteristics, network structure and vulcanizate properties of 50/50 NR/BR blend.

1. The processing characteristics of the blend are much superior to that of polybutadiene.

2. The blending parameters have an important say in the distribution of carbon black in the two phases and the phase inversion behaviour of the blend and hence on the vulcanizate properties.

3. The blend shows fairly good reversion resistance, but is not as good as 50/50 NR/SBR blend.

4. The total crosslink density and the proportions of mono-, di- and polysulphidic linkages of the vulcanizates could be estimated by the chemical probes described in Chapter 2.

5. Varying the amounts of sulphur and accelerator produces smooth variations in the curing behaviour and vulcanizate properties. Hence designing suitable formulations to achieve specific vulcanizate properties is not difficult.

6. The overall crosslink density decreases at the time of thermal ageing accompanied by chain shortening of the polysulphidic linkages with additional crosslinking.

7. The dependence of physical properties on the network structure is more or less similar to that for NR.

8. The physical properties of the vulcanizates deteriorate much more during thermal ageing than the deterioration observed in the case of 50/50 NR/SBR blend.

9. The amounts of free sulphur and zinc sulphide sulphur in the vulcanizates increase with increase in sulphur content but decrease with increase in accelerator content. While there is practically no change in the amount of zinc sulphide sulphur with thermal ageing part of the free sulphur gets used up probably in additional crosslinking.

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Chapter 6

POLYMER-SOLVENT INTERACTION PARAMETER FOR ELASTOMER BLENDS

POLYMER-SOLVENT INTERACTION PARAMETER FOR ELASTOMER BLENDS

The Flory-Rehner equation[1,2] which relates the effective concentration of network chains to the volume fraction of swollen polymer is widely used in the calculation of crosslinking parameters of vulcanized networks. This equation includes the interaction parameter χ which depends on the intermolecular forces between the polymer and the solvent and varies as a function of temperature, nature of the solvent and the type and composition of the polymer. According to the theory[1,2] χ should not depend on the degree of crosslinking. Experimental tests have shown that the interaction parameter of natural rubber with benzene does not depend on the degree of vulcanization for peroxide vulcanizates[3,4] but does depend on it for sulphur vulcanizates.[5,6] The dependence of χ on the concentration of crosslinks has also been demonstrated on vulcanizates of other rubbers like styrene-butadiene[7], polybutadiene[8], ethylene-propylene[9,10] and silicone.[11]

For determining the network structure of vulcanizates of elastomer blends it is required to know their interaction parameters in common solvents. The experimental procedures for determination of the interaction parameter is usually based on the Flory-Huggins theory of polymer solutions.[12-15] According to theory, the free energy of mixing of a polymer solution is given by

$$\Delta F = RT(n_1 \ln V_{r1} + n_2 \ln V_{r2} + \chi n_1 V_{r2})$$

where ΔF is the free energy of mixing of a polymer solution,

R	the gas constant
T	the absolute temperature
n_1	the number of moles of solvent
n_2	the number of moles of solute
V_{r1}	volume fraction of solvent
and V_{r2}	the volume fraction of solute

From this relation useful relationships between χ and various experimentally measurable colligative properties have been derived which could be used for calculation of χ. But often experimental data for a particular polymer/solvent system are not available and one has to rely upon other methods of estimating χ such as resolving χ into entropy and enthalpy components.[16] Otherwise χ must be determined by substituting in M_c values obtained from a method other than swelling in the

Flory-Rehner equation together with the corresponding values of V_r. In this study a simple method suggested by Hayes[17] is used for calculation of the interaction parameters.

The modified Flory-Rehner equation[18],

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

was used for the study. In this equation,

V_r = volume fraction of rubber in swollen sample

V_s = molar volume of solvent

$\frac{1}{2M_c}$ = crosslink concentration

and ρ = density of rubber.

Since the crosslink density of a vulcanizate should not change with the change of solvent, swelling data in two solvents of the same vulcanizate will provide an equation between χ_1 and χ_2, the interaction parameters of the polymer in the solvents. If there are two types of vulcanizates of the same rubber, solvable simultaneous equations will be obtained.

Experimental

The formulations used for preparing the vulcanizates for the swelling study are shown in Table 6.1. Peroxide curing

Table 6.1 Formulations used for the preparation of the vulcanizates

Vulcanizate	1	2	3	4	5	6	7	8	9
NR	100	75	50	25	--	75	50	25	--
SBR	--	25	50	75	100	--	--	--	--
BR	--	--	--	--	--	25	50	75	100
DCP	3	3	3	3	3	3	3	3	3

was employed to make the interaction parameters independent of the crosslink density. The compounds were prepared on a laboratory mixing mill taking care to mix the elastomers homogenously. The cure curves of the compounds were taken on a Monsanto Rheometer model R 100 at 160°C. The compounds were then vulcanized upto the respective optimum cure times, upto 90% of the optimum cure times and upto 80% of the optimum cure times on a steam heated laboratory hydraulic press at 160°C to get 3 sets of vulcanizates with different crosslink densities for each compound. The volume fraction of vulcanizates (V_r) in benzene, toluene and isooctane was determined as per the method described in Chapter 2.

From the V_r values obtained for the same vulcanizate in benzene and toluene an equation connecting χ_1 and χ_2, the interaction parameters of the polymer in these solvents was derived from the Flory-Rehner equation by equating the crosslink density. Since three vulcanizates of different crosslink densities are available for each rubber or rubber blend this procedure yielded three equations with χ_1 and χ_2 as the unknowns for each rubber or rubber blend. Solving these by linear regression gives the values of χ_1 and χ_2 for the particular rubber or rubber blend. The same procedure was repeated by using the solvents isooctane and toluene to get the interaction parameter for the rubbers and rubber blends in these solvents.

Results and Discussion

Figures 6.1 and 6.2 show the values of interaction parameters of the rubbers and rubber blends in benzene and toluene obtained from the swelling data in benzene and toluene. Figures 6.3 and 6.4 show the values of interaction parameters of the rubbers and rubber blends in isooctane and toluene calculated from the swelling data in isooctane and toluene. The interaction parameters of NR and SBR in isooctane and toluene using the isooctane-toluene system are fairly in agreement with those obtained by Hayes.[17] However, the values do not compare favourably with the values recorded in earlier literature.[16] Further the values calculated for the rubbers and rubber blends in toluene employing the benzene-toluene system do not agree with the values calculated from the isooctane-toluene system. This shows that the interaction parameters calculated by this method depend upon the system of solvents employed for the study. This might be due to the differences (eg., chain entanglements) occurring in the network of the vulcanizates in presence of different solvents.[19]

There are some interesting features worth-noting. Benzene and toluene are good solvents for the polymers under study and hence the interaction parameters of the polymers and their blends in these solvents calculated from the swelling

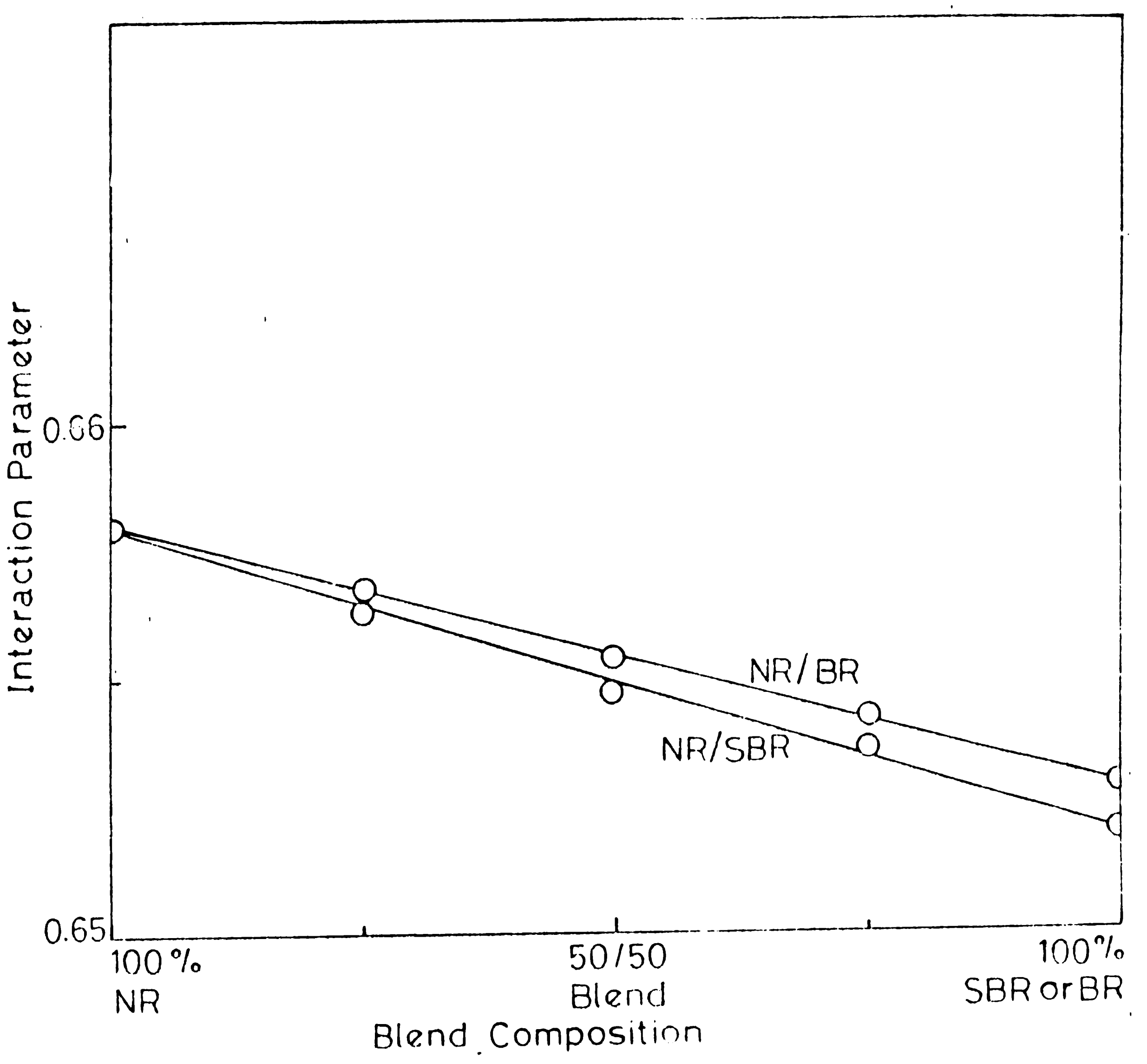

Fig.6.1 Variation of Polymer-Solvent interaction parameter of NR/SBR and NR/BR blend in benzene with the blend composition (Benzene-Toluene system).

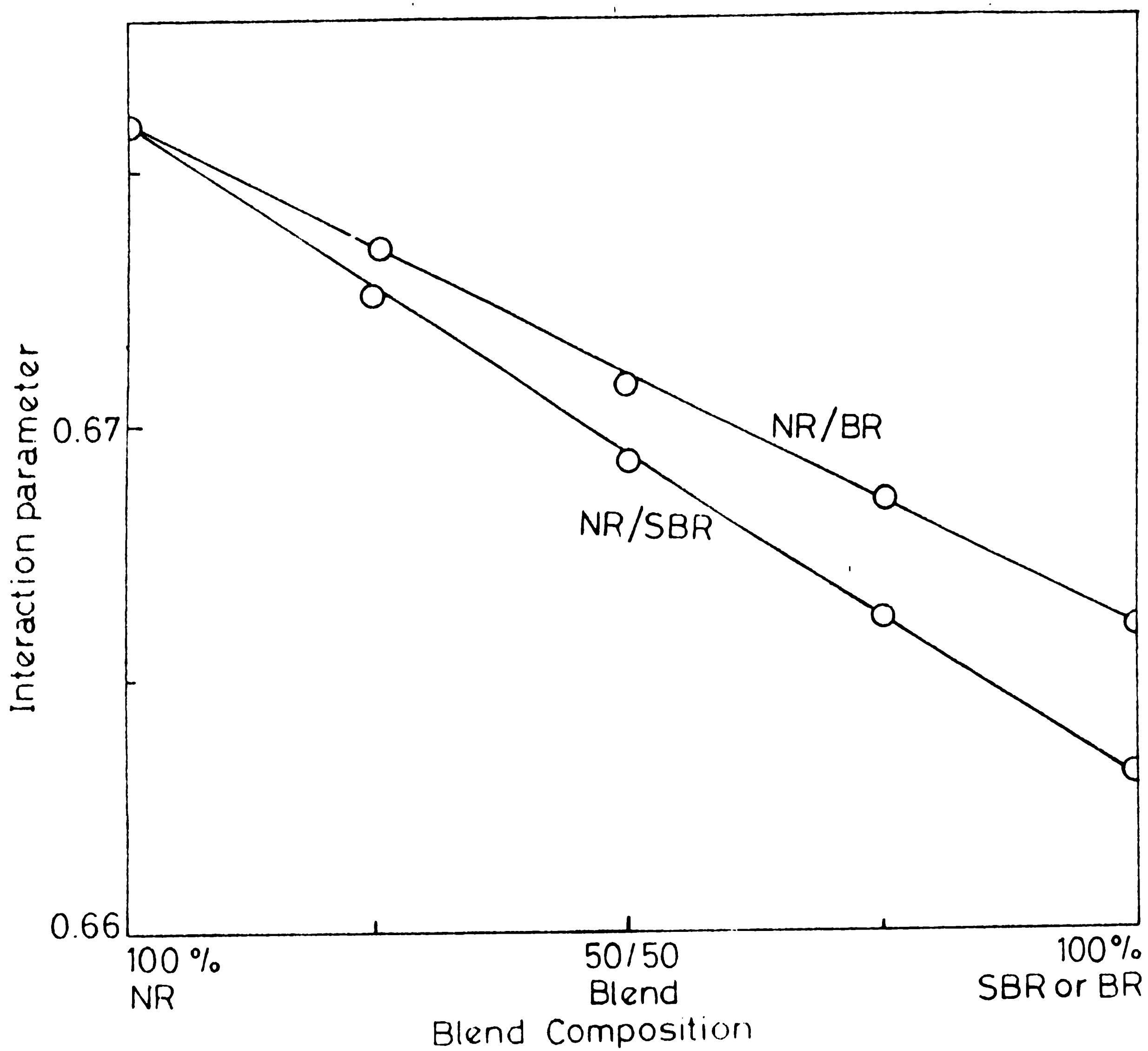

Fig.6.2 Variation of Polymer-Solvent interaction parameter of NR/SBR and NR/BR blend in toluene with the blend

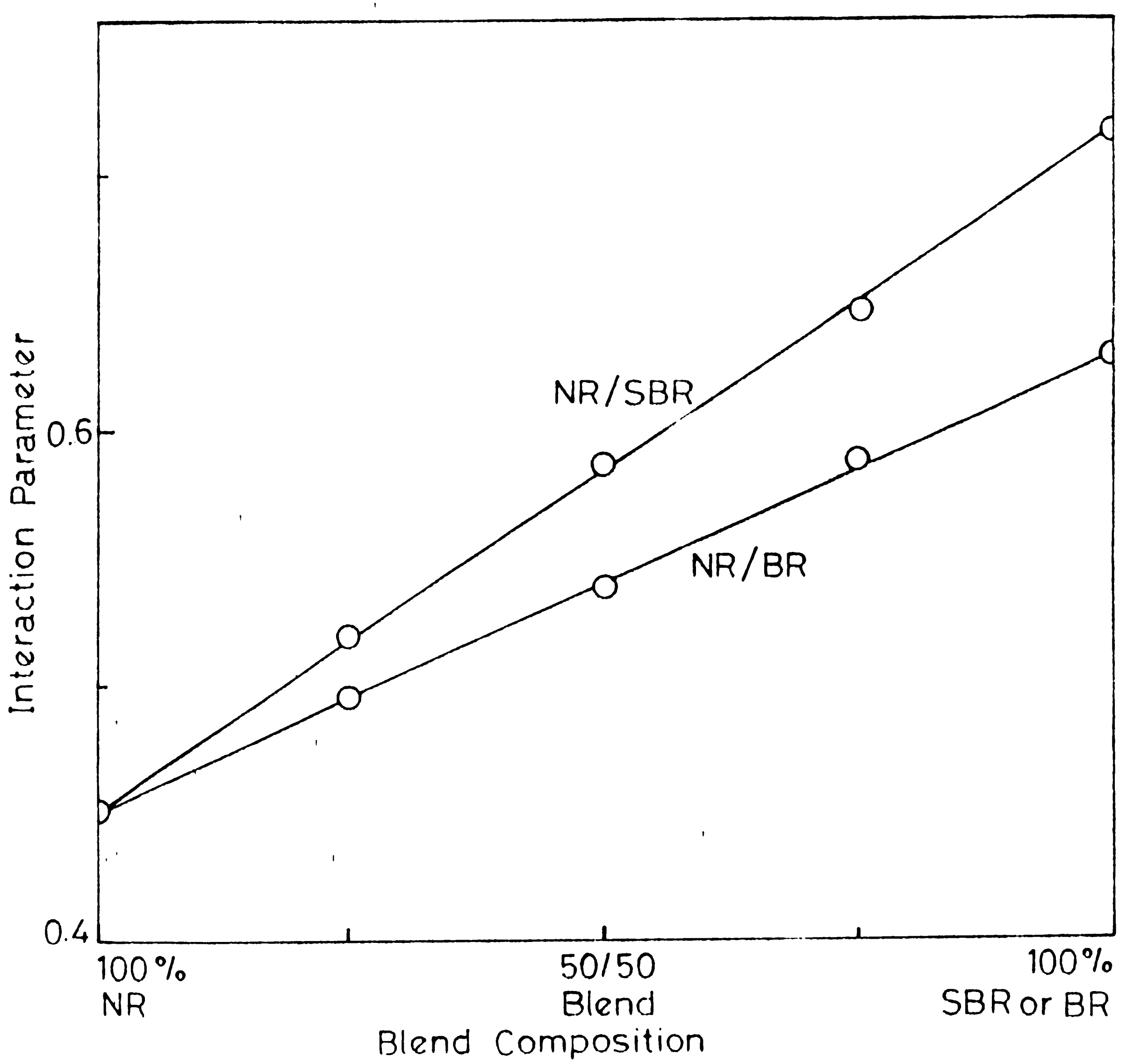

Fig.6.3 Variation of Polymer-Solvent interaction parameter of NR/SBR and NR/BR blend in isooctane with the blend composition (Isooctane-Toluene system)

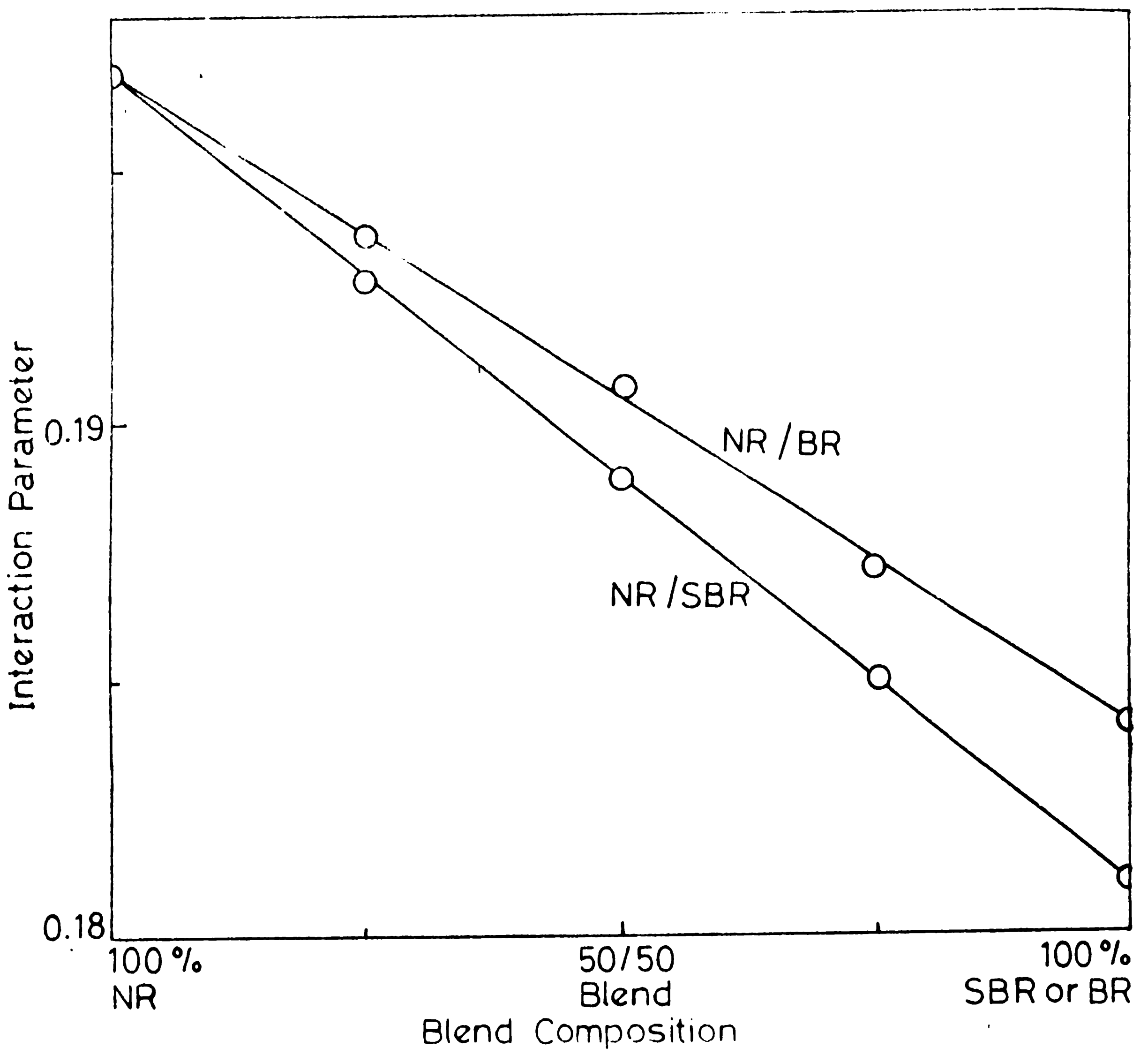

Fig.6.4 Variation of Polymer-Solvent interaction parameter of NR/SBR and NR/BR blend in toluene with the blend composition (Isooctane-Toluene system).

data in the same solvent pair are very close. The spread of values of the interaction parameters for the polymers in each solvent is also very low. Benzene, being a comparatively better solvent than toluene, yields slightly lower values than toluene. The values obtained with the benzene-toluene system are higher than those given in the literature. In the iso-octane-toluene system, toluene is a much better solvent than isooctane and hence the values obtained for the polymers are widely apart. The spread of values obtained for the polymers in isooctane is also high. Toluene, the better solvent yields lower values as before. The values obtained are less than those given in literature in this case. Another point worth noting is regarding the variation of interaction parameters obtained for the elastomer blends with variation in the blend composition. Eventhough the values obtained from the two solvent pairs do not agree, it is interesting to note that in all the cases, the interaction parameter varies linearly with blend composition. This suggests that for blends such as NR/SBR and NR/BR which are fairly compatible the interaction parameter varies linearly with the blend composition and so the values may be calculated if the individual values of the polymers are known.

Conclusions

The following conclusions could be drawn from this study.

1. The values of interaction parameters calculated from the Flory-Rehner equation by equating the network density of vulcanizates in two solvents are highly dependent upon the system of solvents used.

2. The interaction parameters for NR/SBR and NR/BR blends vary linearly with composition.

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Chapter 7

SCANNING ELECTRON MICROSCOPY EXAMINATION OF THE FRACTURE SURFACE OF ELASTOMER BLENDS

SCANNING ELECTRON MICROSCOPY EXAMINATION OF THE FRACTURE SURFACE OF ELASTOMER BLENDS

Scanning electron microscopes (SEM) first became widely available in the late nineteen sixties and they soon found applications in many branches of science and engineering. The resolving power of SEM is much greater than that of an optical microscope, permitting highly detailed study of surface morphology. SEM is more revealing and more convenient to operate. SEM is now widely used for the study of polymer blends. Earlier SEM was used for the study of polymer blend morphology. Walters and Keyte[1] were the first to make an extensive study of the factors that affect the zone size of the dispersed phase in polymer blends by phase contrast microscopy. They observed different polymer phases in polymer blends and found that minimum phase sizes were obtained when the blended polymers had similar viscosities or molecular weights. More recently electron microscopy has been used to study the morphology of polymer blends. Hess and co-workers[2] have obtained excellent phase contrast of natural rubber blends with styrene-butadiene rubber, polybutadiene and chlorobutyl rubber. They confirmed the importance of the viscosity of the polymers on the zone size of the dispersed phase. Marsh and co-workers[3,4] found distinct phase differentiation for all polymer blends studied with the exception of SBR/BR blends and concluded that these blends are homogeneous i.e., they form a molecular solution. However, Callan and co-workers[5] examined blends of SBR with three types of BR and detected discrete polymer zones in each instance. Gardiner[6] has suggested that the smaller the differences in critical surface tension, solubility parameter and solvent interaction parameter between the polymers, the smaller the zone sizes will be. Lewis and co-workers[7] have combined autoradiography with electron microscopy to identify accurately the phases in two component elastomer blends. Kiyek and Schoon[8] found that in polymer blends the harder component is embedded in the softer in the form of spheres.

SEM is also used now for observation of the fracture surfaces in rubber.[9-11] When parts fail in mechanical products the fracture surface of the broken part provides important clues to the cause of the breakdown. The general procedure for examining the fracture surface and analysing the failure so as to deduce the cause of the breakdown involves first of all examining the fracture surface on the macro and micro levels relating the results of these observations with the working environment and the working condition of the part. If this analytical procedure is carried out properly and systematically the cause of the failure can be elucidated and hence it is possible to take remedial action quickly and thus prevent the recurrence of the failure.[9] For many years the study of fractography has been applied to metal and the failure analysis techniques are gradually being established. Manuals for macro- and micro-analysis have been produced and these are actively used. However there have been few systematic investigations or studies in connection with the failure analysis of rubber materials. The SEM observation of fracture surface of rubber is particularly important because the behaviour of rubbers is very sensitive to factors such as the concentration, distribution and orientation of the filler and the adhesion between the rubbery polymer matrix and the filler.[10] The situation is extremely complex in the case of elastomer blends since the mechanical behaviour of blended rubbers is very sensitive to the compatibility of the rubbers, filler distribution and level, curing aspects etc. Hence scanning electron microscopy would be a very useful tool to observe the fracture surfaces of elastomer blends and hence to decipher the fracture mechanisms. In this study an attempt has been made to observe the micro structure of the fracture surface of test samples in tension and abrasion of NR/SBR and NR/BR blends and to correlate it with the strength and type of failure of these materials.

Experimental

The test samples were prepared from gum and filled 50/50 blends of NR/SBR and NR/BR. The formulations employed are shown in Tables 7.1, 7.2 and 7.3. The compounds were prepared on a laboratory mixing mill at near ambient temperature. The rubber blends were prepared initially and then the other additives followed in the usual order. The cure curves of the compounds were taken on a Monsanto Rheometer model R 100 at 150°C. Then the compounds were vulcanized upto their respective optimum cure times on a steam heated laboratory hydraulic press. Dumb-bell samples were punched out along the mill grain direction from the moulded sheets of 15x15x0.2 cm size. Test pieces of 2x2x1 cm size were directly moulded for abrasion testing. The tensile testing and abrasion resistance testing of the samples were done as per ASTM D 412 (1980) and ASTM D 394 respectively.

The failed tensile test pieces and the abraded surfaces were stored in a desiccator to avoid contamination from dust particles. Fracture surfaces were sputtercoated with gold within 24 hours of testing. SEM observations were made using a Philips 500 model scanning electron microscope.

Results and Discussion

The tensile fracture surface of filled NR/SBR vulcanizates 1, 2, 3 and 4 (Table 7.1) are shown in Figs.

Table 7.1 Formulations of filled NR/SBR vulcanizates selected for SEM observation

Vulcanizate	1	2	3	4
NR	50.0	50.0	50.0	50.0
SBR	50.0	50.0	50.0	50.0
ZnO	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0
PBN	1.0	1.0	1.0	1.0
HAF black (N 330)	40.0	40.0	40.0	40.0
Aromatic oil	4.0	4.0	4.0	4.0
CBS	0.8	0.8	0.6	1.4
Sulphur	1.8	3.0	2.0	2.0

Table 7.2 Formulations of filled NR/BR vulcanizates selected for SEM observation

Vulcanizate	5	6	7	8
NR	50.0	50.0	50.0	50.0
BR	50.0	50.0	50.0	50.0
ZnO	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0
PBN	1.0	1.0	1.0	1.0
HAF black (N 330)	40.0	40.0	40.0	40.0
Aromatic oil	4.0	4.0	4.0	4.0
CBS	0.7	0.7	0.6	1.2
Sulphur	1.8	3.0	2.2	2.2

Table 7.3 Formulations of gum NR/SBR vulcanizates selected for SEM observation

Vulcanizate	9	10	11	12
NR	50.0	50.0	50.0	50.0
SBR	50.0	50.0	50.0	50.0
ZnO	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0
CBS	1.2	1.2	1.0	2.0
Sulphur	1.2	2.1	1.6	1.6

7.1, 7.2, 7.3 and 7.4 respectively. Increase in either sulphur or accelerator in the compound increases the crosslink density of the matrix which results in enhanced strength (Chapter 4). This could be observed from the SEM photographs by the progressive increase in the roughness of the fracture surfaces[9-10] between Figs.7.1 and 7.2 and Figs.7.3 and 7.4. This shows that 50/50 NR/SBR blend behaves more or less similar to that of single rubbers producing a regular pattern in the network structure with a change in the concentration of the curatives. This further shows that formulations could be easily designed for NR/SBR blends as in the case of single rubbers to obtain specific vulcanizate properties.

Figures 7.5, 7.6, 7.7 and 7.8 show the tensile fracture surfaces of filled 50/50 NR/BR vulcanizates 5, 6, 7 and 8 (Table 7.2). These figures suggest that the behaviour of 50/50 NR/BR blend is also similar to that of the 50/50 NR/SBR blend. This is expected since the variation of crosslink density of NR/BR vulcanizate with increase in either sulphur or accelerator in the compound is similar to that of the NR/SBR vulcanizate (Chapter 5). The improvement in strength in this case could be observed from the broadening of the tearpath with an increasing number of branches.[9,10] The difference is clearly seen between Figs.7.7 and 7.8. The regular pattern of variation observed in the fracture surface

Fig.7.1 Tensile fracture surface of vulcanizate 1 (Table 7.1)

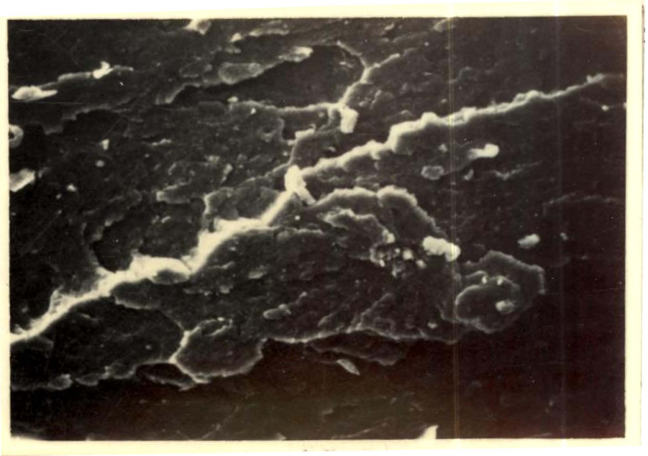

Fig.7.2 Tensile fracture surface of vulcanizate 2 (Table 7.1)

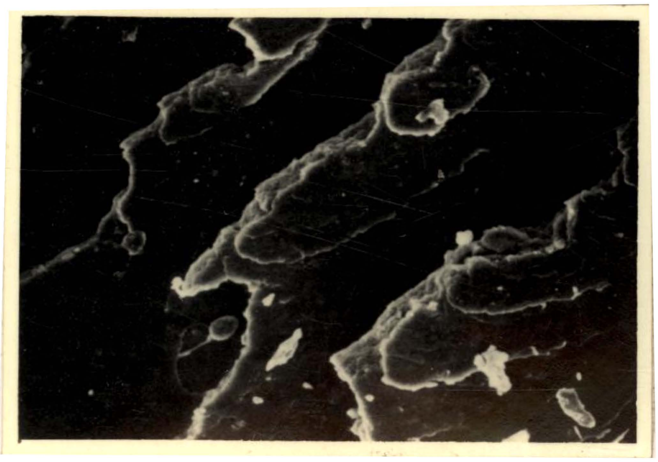

Fig.7.3 Tensile fracture surface of vulcanizate 3 (Table 7.1)

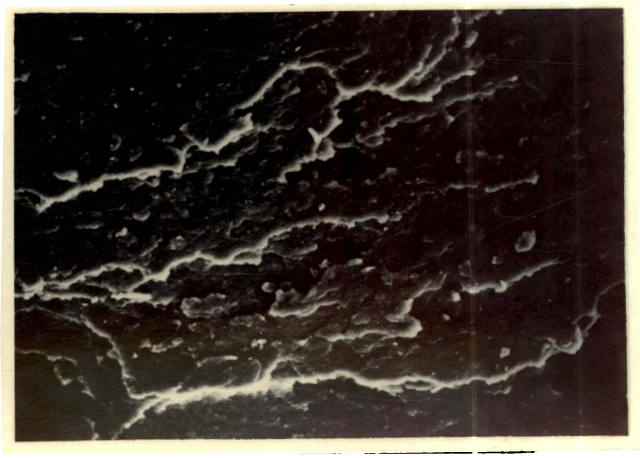

Fig.7.4 Tensile fracture surface of vulcanizate 4 (Table 7.1)

SEM photographs of the tensile fracture surface of filled 50/50 NR/SBR vulcanizates (x 200).

Fig.7.5 Tensile fracture surface of vulcanizate 5 (Table 7.2)

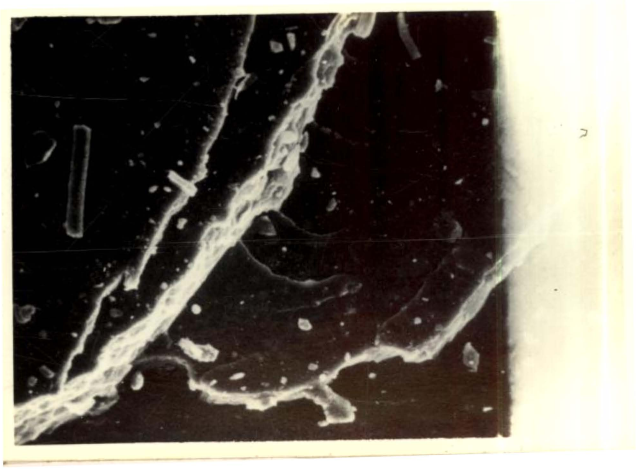

Fig.7.6 Tensile fracture surface of vulcanizate 6 (Table 7.2)

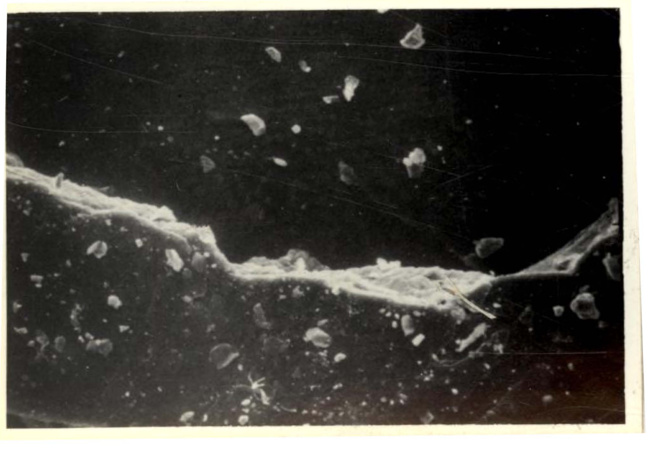

Fig.7.7 Tensile fracture surface of vulcanizate 7 (Table 7.2)

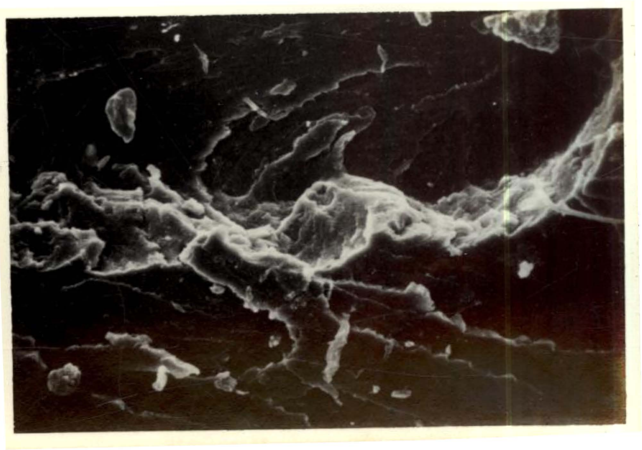

Fig.7.8 Tensile fracture surface of vulcanizate 8 (Table 7.2)

SEM photographs of the tensile fracture surface of filled 50/50 NR/BR vulcanizates (x 200.

with increase in either sulphur or accelerator shows that the behaviour of NR/BR blend is also similar to that of a single elastomer and hence suitable formulations could be chosen for specific applications.

Figures 7.9, 7.10, 7.11 and 7.12 show the abraded surface of 50/50 NR/BR vulcanizates 5, 6, 7 and 8 (Table 7.2). In this case also a significant change is noticeable between Figs.7.9 and 7.10 and Figs.7.11 and 7.12. Figures 7.9 and 7.11 show a pattern indicating less resistance to abrasion whereas Figs.7.10 and 7.12 show no pattern indicating much better abrasion resistance.[9,10] This is obviously due to the increase in crosslink density in turn due to the higher amounts of sulphur/or accelerator in the compound.

Figures 7.13, 7.14, 7.15 and 7.16 show the tensile fracture surfaces of 50/50 NR/BR vulcanizates 5, 6, 7 and 8 (Table 7.2) after ageing. A comparison of these figures with the corresponding figures of the same vulcanizates before ageing shows that the pattern is more or less similar. However, there is a significant increase in the roughness of the surfaces with ageing which indicates that the matrix becomes more brittle with ageing.[9,10]

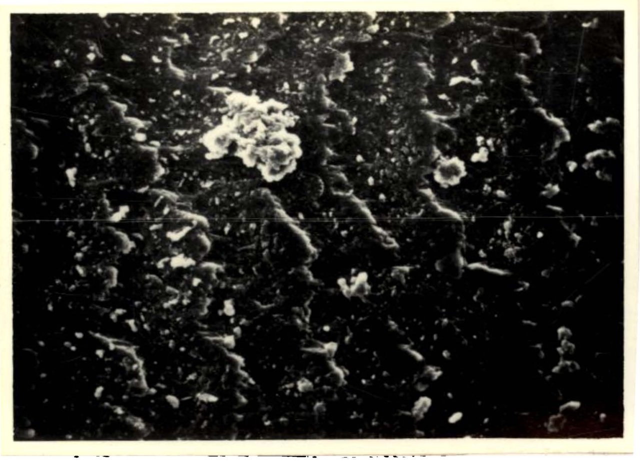

Fig.7.9 Abraded surface of vulcanizate 5 (Table 7.2)

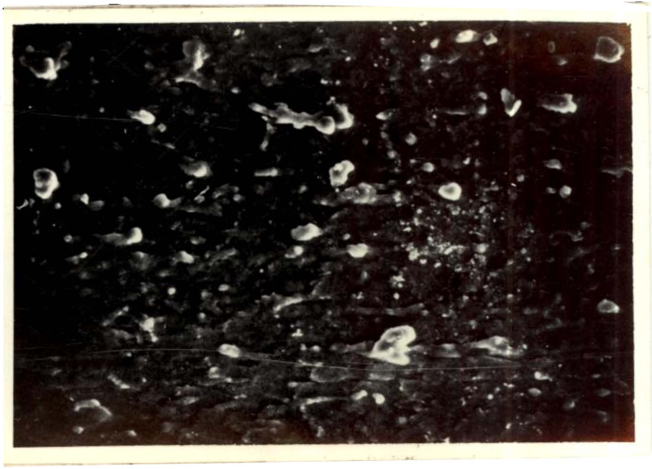

Fig.7.10 Abraded surface of vulcanizate 6 (Table 7.2)

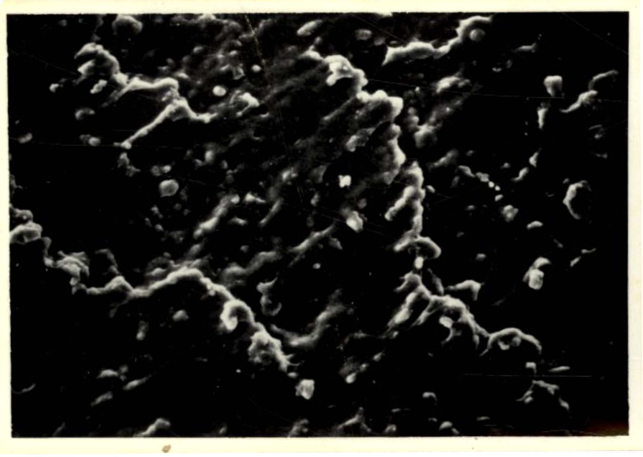

Fig.7.11 Abraded surface of vulcanizate 7 (Table 7.2)

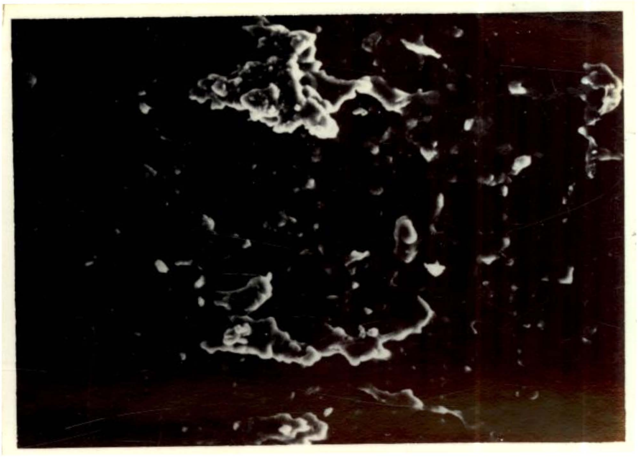

Fig.7.12 Abraded surface of vulcanizate 8 (Table 7.2)

SEM photographs of the abraded surface of filled 50/50 NR/BR vulcanizates (x 200).

Fig.7.13 Tensile fracture surface of vulcanizate 5 (Table 7.2)

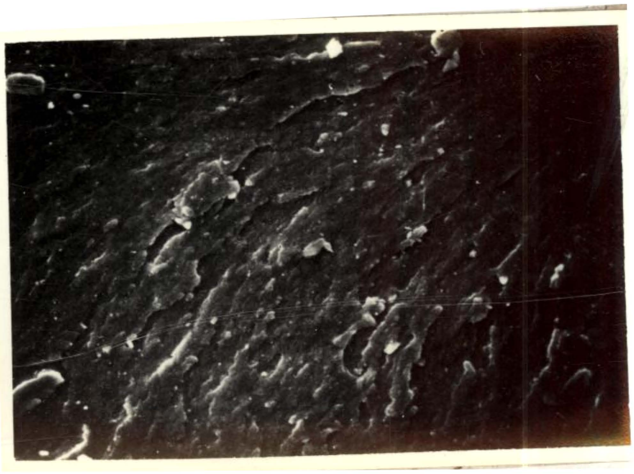

Fig.7.14 Tensile fracture surface of vulcanizate 6 (Table 7.2)

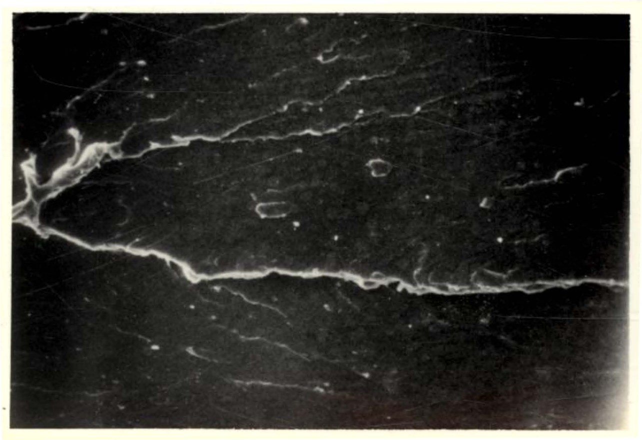

Fig.7.15 Tensile fracture surface of vulcanizate 7 (Table 7.2)

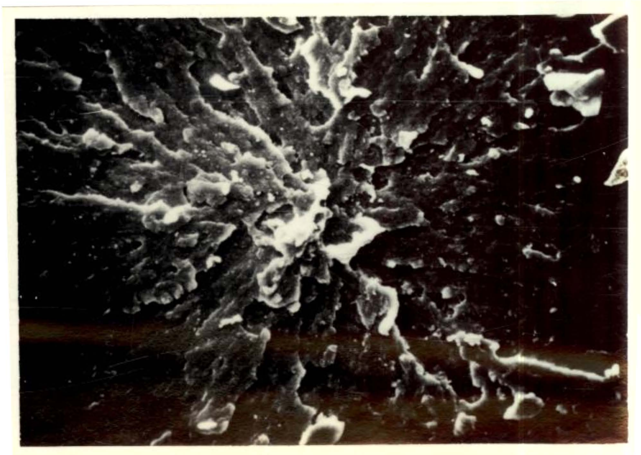

Fig.7.16 Tensile fracture surface of vulcanizate 8 (Table 7.2)

SEM photographs of the tensile fracture surface of filled 50/50 NR/BR vulcanizates after ageing (x 200).

Figures 7.17, 7.18, 7.19 and 7.20 show the tensile fracture surfaces of 50/50 NR/SBR vulcanizates 9, 10, 11 and 12 (Table 7.3) without fillers and are similar to those of the corresponding filled vulcanizates. While Figs.7.17 and 7.19 show a smooth surface indicative of less strength, Figs.7.18 and 7.20 show multiple tear lines indicating much improved strengths.[9,11] The difference is clearly seen between Figs.7.17 and 7.18 in this case.

Conclusions

The study shows that variation of the amounts of sulphur or accelerator in 50/50 blends of NR/SBR and NR/BR produces effects similar to those produced in NR, SBR or BR and hence designing suitable formulations for attaining required vulcanizate properties for these blends could be done as in the case of corresponding single rubbers. The study further shows that scanning electron microscopy studies of the fracture surfaces could be valuably used to determine the fracture mechanisms and mechanical behaviour of rubber blends.

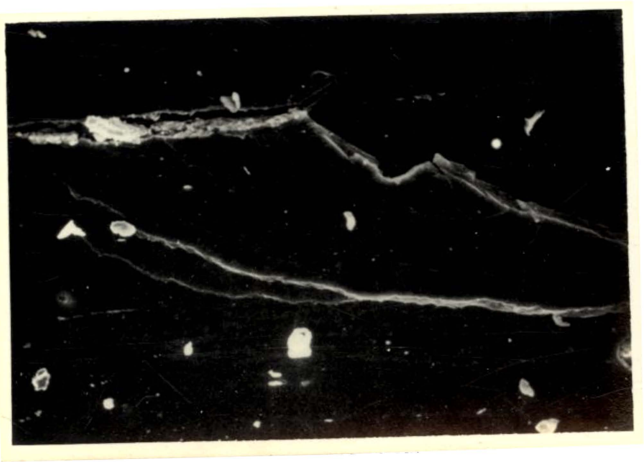

Fig.7.17 Tensile fracture surface of vulcanizate 9 (Table 7.3)

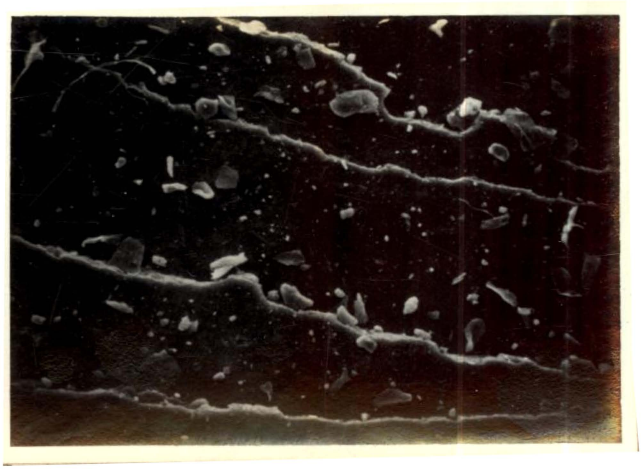

Fig.7.18 Tensile fracture surface of vulcanizate 10 (Table 7.3)

Fig.7.19 Tensile fracture surface of vulcanizate 11 (Tanle 7.3)

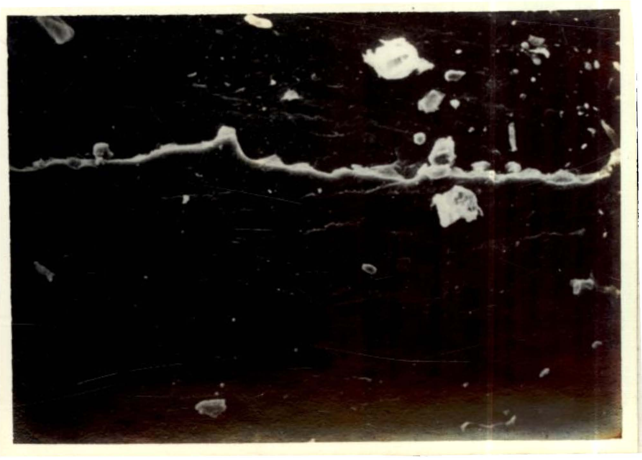

Fig.7.20 Tensile fracture surface of vulcanizate 12 (Table 7.3)

SEM photographs of the tensile fracture surface of gum 50/50 NR/SBR vulcanizates (x 200).

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Chapter 8

SUMMARY AND CONCLUSIONS

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This investigation had led to the following conclusions regarding the curing behaviour and vulcanizate properties of elastomer blends.

The distribution of curing agents in the constituents of an elastomer blend is an important factor which determines the curing behaviour and vulcanizate properties of the blend. The distribution of the curatives largely depends on the nature of the elastomers. The conventional curing agents tend to migrate preferentially to the rubber with higher unsaturation and/or higher polarity. If for a given binary rubber blend the tendency of the curatives for migration to the two rubbers is nearly same,different blending techniques , such as (1) conventional blending viz., rubbers are blended and the total amount of additives for both the rubbers are added together, (2) compound blending in which compounds for the two rubbers are separately prepared and then blended together and (3) master batch blending in which the total amounts of the additives are added to the slower curing rubber and then the other rubber is blended with this compound, can influence the distribution of curatives and hence the curing behaviour and vulcanizate properties of the blend. The vulcanizate properties of elastomer blends are found to be most affected by the degree of crosslinking in the different phases particularly the phase(s) which is continuous.

The curing behaviour of elastomer blends can be employed to determine the relative compatibility of the constituent elastomers. If the constituents are compatible, there will be a smooth variation of the curing behaviour with the composition of the blend from the behaviour of one component at one end and the other component at the other end.

Two industrially important blends viz., NR/SBR and NR/BR were selected for detailed study in this investigation. The behaviour of the NR/SBR and NR/BR blends in many respects are found to be more or less similar to the behaviour of a single elastomer. Variations of curing agents like sulphur or accelerator produce smooth variations in the curing behaviour displaying the same pattern as in the case of single elastomers. Hence designing suitable formulations for these blends to obtain a set of vulcanizate properties for specific applications is possible. Eventhough the NR phase takes a slightly larger share of the curative leaving SBR or BR slightly under crosslinked in conventional compounding, this does not affect the physical properties of the vulcanizates seriously. Both SBR and BR impart some heat resistance to

NR, but the degree of resistance imparted by SBR is found to be much superior. SBR offers good reversion resistance during the curing stage and also good heat ageing resistance for the vulcanizates.

Another significant finding is the observation that the network structure of NR/SBR and NR/BR vulcanizates can be determined from the simplified procedures outlined in this thesis. The total crosslink density and the proportions of mono-, di- and polysulphide linkages explain in most cases the mechanical behaviour of these vulcanizates. The changes occurring in the network structure during thermal ageing explain the deterioration in properties of these vulcanizates with ageing.

A serious drawback in the use of swelling methods for the network structure determination of elastomer blends, is the nonavailability of the rubber-solvent interaction parameter (χ). The observation that χ varies linearly with composition for NR/SBR and NR/BR blends would help to elucidate the network structure of their vulcanizates more easily in future studies.

Since the mechanical behaviour of elastomer blend vulcanizates is very sensitive to compatibility of the elastomers, crosslink densities and network structure of the different phases, filler distribution in the rubbers, amount of interphase crosslinking etc., it is important to have a good means of studying the fracture mechanisms of elastomer blends. Scanning electron microscopy has been found to be a very efficient tool in deciphering the fracture mechanisms of elastomer blends. SEM observations of the microstructure of the fractured surfaces would be the basis of many future studies on the methods of improving the performance of elastomer blends.

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1. Studies on the cure characteristics of elastomer blends,
   Intern.J.Polymeric Mater., 11, 205-209 (1986).

2. Effect of blending techniques on the curing of elastomer blends,
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3. Studies on the cure characteristics and vulcanizate properties of 50/50 NR/SBR blend,
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4. Studies on 50/50 natural rubber/styrene-butadiene copolymer blend,
   Angew.Makromol.Chem., 152, 107-119 (1987).

5. Studies on the cure characteristics and vulcanizate properties of 50/50 NR/BR blend,
   Intern.J.Polymeric Mater., in press.

6. Polymer-solvent interaction parameters for NR/SBR and NR/BR blends,
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7. Scanning electron microscopy examination of the fracture surface of NR/SBR and NR/BR blends,
   Intern.J.Polymeric Mater., in press.