STUDIES ON NEW BASE MATERIALS FOR MICROCELLULAR SOLES

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By

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AUGUST 1998

CERTIFICATE

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

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DECLARATION

I hereby declare that the thesis entitled "**Studies on new base materials for microcellular soles**" is the original work carried out by me under the supervision of Dr.K.E.George, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi 682022, and no part of this thesis has been presented for any other degree from any other institution.

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CONTENTS

CHAPTER 6

LIST OF ABBREVIATIONS USED IN THIS THESIS

Polymers

NR	Natural rubber
NBR	Acrylonitrile butadiene rubber
SBR	Styrene-butadiene rubber
BR	Polybutadiene rubber
HSR	High styrene resin
EVA	Ethylene-vinyl acetate
SBS	Styrene-butadiene styrene
ENR	Epoxidized natural rubber
PE	Polyethylene
LDPE	Low density polyethylene
HDPE	High density polyethylene
S-PVC	Suspension grade poly(vinyl chloride)
E-PVC	Emulsion grade poly(vinyl chloride)

Additives

ZnO	Zinc oxide
MgO	Magnesium oxide
TiO_2	Titanium dioxide
DCP	Dicumyl peroxide
S	Sulphur
ZMBT	Zinc salt of mercaptobenzthiazole
MBTS	Dibenzthiazyl disulphide
TMTD	Tetramethyl thiuram disulphide
ATNR	Amine terminated liquid natural rubber
DEG	Diethylene glycol

DOP	Dioctyl phthalate
SP	Styrenated phenol
HAF	High abrasion furnace black
ADC	Azodicarbonamide
DNPT	Dinitrosopentamethylene tetramine

Other abbreviations

MC	Microcellular soles
TPE	Thermoplastic elastomer
Phr	Parts per hundred rubber/plastic
ISNR	Indian standard natural rubber
ASTM	American society for testing and materials
IS	Indian standards
UTM	Universal testing machine
rpm	Revolutions per minute
T	Absolute temperature
h	Hours
kg	Kilogram
N	Newton
mm	Millimeter
min.	Minutes
ML[(1+4)100°C]	Mooney viscosity determined using large rotor after a dwell time of one minute and rotor run of four minutes at 100°C
IR	Infrared
UV	Ultra violet
TGA	Thermogravimetric analysis
N	Number of cells per unit volume of rubber
ρ_o	Density of solid vulcanizate
ACN	Acrylonitrile

CHAPTER 1

INTRODUCTION

Solid polymers are likely to be replaced by cellular polymers, with 20 to 40 per cent reduction in material without compromising their function or required strength via processes without using any chemicals that are harmful to environment, by the turn of the century [1]. A cellular material may be defined as a solid whose volume contains an appreciable fraction of uniformly dispersed visible or invisible cells or voids. Microcellular (MC) rubbers, as the name implies, contain very small cells. Microcellular soles find use in footwear and has replaced leather to a large extent, because of its light weight which provides wearing comfort, abrasion resistance, long flex life, versatility for hardness range, water proof and its ability to be produced in any colour [2-4].

The three main classes of cellular rubbers are foam, sponge and expanded rubber and MC rubber belong to the third category. Foam rubber is defined as a product made from rubber latex, in which the cellular structure is intercommunicating [3]. Sponge rubber is a general term used for partially open cell (and partially closed cell) materials usually made with chemical blowing agent (usually sodium bicarbonate) from dry rubber. Expanded rubber is also made directly from solid starting materials by using chemical blowing agents (usually nitrogen gas evolving) and are closed-celled. The essential difference among the three is in the production process. The three categories can be distinguished by their water absorption properties. Expanded rubber absorbs less than 10%, sponge more than 15%, while foam absorb more than 40% of water [3]. Closed cells are network of nonintercommunicating cells by the entrapment of inert gases as discrete bubbles in a matrix of rubber. So water absorption is low [5]. In open cell structure the walls between the cells are broken and air passes freely between the cells, which accounts for its high water absorption. A brief description on the manufacture and properties of the three types of cellular rubbers are given below.

1.1 Foam rubber

Foam rubber is a cellular rubber made from liquid latex, in which the cells are all intercommunicating and open or partly intercommunicating (and partly non-intercommunicating). The principle of manufacture is dispersing a gas in a fluid to produce a foam of transient stability and then stabilizing it by chemical reaction. Latex foam was the first cellular polymer produced by frothing. When the gas is dispersed in the latex, rubber particles coalesce and form a continuous rubber phase in the water phase. The aqueous soap film breaks because the surfactants get deactivated in the water. The latex film breaks causing retraction into the connecting struts of the bubbles, and the expanded matrix is cured and stabilized by drying [3,6].

Flexible polyurethane foam is seen as a serious competitor for latex foam rubber. However, moulded latex foam rubber is still preferred where considerations of utility and comfort outweigh those of economics [6]. The unique combination of properties such as softness to touch, resilience, better damping compared with metal spring and easy mouldability to a variety of shapes, sizes and foam densities etc. makes latex foam superior to urethane foam.

1.2 Sponge

The term sponge rubber has been applied to various types of cellular rubber products made directly from solid starting materials. By definition, it is an elastic mass made porous by interconnecting or open cells. For the production of sponge one of the main requirement is a low viscosity compound [7]. To achieve this low viscosity, high proportions of oil is incorporated into the compound. At low levels of viscosity, the low strength of the rubber matrix allows the gas bubbles to coalesce and escape from the matrix, leaving a coarse open structure with a high density. At high level of viscosity, the matrix withstands the expansion forces of the gases enough to increase the degree of expansion but cells break down. At still higher level of viscosity, the forces within the rubber are large which prevent the sponge formation.

Sponge rubber is made directly from a solid material by incorporating in to the compound sodium bicarbonate which expands the mass during the curing cycle [3]. The sodium bicarbonate releases CO_2, which produces open cells level best suited to the product being expanded due to its high permeability. A careful balance of curing combinations and blowing agents is required so that the compound will expand and then set up rapidly to prevent the sponge structure from collapsing before vulcanization takes place. The blowing of the sponge is carried out in a mould which is only partially filled with the moulding compound. Sponge compounds are usually highly blown, and a volume loading of 40-60% is common [5,7,8].

1.3 Expanded rubber

A decomposable blowing agent along with vulcanizing system and other additives is compounded with the uncured elastomer. The process involves an excess weight of the compound being placed in the mould cavity [9]. When the press is closed, the compound completely fills the mould expelling the air and sealing the cavity area. Since the compound is relatively low in plasticity, it flows readily in the mould, coalesces and eliminates trapped air blisters [5]. The rubber expands upon release of pressure and cellular structure is formed.

Closed cell products can be manufactured either by a low pressure or high pressure moulding and extruding. In low pressure moulding mould cavity is partially filled and the process relies on expansion to fill the mould. In high pressure moulding process a two step cure is used. In the first step, the mould cavity is completely filled and a pressure sufficient to partially set the rubber and completely activate the blowing agent is applied. In the second step, the mould is opened to release the pressure and allow the compound to expand greatly beyond the original mould dimensions. The product is then post cured to improve certain physical properties [9]. While the microcellular plastics have been the subject of research in recent years, microcellular rubber have received less attention. The microstructure and the mechanical properties of microcellular rubber have been studied by Gent et al.[10,11] and Kinkar Mukherjee et al. [12]. The study suggests that mechanical properties of the expanded rubber depends on the blowing agent concentration and nature of cell structure and cell size. Due to the cushioning ability, wear resistance and low cost expanded rubber has been extensively used for shoe soles [13].

1.4 Microcellular soles

Microcellular (MC) sole is a special class of expanded rubber whose hardness is different from other expanded rubber, foam or sponge. MC soling made an appearance in the late 1940s [5] and has become very popular in footwear industry. Its use is most hygenic. According to IS specification there are two types of microcellular rubber type I with minimum hardness 65 IRHD and type II with minimum hardness 50 IRHD [14,15]. Microcellular soling based on general purpose polymers can be divided into three categories [16] shown in Table 1.1. Manufacturing process is the same as that described under expanded rubber.

Table 1.1

Different types of microcellular soling based on general purpose polymers

	Approx. Density (g/cc)	Hardness (Shore A)
Beach sandal	0.3	30
Normal expanded soles	0.6	60
Leather shoe soles	0.9	90

1.5 Cell structure

Cell is a single small cavity surrounded partially or completely by its walls. The term cellular polymer is used interchangeably to denote all two. Phase gas-solid systems in which the solid is continuous and composed of a synthetic polymer or rubber.

A true knowledge of the cell structure of a particular cellular polymer would require the size, shape and location of each cell. It is very difficult to locate or characterize the cell, so approximations are employed. Cell size has been characterized by measurements of the cell diameter [17] as a measurement of average cell volume [18,19]. Using the formula number of cells per unit volume of rubber can be calculated [20].

$$N = \frac{6}{\pi d^3}\left(\frac{\rho_o}{\rho_s} - 1\right)$$

where N is the number of cells per unit volume of rubber, d is the average cell diameter, ρ_o and ρ_s are the density of solid vulcanizates and microcellular vulcanizates respectively. It is seen that N is affected by the blowing agent concentration. Mechanical, optical and thermal properties of sponge, expanded and microcellular rubber depend on cell size.

Cell shape is governed predominantly by density and the external forces exerted on the cellular structure before its stabilization in the expanded state. Photographs of cells show the various shapes. An important characteristic of the cell structure is the extent of communication with other cells. This is expressed as fraction of open cells. When many cells are interconnected, the material has a large fraction of open cells and is called open-celled. Conversely, numerous non-interconnecting cells result in a large fraction of closed cells and is termed closed-celled. In closed celled expanded material the gas phase in the cells can contain blowing agent (so called captive blowing agent), air or other gases generated during expansion [13].

Various factors determine the cell structure of a cellular material. To obtain good cell structure it is necessary to have a right balance between the rate of cure of the compound and temperature and rate of decomposition of blowing agent. Selection of blowing agent and an understanding of their decomposition products is important in use of particular application. Inorganic blowing agents such as sodiumbicarbonate, which gives off carbon dioxide gas were used in the manufacture of open celled cellular rubber, i.e. sponge. In contrast, organic blowing agents are capable of producing fine, closed-cell structure in rubber.

The specific pressure of the press is very important in getting a fine cell structure when the pressure is less, the cells are much larger and expansion is high. For higher pressures the expansion is less but cells are very fine and invisible.

The production of open celled or closed celled rubber depends on mould filling and viscosity of the compound. The determination of mould volume loading is necessary to produce product with desired properties. In the case of sponge compounds which are not highly blown mould is partially filled (40-60%) and during curing compound expands and fills the mould which results in the formation of an open cell structure. But in the case of expanded rubber, the compound is filled in the mould with 3-5% excess of the mould volume. For the production of closed-cell rubber the timing for blowing agent decomposition is more critical and must occur early to cause expansion, but late enough to allow the cell walls to strengthen, so that they will not rupture under the blowing stress. In the case of latex foam or urethane foams nucleating agents are added to achieve uniform and consistent cell size [21]. The cell structure of MC soling depends on the dosage of the blowing agent, the volume loading of the mould cavity, the precuring time and temperature and the specific moulding pressure. Finally, to obtain a uniform cell structure uniform distribution of blowing agent in rubber phase is necessary [16].

1.6 Expansion technology

The expansion technology of cellular rubber is conveniently divided into two sections, covering foams on the one hand and sponge and expanded rubbers on the other. The link between the two is the gas phase, which may be air, carbondioxide, nitrogen or ammonia, each of which has special functions in individual circumstances [3]. They are not always interchangeable.

The expansion process has been the subject of extensive investigation because it is the foundation of all cellular polymers [22,23]. In general, the expansion process consists of three steps: creation of small discontinuities or cells in a polymer phase, growth of these cells to a desired volume, and stabilization of the resultant cellular structure by physical or chemical means. Cellular rubbers are produced by chemical stabilization processes [13,22,23]. The general procedure used for the production of cellular rubbers from a variety of rubbers is as follows. A decomposable blowing agent, along with the vulcanizing systems and other additives, is compounded with the uncured elastomer at a temperature below the decomposition temperature of blowing agent [24]. The gas is dissolved in the elastomer under high pressure and expands the compound after depressurization because of gas formation [25]. In the formation of a microcellular rubber blowing and vulcanization take place almost simultaneously. Too early a blowing produces an article of undesirable shape whereas premature vulcanization impedes proper blowing [26]. While vulcanization time can be obtained by cure meters, it is harder to determine the onset of blowing.

When the uncured elastomer is heated in a forming mould it undergoes a viscosity change shown in Fig.1.1 [27]. For a closed celled cellular rubber, the time of blowing agent decomposition is more critical - it must occur soon enough after point A to cause expansion of the elastomer, but far enough past point A to allow the cell walls become strong enough not to rupture under the blowing stress. The expansion of closed celled rubber (MC rubber) is often carried out in two steps. The initial step is a partial one and is carried out in a mould. On removal from this mould the specimen expands partly to its final form. It is then placed in mould of exactly the desired size and is heated more thoroughly to complete the expansion and cure [24,25].

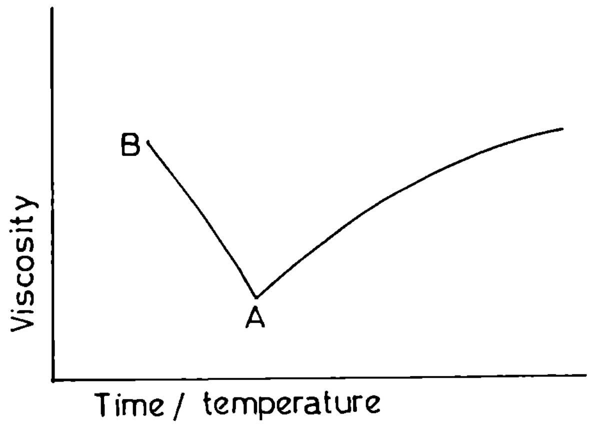


Fig. 1.1 Viscosity of cellular rubber stock during production cycle.

To produce open-celled cellular rubber like sponge the blowing agent is decomposed just prior to point B in Fig. 1.1, so that the gas released at the point of minimum viscosity. As the polymer expands the cell walls become thin and rupture, the connecting struts have developed enough strength to support the sponge. This process is ordinarily carried out in one step inside the mould under pressure.

1.7 Blowing agents

A chemical which acts as a blowing agent produces gas when heated to normal vulcanizing temperatures (120-170°C) and thus may be used to generate cells (gas pockets) in polymeric materials. They are classified as either physical or chemical blowing agent (CBAs). A good blowing agent should fulfil the following requirements:

- Contain a large amount of releasable gas
- Gas release over a controlled time and temperature range
- The ability to produce cells of uniform size
- No deleterious effects on the stability and processing characteristics of the polymer
- Low toxicity, odour and colour of both the blowing agents and its decomposition products
- Should not discolour the vulcanizate
- Good cost performance relation and availability

Since it is difficult to combine all these properties in one product, special blowing agents have been developed for different areas of application [28]. They are classified as either physical or chemical blowing agents.

Blowing in cellular rubber

During the expansion of the substrate by the blowing agent, cells are initiated and grow to produce the final cellular product. As gas is produced an equalibrium is established between the material in the gas phase and material dissolved in the solid phase. The cells formed initially are under higher pressure than the ambient pressure. Since the pressure due to the surface tension depends on the reciprocal of the cell radius, the pressure within the cell is reduced as the cell grows [28].

A proper balance of blowing and curing systems is necessary to obtain a closed cell structure. The density and cell size of the cellular products are controlled by balancing the reaction rates of blowing and curing systems [29,30]. During blowing, two physical changes usually take place, heat is evolved together with a loss in weight of the sample due to gas evolution. These physical changes are studied by thermal analysis. Blowing is influenced by the type of sulphur curing system [26]. If the cure progresses too far before the release of the gases, the expansion will be restricted and a high density product with a blistered surface will be formed. Premature decomposition of the blowing agent generally will result in the rupture of cell walls [31].

1.7.A Physical blowing agents

Physical blowing agents form cells by a phase change, eg. a liquid may be volatilized or a gas dissolved in a polymer under higher pressure may be desorbed by decomposition. A physical blowing agent should be odourless, nontoxic, non-corrosive and non-inflammable. It should be thermally stable and chemically inert in the gaseous form, should not affect the physical or chemical properties of the polymer and offer advantage of leaving no solid residue and generally inexpensive [28]. Examples are pentanes, hexanes, heptanes etc.

1.7.B Chemical blowing agents

Chemical blowing agents produce gas by a thermal decomposition or a reaction between two components. It should occur over a well-defined temperature and time range. The rate at which the blowing agent decomposes must be compatible with the polymer-processing temperature, at which the blowing agent should decompose rapidly but not violently. Chemical blowing agents are of two types—inorganic and organic blowing agents. For the production of sponge rubber, inorganic blowing agents are used which produce carbon dioxide gas and H_2O at 140°C whose gas yield is 135 cm^3/g. The rapid diffusion of CO_2 makes production of stable closed-cell extremely difficult. Incorporation of inorganic blowing agents in rubber is comparatively difficult, their dispersion is poor, causing irregular pore structure [30]. Organic blowing agents show important advantages over inorganic blowing agents. They produce nitrogen gas which produce a fine closed-cell structure in rubber and plastics. Nitrogen diffuses slowly through rubber cell walls than carbon dioxide [32,33]. The decomposition temperature and gas yield of a number of chemicals are given in Table 1.2 [29,30,31].

Table 1.2

Decomposition temperatures and gas evolution rate of various blowing agents

Type	Code	Decomposition temperature °C	Gas evolution cm^3/g
Azodicarbonamide	ADC	200-210	190-220
Benzene sulfonyl hydrazide	BSH	90-100	115-130
P-P'-oxybis(benzene sulfonyl hydrazide)	OBSH	153-160	120-125
P-toluene sulfonyl hydrazide	TSH	105	120
N,N'-Dinitrosopentamethylene tetramine	DNPT	205	260

Kickers

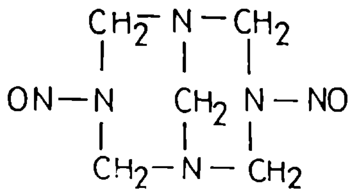
The temperature of decomposition of certain blowing agents are high as shown in Table 1.2, which can be substantially lowered and the decomposition accelerated at constant temperature by certain substances which are known as "kickers" or activators. Acidic substances such as salicylic acid, phthalic anhydride and hydroxy compounds as ethylene glycol, ZnO and Zn-salts etc. are commonly used as kickers. Higher amounts of stearic acid/fatty acids are used as activators for decomposition of the DNPT and ADC type of blowing agents. Decomposition temperature of ADC can be lowered by ZnO, and ZnO and Zinc stearate are very strong activators for ADC. A new chemical diamine bis(cyanato-N) zinc is used as a novel activator for ADC. Its action was studied by S.K.Bose [34].

By using the so called "Kickers" the decomposition temperature can be lowered by some 20-30°C and the decomposition rate increased at constant temperature [30]. In the present study DNPT and ADC are used as blowing agents.

1. Dinitrosopentamethylene tetramine (DNPT)

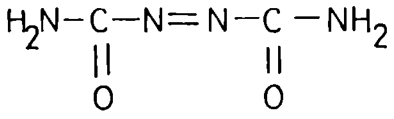
The gas evolution and decomposition temperature of DNPT is shown in Table 1.2.

The structure of DNPT is



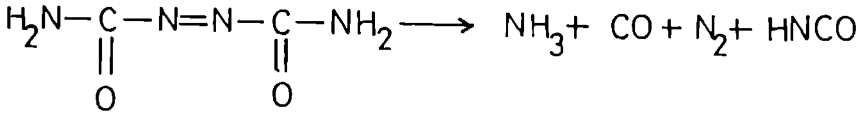
DNPT was the key to the early growth of the closed cell industry. The stability and shelf life of DNPT is excellent when the material is stored properly. The decomposition products of DNPT have not been fully elucidated. It has been reported that nitrogen, and nitrous oxide are formed as well as amine and water [32,33]. The decomposition products for example, show a definite cure activation. The main disadvantage with DNPT is the pronounced amine or fish type odour in the product. The use of urea and borates reduces the level of this odour. The advantages with DNPT is low cost, high gas releasing ability and good dispersion in rubber and plastics.

2. Azodicarbonamide (ADC)

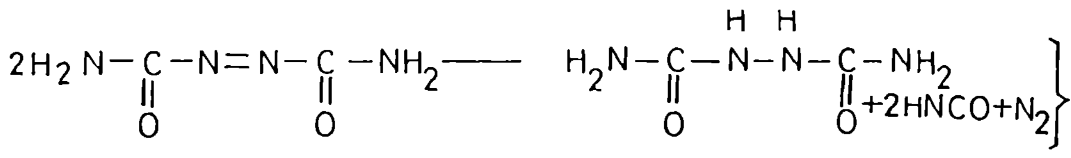


$$H_2N-\underset{\underset{O}{\|}}{C}-N=N-\underset{\underset{O}{\|}}{C}-NH_2$$

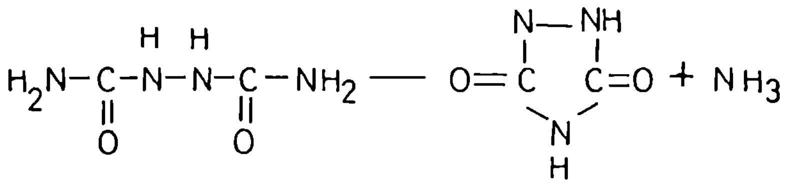
ADC was first suggested as a potential blowing agent for plastics unlike most other blowing agents ADC does not support combustion and is self extinguishing. The decomposition of ADC produces a gaseous mixture of nitrogen, carbon monoxide, ammonia and carbon dioxide [35]. Reed has suggested that primary decomposition of ADC can follow the two steps shown below [33].



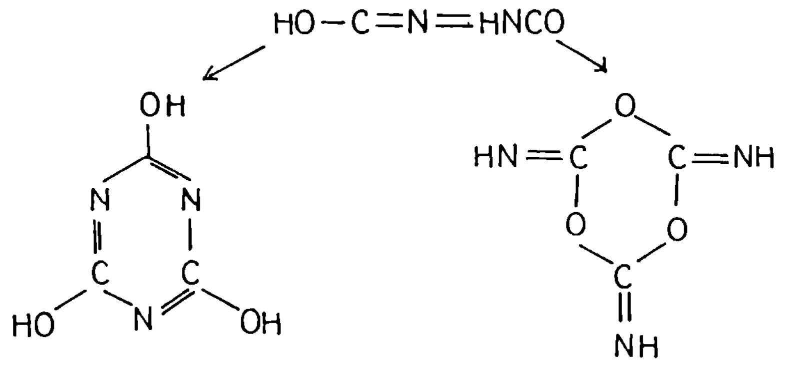
$$H_2N-\underset{\underset{O}{\|}}{C}-N=N-\underset{\underset{O}{\|}}{C}-NH_2 \longrightarrow NH_3 + CO + N_2 + HNCO \text{ -------(1)}$$



$$2H_2N-\underset{\underset{O}{\|}}{C}-N=N-\underset{\underset{O}{\|}}{C}-NH_2 \longrightarrow H_2N-\underset{\underset{O}{\|}}{C}-\overset{H}{N}-\overset{H}{N}-\underset{\underset{O}{\|}}{C}-NH_2 + 2HNCO + N_2 \qquad (2)$$



---------- (3)



Cyanuric acid

Cyamelide

One of the by-products in the decomposition of ADC is cyanic acid shown equation (1). Thermogravimetric studies show that blowing is influenced by the type of sulphur curing systems. Blowing also depends on the acidic or basic character of the decomposition products of blowing agents [26]. Gas generation of ADC begins in rubber compounds at approximately 140°C, it is completed only at vulcanization temperatures of 160°C and above [31]. For this reason no gas loss occurs when the uncured rubber compounds containing ADC are stored. It is especially suitable for plastics, because dispersion of ADC in plastic phase is better.

1.8 Manufacture of microcellular soles

Following are the details of the steps involved for the manufacture of microcellular soles.

1.8.1 Compounding

Common mixing equipments such as mixing mill or Kneader are used for mixing MC sole compound. The roll temperature has to be maintained at 80-85°C throughout the mixing cycle. Blowing agent is added towards the end of the mixing cycle. Proper dispersion of ingredients especially the blowing agent is necessary to prevent the production of coarse cellular structure. For maturation compound is kept for 16-24h at room temperature which will improve the dispersion of ingredients by diffusion process.

1.8.2 Moulding of MC sheets

For the production of MC sheets compression moulding is used. The moulds used are carefully designed and finished to obtain products with correct dimensions and surface finish. The mould cavity is filled with 3 to 5% excess of the compound on volume basis. The slight flash formed by excess filling acts as a seal between the mould and press platen which prevents the loss of gas, formed within the sheets during cure. Control the temperature and pressure during vulcanization are very important for obtaining good quality sheets. MC sheets removed from the press after precuring, the sides have to be trimmed by removing the flash to avoid cracking of sides and bending of the sheets [16].

To facilitate easy release of the sheet the mould cavity has tapered edges. Also the tapered angle determines the relative expansion of the sheet in the three directions. Lower angle (the acute angle between the cavity wall and cavity bottom surface) gives expansion in the lateral dimension, while higher angles gives better height. The moulding procedure of MC sheets is given in Fig.1.2. As soon as the mould is opened the sheet expands and jumps out of the cavity, the edges of which are angled to aid release and thereby minimise the distortion of the sheet which tends to be somewhat thermoplastic in nature. As the sheet cools it shrinks and gas permeation from the cells causes further gradual shrinkage over a long period. The density and cell structure of the MC soling depends on certain factors which are described in detail.

1. Moulding pressure

The specific moulding pressure required depends on the viscosity of the compound and complexity of the mould. During the vulcanization of MC sole compound the nitrogen gas liberated by the blowing agent generates internal pressure in the compound tending to open the mould. The external closing pressure on the mould must be adequate enough to keep the mould closed and high enough to liberate nitrogen gas dissolved in the rubber compound. If the pressure used is lower than this, the liberated nitrogen does not get dissolved in the compound. On completion of expansion a coarse cell structure is obtained. When the pressure used is high, expansion is less [36] but cells are very fine and invisible [3,11,19]. Also adequate press pressure during vulcanization is essential in order to avoid gas loss.

2. Precuring

In the precuring step, a partial vulcanization is given so that the rubber gets adequate strength to contain nitrogen gas released after expansion. If the pressure is high the modulus of

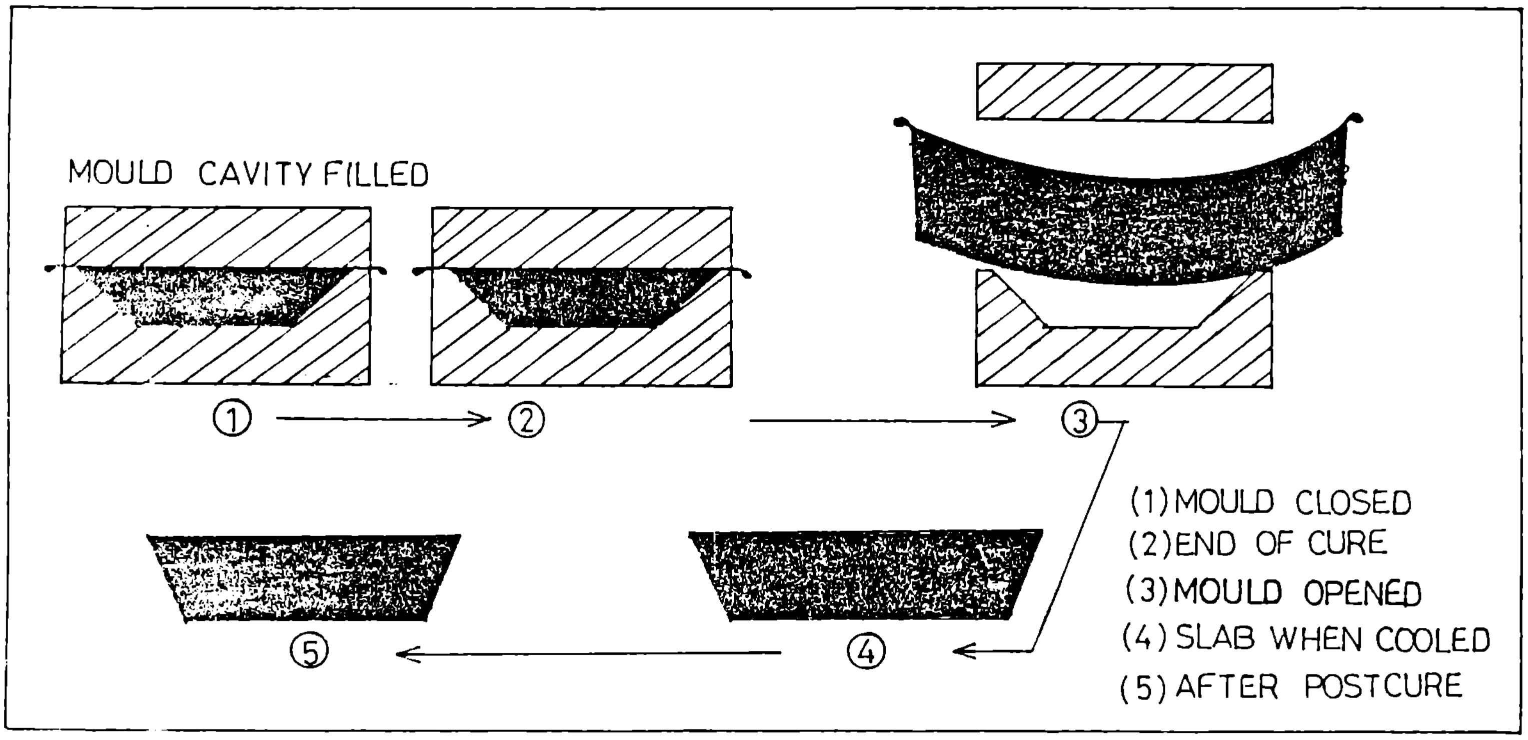


FIG.1.2. PRODUCTION OF MICROCELLULAR RUBBER SHEET

rubber becomes higher and the expansion would be low. When the degree of precure is low, higher volume of expansion is obtained. This means the vulcanizate will become softer and lighter. The precure is carried out in curing press under a high specific moulding pressure. The precuring time and temperature are determined by the decomposition behaviour of blowing agent and the curing characteristics of the rubber compound.

3. Post cure

After removal of the precured sheets from the moulds cools to room temperature, and shrinks. The shrinkage continues for 10 to 15 days. In closed cell sole the gas phase in the cells can contain nitrogen gas, air, or other gases generated during expansion. This nitrogen gas under pressure slowly diffuses through the cell walls during storage and hence further shrinkage occurs during service life. After post cure the sheet becomes permanently stabilized in the expanded size. Post cure can be done in moulds of larger size or in open air [19].

1.8.3 Quality control

The manufacture of MC soles is more complicated than that of solid soles due to many factors which must be controlled within narrow limits to get consistent quality product. Good dispersion of blowing agent in the mix, the time and temperature of vulcanization process and rate of decomposition of blowing agent, volume of loading of the mould cavity are the main factors for the good expanded material. The cell structure and the density of the MC sheet depend on the above factors. Therefore for consistent production of good quality of MC sheets reasonable care at various stages of production is necessary [11].

1.9 Materials used for making microcellular soles

Natural rubber is the most important polymer used for making MC soles. NR is cheaper than most of the synthetic rubbers and possesses good vulcanizate properties. Various polymers and their blends are used for making MC soles in order to attain specific combinations of properties.

1.9.1 Polymer blends

The commercial development of polymer blends and alloys is driven by more favourable economics than in the more conventional chemical routes to new products [37]. Blend systems, comprising, existing materials, can be developed about twice as rapidly as new polymers due to reduced cost and improved mechanical properties [38].. Commercial blends are nearly evenly divided between miscible and immiscible binaries. The mechanical properties of immiscible systems strongly depend on flow induced morphology and interfacial adhesion as well as composition [39-41], whereas the properties of miscible blends are no more ~~affected by~~ those of homopolymers. The glass-transition temperature (T_g) is the primary thermal transition for these blends and it varies monotonically with composition [42]. An immiscible mixtures of polymers shows multiple amorphous phases by the presence of multiple glass transition temperatures. In amorphous immiscible binary mixtures, the stiffness, strength and HDT properties of the principal component largely determine properties of the blend [43,44]. Immiscible blend shows poor mechanical properties as the following equation suggests

$$a = \frac{C}{(\chi_{AB})^m}$$

where 'a' is the interfacial thickness, 'C' and 'm' are slightly different Constants and χ_{AB} is Flory-Huggins interaction parameter for immiscible mixture.

The equation suggests that the properties of immiscible mixtures would be improved if the interfacial zone could be strengthened or increased by incorporating an interfacially active block or graft copolymer as compatibilizer. The compatibilizer added during processing, eliminate the macroscopic inhomogeneities and increase the stability and morphology reduces the interfacial tension and size of the dispersed phase [45-53].

Microscopical methods are most suitable to study the homogeneity of polymer blends because they provide information on the overall homogeneity and phase morphology. Optical microscope and scanning electron microscope have been widely used to observe the surface morphology of polymeric materials [54-56}.

1.9.2 Elastomer blends

All rubbers have shortcomings in one or more properties. Therefore, on blending two rubbers, it should be possible to obtain the right compromise in properties [57]. The difficulties experienced in processing some rubbers also necessitate blending. There are also appreciable differences in price between rubbers emphasizing economic reasons for blending. Most blends of elastomers are immiscible because mixing is endothermic and the entropic contribution is small because of high molecular weight. The complete miscibility of polymers requires that the free energy of mixing be negative, which can only be achieved by exothermic mixing or a large entropy of mixing [58-62]. True miscibility is not required for good rubber properties eventhough, adhesion between the polymer phases is necessary and the respective interfacial energies are important in this respect [63].

Due to high structural regularity of natural rubber, natural rubber based elastomer blends are used for a variety of purposes. One important example is the blend of NR with SBR. SBR is blended with NR to attain fairly constant Mooney and cure characteristics, better abrasion and crack initiation resistance, NR/SBR blends are widely used for the manufacture of MC soles. For reducing the compound cost and to conserve raw material and energy the utilisation of latex reclaim in microcellular soles was reported by R.S.George et al. [64].

1.9.3 Thermoplastic elastomers

Thermoplastic elastomers are a new class of materials in which the properties of vulcanized rubber are embodied with the ease of processing of thermoplastics. These novel materials have numerous processing and performance advantages, and some disadvantages. Their chief advantage, however, is the ease of reproducibility and economy of thermoplastic processing. The disadvantages associated with thermoplastic elastomers are that they soften/melt at elevated temperature, and show creep behaviour on extended use. The unique combination of thermoplastic processing and subsequent rubber properties is derived from the two-phase morphology of these materials. Virtually all TPEs consist of a hard thermoplastic phase, and a soft elastomeric phase [65-69]. Five classes of thermoplastic elastomers are commercially important. They are

1. Polystyrene/elastomer block copolymers
2. Polyurethane/elastomer block copolymers
3. Polyether/elastomer block copolymers
4. Polyamide/elastomer block copolymers
5. Hard thermoplastic/elastomer blends

The first four classes of thermoplastic elastomers listed above are all block copolymers eventhough, they have important structural differences. Most of the polystyrene/elastomer class have the general formula S-E-S, where S represents a polystyrene block and E an elastomer block. Others have a branched structure with the general formula $(S\text{-}E)_nx$, where x represents a multifunctional junction point. The next three classes have the general formula $(H\text{-}E)_n$, where H represents a hard thermoplastic block. The last class, the hard thermoplastic/elastomer blends, are usually intimate mixtures of the two phases, although in some cases grafting of one polymer onto the other can take place [70].

1.9.4 Thermoplastic elastomers based on elastomer-thermoplastic blends

Elastomer-thermoplastic blends have become technologically useful as thermoplastic elastomers in recent years [71-74]. They have many of the properties of elastomers, but they are processable as thermoplastic [74-78]. Thermodynamic compatibility of the two phases demands that the solubility parameters be reasonably close. The polymer present in largest amount is generally the continuous phase. The discontinuous phase of the other polymer is in fine particles with sufficient surface area for the attractive forces between the two phases to prevent coalescence of the dispersed phase [65]. The thermoplastic elastomers described can be divided in to two categories: those in which the thermoplastic used contains a low level of crystallinity such as PVC, and those in which the thermoplastic is a highly crystalline such as polyethylene. The crystalline thermoplastic are typically mixed with elastomers with which they are not molecularly compatible to form thermoplastic elastomers which are multiphased. PVC and its copolymers are often converted to thermoplastic elastomers by mixture with plasticizers which are compatible with PVC, resulting in a blend having a T_g intermediate between that of the components [79]. A brief description of the TPEs used in this study are given below.

A. Polystyrene-polydiene block copolymers

Of the various types of thermoplastic elastomers, those based on triblock copolymers of polystyrene and polydienes are the largest in terms of commercial production [77] because of their relatively simple molecular structure and the fact that this structure is uniform, unequivocal and reproducible. Most of the polystyrene/polydiene block copolymers that are thermoplastic elastomers have basic structure Poly(styrene-b-butadiene b-styrene) (S-B-S) or poly(styrene-b-isoprene-b-styrene) (S-I-S). They are phase separated systems, quite unlike the corresponding random copolymers. The two phases, polystyrene and polydiene, retain many of the properties of the respective homopolymers [72]. The polystyrene-elastomer block copolymers are technologically compatible with a surprisingly wide range of other polymers, and is the blends show improved properties when compared to original polymers. Impact strength usually is the most obvious improvement, but others include tear strength, stress crack resistance, low temperature flexibility and elongation. The most important application of TPEs is in shoe-soling applications. The styrene TPEs have achieved a major market share [80]. This is because they are suitable for the production of light weight soles with good grip and elasticity at low temperatures.

B. NBR/PVC blends

NBR blended with PVC to achieve certain properties for a number of purposes. Small amount of NBR in PVC can improve the impact strength of rigid PVC compositions. Ozone resistance of NBR can be improved by incorporation of 10-15 wt. % PVC [81,82]. NBR of certain composition, exhibits compatibility with PVC which is unusual among polymers [83-85]. Blends of NBR and PVC were reported by Nielsen and others [86,87] to have a single broad glass transition over a temperature range between the T_g's of the unblended components. Takayanagi et al. [86] qualitatively describing the blends as micro-heterogeneous, applied a mechanical model which predicted dynamic mechanical properties of NBR/PVC blends through the glass transition region over a range of blend ratios.

PVC has assumed a leading position among other plastics because of its economic and design advantages. It is a material of choice due to lower cost, greater availability or improved performance. NBR can produce compatible and semicompatible blends with PVC according to the acrylonitrile content of the rubber.

C. NR/Polyethylene blends

Thermoplastic elastomers have been prepared by blending natural rubber with crystalline polyolefins named as thermoplastic natural rubber (TPNR). The addition of small amounts of peroxide crosslinking agents during blending has been found to be effective in improving the moulding behaviour and resistance to compression set [88,89]. Blends with high density polyethylene or with low density polyethylene have been studied. With gradual incorporation of rubber like NR in HDPE or LDPE tensile strength and modulus decrease but the elongation at break increases. The decrease in strength with increase in rubber has been ascribed to the drop in crystallinity [90-91]. A range of NR-PE blends can be prepared by variation of rubber content and the crosslinking agent and have the advantages of low density, good low-temperature flexibility, elastic recovery, heat resistance, low material cost, low processing cost with reusable scrap etc.

1.10 Preparation of blends

The general mixing methods for preparing elastomer blends include mixing of latices, solutions and mechanical and mechano-chemical mixing. The simplest and most direct method is mechanical blending. This may be accomplished on a two roll mill or an internal mixers, eg. Banbury. The nature of resulting dispersion depends on the time of mixing, the shear field in equipment, temperature, rheological properties of the component polymers etc. Thermoplastic elastomers from elastomer/thermoplastic blends are prepared by mechanical means. The processing temperature must be well above the glass transition temperature (T_g) of each constituent for mixtures of amorphous polymers and above the melting temperature (T_m) of mixtures containing semicrystalline polymers.

1.11 TPEs used for making MC soles

Blending of syndiotactic 1,2-polybutadiene having a 1,2 content of more than 90% with NR have been reported by Kuriakose [92]. MC soles based on 1,2 polybutadiene/NR blend shows higher expansion ratio, higher flex life and lower blooming. But the slow cure rate and lower degree of crosslinking will give slightly inferior properties to the MC sheets [93].

Ethylene vinyl acetate polymer having 45% vinyl acetate content can be used for making very low density soling. Outstanding resistance to oxygen, ozone, weathering ageing are the additional properties. EVA is blended with PE and HSR and the blend based MC soles shows good mechanical properties [94].

1.12 Rubber footwear and footwear industry

Rubber footwear has become a part of our day to day life from children's cosmetic footwear to pull-ons for adults [95]. Production of rubber footwear and those containing rubber soles and heels increases every year. Wood, leather, plastic and rubber are the soling material used in footwear industry. While wood, being completely non-flexible, leather, though flexible is not preferred on economical grounds and variability in supply and its susceptibility to moisture, water and oils. Use of plasticized PVC is restricted because of its poor tear and cut growth resistance, higher thermoplasticity and its tendency to slip while walking. Rubber soling surpass all the soling materials and as regards to cost, it is the rubber soled footwear alone that may be considered within the reach of a common man. The modern rubber technology produces rubber soling material with leathery feel, with outstanding wear resistance, excellent wearing comfort, resistance to moisture, water, oil and weather conditions. Additional advantages of rubber are the ease of colourability and ease of fabrication [2].

Rubber in footwear includes unit soles (integrally-moulded sole and heal combinations); microcellular and other sheet soling supplied in vulcanized form to wear manufacturers [96]. Rubber footwear can be of the following types: plim solls, built-up shoes, all-rubber shoes, direct vulcanization process (DVP) shoes, direct injection process (DIP) shoes. Rubber at least forms a part of the majority of footwear in market today [95-99].

Table 1.3 shows different types of footwear and use of rubber component in them. The term 'rubber footwear', in its broad sense, signifies a composite article using rubber components completely, as well as many types of footwear having rubber component and non-rubber constituent like textiles and leather.

Table 1.3

Different types of footwears and use of rubber components in them

Type of footwear	Rubber components
Leather shoes and sandal	Sole, packing insole, top lefts in ladies high heel sandals
Chappals	Resin soling, MC soling, plateforms in ladies chappals, straps in hawai chappals.
Canvas shoes (PT and sports shoes and military shoes)	Sole and heel, toe cap, foxing, rag component, insole, heel stiffner, packing cement for doubling textiles, adhesives for building the shoe
Protective footwear (Rain wear and safety shoes)	Upper, vamp, back quarters etc. sole and heel, rag component and cement and adhesive for building shoes.

The Indian rubber footwear industry constitutes the largest segment of the nontyre products manufacturing industry. At present 12-13% of the total rubber is consumed for the manufacture of rubber footwear. Footwear is not only a rubber based product but also a very labour intensive product [100,101]. Footwear is becoming more and more a fashion and functional item, so the rise per consumption is inevitable and with the increased world population, the market potential for footwear is tremendous.

OBJECTIVES AND SCOPE OF THE PRESENT STUDY

The most important part of any footwear is the sole (or sole and heel) which withstands all the harmful external factors such as roughness of the ground or road, sharp objects, thorns and stones, heat, dampness and cold during walking. The properties desirable in soling material, therefore, would be

1. lightness
2. resistance to wear and tear for long service life
3. flexibility/softness for wearing comfort
4. thermal insulation

Rubber soling surpasses all other soling materials in better performance and lower cost. Because MC sole is soft and very light, and has good abrasion resistance, flex properties and set behaviour it has become very popular all over the world and demand for better quality product is ever increasing. Due to the traditional approach adopted by the footwear industry in foot wear design, the rubber based footwear export surprisingly contributes only a small percentage. The essence of success for any industry lies in the expansion of the export market. Microcellular soles are manufactured for the last three decades without much change in the traditional design and colour pattern. In recent years domestic customers have also started demanding better quality products. In view of the changing taste of the customer and growing competition from other countries, substantial improvement in the export potential will require new base materials for regular or fashion rubber based footwears. The main objective of the present study is to develop new base materials for making MC soles with good quality, viz., light weight, durability and bright colours.

The present study on the development of new base materials for making MC soles has been undertaken with the following objectives.

1. To study the properties of NBR/PVC based MC soles and to develop novel formulations for developing better quality microcellular soles. Other rubber/plastic blends such as NR/PVC are also proposed to be tried as base materials.

2. To develop MC soles based on thermoplastic elastomers such as styrene-butadiene-styrene (SBS) and their blends such as SBS/SBR, SBS/NR and SBS/NR/HSR and to evaluate their suitability for high performance soles.

3. To investigate the properties of NR/EVA based MC soles and to suggest modification for improving their performance.

4. To develop NR/polyethylene blend based MC soles and to evaluate their suitability.

5. To develop BR/PE and NR/BR/PE blend based MC soles for low temperature applications.

5. To investigate the suitability of BR/HSR blend as a base material for MC soles and to evaluate their properties.

7. To modify the conventional NR/HSR based MC soles for more improved performance.

8. To investigate in detail the structure, performance characteristics and other features of successful base materials.

This thesis is divided into the following chapters:

Chapter 1	Introduction
Chapter 2	Experimental techniques
Chapter 3	
Part I	Studies on the properties of microcellular soles based on NBR/PVC blends
Part II	Studies on the properties of microcellular soles based on NR/PVC blends
Chapter 4	
Part I	Studies on the properties of microcellular soles based on SBS/SBR blends
Part II	Studies on the properties of microcellular soles based on SBS/NR and SBS/NR/HSR blends
Chapter 5	
Part I	Use of NR/EVA and NR/HSR/EVA blends as novel base materials for microcellular soles
Part II	Studies on the properties of microcellular soles based on NR/polyethylene blends
Part III	Development of microcellular soles based on BR/PE blends for low temperature applications
Part IV	Development of microcellular soles based on BR/HSR blends
Chapter 6	
Part I	Modification of NR/HSR MC sole waste and latex foam waste for utilisation in microcellular soles based on NR/HSR blends

Part II	Rice hull ash and coir pith as fillers in microcellular soles based on NR/HSR blends
Part III	Preparation and use of cyclized rubber in microcellular soles
Chapter 7	Summary and conclusions

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CHAPTER 2

EXPERIMENTAL TECHNIQUES

Materials used and the experimental procedures adopted for the present investigations are given in this chapter.

2.1 Materials

Polymers

1. Natural rubber (NR)

ISNR-5 was supplied by the Rubber Research Institute of India, Kottayam, Kerala. The Indian standard specifications for this grade of rubber are given below:

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

2. Butadiene-acrylonitrile rubber (NBR, or nitrile rubber)

Nitrile rubber used in the study was Aparene N-553 NS supplied by Apar India, Mumbai. Acrylonitrile (AN) content (%) 33, Mooney viscosity [ML(1+4) at 100°C] = 45-55.

3. Styrene-butadiene rubber (SBR)

SBR used was Synaprene S-1502 supplied by Synthetics and Chemicals Ltd., Bareilly. Styrene content, (%) by mass - 23.5; Mooney viscosity [ML(1+4) at 100°C] = 52.00.

4. Polybutadiene (BR)

Polybutadiene used in the study were the following grades:

(i) Cisamer-01 supplied by Indian Petrochemicals Corporation Ltd., Vadodara cis 1,4 configuration (%) 96, Raw Mooney viscosity[ML(1+4) 100°C]= 44.

(ii) Cisamer-1220, supplied by Indian Petrochemicals Corporation Ltd., Vadodara. Raw Mooney viscosity [ML(1+4) 100°C] = 45.

5. Centrifuged NR latex

High ammonia type 60 per cent centrifuged latex obtained from M/s. Padinjarekara Agencies, Kottayam. Dry rubber content, (%) by mass - 60.

6. Field latex

Field latex which has a dry rubber content of 33% and obtained from M/s.Kattakkayam Latex, Aluva was used in this study.

7. High-styrene resin (HSR)

HSR used was Synaprene 1958 grade supplied by Synthetics and Chemicals Ltd., Bareilly. Styrene content, (%) by mass - 49.

8. Cyclized rubber

Cyclized rubber used was prepared in the lab. Softening point = 130-140°C.

9. Styrene-butadiene-styrene (SBS)

SBS used in this study were ATV Prene A475 and ATV Prene 411 was supplied by ATV Projects India Ltd., Marol, Mumbai. The specifications of ATV-Prene A475 and ATV-Prene 411 are given below.

	ATV-Prene A 475	ATV-Prene 411
Butadiene/styrene ratio	60/40	70/30
Block polystyrene %	39	29
Volatile matter %	0.5	0.75
Specific gravity	0.94	0.94
Melt flow index (190°C/5 kg), g/10 min.	6±2	--

10. Ethylene-vinyl acetate (EVA)

EVA 1202 was supplied by National Organic Chemicals Ltd., Thane, Mumbai. The specifications are given below:

Vinyl acetate (%)	12
Melt flow index (g/10 min.)	2
Density (gm/cc)	0.931

11. Poly(vinyl chloride) (PVC)

PVC grades used in the study were the following:

(i) Suspension polymer in powder form with a K value of 65. The resin was obtained from IPCL, Vadodara.

(ii) Emulsion grade in powder form with a K value of 70.5.

The resin was obtained from Chemplast, Chennai.

12. Polyethylene

(i) High density polyethylene HDPE

HDPE used was Indothene HD supplied by Indian Petrochemical Corporation Ltd., Vadodara, which had the following properties.

Density at 23°C, gm/cm^3	0.957
Melt flow index (gm/10 min)	5.2

(ii) Low density polyethylene LDPE

LDPE used in this study was Indothene 24 FS 040 grade obtained from Indian Petrochemicals Ltd., Vadodara, which had the following properties.

Density at 23°C, gm/cm^3	0.922
Melting range °C	105-110
Melt flow index at 190°C (gm/10 min.)	4.0

Additives

1. Zinc oxide

Zinc oxide (ZnO) was supplied by M/s.Meta Zinc Ltd., Mumbai, having the following specifications:

Specific gravity	5.5
Zinc oxide content	98%
Acidity	0.4% max.
Heat loss (2 hrs at 100°C)	0.5% max.

2. Magnesium oxide

Magnesium oxide (MgO) used in the study was commercial grade calcined light magnesia with a specific gravity of 3.6, supplied by Central Drug House (P) Ltd., Mumbai.

3. Titanium dioxide

Titanium dioxide used in the study was commercial grade supplied by Suvidhinath Laboratories, Vadodara.

4. Zinc stearate

Zinc stearate used in the study was laboratory reagent supplied by Reidel (India) Chemicals, Hapur, U.P.

5. Stearic acid

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

Melting point	50-69°C
Acid number	185-210
Iodine number	9.5 max.
Specific gravity	0.85±0.01
Ash content	0.1, % max.

Accelerators

A short description of the important accelerators used are given below:

6. F

Accelerator used in the present study was Vulcafor F, supplied by Bayer India Ltd., Mumbai. F is a versatile, widely used, general purpose, medium speed accelerator. F is particularly useful for curing thick cellular rubbers and is popular with the footwear industry and had the following specifications:

Composition	An activated thiazole
Appearance	Cream-coloured powder
Specific gravity at 25°C	1.46

7. Dibenzthiazyl disulphide (MBTS)

MBTS was supplied by Bayer Chemicals, Mumbai. It had the following specifications:

Specific gravity	1.34
Melting point	165°C

8. 2-Mercaptobenzthiazole (MBT)

MBT was supplied by ICI India Ltd., Mumbai. It had the following specifications

Specific gravity	1.49
Melting point	177°C

9. Zinc salt of mercaptobenzthiazole (ZMBT)

ZMBT was supplied by ICI India Ltd., Mumbai. It had the following specifications:

Specific gravity	1.64
Melting point	178°C

10. Tetramethyl thiuram disulphide (TMTD)

TMTD was supplied by ICI India Ltd., Mumbai. It had the following specifications:

Specific gravity	1.42
Melting point	140°C

11. Sulphur

Sulphur used was supplied by Standard Chemical Company (Pvt.) Ltd., Chennai. It had the following specifications:

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

12. Dicumyl peroxide (DCP)

DCP used was supplied by Bengal Water Proof Ltd., Panihati. It had 40% active ingredient.

Blowing agents

13. Azodicarbonamide (ADC)

ADC was supplied by High Polymer Labs-India. It had the following specifications:

Decomposition temperature (approx.)	210°C
Gas evolution (approx.)	190 cm^3/g

14. Dinitrosopentamethylene tetramine (DNPT)

DNPT used in the study was commercial grade supplied by Deepak Nitrite, Mumbai. It had 40% active ingredient. The other properties were

Decomposition temperature	195°C
Gas evolution (approx.)	185 cm^3/g

15. Styrenated phenol (SP)

Styrenated phenol used was supplied by Synthetics and Chemicals Ltd., Bareilly. It had the following specifications:

Relative density	1.08
Viscosity at 27°C, cps	2000-6000

16. Naphthenic oil

It was supplied by M/s.Hindustan Petroleum Ltd., India. It had the following specifications:

Colour	Light coloured oil
Viscosity gravity constant (VGC)	0.85-0.9
Aniline point °C	75

17. Dioctyl phthalate (DOP)

DOP used was commercial grade supplied by Rubo-Synth Impex Pvt. Ltd., Mumbai. It had the following specifications:

Specific gravity	0.986
Viscosity, cps	60

18. Paraffinic oil

Paraffinic oil was supplied by M/s.Hindustan Petroleum Ltd., India. It had the following specifications:

Colour	Light coloured oil
Viscosity gravity constant (VGC)	0.8-0.85
Aniline point °C	96

19. Amine terminated liquid natural rubber (ATNR)

ATNR used in the present study was prepared in the Laboratory as per the procedure outlined below.

Preparation of ATNR

Natural rubber was masticated for 30 min. at 50°C. 100g of masticated rubber was dissolved in 450ml toluene and the solution was charged into a flat bottomed borosilicate flask. 50 ml of the ethylene diamine together with 50 ml of tetrahydrofuran was added and thoroughly mixed with the rubber solution. This solution was kept in sunlight for irradiation. After about 60h of irradiation, the product was precipitated using methanol and dried in vacuum. The sample for analysis was purified by repeated precipitation by methanol from toluene solution and dried in a vacuum oven [1].

ATNR used in the present study had the following properties:

Average molecular weight (M_w)	2100
Functionality	1.79

Fillers

20. Precipitated silica

Precipitated silica used in this study was GSL-150 Grade obtained from Gujarat Silicon Pvt. Ltd., Gujarat. Its specific gravity was 1.95.

21. China clay

It was supplied by English Indian Clays Ltd. Veli, Trivandrum. The specific gravity was 2.6.

Precipitated calcium carbonate, and aluminium silicate used in this study were of commercial grade. High abrasion furnace black (HAF-N330) was supplied by M/s.Carbon and Chemicals (India) Ltd., Kochi.

22. NR/HSR microcrumb

Ground microcellular sole scrap of NR/HSR having 200 mesh size was used for this study was supplied by M/s.Paragon Rubbers, Kottayam.

23. Rice hull ash

Rice hull ash used in this study was supplied by Paddy Research Institute, Thanjavoor. Rice hull ash contained about 85% silica.

24. Latex foam waste

Latex foam waste used in this study was supplied by Galaxy Foams, Industrial Estate, South Kalamassery, Kochi.

25. Epoxidised natural rubber (ENR)

ENR-50 (with 50 mol % epoxidation) was supplied by RRII, Kottayam.

Other additives

Other additives such as diethylene glycol and wood rosin used were commercial grade. Dispersol VL-specific gravity 1.0 was supplied by ICI India Ltd., Mumbai.

Solvents

Tetrahydrofuran, and ethylene diamine used were analytical grade. Methanol and toluene were commercial grade.

2.2 Experimental procedure

2.2.1 Melt mixing using Brabender plasticorder

A Brabender plasticorder (torque rheometer) model PL 3S was used for the melt mixing of the polymers and blends. This instrument manufactured by M/s.Brabender OHG Duisburg, Germany has been widely used for measuring processability of polymers, rheological properties of polymer melts, for blending of polymers, modelling processes such as extrusion etc. [2-6].

The Brabender torque rheometer is essentially a device for measuring torque generated due to the resistance of a material during mastication or flow under pre-selected conditions of shear and temperature. A jacketed mixing chamber with a volume capacity of 40 cc is the heart of the plasticorder which is heated by oil circulating thermostat heating tank. The mixer temperature can be adjusted with the contact thermometer in the heating tank. High temperature silicone oil is used as heating liquid and the temperature on the mixer can be varied up to 300°C. The measuring heat is equipped with a stock temperature thermocouple coupled with a temperature recorder for temperature measurement. The torque required for mixing or shearing of the material in the mixing chamber is made visible with the help of a dynamometer balance. The dynamometer is attached to a precise mechanical measuring system which indicates and records the torque. The torque is plotted continuously against time. Torque up to 20,000 meter grams can be measured by the torque rheometer.

The mixing or shearing of the polymers in the mixing chamber is done by two motors rotating in opposite directions. Various types of rotors can be used, depending upon the nature of the polymers used. The speed control of the rotors (range 0-150 rpm) is done by means of a DC thyristor controlled drive. The measurement is based on the fact that the resistance which is put up by the material against the rotors in the chamber is made visible as a means of viscosity dynamometer.

In the present study, Brabender plasticorder was used for blending NBR/PVC, NR/PVC, NR/PE, SBS/SBR, SBS/NR blends to study the mechanical properties of these blends. It was also used to develop the MC soles based on these blends.

Thermoplastic/elastomer blends were prepared in the Brabender plasticorder equipped with roller mixing heads according to ASTM D-3184 (1980) and 3182 (1982). Blending parameters were selected based on torque temperature data of the individual components and the particular blend. The basic principle followed in every blending was to ensure the melting of the polymers and to keep polymer degradations to minimum.

2.2.2 Mixing and homogenisation

Mixing and homogenisation of elastomers and compounding ingredients were done on a laboratory size (15x33 cm) two roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through the nip of (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 had disappeared, the compounding ingredients were added as per ASTM D-3184 (1980) in the order of activators, fillers, accelerators, curing agents and blowing agents. Before the addition of accelerators, curing agents and blowing agents the batch was thoroughly cooled. After the addition of accelerators and curing agent, the blowing agent was added. The band was properly cut from both sides to improve the homogeneity of the compound.

After completion of the mixing, the compound was homogenised by passing six times endwise through a tight nip and finally the batch is sheeted out as very thin sheet (2mm thickness). The surface of the sheeted out compound must be very smooth. For the preparation of compounds of elastomer blends,NR was masticated to the mooney viscosity level of the synthetic rubber, and then the other additives were added as described above unless otherwise specified.

In the present study NR/HSR and BR/HSR blend was prepared using mixing mill to develop MC soles based on these blends. It was also used to assess the mechanical properties of these blends.

2.2.3 Cure characteristics

Using Goettfert Elastograph

The cure characteristics of the compounds were determined using a Goettfert Elastograph model 67.85. It is microprocessor controlled rotorless cure meter with a quick temperature control mechanism and well defined homogeneous temperature distribution in the die or test chamber. In this instrument, a specimen of definite size is kept in the lower half of the cavity which is oscillated through a small deformation angle (±0.2°). The frequency is 50 oscillations per minute. The torque is measured on the lower oscillating die half. The following data can be taken from the torque-time curve.

1. Minimum torque: Torque obtained by the mix after homogenising 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. Scorch time (t_{10}): This is the time for attaining 10% of the maximum torque.

4. Optimum cure time (t_{90}): This is the time taken for attaining 90% of the maximum torque.

5. Cure rate: Cure rate was determined from the following equation:

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

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

The elastograph microprocessor evaluates the vulcanization curve and prints out these data after each measurement.

2.2.4 Moulding of test specimens

The test specimens for determining the physical properties were moulded in standard mould by compression moulding in an electrically heated hydraulic press having 30x30 cm platens at a pressure of 180 kg/cm^2 in the mould. The rubber compounds were vulcanized up to their respective optimum cure times and at specified temperatures. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold and dark place for 24h and were used for subsequent physical tests.

For compression moulding of thermoplastic/elastomer blends, specially designed moulds with provision for cooling under pressure were used.

2.2.5 Moulding of microcellular sheets

Microcellular sheets were compression moulded in an electrically heated hydraulic press having 30x30 cm platens. The moulding pressure was 120-140 kg/cm^2. The moulds are carefully designed and finished to products with correct dimensions and surface finish. The moulds can be made gas tight and have tapered edges (usually more than 45°). The mould size should be properly calculated to accommodate 100 percent initial expansion in cooling and the sheet does not wedged between the guides of the press. Around the edge of the mould a "well" should be provided to accommodate excess compound which acts as a seal.

The MC sole compound was placed in the mould with about 3 to 5% excess of the compound on volume basis. The mould was then transferred to the platens of the press maintained at required moulding temperatures and the mould was closed under pressure. When the compound was sufficiently cured, the press was opened rapidly to allow maximum expansion. The expanding sheet sprangs out of the mould by itself in all directions without any distortion, due to the bevelled edges. As the MC sheets were removed from the mould, then sides were trimmed by removing the flash so as to avoid cracking of the sides and bending of the sheets.

2.2.6 Post curing

The precured sheets are post cured in an air oven for required time and temperature. The sheets are stored for 24h before physical tests. Post curing was done to complete the cure of precured sheets and to help in attaining maximum physical properties.

2.2.7 Problems in MC soling sheet production

(1) Inconsistent production (varying sheet size):

This is mainly due to the variation in curing temperature, pressure, time and uneven cure characteristics of the compounds. To overcome this defect, temperature and time of the moulding were carefully controlled.

(2) Coarse/open cell structure

This defect can arise when (a) low moulding pressure is employed, (b) mould cavity is not filled properly, (c) mould is not closed properly, (d) ingredients are not properly dispersed, especially blowing agents.

(a) The external closing pressure on the mould must not only be adequate enough to keep the mould closed but must also be high enough to keep the liberated nitrogen gas dissolved in the compound. Otherwise proper expansion may not be obtained and, a coarse cell structure will result.

(b) Mould cavity not filled properly, flash is not formed. In MC sole moulding mould cavity has to be filled with 3-5% excess, this excess leads to the formation of a slight flash which prevents the gas loss.

(c) If the mould is not closing properly, the seal along the edge is not perfect. When the internal pressure in the compound shoots up after the decomposition of blowing agent, oozing of the compound starts.

(3) Blister formation/Bulging in sheets

This is a case of under cure or too low degree of precure and an entrapment in between the layers of the blank. To overcome these defects precure time should be lengthened and when the blank is built up of layers it is stored for few hours so that the air in between the layers diffuses out.

(4) Pinholes and holes in the sheet

This defects can arise due to (a) entrapped air in the compound, (b) undispersed compounding ingredients.

If thick compound is sheeted out directly from the mill it is very likely that the blank will contain air bubbles which enlarge on expansion of the sheet. So it is essential to run the compound on the roll for sometimes and then only mould it.

Any filler, sand or any other particle will not expand along with the sheet and will form a pinhole in the sheet.

(5) Warped or wavy sheets

This defect is due to the fact that on release of pressure the sheet is unable to come out of the mould immediately. This may happen if the opening of the press is not quick.

(6) Bubbles on the sheet during post cure

This is due to the incomplete decomposition of the blowing agent during precure. The precure time can be increased and the decomposition of the blowing agent can be activated by increasing the amount of acidic substances, eg. Stearic acid [7].

2.3 Physical test methods

For parameters described below, atleast four specimens per sample were tested for each property and the mean values are reported.

2.3.1 Tensile strength, elongation at break and modulus

These three parameters were determined according to ASTM D-412 (1980) test method, using dumb-bell shaped test pieces. The test pieces were punched out from the moulded sheets using C-type die along the mill grain direction of the vulcanized sheets. The thickness of the narrow portion of specimen was measured using a dial gauge. The specimen were tested in a Zwick universal testing machine (UTM) model 1445 at 28±2°C and at a crosshead speed of 500 mm per minute. The tensile strength, elongation at break and modulus were recorded on a strip chart recorder. The machine had a sensitivity of 0.5 percent of full scale load.

2.3.2 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/min. and the test temperature 28±2°C.

2.4 Testing of microcellular sheets

For parameters described below, at least four specimens per samples were tested for each property and the mean values are reported.

2.4.1 Split tear strength

It is the maximum load required to split off a test piece of specific size, which was separated at a constant speed of 75 mm per minute. The split tear strength determination of MC sheets was carried out as per IS: 10702-1985.

25x100x7±0.2 mm test pieces were cut along and across the direction of the compression moulded microcellular sheet. Each test piece was prepared by splitting it midway between the top and the bottom surface for a distance of 30 mm from one end and thus form two tongues at the end. The tongues of the test pieces were clamped in the jaws of the Zwick UTM 1445 and the jaws were allowed to separate at a constant rate of 75 mm/min. The maximum load was noted and the arithmetic average of the test in kg was recorded as the split tear strength.

2.4.2 Hardness

The hardness of the microcellular samples was tested using Zwick 3114 hardness tester in accordance with IS: 3400 (part-II) 1965 and IS: 10702-1985. The tests were performed on mechanically unstressed samples of 50x50 mm. A load of 12.5N was applied and place the indentor normal to the sole side at the top and press the instrument evenly without shock on to the rubber with just sufficient force to ensure complete contact of the foot with rubber. The readings were taken after 10 seconds of indentation after firm contact had been established with the specimens. Take two such readings of each test piece and average of three test pieces. Hardness is expressed directly in Shore-A.

2.4.3 Change in hardness after ageing at 100°C for 24h

The change in hardness of microcellular samples was determined according to IS: 3400 (part-III) - 1965 method. Test pieces 50x50 mm size were cut from microcellular sheets and heated in an air oven at 100±°C for 24h. The test pieces were then removed and cooled for 1 hour at 27±1°C and the final shore hardness was checked. The average of three readings (R_2) was noted and the change in hardness from that of the original hardness (R_1) was noted.

Increase in hardness due to ageing = $(R_2 - R_1)$.

where R_2 = final reading of Shore A durometer, and

R_1 = initial reading of Shore A durometer.

2.4.4 Abrasion resistance

Abrasion test was conducted using a DIN Abrader as per DIN 53516 with a load of 5N. Abrasion loss was expressed as the volume of the test piece getting abraded by its travel through 42m on a standard abrasive surface.

Cylindrical sample was punched out from the vulcanizate. It had a diameter of 6±0.2 mm and a thickness of 6 to 10 mm. It was kept on a rotating sample holder and a load of 5N was applied. Initially a pre-run was given for the sample and its weight was taken. Then the test run was conducted and the weight was again noted. The difference in weight is abrasion loss. Abrasion loss was calculated as follows:

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

where, Δm = mass loss, ρ - density of the sample and V = abrasion loss in volume.

The result is expressed in mm^3.

2.4.5 Compression set

Two identical microcellular samples (9.5 mm thick and 30 mm diameter) were compressed to constant deflection (25%) and were kept for 24 hours at 27 ±1°C and then the samples were taken out and allowed to recover for an hour and the final thickness was measured. Compression set is the difference between the original thickness and that after the application of a specified load for a specified period of time and is expressed as a percentage of the initial thickness of the sample. Compression set was calculated using the formula

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

where, t_o = initial thickness in mm

t_1 = final thickness in mm.

2.4.6 Heat shrinkage

It is the reduction in length that may occur to a sample of specified size when it is cooled after being kept in heating chamber maintained at 100 ±1°C for one hour.

Heat shrinkage of microcellular sample was determined according to IS: 6664-1972 procedure. The test samples of size 125x5x15 mm were conditioned at a temperature of 27±2°C for at least 24 hours, prior to testing. Then the length of the test piece was measured nearest to 0.1 mm. The test piece was kept in an air oven at 100±1°C for 1 hour. Then it was taken out from the oven and allowed to cool for 2 hours at 27±2°C. The final length of the test piece was measured and the heat shrinkage was calculated as follows:

$$\text{Heat shrinkage (\%)} = \frac{(L_o - L_1)\times 100}{L_o}$$

where,

L_o = length of the test piece in mm before heating, and

L_1 = length of the test piece in mm after heating.

2.4.7 Room temperature shrinkage

It is the percentage linear shrinkage that occurs to the sample after keeping the sample at 27±2°C for two weeks.

Room temperature shrinkage of microcellular sample was determined according to IS: 10702-1985. Test pieces of size 125x5x15 mm were cut from the sample after splitting off all the sides. It was then conditioned at a temperature of 27±2°C for 24h prior to testing. Initial length of the test piece was noted to the nearest of 0.1 mm. The test piece was placed in a chamber maintained at 27±2°C for 2 weeks. It was then removed and its length noted. Room temperature shrinkage was calculated and expressed as

$$\text{Shrinkage (\%)} = \frac{(L_o - L_1)\times 100}{L_o}$$

where L_o = Original length of the test piece in mm

L_1 = Length of the test piece in mm after 2 weeks.

2.4.8 Water absorption

Water absorption of the microcellular test pieces was carried out according to IS: 6664-1972. Sample test pieces of size 5x5x5 mm were taken after splitting all sides of the samples to remove the skin. The test pieces were conditioned at a temperature of 27±2°C for at least 24 hours prior to testing. The weight of samples was accurately measured and immersed in distilled water for a period of 24 hours at 27±2°C. Then the samples were removed from water and, wiped with a blotting paper. The sample was reweighed accurately within two minutes of the removal of the test pieces from water. The water absorption was calculated as follows:

$$\text{Water absorption, \% by mass} = \frac{M_1 - M_0}{M_0}$$

where M_1 = mass in g of the test piece after immersion in water, and

M_o = mass in g of the test piece before immersion in water.

2.4.9 Relative density

Relative density of the microcellular sheets was determined out according to IS: 10702-1985. A sample of size 50x50 mm was cut from vulcanized microcellular sheets. The test piece was conditioned at a temperature of 27±2°C for 24h prior to testing. After conditioning the mass, length, breadth and thickness of the samples were noted. Relative density was then calculated as follows:

$$\text{Relative density} = \frac{M}{L \times B \times T}$$

where,

M = the mass of the test piece in g after conditioning

L = length of the test piece in mm after conditioning,

B = breadth of the test piece in mm after conditioning,

T = average thickness of the test piece in mm in three different places after conditioning.

2.4.10 Expansion ratio

The linear expansion of the MC sheet was measured immediately after taking from the press. This is the initial expansion of the MC sheet, then linear expansion was measured after 5 min and 24 h respectively.

$$\text{Linear expansion (\%)} = \frac{L_0 \text{x} 100}{L} - 100$$

L_0 = length of the MC sheet after taking from the mould in cm

L = length of the mould in cm.

The expansion ratio of the microcellular sheets was calculated according to the formula:

$$\text{Expansion ratio} = \frac{\text{Area of the microcellular sheet}}{\text{Area of the mould}}$$

The linear expansion of the sheets before post curing was controlled to about 100 percent of the mould dimensions.

2.4.11 Flexing resistance

Flexing resistance of the microcellular samples was determined using Ross flexing machine. In this method, the number of flexing cyclesrequired for the sample with an initial cut of definite size to grow to a definite length and for failure, were determined. The flexing resistance test was carried out according to IS: 3400 (part XVI) - 1974 method.

The test specimen of 25 mm in width, 150 mm in length and 6.3 mm in thickness was prepared from the microcellular sheet so that the longitudinal dimension was parallel with the direction of the grain. The test specimen was pierced by using a piercing tool and the cut made by it was made parallel to the width of test specimen at a point 62 mm from the clamped end. The test specimens were clamped to the holder arm of the flexing machine in such a position that when the specimens were flexed at 90°, the cuts were at the centre point of the arc of flexure. Then the machine was started and run at a rate of 100±5°C cycles per minute. The number of cycles was recorded by the use of counter. Frequent observations were made, recording the number of cycles and the increase in cut length for the purpose of determining the rate of increase in cut length. Number of cycles for the initiation of the crack from the pierced hole was also recorded.

The results from the observations of two test specimens were averaged and reported as

1. Number of cycles for the initiation of crack.

2. Extent of crack size growth in mm after 1,00,000 cycles or the number of cycles for each 100 percent increase in cut growth upto and including 600 percent.

2.4.12 Low temperature flexibility

Low temperature flexibility of a microcellular sheet was determined using Ross flexing machine. The test was carried out at a temperature of –5°C according to SATRA PM60-1992 method.

Rectangular specimens of the material were either cut from a sheet or a moulded sole were specially moulded for the test. A narrow cut is made through the full thickness of the specimen in the centre of its width. The specimen is then repeatedly flexed at the cut position, through 90° until the length of the cut has grown to a predetermined length. The arithmetic mean cut growth rate per 1000 flexing cycles is then calculated.

Ross Flex Machine with a mandrel of diameter 10±0.6 mm around which the specimen were flexed. A means of holding the specimen so that in the unflexed state the cut is directly in line with the edge of the mandrel nearest to the rollers. One end of the specimen is firmly clamped and the other end is free to move in a lengthwise direction between rollers. The vertical position of the upper roller must be adjustable to the thickness of the test specimen.

The sheet material cut six test specimens 25±2 mm wide and 150±5mm long three cut so that their longest edges are parallel to the length direction of the sheet, the thickness of material is 5.0±0.2 mm place each test specimen in the chisel jig with the wearing surface uppermost, and make a cut which across the longitudinal central line of the specimen and is at 90° to it. Colour the area around the cut with a contrasting marking pen or chalk. This colouring assists the visibility of the cut band each specimen through an angle of 45° around the mandrel and use the optical magnifier to measure the length of the cut to an accuracy of 0.1 mm.

Load the test specimens in to the flexing machine in the unflexed position with their wearing surface uppermost and cuts directly in line with the edge of the flexing mandrel. Reset the counters on the machine the test specimen should be at right angle to the axis mandrel. When the specimens have been in the temperature controlled environment for atleast ten minutes run the flexing m/c for 3600 cycles.

Stop the flexing machine so that the specimens were flexed through an angle of 45° use the steel rule to measure the length of cut in each specimen to an accuracy of 0.5 mm without removing them from the machine.

Start the flexing machine again and repeat the procedure. Stop the test when either the length of the cut has reached 8 mm (6 mm cut growth) or specimen has been subjected to a total of 150,000 cycles.

2.4.13 Cell structure study

The cell structure of the microcellular sheets were done using a Leica Wild M8 Zoom stereomicroscope and Wild MPS 4.6/5.2 photoautomat. For this, a compression moulded test piece was cut into a convenient size and mounted on a microscope slide. Photographs were taken at a magnification of 40.

2.5 Thermogravimetric analysis

The thermogravimetric analysis of the sample was done using a Shimadzu-50 Thermogravimetric analyser. About 10 mgs of the sample was taken in a platinum crucible and the experiment was done in air at a heating rate of 10°C/min. The weight loss of the sample was taken and then plotted against temperature.

2.6 Infrared spectroscopy

Infrared (IR) spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm^{-1} by organic molecules. Different functional groups and structural features in the molecule absorb at characteristic frequencies. The frequency and intensity of absorption are indication of the bond strengths and structural geometry in the molecule. IR spectra given in this investigation were taken in KBr pellets using Perkin Elmer Model 983.

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CHAPTER 3

PART I: STUDIES ON THE PROPERTIES OF MICROCELLULAR SOLES BASED ON NBR/PVC BLENDS

Blends of poly(vinyl chloride) (PVC) and acrylonitrile butadiene rubber (NBR) are compatible in all proportions. The rubber functions as a 'solid plasticizer' for the PVC and PVC as a reinforcing agent for the rubber [1,2]. In NBR vulcanizates PVC acts as a reinforcing material [3-6] increasing tensile strength and tear resistance, improving resistance to flex cracking and solvents and giving the vulcanizates improved protection against the atmosphere and ozone [7]. Lower abrasion resistance, lower tensile strength and higher compression set are the disadvantages of adding higher amounts of PVC. The advantages are utilised in applications like wire and cable jacketing, gaskets, football covers, shoe uppers, tubing etc. [8].

Miscibility of polymer blends was first observed with NBR/PVC systems. These blends probably have been the most widely studied, due to the significant commercial interest. In well mixed blends of most polymer pairs, the presence of two phases is evidenced by two glass transitions [9,10]. In contrast blends of NBR and PVC have a single broad glass transition over a temperature range between T_g's of the unblended components [11-13]. The compatibility of NBR/PVC blends depends on the ACN content in the NBR. NBR having an ACN content in the range of 25 to 40 wt. % is completely compatible with PVC [14,15]. The properties of NBR/PVC blends are sensitive to blending conditions and variations in the individual polymers used. The optimization of parameters available to the processors of NBR/PVC blends has been reported [13,16].

NBR/PVC blends can be used in MC sole industry due to their attractive properties, such as light weight, adequate abrasion resistance, and low shrinkage on storage. The main disadvantages with microcellular soles based on NBR/PVC blends are crack formation and crack growth during service. The main objective of this study is to develop crack resistant and light weight MC sole based on NBR/PVC blends with good technical properties. For this end, influence of several parameters like PVC type and content, blending temperature, amount of plasticizer, amount of blowing agent etc. are proposed to be investigated. A suitable formulation for making light weight MC soles is proposed to be developed. A polymeric plasticizer, amine terminated liquid natural rubber (ATNR), is proposed to be used as a plasticizer in NBR/PVC blend and the effect of replacement of DOP by ATNR on the properties of NBR/PVC blend based MC soles is also proposed to be investigated. Cell structure of the MC soles is proposed to be investigated to correlate it with the mechanical properties.

This part of the study is divided into the following sections:

A. Development of crack resistant microcellular soles based on NBR/PVC blends

B. Effect of fillers on the properties of microcellular soles based on NBR/PVC blends

C. Effect of replacement of NBR by NR, SBR and HSR on properties of microcellular soles based on NBR/PVC blends.

3A. Development of crack resistant microcellular soles based on NBR/PVC blends

Experimental

Preparation of PVC compound

A stabilizer system consisting of ZnO, MgO and stearic acid was used for PVC [Table 3.1.1]. The dry blending technique was used for the preparation of PVC compounds [17]. PVC was premixed with stabilizers and was subjected to vigorous stirring. Then plasticizer was added which got absorbed into the polymer particles and a free flowing powder was obtained.

Preparation and characterization of NBR/PVC blends

Blends of NBR and suspension PVC (hereafter referred to as NBR/S-PVC) were prepared in a Brabender plasticorder model PL 3S. The mixing head was heated to the required temperature and the rotor speed was adjusted to 30 rpm. NBR was first added and allowed to heat up and homogenize for one minute, PVC compound was then added and mixing was continued for seven more minutes.

Blends of NBR/S-PVC were also prepared in a laboratory model Shaw Intermix-MK-3, size KO, set at 40 rpm and at an initial temperature of 130°C.

Blends of NBR and emulsion PVC (hereafter referred to as NBR/E-PVC) were prepared on a laboratory model two-roll mill at the optimum blending temperature [18,19]. The rolls were heated by steam to 90°C. NBR/E-PVC blends were also prepared in a Brabender plasticorder at 120°C and at 30 rpm employing a blending time of 5 minutes.

Table 3.1.1: Formulation of PVC compound

PVC Grade	Suspension (Phr)	Emulsion (Phr)
Poly(vinyl chloride)	100	100
ZnO	4	4
MgO	4	4
Stearic acid	2	2
DOP	40	30

Table 3.1.2: Formulation for microcellular sole compound

Ingredients	Phr
NBR (in NBR/PVC blend)	100
Sulphur	1.5
ZnO	3
Stearic acid	1
Zinc stearate	1
Titanium dioxide	4
Precipitated silica	40
Calcium carbonate	60
Diethylene glycol (DEG)	1.5
Dioctyl phthalate (DOP)	5
Wood rosin	2
Vulcafor F	1.5
TMTD	0.5
Styrenated phenol (SP)	1
Azodicarbonamide (ADC)	10

Preparation of amine terminated liquid natural rubber

ATNR was prepared by UV irradiation of NR solution in toluene in presence of ethylene diamine. The details of preparation are given in chapter 2.

Preparation of microcellular sheets

The NBR/S-PVC and NBR/E-PVC blends were compounded on a laboratory two roll mixing mill (150x330 mm) at a friction ratio 1:1.25 as per ASTM D-3182. Curatives, blowing agents etc. were added on a cold mill, as per formulation given in Table 3.1.2. The final compound was kept for maturation at room temperature for a period of 16-24h. The cure characteristics of the compounds were determined at 160°C on a Goettfert Elastograph Model 67.85. The mould was filled with 3-5 percent excess of the compound on volume basis. The compounds were precured upto an optimum level of precuring. The expanded sheets were then post cured for 2h at 70°C.

The sheets were tested for technical properties as per relevant Indian standards. The details of tests are given in chapter 2. The cell structure of the MC sheets was studied using an optical microscope, from razor cut samples.

3A.1 Effect of PVC content on properties of microcellular soles based on NBR/PVC blends

Experimental

NBR/S-PVC and NBR/E-PVC blends were prepared in a Brabender plasticorder with varying amounts of NBR and PVC viz., 70:30, 60:40, 50:50, 40:60 at 150°C. These blends were compounded in a laboratory model two-roll mill at a temperature of 80°C as per formulation given in Table 3.1.2. Preparation of MC sheets and determination of their technical properties were done as per the procedure described in section 3A.

Results and Discussion

Fig.3.1.1 shows the variation of heat shrinkage and relative density with increase in the amount of PVC. Heat shrinkage is found to decrease as the PVC content increases from 30 to 60 phr. The relative density decreases with increase in PVC content, possibly due to the higher expansion of the sheet (as shown in Table 3.1.3) and may be attributed to the thermoplastic nature of PVC [20].

Fig.3.1.2 shows the changes in split tear strength and abrasion loss with increase in PVC content. The observed increase in split tear strength of the cellular product with increase in the amount of PVC is due to the higher tear strength of PVC [7,21]. The abrasion loss is found to be minimum when the PVC content is 50% or less in both cases. This may be due to the higher expansion of the MC sheets. At higher levels of PVC, expansion of MC sheet is higher, and consequently abrasion loss is high [22,23].

Fig.3.1.3 shows the changes in hardness and water absorption with the amount of PVC in the blend. When the amount of PVC in NBR/S-PVC blend increases, the water absorption increases. This shows that at higher PVC compositions there is more chance for the formation of open cell structure [22]. The hardness slightly decreases when the amount of PVC increases. This may be due to the higher expansion at higher PVC content. The same trend is observed in the case of NBR/E-PVC blend.

The compression set is also high for blends containing higher amount of PVC as shown in Table 3.1.3. This may be attributed to the thermoplastic nature of PVC and to the lower extent of crosslinking with increased PVC content. At higher levels of PVC, NBR is no longer crosslinked and it serves as a polymeric plasticizer [23].

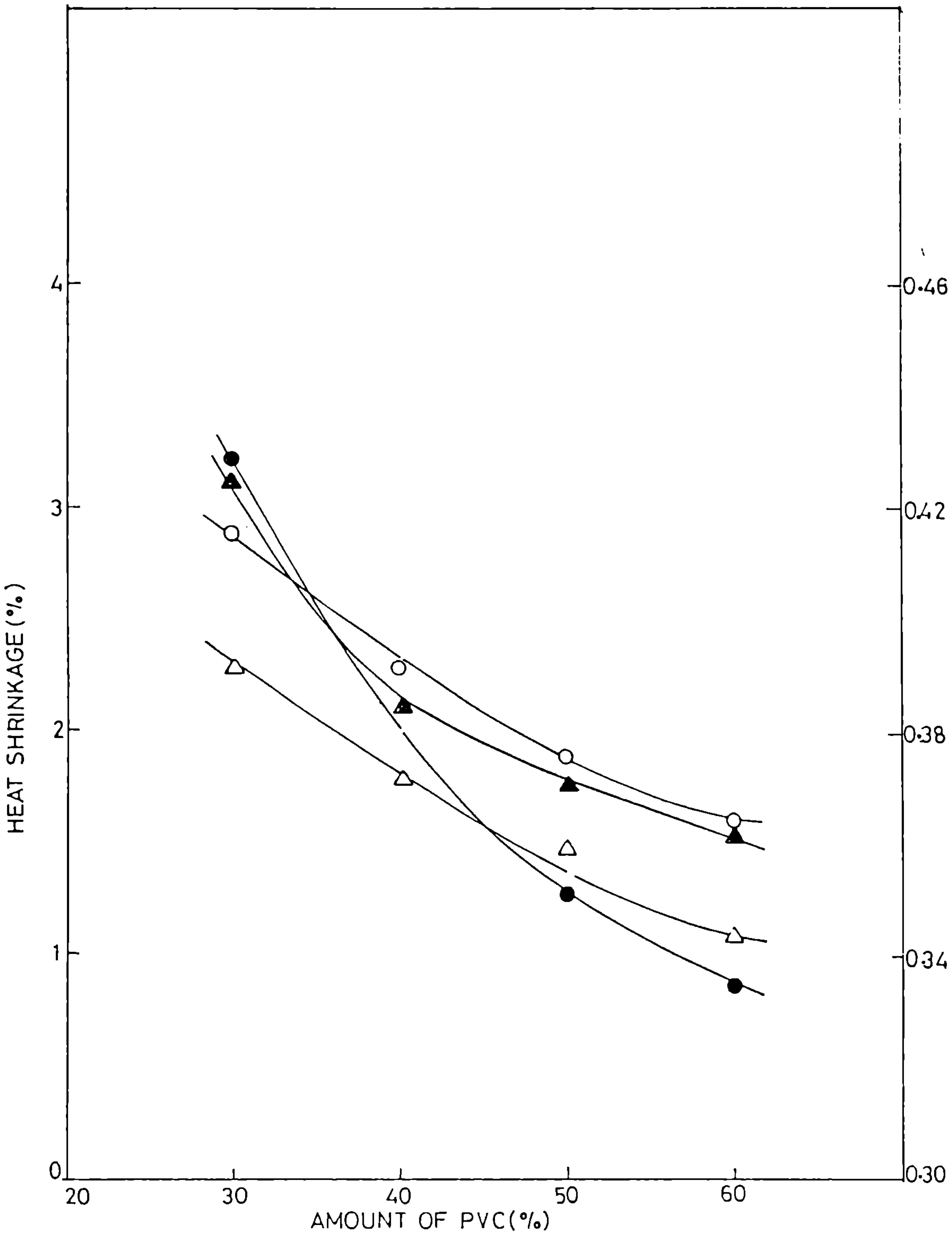

Fig.3.1.1 Variation of heat shrinkage and relative density with increase in the amount of PVC. NBR/S-PVC: (○) heat shrinkage, (●) relative density. NBR/E-PVC: (△) heat shrinkage, (▲) relative density.

Table 3.1.3

Effect of PVC ratio on technical properties of NBR/PVC blend MC sheets

Blend	Properties	Percentage of PVC			
		30	40	50	60
NBR/ S-PVC	Optimum cure time at 160°C (min.)	10.9	10.7	10.5	9.85
	Initial expansion (%)	75.79	79.17	81.55	82.74
	Final expansion (%)	42.26	47.62	48.09	50
	Compression set (%)	5.13	5.21	5.8	6.77
	Shrinkage after post curing (%)	3.45	3.49	3.5	3.69
	Flex resistance				
	a) Crack initiation in cycles	270,746	270,746	267,450	240,100
	b) Crack growth at the end of 100,000 cycles (mm)	0.05	0.05	0.05	0.1
NBR/ E-PVC	Optimum cure time at 160°C (min.)	9.9	9.95	10.00	10.1
	Initial expansion (%)	76.78	84.52	89.28	90.48
	Final expansion (%)	58.33	59.52	60	60.71
	Compression set (%)	8.19	8.3	8.58	9.44
	Shrinkage after post curing (%)	3.84	4.12	4.4	4.6
	Flex resistance				
	a) Crack initiation in cycles	290,140	290,176	289,200	270,195
	b) Crack growth at the end of 100,000 cycles (mm)	0.05	0.05	0.1	0.1

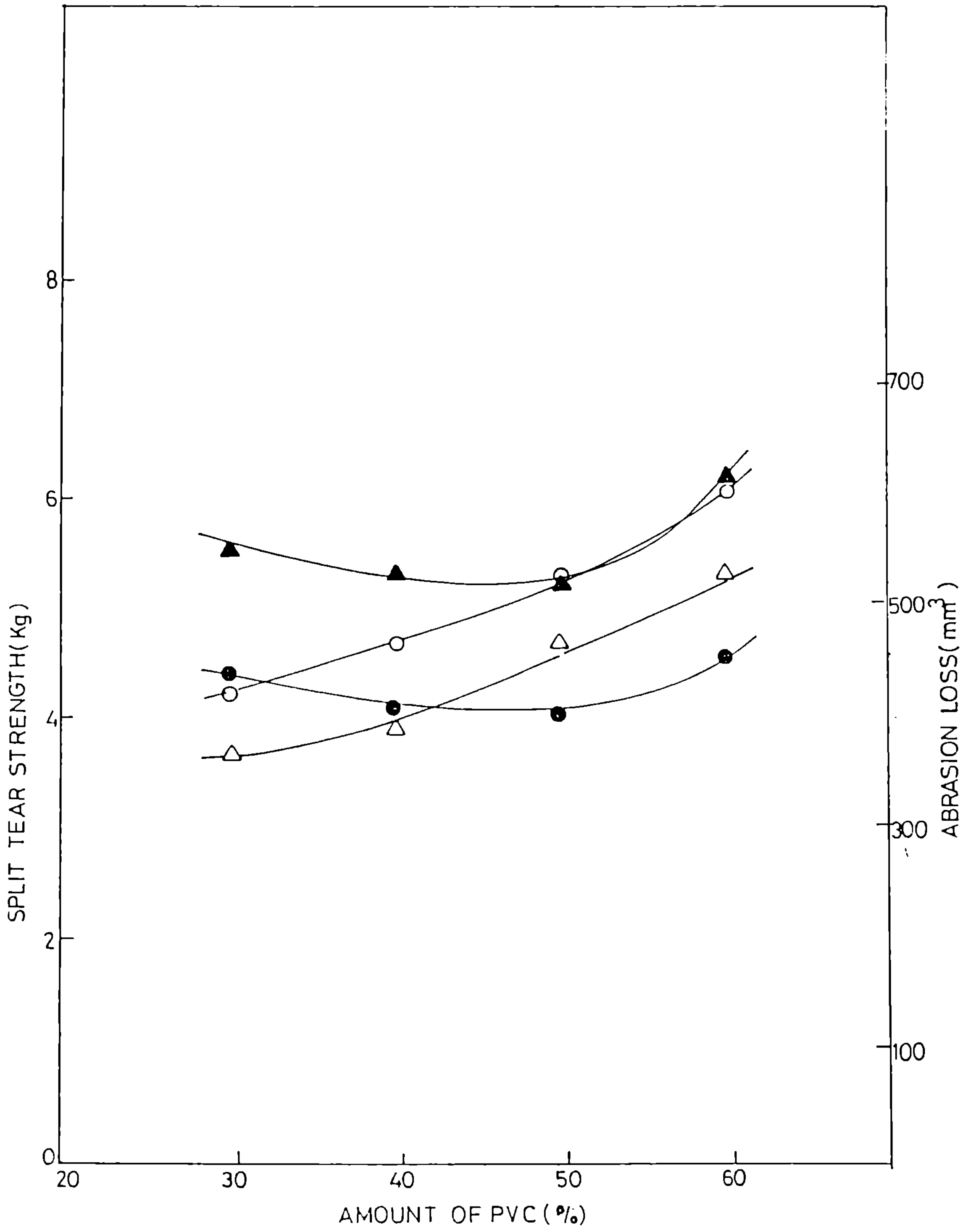

Fig.3.1.2 Variation of split tear strength and abrasion loss with increase in the amount of PVC. NBR/S-PVC: (○) split tear strength, (●) Abrasion loss, NBR/E-PVC: (△) Split tear strength (▲) Abrasion loss.

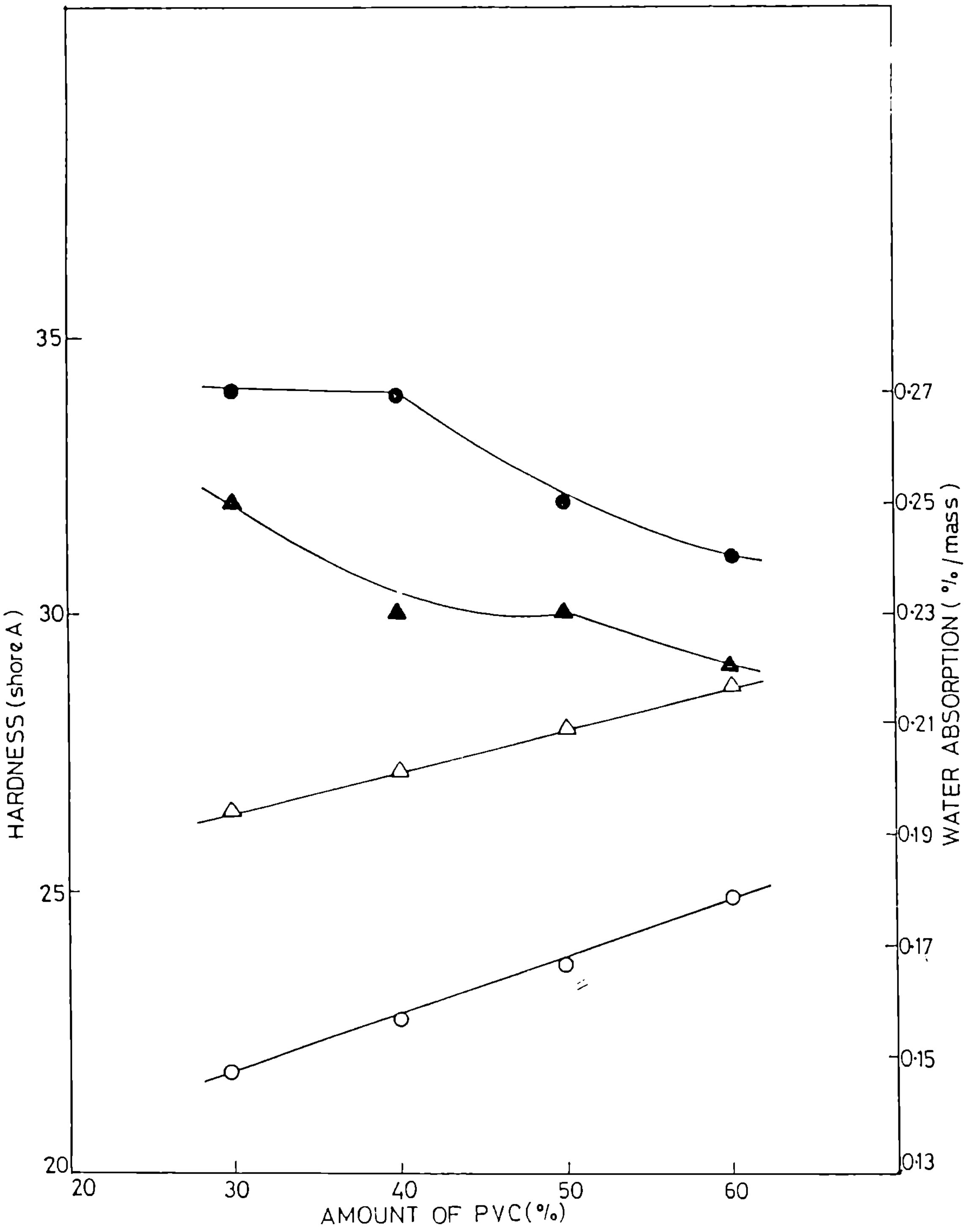

Fig.3.1.3 Variation of hardness and water absorption with increase in the amount of PVC. NBR/S-PVC: (●) Hardness, (○) Water absorption, NBR/E-PVC: (▲) Hardness, (△) Water absorption.

Shrinkage after post curing remains almost unchanged upto 50% PVC content, while at higher levels of PVC there is a slight change. Flex resistance of the samples are shown in Table 3.1.3. When the PVC content is low crack initiation is observed after 270,746 cycles. But when the PVC content is moderate, initial crack is observed after 267,450 cycles and when the PVC content is 50% initial crack formation occurs after 240,100 cycles. This shows that as the PVC content increases flex resistance decreases. Crack growth is also found to be high at 60% PVC, but all the values are within the specification limits.

NBR/E-PVC blend based MC sheets show similar behaviour. MC sheets based on NBR/E-PVC blend show higher expansion compared to NBR/S-PVC blends. Consequently relative density is low and hardness, split tear strength etc. are also lower compared to NBR/S-PVC blend. The differences between the emulsion and suspension PVCs used in blend are reported [16,24-26]. The suspension resin gives slightly better physical properties, abrasion resistance and ozone resistance. The study shows the 50:50 blend ratio is ideal for obtaining optimum technical properties.

Figs.3.1.4 to 3.1.6 are the optical microscope photographs of the microcellular sheets prepared from 70/30, 50/50 and 40/60 NBR/PVC blends. As the amount of PVC increases, the size and number of cells become larger and the cells attain a more uniform structure due to the increased expansion, resulting from the lower viscosity of the thermoplastic phase. However, when PVC forms a continuous phase a decrease in cell size is observed as shown in Fig.3.1.6 probably due to the lower amount of blowing agent used. The observed high technical properties of the MC sheets containing higher proportion of PVC thus correlates well with their cell structure.

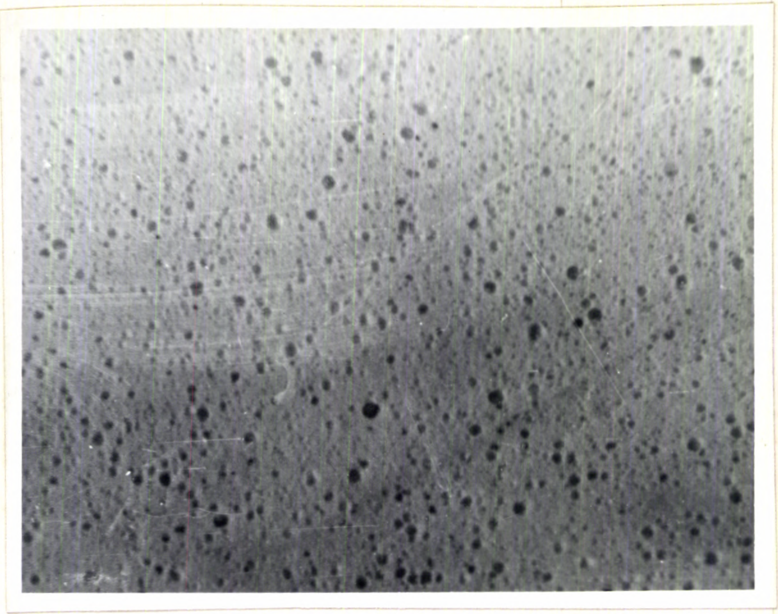

Fig.3.1.4
70/30 NBR/PVC

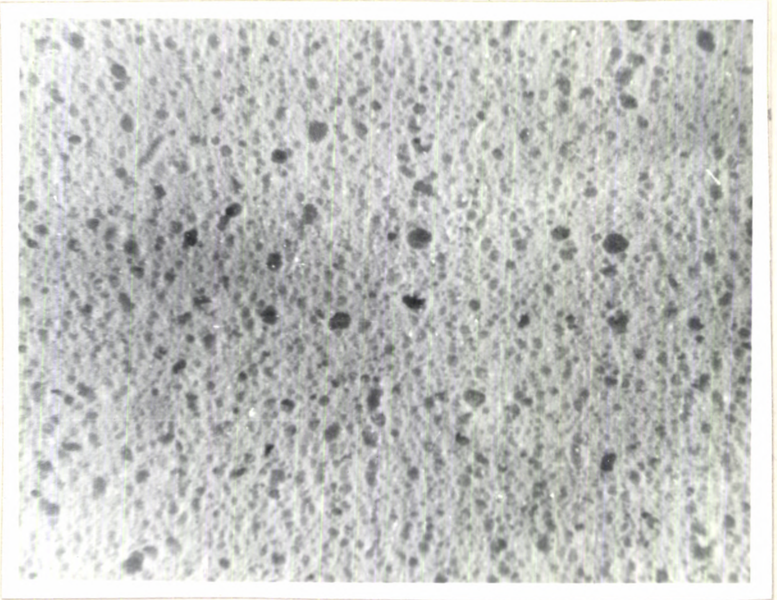

Fig.3.1.5
50/50 NBR/PVC

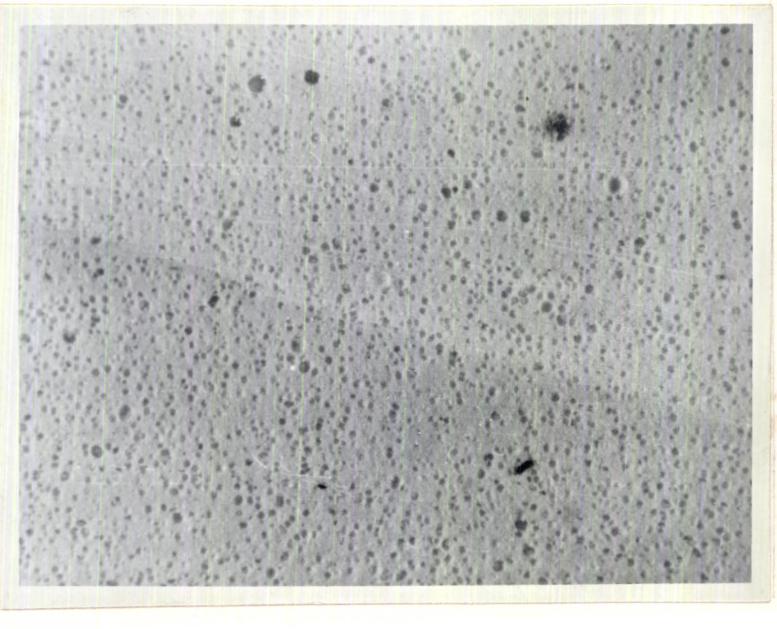

Fig.3.1.6
40/60 NBR/PVC

Optical microscope photographs of MC sheets

3A.2 Effect of blending temperature on properties of microcellular soles based on NBR/PVC blends

Experimental

A 50:50 NBR/S-PVC blend was used for these studies. Blending was done on a Brabender plasticorder model PL 3S. Blending was carried out at 130, 140, 150 and 160°C respectively to study the effect of blending temperature. Compounding and moulding of MC sheets were done as per the procedure given in Section 3A.

Results and Discussion

Fig.3.1.7 shows the variation of relative density and heat shrinkage with increase in blending temperature. Relative density of MC sheets decrease with increase in blending temperature, while the linear expansion increases. The viscosities of the compounds increase considerably by hot mixing or flexing of the resin [24]. This may be the reason for the increased expansion. Heat shrinkage marginally decreases with increase in blending temperature.

Fig.3.1.8 shows the variation of split tear strength and abrasion loss with increase in blending temperature. Split tear strength increases up to a blending temperature of 150°C and then decreases. This may be due to the better homogenisation of PVC particles at higher blending temperature. W.J.Abrams has reported that, the compound containing suspension resin possess only very low tensile strength when mixed at low temperature. Abrasion loss shows marginal reduction up to a blending temperature of 150°C and then increases. The decrease in split tear strength and increase in abrasion loss after 150°C may be due to the onset of degradation in the rubber phase at higher temperature.

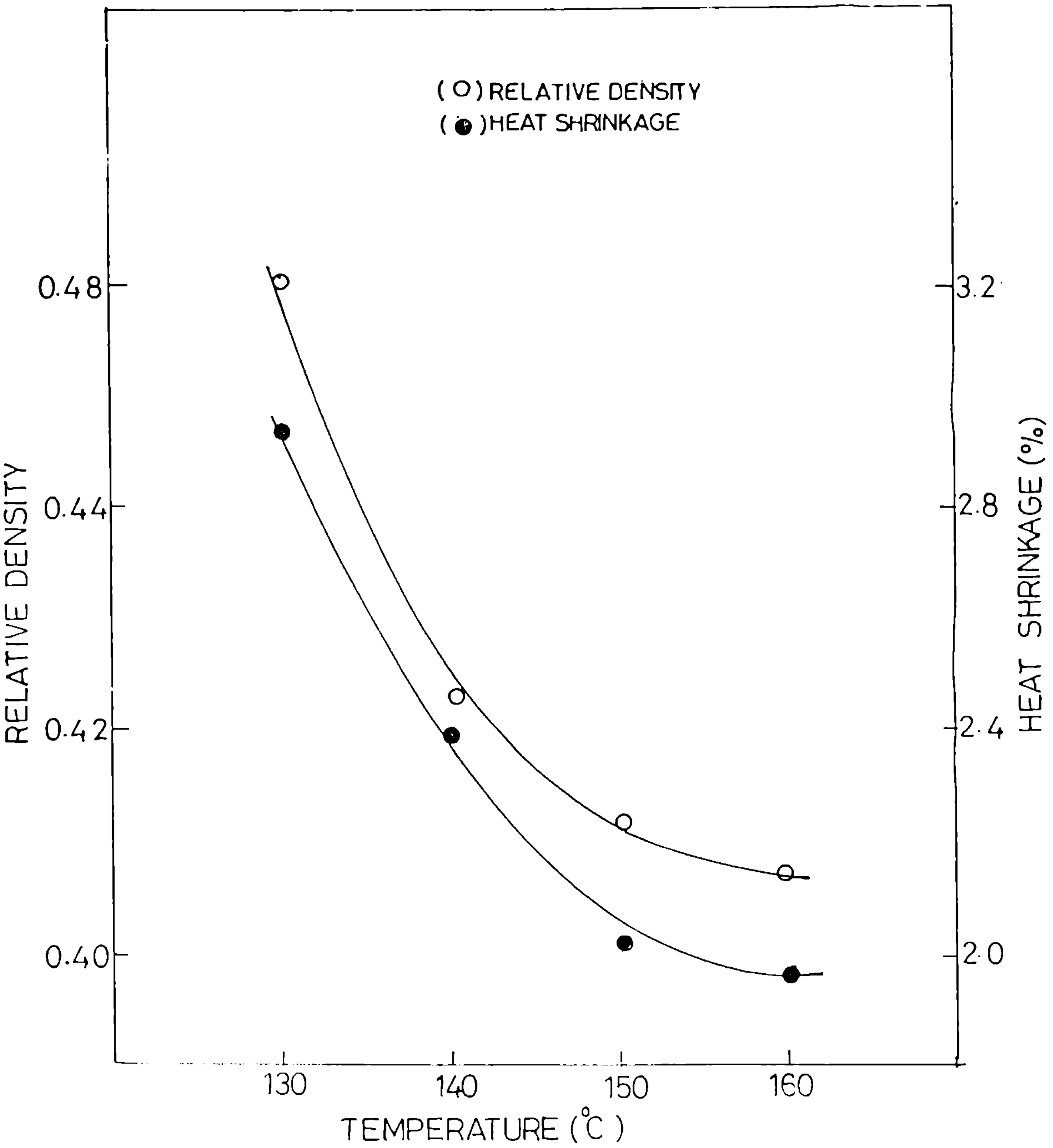

Fig.3.1.7 Variation of relative density and heat shrinkage with increase in blending temperature. NBR/S-PVC: (O) relative density, (●) heat shrinkage.

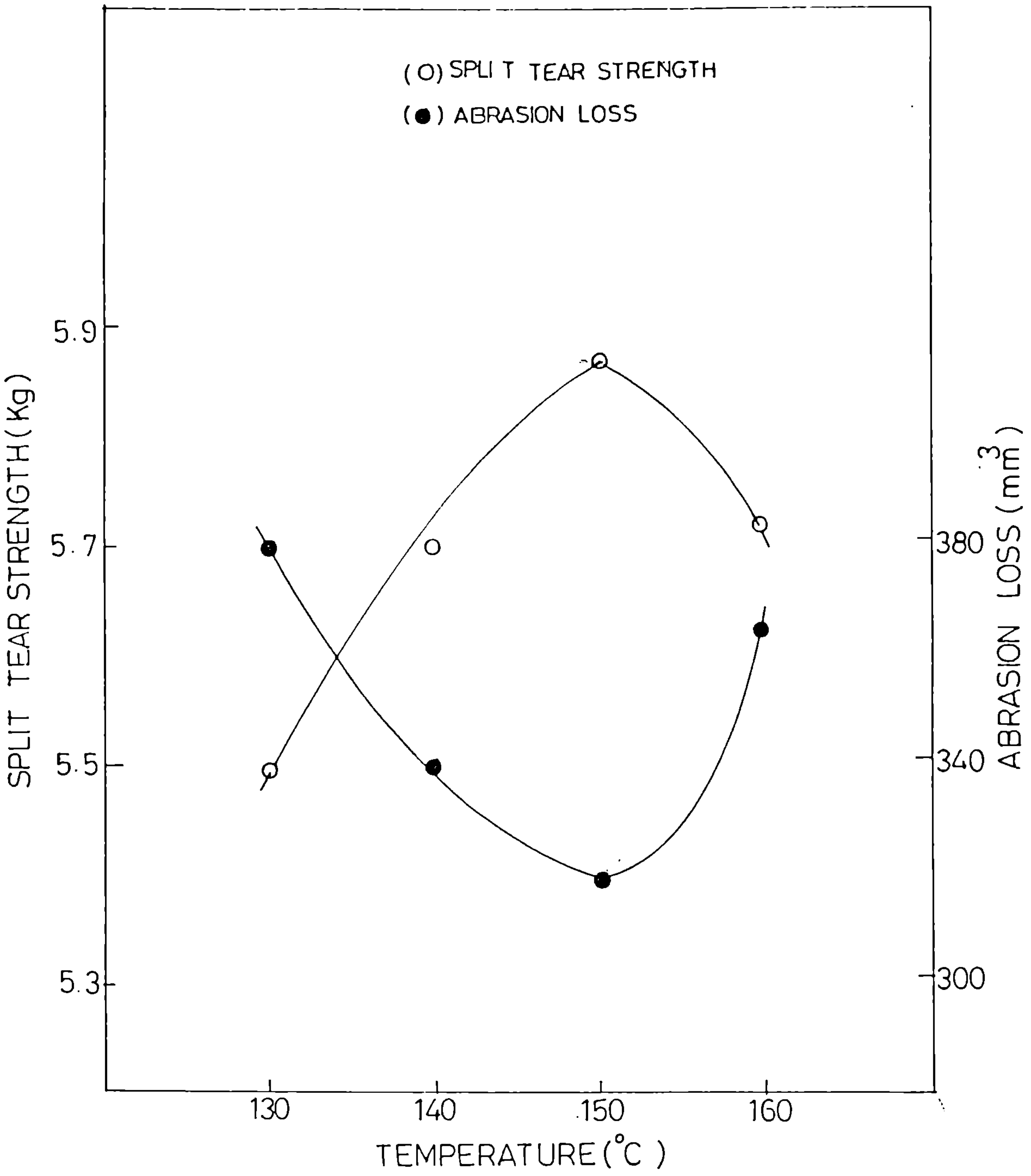

Fig.3.1.8 Variation of split tear strength and abrasion loss with increase in blending temperature. NBR/S-PVC: (O) Split tear strength, (●) abrasion loss.

Fig.3.1.9 shows the variation of water absorption and hardness with increase in blending temperature. Water absorption and hardness decrease with increase in blending temperature. The decrease in hardness may be due to the higher expansion shown by the blends at higher temperature.

Compression set increases with blending temperature as shown in Table 3.1.4. This behaviour may be due to the thin cell walls resulting from higher expansion. Shrinkage after post curing is also found to decrease with increase in blending temperature.

It may be noted that as the blending temperature increases properties like split tear strength increases up to 150°C and thereafter decreases. Abrasion loss also decreases upto 150°C then increases. But shrinkage decreases right from the beginning as the blending temperature increases. This shows that a uniform blend is formed at 150°C. Usually a temperature above the glass transition temperature of PVC is required for proper blending of two component. But when the temperature is too high it may cause degradation of the polymer. Hence it is advisable to carryout blending at the lowest temperature possible and so, the optimum temperature for blending NBR and S-PVC may be taken as 150°C.

Y.Nakamura et al.have reported the blending temperature for NBR/E-PVC blends. A uniform blend of NBR and E-PVC is obtained by mixing the two materials for 15 min. at 90°C [25]. NBR/E-PVC is obtained as a uniform blend even at 120°C.

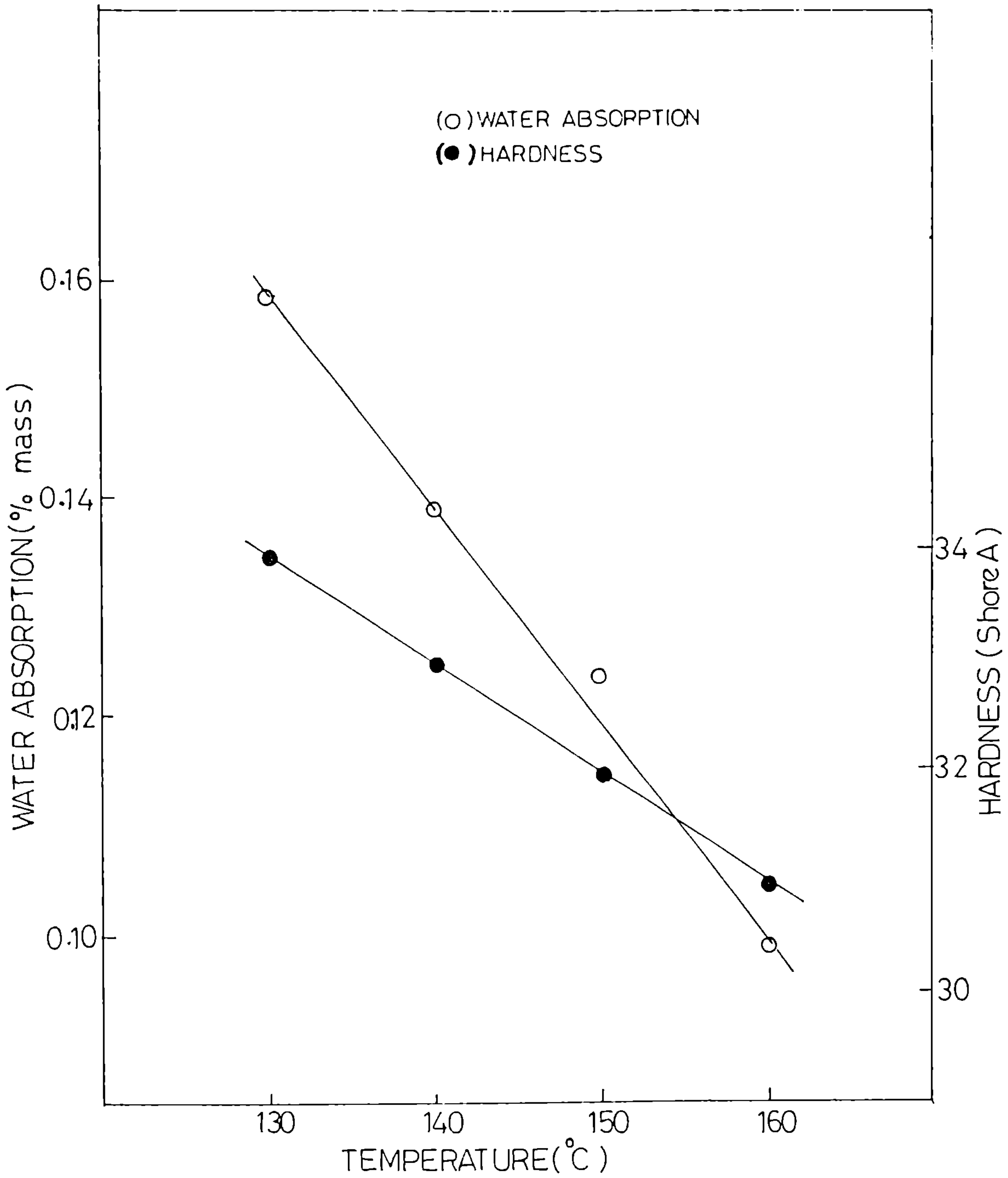

Fig.3.1.9 Variation of water absorption and hardness with increase in blending temperature. NBR/S-PVC: (O) water absorption, (●) hardness.

Table 3.1.4

Effect of blending temperature on the technical properties of NBR/S-PVC based MC sheets

Properties	Blending temperature (°C)			
	130	140	150	160
Time required for optimum cure at 160°C (min.)	10.5	10.5	10.6	10.7
Initial expansion (%)	57.05	60.01	62.91	65.81
Final expansion (%)	48.90	50.91	51.31	52.42
Shrinkage after post curing (%)	3.75	3.12	2.79	2.25
Compression set (%)	4.38	4.44	4.61	4.93

3A.3 Effect of percentage precure on properties of microcellular soles based on NBR/PVC blends

Experimental

50:50 NBR/S-PVC and NBR/E-PVC blends were used for this study. Blending was done in the Brabender plasticorder model PL 3S. Blending of NBR and S-PVC was carried out at 150°C and NBR and E-PVC at 120°C. These blends were compounded as per formulation given in Table 3.1.2. Compounding and moulding of MC sheets were done as described in Section 3A. In order to study the effect of degree of precuring on MC soles based on NBR/S-PVC and NBR/E-PVC blends, the sheets were precured to different percentages of their optimum cure times and the expanded sheets were post cured for 2h at 70°C.

Results and discussion

Table 3.1.5 shows that the expansion of the MC sheet decreases with increase in precure. As precure increases, modulus of rubber becomes higher causing more resistance for the sheet to expand and the resulting size of the sheet is lower.

Fig.3.1.10 shows the variation of relative density and split tear strength with percentage precuring. The relative density is minimum when 75% precuring is given for NBR/E-PVC and 50% for NBR/S-PVC. This shows that the maximum percentage of expansion occurs at 75% precuring for NBR/E-PVC and at 50% for NBR/S-PVC, as shown in Table 3.1.5. Split tear strength is maximum when the percentage precuring is not less than

Table 3.1.5

Effect of percentage of precuring on the technical properties of NBR/PVC blend based MC sheets

Blend	Properties	Percentage precure				
		80	70	60	50	40
NBR/ S-PVC	Initial expansion (%)	65.48	69.05	72.62	100	96.43
	Final expansion (%)	45.24	47.62	51.19	55.98	52.38
	Compression set (%)	8.4	9.12	10.95	11.5	10.9
	Shrinkage after post curing (%)	3.51	3.67	3.7	4.59	4.85
	Hardness (Shore A)	32	30	27	24	23
			Percentage precure			
			90	80	75	65
NBR/ E-PVC	Initial expansion (%)		83.3	91.67	101.19	66.67
	Final expansion (%)		57.14	59.5	64.28	48.81
	Compression set (%)		9.24	10.5	10.92	10.8
	Shrinkage after post curing (%)		3.69	3.85	4.8	4.95
	Hardness (Shore A)		30	29	27	27

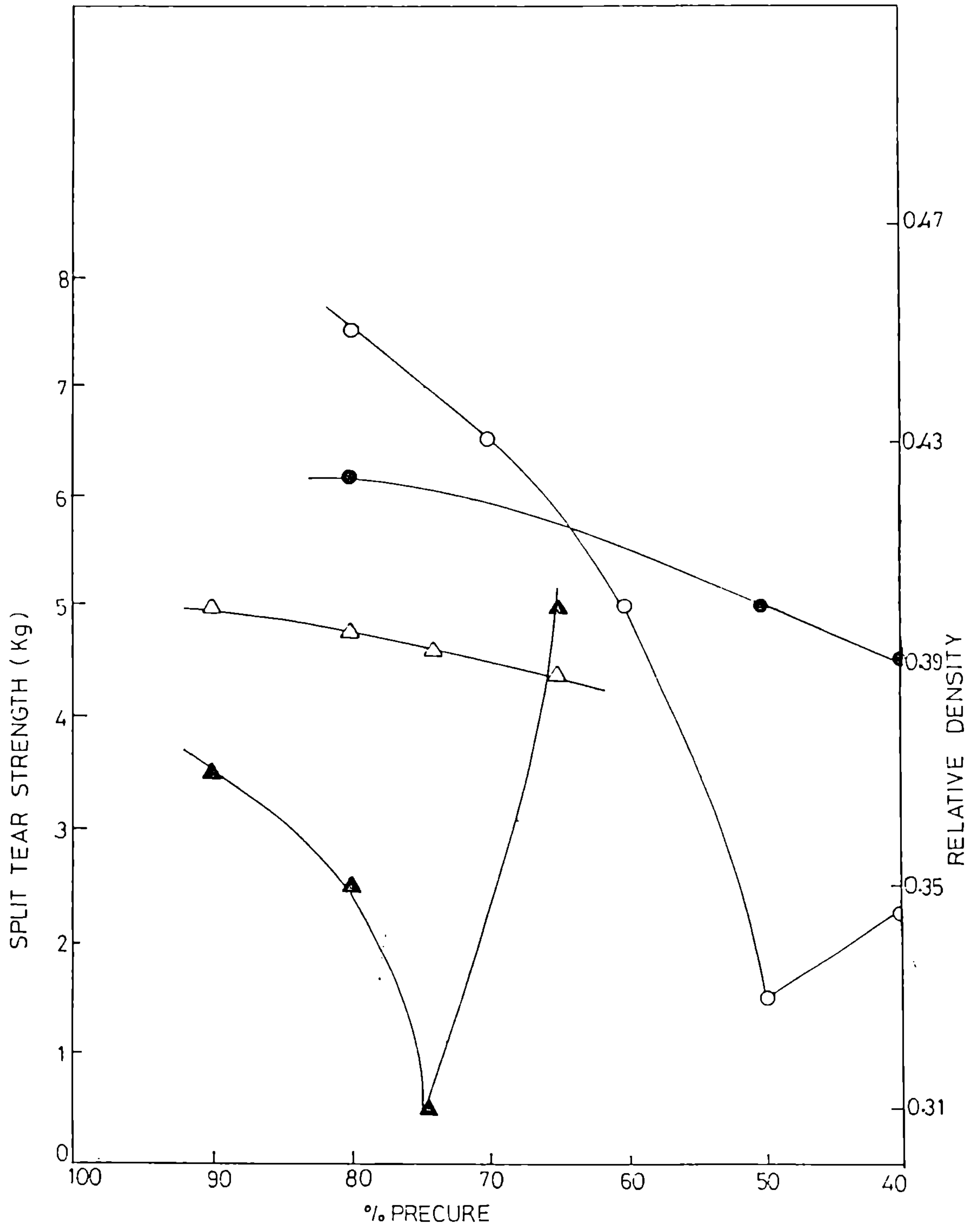

Fig.3.1.10 Variation of split tear strength and relative density with percentage precure. NBR/S-PVC: (●) split tear strength, (○) relative density. NBR/E-PVC: (△) split tear strength, (▲) relative density.

70% in both cases. This shows that only at 70% precuring does the matrix attain the required amount of crosslinking in both suspension and emulsion grade PVC/NBR blends.

Fig.3.1.11 shows the variation of heat shrinkage and water absorption with percentage precuring. The water absorption is found to be minimum when the amount of precuring is around 80%. This shows that when a low percentage of precuring is given, there is more chance for the formation of open cell structure. The heat shrinkage is found to be minimum at about 70% precuring, which again shows that a strong matrix is formed when the percentage of precuring is around 70% in both cases.

Minimum hardness and maximum compression set are observed at 50% precure for NBR/S-PVC and at 65% for NBR/E-PVC. Shrinkage after post curing is maximum at 40% for NBR/S-PVC and at 65% for NBR/E-PVC as shown in Table 3.1.5. As the percent precure increases size of the sheet decreases. This is due to the high internal pressure of the gas after expansion and when the gas releases on storage, the shrinkage becomes more. Hence to control shrinkage it is necessary to give low degree of precure as possible. Considering all the properties 70% precuring is given for NBR/S-PVC blend and 75% precuring for NBR/E-PVC blend.

3A.4 Effect of amount of plasticizer (DOP) on properties of microcellular soles based on NBR/PVC blends

Experimental

50:50 NBR/S-PVC and NBR/E-PVC blends were used for this study. Blending was done in the Brabender plasticorder model PL 3S at 150°C for NBR/S-PVC and 120°C for NBR/E-PVC respectively at a rotor speed of 30 rpm. These blends were compounded as per formulation given in Table 3.1.2. The compounding and moulding of MC sheets were

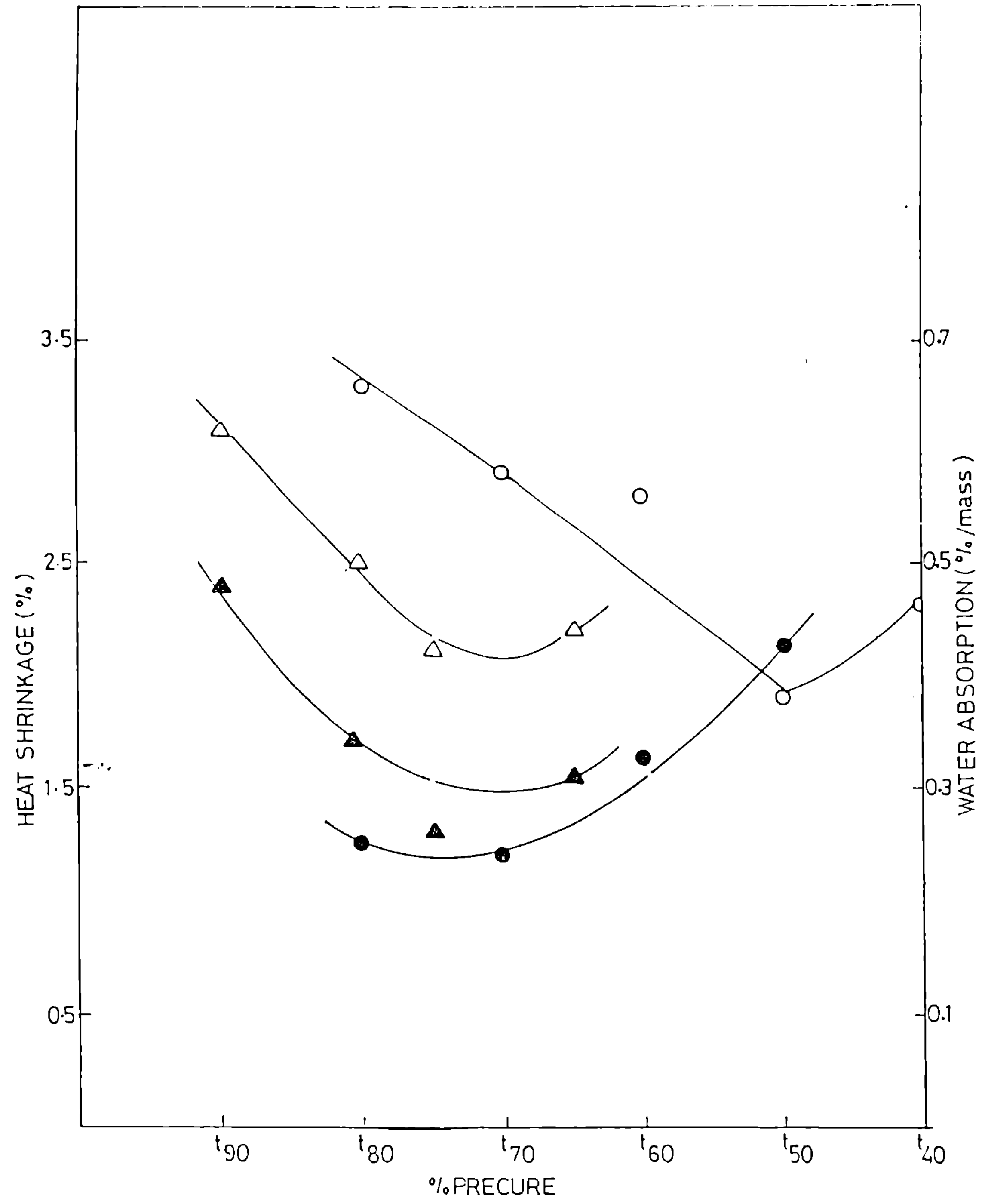

Fig.3.1.11 Variation of heat shrinkage and water absorption with percentage precure. NBR/S-PVC: (○) heat shrinkage, (●) water absorption. NBR/E-PVC: (△) heat shrinkage, (▲) water absorption.

described in Section 3A. In order to study the optimum level of plasticizer (DOP) required for getting good technical properties, the DOP content in blend was varied from 20 to 40 phr. The technical properties of the microcellular sheets were determined as per relevant Indian standards. The cell structure of the selected microcellular sheets were observed using an optical microscope.

Results and discussion

Table 3.1.6 shows the cure characteristics and technical properties of MC soles based on NBR/PVC blends. As the amount of plasticizer in the blend increases, the cure time of the compound also increases.

Fig.3.1.12 shows the variation in relative density and heat shrinkage with increase in the amount of plasticizer (DOP). As the amount of DOP increases, the expansion of MC sheets increases and consequently relative density decreases in NBR/S-PVC blends. This is obviously due to the improvement in the softness of sheet by the progressive addition of plasticizer [27]. There is only a marginal increase in shrinkage when the amount of DOP is varied from 25 to 35 phr in NBR/S-PVC blends.

Fig.3.1.13 shows the variation in split tear strength and abrasion loss with increase in the amount of DOP. Split tear strength decreases as the amount of DOP increases. This is obviously due to the higher softness of the matrix with increase in DOP content. The abrasion loss of the MC sheet increases with increase in the amount of DOP. This may be due to the higher expansion, resulting in thinner walls and the increased chances for breakage of the cell walls.

Table 3.1.6

Effect of amount of plasticizer (DOP) on the technical properties of NBR/PVC blend based MC sheets

Blend	Properties	Amount of DOP (Phr)		
		25	30	35
NBR/ S-PVC	Time required for optimum cure at 160°C (min.)	12.1	12.9	13.2
	Initial expansion (%)	67.86	72.02	82.13
	Final expansion (%)	44.05	45.24	50
	Compression set (%)	5.57	5.44	5.16
	Shrinkage after post curing (%)	3.14	3.59	3.99
	Flex resistance			
	a) Crack initiation in cycles	245,045	220,000	209,000
	b) Crack size growth at the end of 100,000 cycles (mm)	0.05	0.1	0.1
		Amount of DOP (Phr)		
		20	30	40
NBR/ E-PVC	Time required for optimum cure at 160°C (min.)	11.8	12	12.5
	Initial expansion (%)	88.1	90	98.8
	Final expansion (%)	58.3	60.7	63.09
	Compression set (%)	5.47	5.32	5.24
	Shrinkage after post curing (%)	3.9	4.25	4.91
	Flex resistance			
	a) Crack initiation in cycles	239,450	210,145	200,470
	b) Crack size growth at the end of 100,000 cycles (mm)	0.05	0.1	0.1

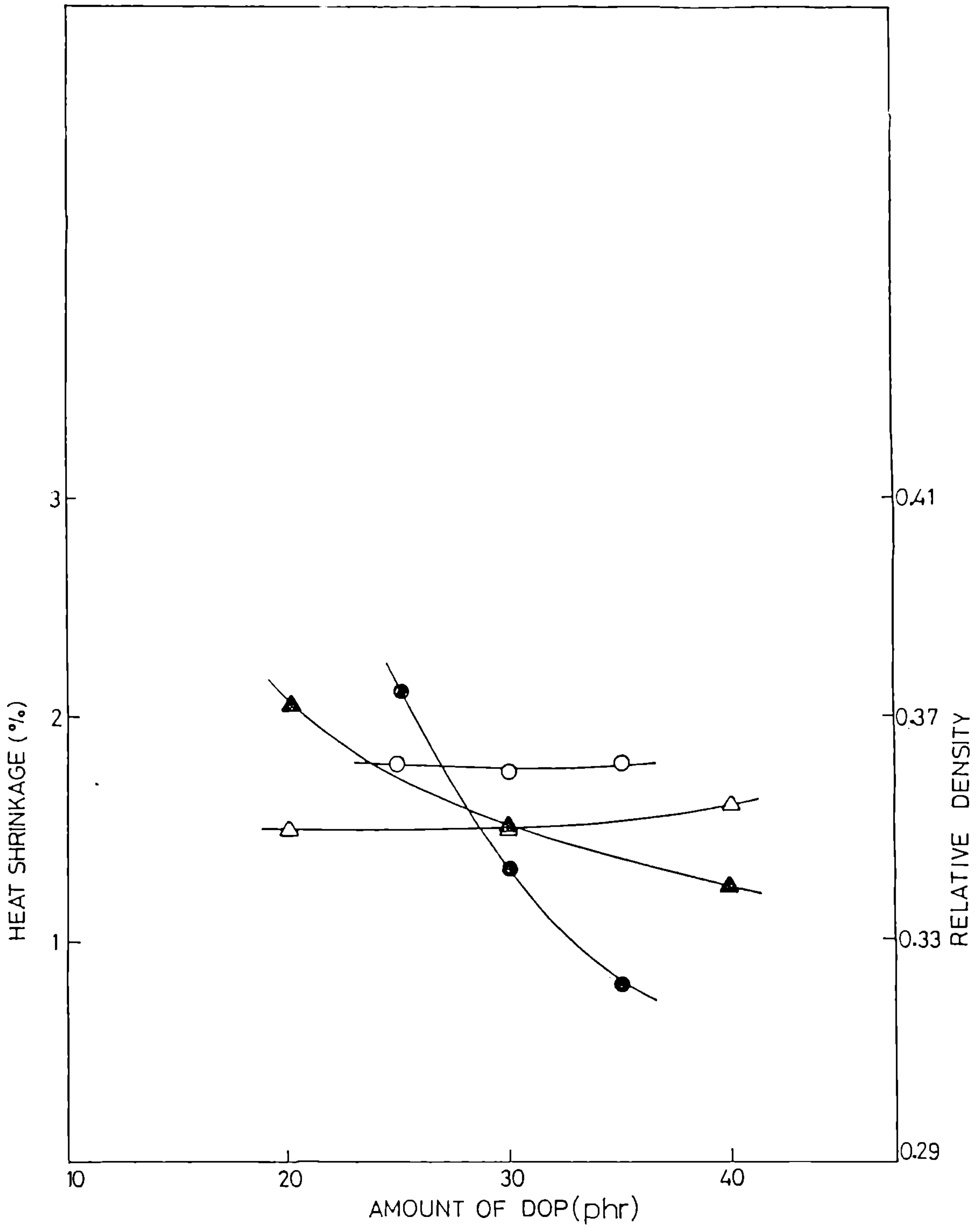

Fig.3.1.12 Variation of heat shrinkage and relative density with increase in the amount of DOP. NBR/S-PVC: (○) heat shrinkage, (●) relative density. NBR/E-PVC: (△) heat shrinkage, (▲) relative density.

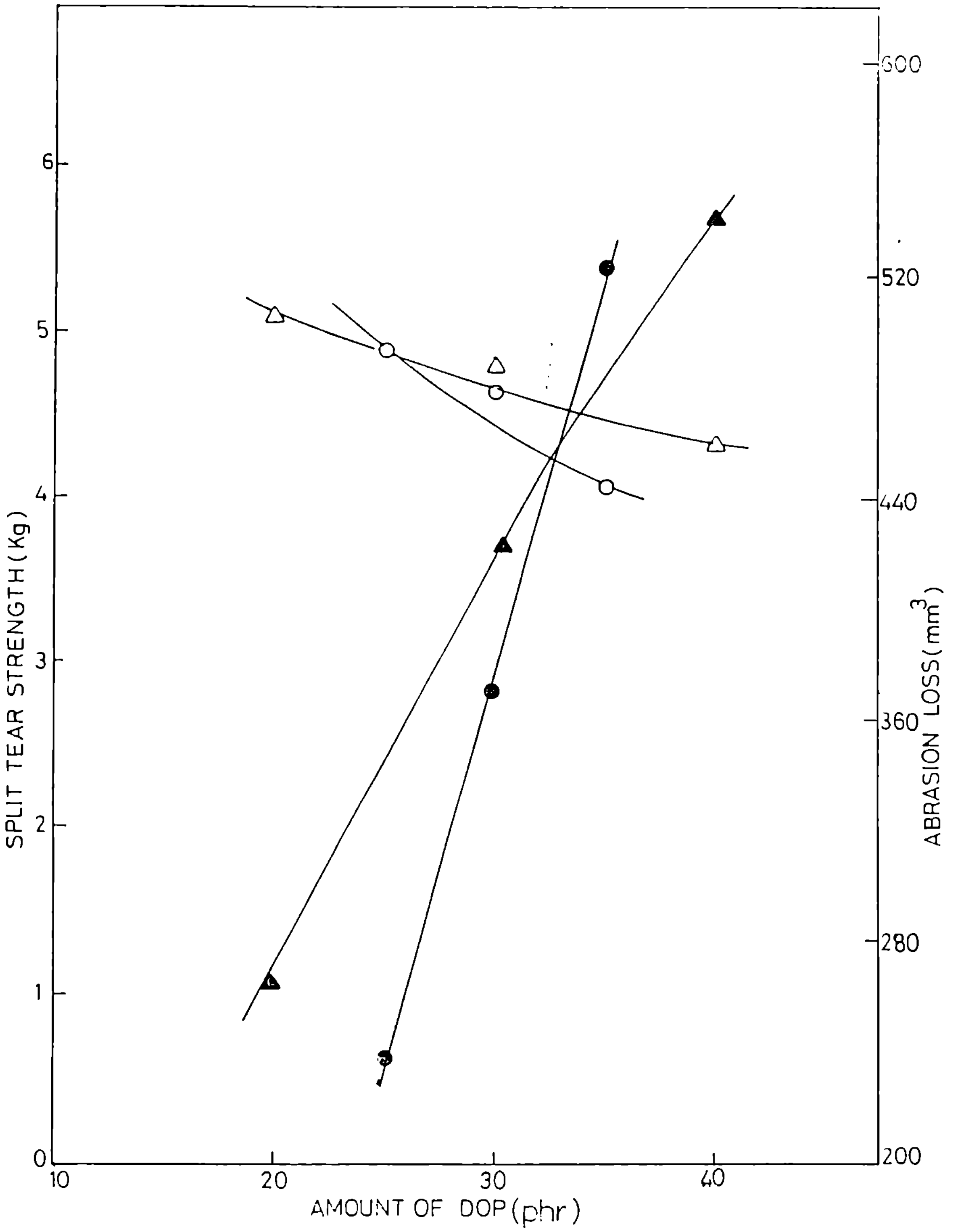

Fig.3.1.13 Variation of split tear strength and abrasion loss with increase in the amount of DOP. NBR/S-PVC: (○) split tear strength, (●) Abrasion loss, NBR/E-PVC: (△) Split tear strength (▲) Abrasion loss.

Hardness of the MC sheet shows a marginal decrease as the amount of DOP increases whereas water absorption shows an increase with increase in DOP content as shown in Fig.3.1.14. This reduction in hardness may be due to the increase in expansion of the MC sheet. Water absorption increases due to the increased number of open cells produced in the expanded sheet.

Compression set decreases with increase in the amount of DOP as shown in Table 3.1.6. The decrease in compression set may be due to the higher elastic nature imparted by DOP to PVC. Shrinkage after post curing can also be increased with increase in DOP content. Initial crack is observed only after a large number of cycles (245,045 cycles) in the case of 20 parts DOP. As the amount of DOP increases, crack initiation occurs after 220,000 cycles for 30 parts and 209,000 for 35 part DOP. This shows that higher expansion of MC sheets results in poor flexing resistance. It can be seen that the crack growth rate is slowest for 25 part DOP containing MC sheets since crack initiation depends on the yield and failure properties of the plasticised PVC compounds [28]. The same trend is observed in the case of NBR/E-PVC blend based MC sheets. The reduction in properties due to addition of plasticizer is more in the case of NBR/E-PVC blends. The above results show that a limited amount of plasticizer will give better properties in both cases. About 30 parts DOP on PVC seems to be the optimum plasticizer level for NBR/PVC blends.

Figs.3.1.15 and 3.1.16 show the optical microscope photographs of 50/50 NBR/PVC blend based MC sheets containing 25 and 35 phr DOP. As the amount of DOP increases from 25 to 35 phr cells become small and uniform obviously due to the lower viscosity of the matrix. However the uniform cell structure in the case does not give rise to better technical properties due to the low viscosity and high expansion of the matrix.

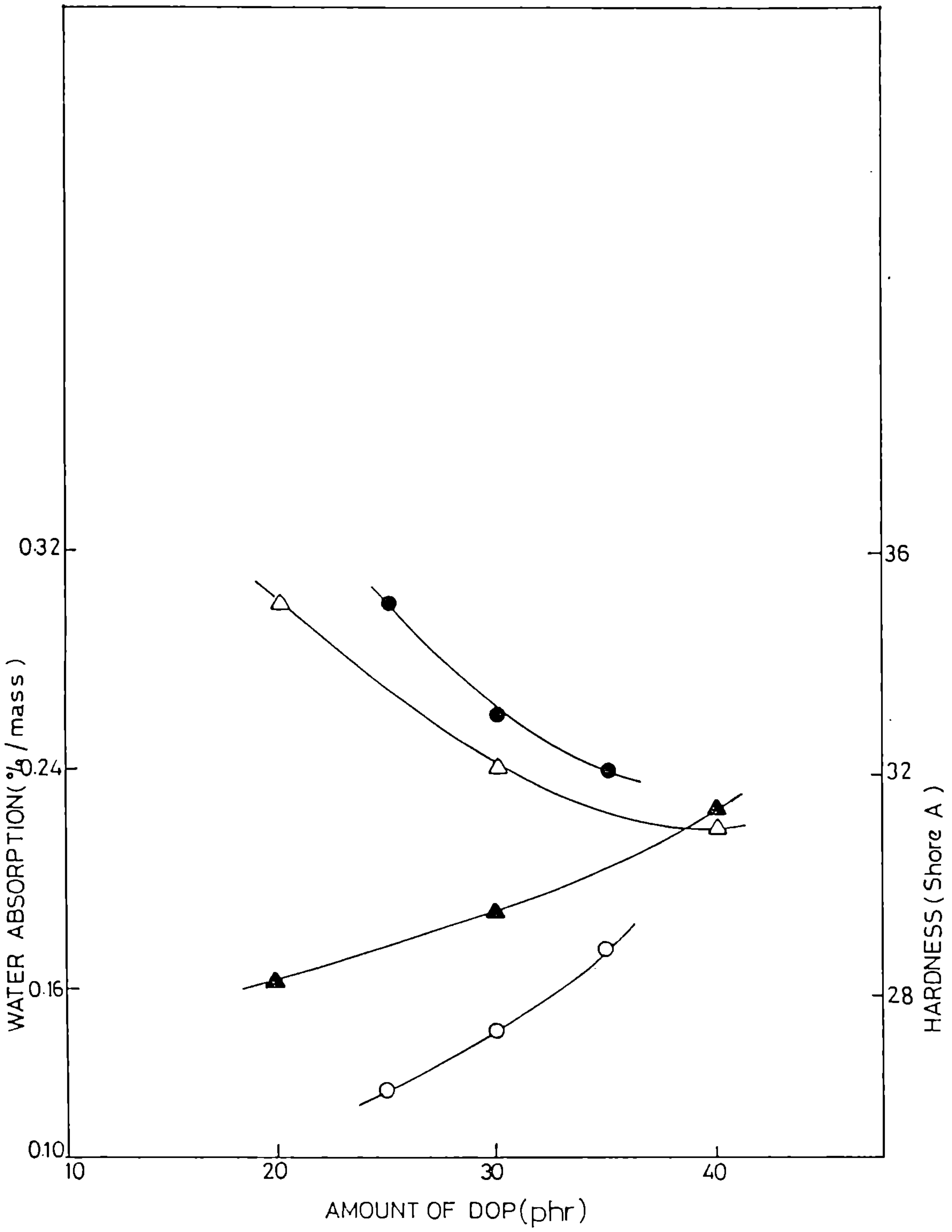

Fig.3.1.14 Variation of water absorption and hardness with increase in the amount of PVC. NBR/S-PVC: (○) water absorption (●) hardness. NBR/E-PVC: (▲) water absorption (△) hardness.

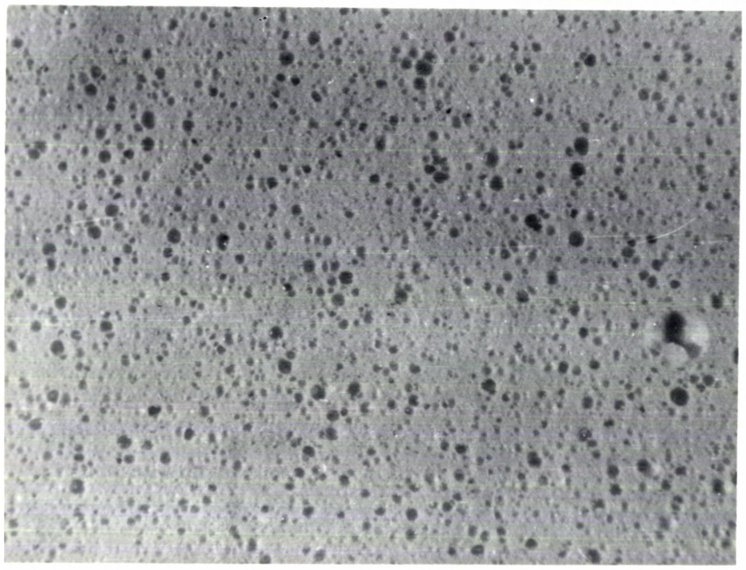

Fig.3.1.15: 25 phr DOP

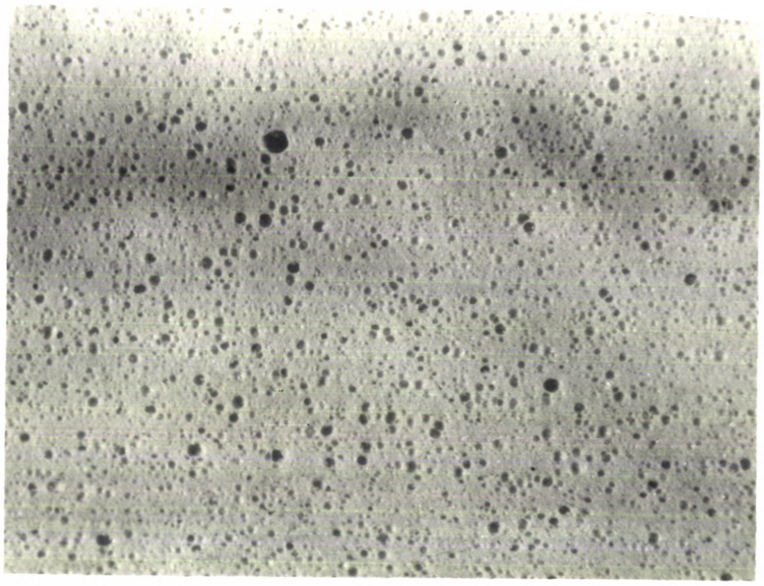

Fig.3.1.16: 35 phr DOP

Optical microscope photographs of NBR/PVC MC sheets

3A.5 Effect of concentration of blowing agent on properties of microcellular soles based NBR/PVC blends

Experimental

The compound containing optimum amount of PVC was selected for this study. All ingredients except blowing agent (ADC) were kept at the same level. The formulation of the compound is given in Table 3.1.2. The amount of blowing agent required for achieving optimum expansion and technical properties was evaluated by varying the amount of ADC from 8 to 12 phr. The compounding and moulding were done as described in section 3A. The technical properties were measured according to relevant Indian Standards. The cell structure of the selected MC sheets were observed using an optical microscope.

Results and discussion

Table 3.1.7 shows the cure characteristics and technical properties of NBR/PVC based MC sheets with varying amount of blowing agent. The optimum cure time increases as the amount of ADC is increased from 8 to 12 phr.

Fig.3.1.17 shows the changes in relative density and heat shrinkage with increase in concentration of blowing agent. Heat shrinkage increases as the concentration of blowing agent increases. As the amount of blowing agent increases from 8 to 12 phr expansion of the MC increases upto 11 phr and on further addition expansion decreases. Relative density of the MC sheets decrease with increase in concentration of blowing agent.

Table 3.1.7

Effect of concentration of blowing agent on the technical properties of NBR/PVC blend based MC sheets

Blend	Properties	Amount of blowing agent (ADC) (Phr)				
		8	9	10	11	12
NBR/ S-PVC	Time required for optimum cure at 160°C (min.)	8	8.4	8.6	8.7	9.4
	Initial expansion (%)	64.28	75.00	79.05	90.47	88.69
	Final expansion (%)	38.09	48.81	49.21	59.22	60.09
	Compression set (%)	4.81	5.28	5.48	5.70	5.60
	Shrinkage after post curing (%)	2.97	2.99	3.1	3.29	3.5
	Flex resistance					
	a) Crack initiation in cycles	300,700	300,000	299,750	281,400	275,500
	b) Crack size growth at the end of 100,000 cycles (mm)	0.05	0.05	0.05	0.1	0.1
NBR/ E-PVC	Time required for optimum cure at 160°C (min.)	5.8	7.2	7.5	8	8.8
	Initial expansion (%)	64.28	79.19	89.28	90.48	84.52
	Final expansion (%)	38.69	45.83	52.1	53.57	52.38
	Compression set (%)	4.71	5.89	6.2	6.79	6.12
	Shrinkage after post curing (%)	3.01	3.15	3.29	3.38	3.81
	Flex resistance					
	a) Crack initiation in cycles	360,000	324,985	320,685	310,510	301,700
	b) Crack size growth at the end of 100,000 cycles (mm)	0.05	0.05	0.05	0.1	0.1

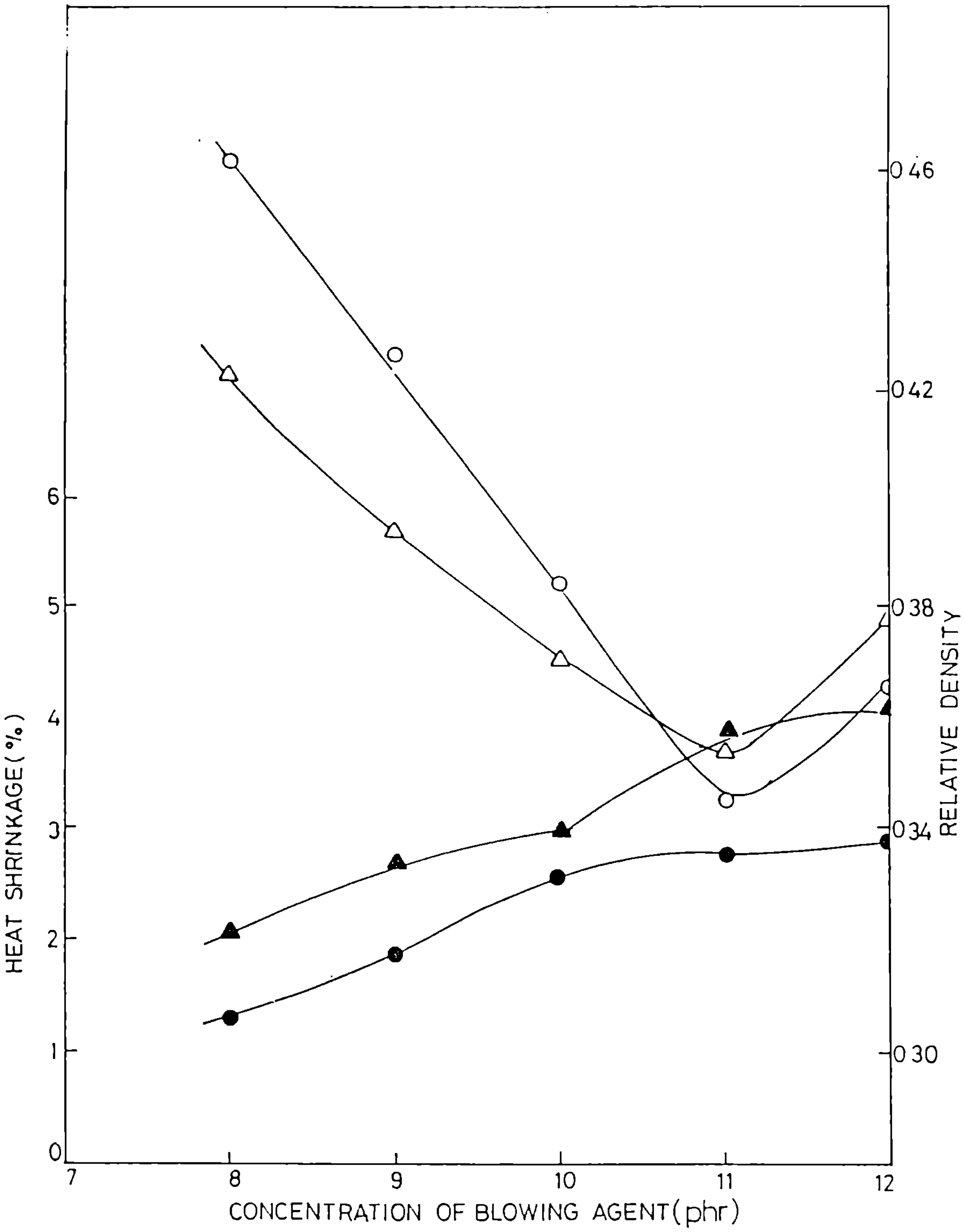

Fig.3.1.17 Variation of heat shrinkage and relative density with increase in the concentration of blowing agent. NBR/S-PVC: (●) heat shrinkage, (○) relative density. NBR/E-PVC: (▲) heat shrinkage, (△) relative density.

Split tear strength and hardness decrease as the amount of blowing agent (Fig.3.1.18) increases. Decrease in tear strength is due to the decrease in solid rubber content. The obstruction to the tear path is due to solid rubber surrounding the cells (cell wall thickness). Cell wall thickness decreases with volume of expansion as well as increase in number of cells per unit volume. The number of cells increases with increase in blowing agent concentration from 8 to 12 phr [29]. Hardness of the MC sheet decrease with increase in blowing agent concentration. The rate of decrease is slow up to 10 phr.

Fig.3.1.19 shows the variation in abrasion loss and water absorption. Abrasion loss and water absorption increase as the amount of blowing agent increases. This is due to the higher expansion, and open cellular structure.

Shrinkage after post curing increases with increase in concentration of blowing agent. Crack initiation occurs at a much faster rate when the concentration of blowing agent is high as shown in Table 3.1.7. NBR/E-PVC blend based MC sheets show similar behaviour. Expansion, water absorption, shrinkage and abrasion loss are found to be higher for MC sheets based NBR/E-PVC blends whereas relative density, hardness, compression set are found to be low with blowing agent concentration.

On adding 8-12 phr blowing agent, expansion increases up to 11 phr, and upon further addition, expansion decreases, as shown in Table 3.1.7. Consequently relative density decreases up to 11 phr and then marginally increases. Though higher expansion occurs at 11 phr split tear strength and hardness are found to be low and the abrasion loss is found to be maximum. At 8 phr level abrasion loss is found to be minimum and relative density and

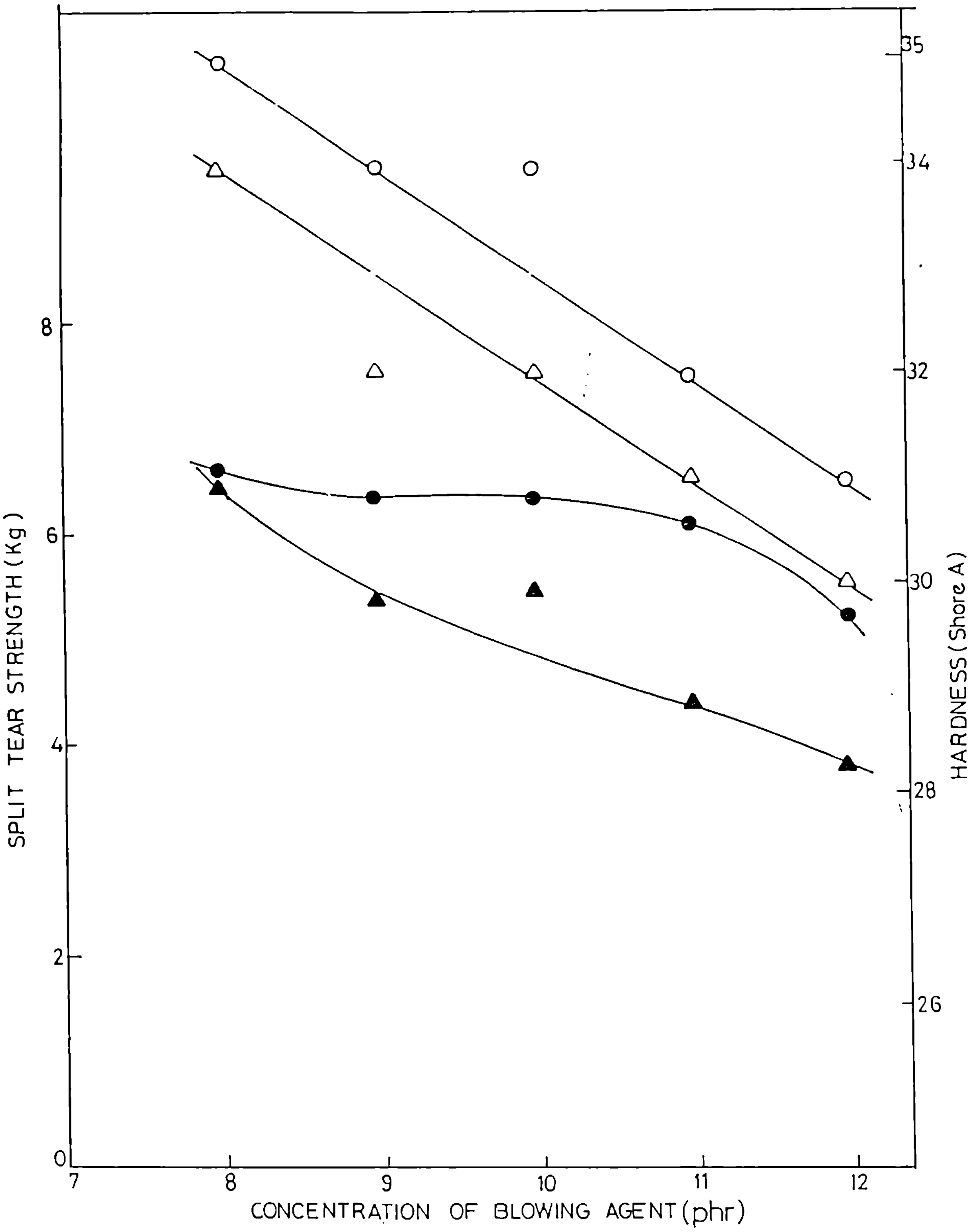

Fig.3.1.18 Variation of split tear strength and hardness with increase in the concentration of blowing agent. NBR/S-PVC: (●) split tear strength, (○) hardness. NBR/E-PVC: (▲) Split tear strength (△) hardness.

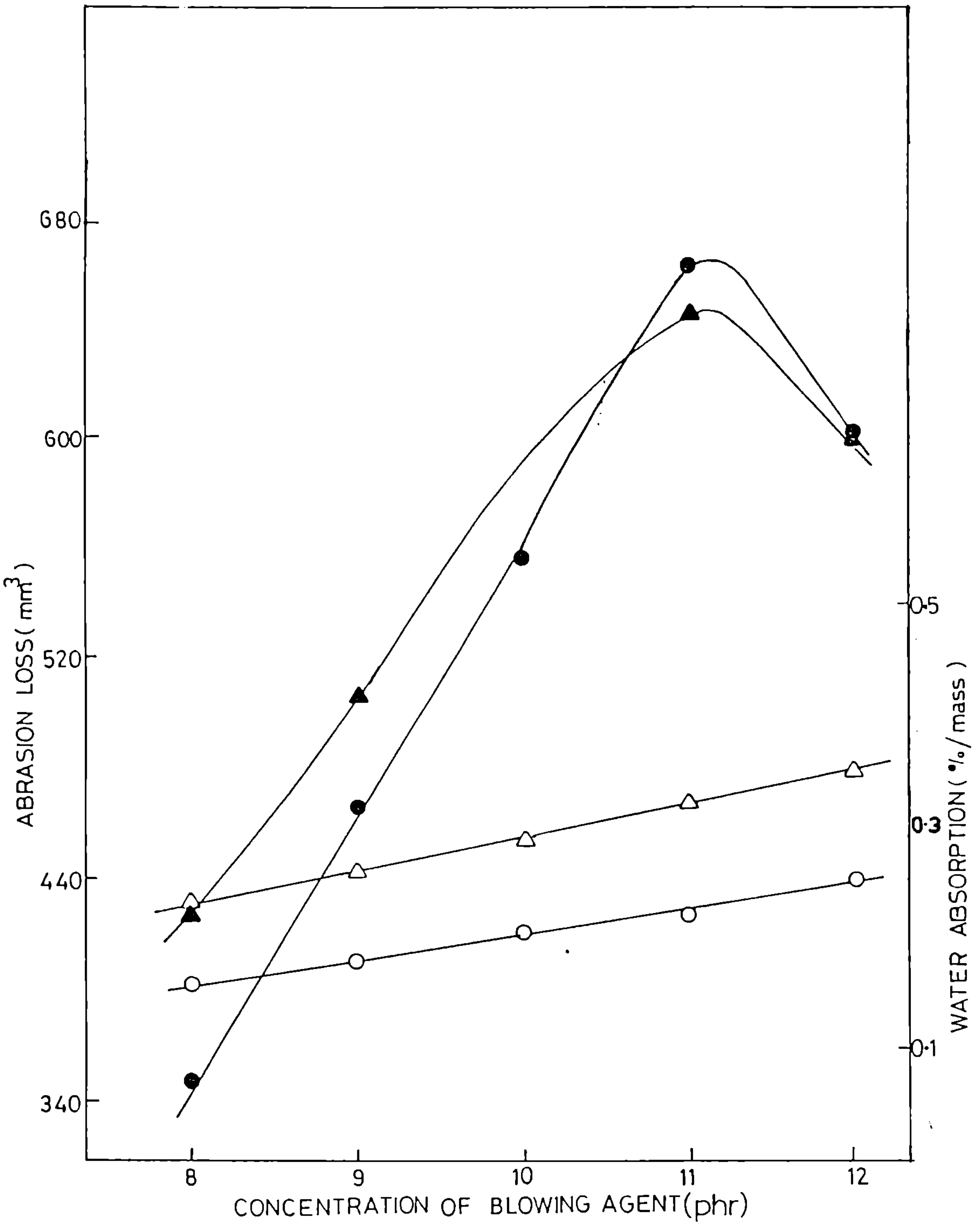

Fig.3.1.19 Variation of abrasion loss and water absorption with increase in the concentration of blowing agent. NBR/S-PVC: (●) abrasion loss, (○) water absorption. NBR/E-PVC: (▲) abrasion loss, (△) water absorption.

hardness are high while expansion is low. At 10 phr level, the properties of MC sheets conform to the specification limits.

Figs.3.1.20 and 3.1.21 show the optical microscope photographs of 50/50 NBR/PVC blend based MC sheets containing 10 and 12 phr blowing agent. It is evident from the figures that as the amount of blowing agent increases, cells become larger, but at the expense of a uniform structure. A uniform cell structure is shown at the optimum level of blowing agent (10 phr) observed from the technical properties.

3A.6 Use of amine terminated liquid natural rubber (ATNR) as a plasticizer in NBR/PVC blends

As mentioned earlier the main problem of microcellular soles based on NBR/PVC blends is crack formation and growth during service. This crack formation and growth are mainly due to the migration of plasticizer from PVC phase or due to the degradation of PVC. When plasticized PVC comes in to contact with other materials, plasticizer may migrate from the plasticized PVC to the other polymer. Plasticizer can also be extracted from PVC by organic solvents and water [30]. Water extracts plasticizer very slowly, compared to oils. Due to this migration to the surrounding medium, the polymer itself shows considerable change in mechanical properties while surrounding medium gets contaminated [31]. Loss of plasticizer results in loss of flexibility of the material, and this may be the reason for crack initiation and growth. The key characteristic for migration and extraction resistance is molecular size. The larger the molecular size of the plasticizer the less it tends to migrate or get extracted [30].

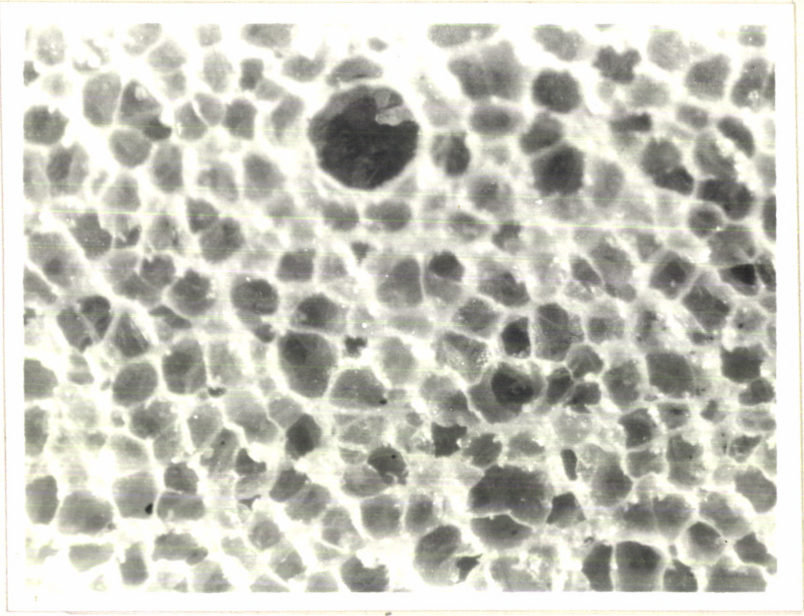

Fig.3.1.20: 10 phr Blowing agent

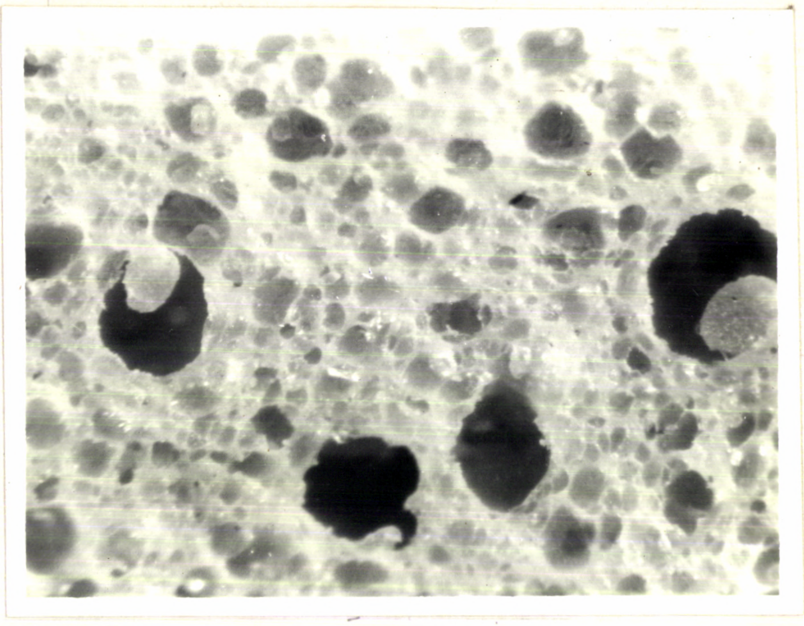

Fig.3.1.21: 12 phr Blowing agent

Optical microscope photographs of NBR/PVC MC sheets

A polymeric plasticizer is more resistant to migration and extraction. In this part of the study amine terminated liquid natural rubber (ATNR) is tried as a plasticizer in NBR/PVC blends.

Experimental

Blends of NBR and suspension PVC were prepared in a Brabender plasticorder model PL 3S at a rotor speed of 30 rpm and at 150°C. NBR was added and was allowed to homogenize for 1 minute. Then PVC compound was added and blended for 5 min. ATNR was then added and blending was continued for in another 2 min. The formulation for PVC compound is given in Table 3.1.8. The formulation for MC sole compounds is given in Table 3.1.9.

The compounding and preparation of MC sheets were done as per the procedure described in section 3A. Cell structure of a razor cut samples of the MC sheets was investigated using an optical microscope.

Results and discussion

Table 3.1.10 shows the effect of replacement of DOP by ATNR on cure characteristics and technical properties of NBR/S-PVC based MC soles. When part of DOP in the blend is replaced by ATNR, the time required for optimum cure decreases. This is probably due to the presence of polar amino group in ATNR, which accelerates the vulcanization [32,33].

Table 3.1.8: Formulation for PVC compound

Ingredients (Phr)	Mix Number			
	1	2	3	4
PVC	100	100	100	100
ZnO	4	4	4	4
MgO	4	4	4.	4
Stearic acid	2	2	2	2
DOP	40	35	30	25
ATNR	--	5	10	15

Table 3.1.9: Formulation for NBR/PVC microcellular sole compound

Ingredients	Phr
NBR (in NBR/PVC blend)	100
Sulfur	1.5
ZnO	3
Stearic acid	1
Zinc stearate	1
Titanium dioxide	4
Precipitated silica	40
China clay	100
Diethylene glycol	1.5
Wood rosin	2
DOP	5
Styrenated phenol	1
Vulcafor F	1.5
TMTD	0.5
ADC	10

Table 3.1.10

Effect of replacement of a part DOP by ATNR in the blend on the technical properties of MC soles based on NBR/S-PVC blends

Properties	Amount of ATNR			
	0	5	10	15
Time required for optimum cure at 160°C (min.)	14.9	13.9	13.5	12.8
Initial expansion (%)	64.28	47.62	46.43	42.86
Expansion after 5 min. (%)	52.24	40.68	39.28	35.71
Expansion after 24 h (%)	41.66	35.71	34.52	30.95
Expansion ratio	2.93	2.50	2.33	2.09
Relative density	0.437	0.494	0.514	0.556
Split tear strength (kg)	3.76	3.90	4.15	4.5
Abrasion loss (mm^3)	472.1	401	381.45	374.6
Heat shrinkage (%)	2.81	2.43	2.1	1.83
Hardness (Shore A)	45	47	48	49
Compression set (%)	10.02	9.13	9.02	9.02
Water absorption (percent by mass)	0.112	0.109	0.09	0.085
Shrinkage after post curing (%)	3.24	3.2	3.19	2.94
Flex crack resistance				
a) Crack initiation in cycles	400,000	650,000	690,170	750,000
b) Crack size growth at the end of 100,000 cycles (mm)	0.05	Nil	Nil	Nil

Table 3.1.10 shows the variation of expansion ratio and relative density. Expansion of MC sheets decrease when DOP is replaced by ATNR. As the amount of ATNR in the blend increases, expansion marginally decreases, and consequently relative density increases.

Split tear strength of the MC sheets increase when part of DOP is replaced by ATNR while abrasion loss decreases. As the amount of ATNR in the blend increases, the split tear strength increases and reaches a maximum at an ATNR content of 15 phr. The observed increase in split tear strength may be due to the presence of ATNR, which has a polymeric entity that may get co-crosslinked with NBR. The decrease in abrasion loss may be due to the lower expansion and higher extent of crosslinking in presence of ATNR.

Change in heat shrinkage and water absorption with the addition of ATNR are shown in Table 3.1.10. Heat shrinkage and water absorption decrease with increase in ATNR content. This may be due to the lower expansion of the MC sheets. As the quantity of ATNR increases the expansion decreases and the number of open cells formed also decreases. This is obviously the reason for the lower water absorption.

Hardness of the MC sheets increase with increase in the amount ATNR in the blend and compression set decrease with increase in ATNR content. This may be due to the lower expansion and higher extent of crosslinking as the quantity of ATNR increases. Shrinkage after post curing decreases with increase in ATNR content in the blend.

Initial crack formation occurs at a lower number of cycles when the blends contain DOP alone. The crack depth increases with DOP after 100,000 cycles. But when a part of DOP is replaced by ATNR (5 parts) crack initiation occurs only after a higher number of cycles as shown in Table 3.1.10. As the ATNR content increases in the blend, a single crack initiation occurs in the flexed region at a much higher number of cycles. The number of cracks decreases with high ATNR content and no crack growth is observed with further increase in ATNR content in the blend. The above results shows that ATNR does not migrate, in contact with other material and at lower level it can be co-crosslinked with NBR and due to this migration of DOP also is arrested. ATNR also shows antioxidant property due to the presence of NH_2 group and can improve the resistance to degradation of the polymer formation, which may be the reason for the improvement in resistance to crack. Addition of ATNR in NBR/E-PVC blend also shows similar behaviour (results not shown).

Fig.3.1.22 shows the cell structure of MC sheets containing DOP alone and Fig.3.1.23 the corresponding cell structure when a part of DOP is replaced by ATNR. The cell structure of the MC sheets containing ATNR is more uniform supporting the earlier observation of better mechanical properties.

CONCLUSION

1. NBR/PVC blends can be used as a base material for microcellular soles.
2. The 50/50 NBR/PVC blend is ideal for obtaining optimum technical properties.
3. At 150°C blending temperature NBR/S-PVC blend shows optimum technical properties.
4. The optimum percentage of precuring required for microcellular sheets is 70% for NBR/S-PVC based compounds and 75% for NBR/E-PVC based compounds.
5. The amount of plasticizer required for obtaining optimum technical properties is 30 parts of DOP.
6. The amount of blowing agent required for obtaining optimum technical properties is 10 phr in both cases.
7. The NBR/S-PVC based microcellular sheets give lower water absorption and lower shrinkage and better abrasion resistance, split tear strength and hardness. NBR/E-PVC

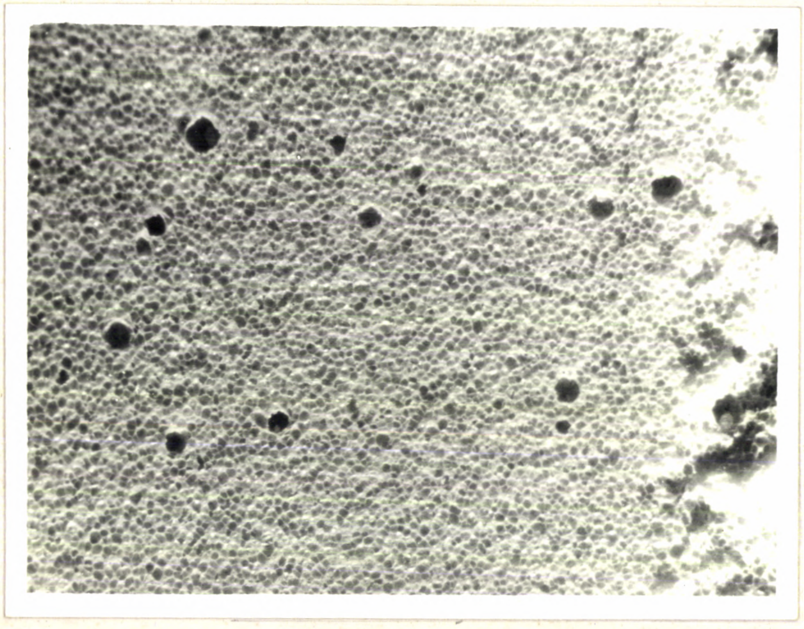

Fig.3.1.22: 40 phr DOP

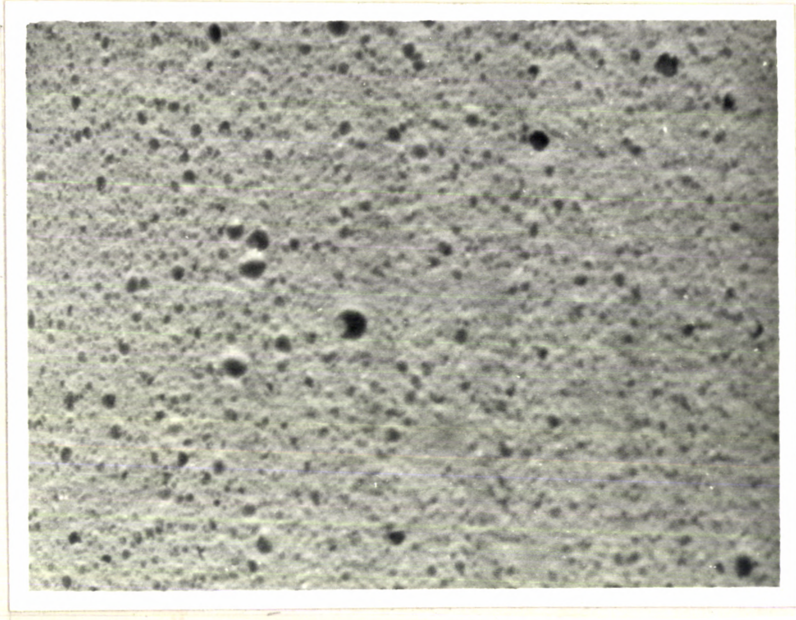

Fig.3.1.23: 30 phr DOP/10 phr ATNR

Optical microscope photographs of NBR/PVC MC sheets

based MC sheets show higher volume expansion, lower density and extra light weight. NBR/S-PVC blends are usually prepared by melt mixing but NBR/E-PVC blends can be prepared on a mixing mill.

8. Replacement of DOP by a polymeric plasticizer in NBR/PVC blend reduces the crack initiation and growth during service. Also addition of ATNR improves the properties like hardness, abrasion resistance and split tear strength.

3B. Effect of fillers on the properties of microcellular soles based on NBR/PVC blends

The use of fillers in rubber is almost as old as the use of rubber itself [34]. Among the fillers used in rubber industry, carbon black have a unique ability to enhance the physical properties of vulcanizates and the service performance of rubber products [35]. Fillers are commonly employed to reduce the cost and improve the mechanical properties and to reduce the tackiness of highly plasticized compounds.

Reinforcing fillers are necessary to achieve optimum properties with NBR and its blends [36]. Microcellular soles represent one class of rubber products in which non black fillers dominate [36,37]. Common fillers like silica, aluminium silicate, china clay, calcium carbonate etc. are used in MC soles. The objective of this study is to evaluate the influence of such fillers and NBR/PVC based MC sole waste (hereafter referred to as NBR/PVC microcrumb) on properties of MC soles and to find the optimum levels of loading in the case of such fillers.

Experimental

Blends of NBR and S-PVC (50:50) were prepared on a Brabender plasticorder, model

PL 3S using roller type mixing head at a speed of 30 rpm and 150°C. NBR was added, and allowed to heat up and homogenize for 1 min. and then PVC premixed with stabilizers and plasticizer was added (formulation shown in Table 3.1.1). The blending was completed in another 7 min. Blends of NBR and E-PVC were prepared in the same way, but at 120°C, and in 5 min. These blends (NBR/S-PVC and NBR/E-PVC were compounded on a two roll mill (150x300mm) at a friction ratio 1:1.25 according to the formulation given in Table 3.1.11.

The amount of silica was varied from 50 to 70 phr and the technical properties were evaluated. The effect of replacing part of silica by aluminium silicate was also investigated. Silica was also completely replaced by aluminium silicate. The amount of china clay was varied from 100 to 200 phr while calcium carbonate was varied from 60 to 100 phr. The amount of NBR/PVC microcrumb loading was varied from 20 to 150 phr to study its effect on the properties of the MC sheets. In NBR/PVC blends both suspension grade and emulsion grade PVC were used.

The moulding of the MC sheets and determination of properties were done as per the procedure described in section 3A.

Results and discussion

Fig.3.1.24 shows the variation of split tear strength and hardness with increasing amount of china clay in NBR/S-PVC based MC sheets. Split tear strength increases with clay loading upto 150 phr and then decreases on further loading. Hardness of the MC sheet increases with clay loading as expected. Fig.3.1.25 shows the variation of abrasion loss and heat shrinkage with increase in the amount of clay. Abrasion loss decreases upto a loading of 150 phr and then increases. The increase in abrasion loss after 150 phr may be due to the

Table 3.1.11 Formulation for NBR/PVC microcellular sole compounds

Ingredients (Phr)	China clay			Precipitated silica			Aluminium silicate		Calcium carbonate		NBR/PVC microcrumb					
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
NBR in the blend	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
ZnO	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Stearic acid	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Zinc stearate	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Titanium dioxide	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Precipitated silica	40	40	40	50	60	70	20	—	40	40	40	40	40	40	40	40
China clay	100	150	200	100	100	100	100	100	--	--	--	--	--	--	--	--
Aluminium silicate	--	--	--	--	--	--	20	40	--	--	--	--	--	--	--	--
Calcium carbonate	--	--	--	--	--	--	--	--	60	100	60	60	60	60	60	60
NBR/PVC crumb	--	--	--	--	--	--	--	--	--	--	20	40	60	80	100	150
Diethylene glycol	1.5	1.5	1.5	2.0	2.5	3	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
ATNR	5	7.5	10	5	5	5	5	5	5	5	5	5	5	5	5	5
Wood rosin	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Styrenated phenol	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Vulcafor F	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Azodicarbonamide (ADC)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10

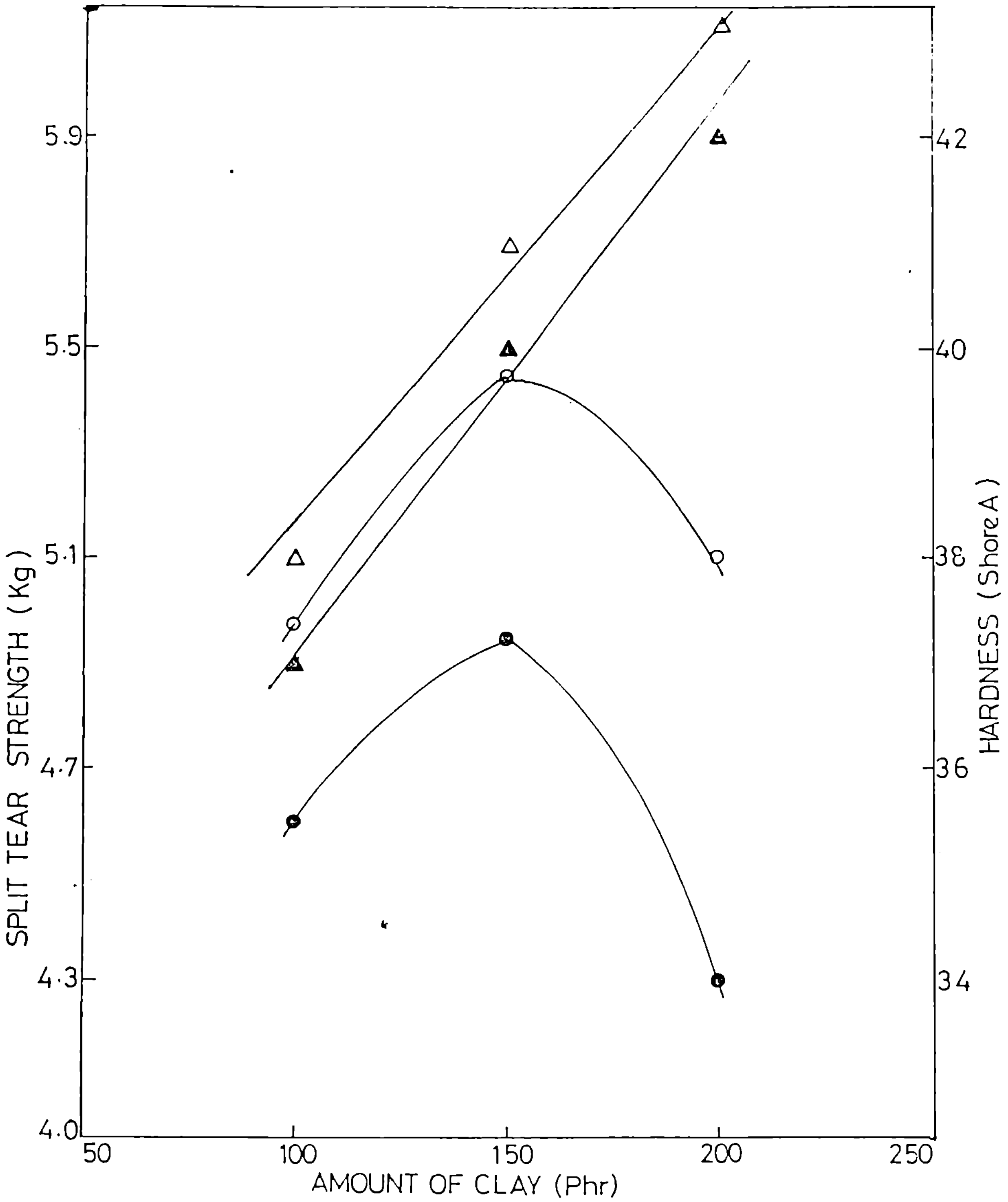

Fig.3.1.24 Variation of split tear strength and hardness with increase in the amount of china clay. NBR/S-PVC: (○) split tear strength, (△) hardness. NBR/E-PVC: (●) split tear strength, (▲) hardness.

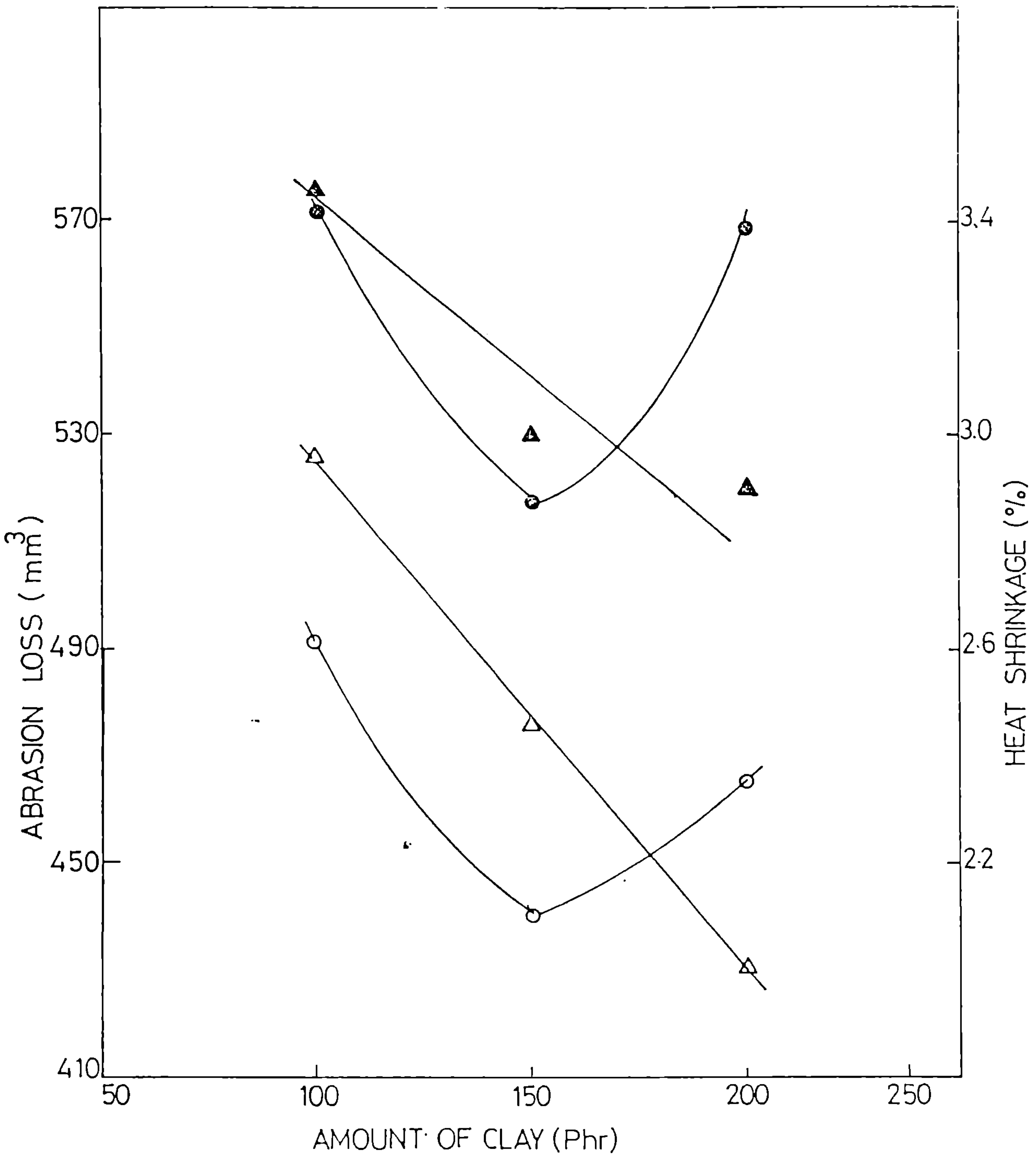

Fig.3.1.25 Variation of abrasion loss and heat shrinkage with increase in the amount of china clay. NBR/S-PVC: (○) abrasion loss, (△) heat shrinkage. NBR/E-PVC: (●) abrasion loss, (▲) heat shrinkage.

poor reinforcement of clay and poor distribution at higher concentration. Heat shrinkage also decreases as the amount of clay increases.

Water absorption and compression set decrease with increase in clay content as shown in Table 3.1.12. This may be due to the lower expansion of the MC sheet. The expansion of the MC sheet decreases with increase in the amount of china clay and consequently relative density increases. Higher levels of addition of filler severely reduces the thermoplasticity of blends [38]. This may be the reason for reduced expansion. The flex resistance of the MC sheets are shown in Table 3.1.12. Crack initiation occurs at higher number of cycles for 150 phr clay, but further increase in the amount of clay reduces crack initiation resistance marginally. Crack growth resistance is high for compounds containing lower amount of clay. NBR/E-PVC based MC sheets also show a similar behaviour.

Fig.3.1.26 shows the variation of split tear strength and hardness with amount of silica in NBR/S-PVC based MC sheets. Split tear strength and hardness increase with increase in the amount of silica as in the case of clay. Above 60 phr silica split tear strength decreases and this may be due to the poor distribution at higher concentration. Fig.3.1.27 shows the variation of abrasion loss and heat shrinkage. Abrasion loss decreases with increase in the amount of silica upto 60 phr and then increases. Heat shrinkage also decreases with an increase in silica loading as expected. Compared to silica, clay shows marginal improvement in split tear strength. Hardness of the clay filled MC sheets are found to be higher than that of silica.

Expansion, water absorption and compression set etc. decrease with an increase in the amount of silica as shown in Table 3.1.13. Relative density of the MC sheets increase with

Table 3.1.12

Effect of amount of China clay on the properties of NBR/PVC based microcellular soles

Properties	Amount of China clay (Phr)					
	NBR/S-PVC blend			NBR/E-PVC blend		
	100	150	200	100	150	200
Time required for optimum cure 160°C (min.)	10.1	8.33	8.0	9.7	9.21	8.3
Initial expansion (%)	79.05	75.5	70.12	79.76	76.19	70.23
Final expansion (%)	51.19	45.24	44.14	52.67	46.48	45.83
Relative density	0.376	0.412	0.428	0.374	0.405	0.412
Water absorption (percent by mass)	0.18	0.17	0.163	0.192	0.185	0.163
Compression set (%)	7.98	7.67	7.12	8.38	8.28	8.28
Flex resistance						
a) Crack initiation in cycles	395,410	395,970	389,963	389,990	399,000	389,501
b) Crack size growth in mm at the end of 100,000 cycles	0.05	0.05	0.1	0.05	0.05	0.1

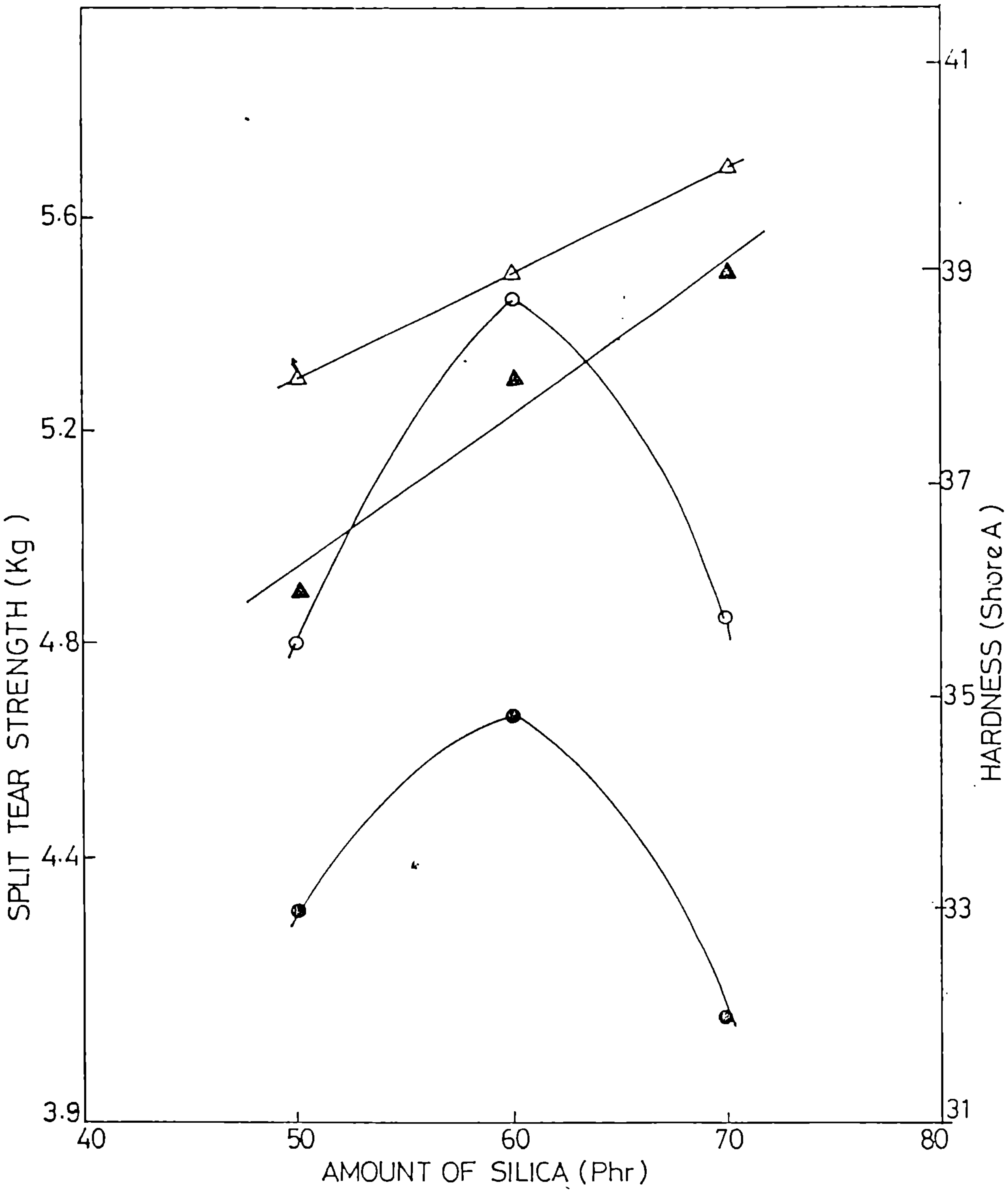

Fig.3.1.26 Variation of split tear strength and hardness with increase in the amount of silica. NBR/S-PVC: (○) split tear strength, (△) hardness. NBR/E-PVC: (●) split tear strength, (▲) hardness.

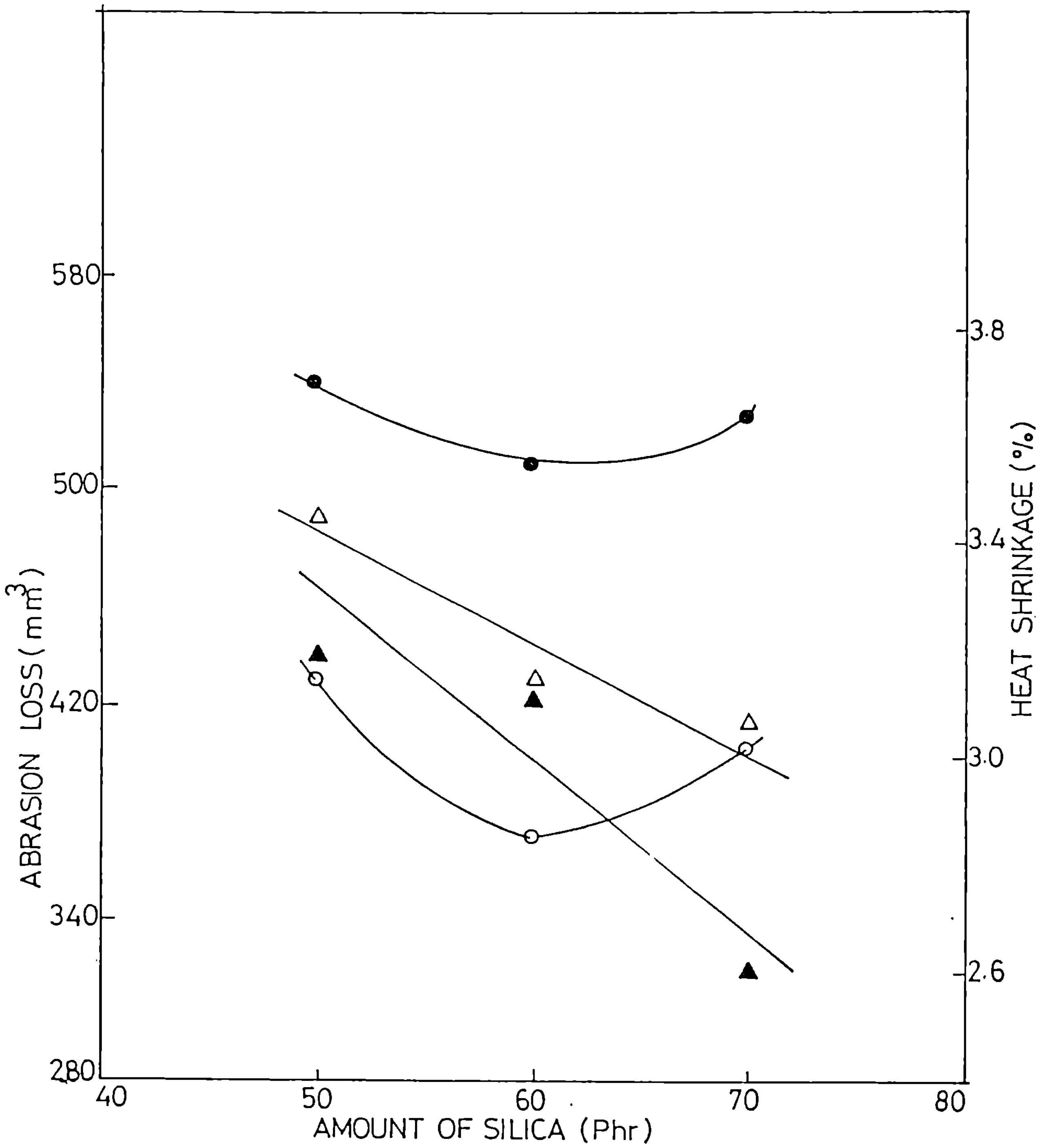

Fig.3.1.27 Variation of abrasion loss and heat shrinkage with increase in the amount of silica. NBR/S-PVC: (○) abrasion loss, (△) heat shrinkage. NBR/E-PVC: (●) abrasion loss, (▲) heat shrinkage.

Table 3.1.13

Effect of amount of precipitated silica on the properties of NBR/PVC based microcellular soles

Properties	Amount of precipitated silica (Phr)					
	NBR/S-PVC blend			NBR/E-PVC blend		
	50	60	70	50	60	70
Time required for optimum cure 160°C (min)	8.0	7.4	5.7	9.0	8.4	8.3
Initial expansion (%)	80.95	77.38	72.62	81.81	79.9	73.81
Final expansion (%)	61.19	59.38	58.0	62.19	60.0	59
Relative density	0.348	0.378	0.395	0.335	0.35	0.372
Water absorption (percent by mass)	0.175	0.153	0.14	0.18	0.173	0.163
Compression set (%)	8.12	7.64	7.12	8.2	7.93	7.28
Flex resistance						
a) Crack initiation in cycles	400,145	400,145	400,150	400,000	400,500	400,700
b) Crack size growth in mm at the end of 100,000 cycles	0.05	0.05	0.1	0.05	0.1	0.1

increasing amount of silica. The silica filled MC sheets show marginally higher expansion compared to clay. The crack initiation occurs after higher number of cycles. Silica filled sheets show similar behaviour to clay filled compounds in crack growth.

Fig.3.1.28 shows the variation of split tear strength and hardness with the amount of aluminium silicate. Split tear strength decreases when a part of silica is replaced with aluminium silicate. The rate of decrease in split tear strength is high when silica is completely replaced by aluminium silicate. This is because aluminium silicate is less reinforcing compared to other silicates and silica [36]. Hardness of the sheets show no appreciable change when silica is completely replaced by aluminium silicate.

Fig.3.1.29 shows the variation of abrasion loss and heat shrinkage with amount of aluminium silicate. Abrasion loss increases when silica is completely replaced by aluminium silicate. This may be due to the formation of weaker cell walls resulting in easy wearing of the product. There is a slight reduction in heat shrinkage as the amount of aluminium silicate increases.

Expansion of MC sheets show a marginal increase when silica is replaced by aluminium silicate and consequently relative density decreases and water absorption increases as shown in Table 3.1.14. Compression set always decreases with filler content as expected. The crack initiation occurs at lower number of cycles compared to silica and clay. Crack growth rate is found to be marginally high.

Split tear strength remains unchanged and hardness increases as the amount of calcium carbonate increases as shown in Fig.3.1.30. Abrasion loss and heat shrinkage show

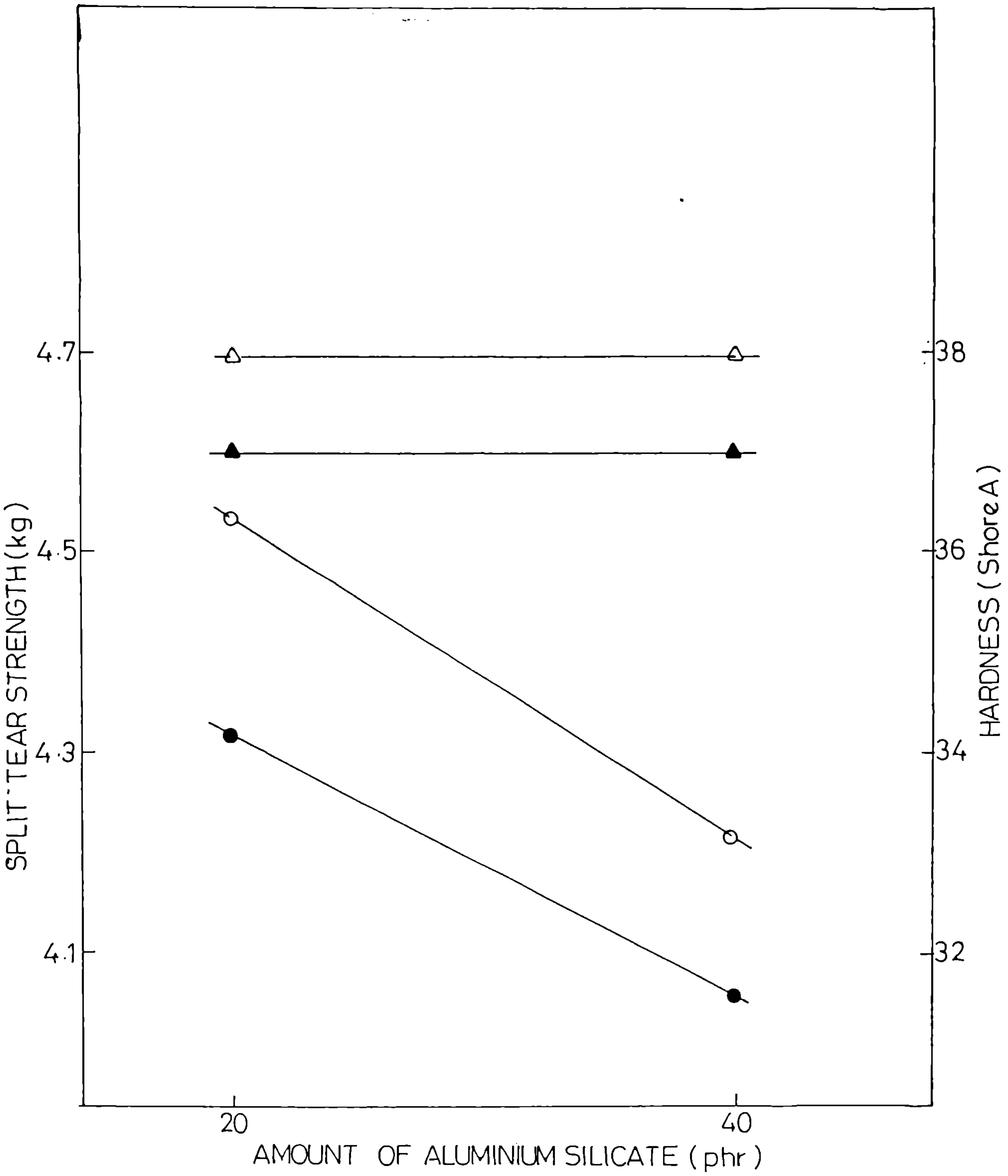

Fig.3.1.28 Variation of split tear strength and hardness with increase in the amount of aluminium silicate. NBR/S-PVC: (○) split tear strength, (△) hardness. NBR/E-PVC: (●) Split tear strength (▲) hardness.

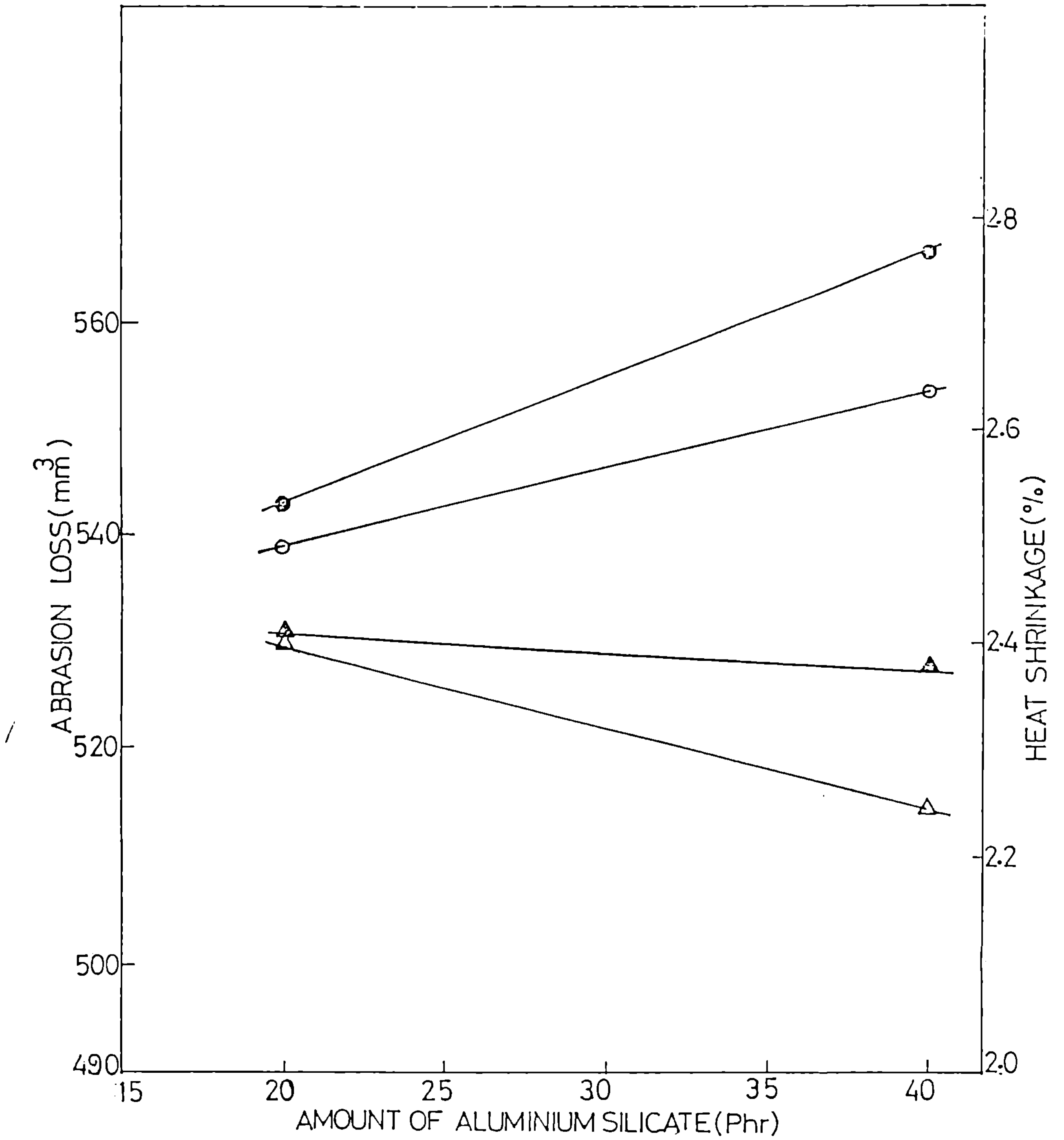

Fig.3.1.29 Variation of abrasion loss and heat shrinkage with increase in the amount of aluminium silicate.NBR/S-PVC: (○) abrasion loss, (△) heat shrinkage. NBR/E-PVC: (●) abrasion loss, (▲) heat shrinkage.

Table 3.1.14

Effect of amount of aluminium silicate on the properties of NBR/PVC based microcellular soles

Properties	Amount of aluminium silicate (Phr)			
	NBR/S-PVC		NBR/E-PVC	
	20	40	20	40
Time required for optimum cure 160°C (min)	10.2	9.8	9.1	8.6
Initial expansion (%)	78.57	78.98	80.95	81.06
Final expansion (%)	45.59	46.98	45.83	45.94
Relative density	0.367	0.384	0.383	0.389
Water absorption (percent by mass)	0.134	0.154	0.185	0.217
Compression set (%)	5.69	5.49	5.79	5.68
Flex resistance				
a) Crack initiation in cycles	365,000	360,650	385,100	368,090
b) Crack size growth in mm at the end of 100,000 cycles	0.1	0.5	0.1	0.1

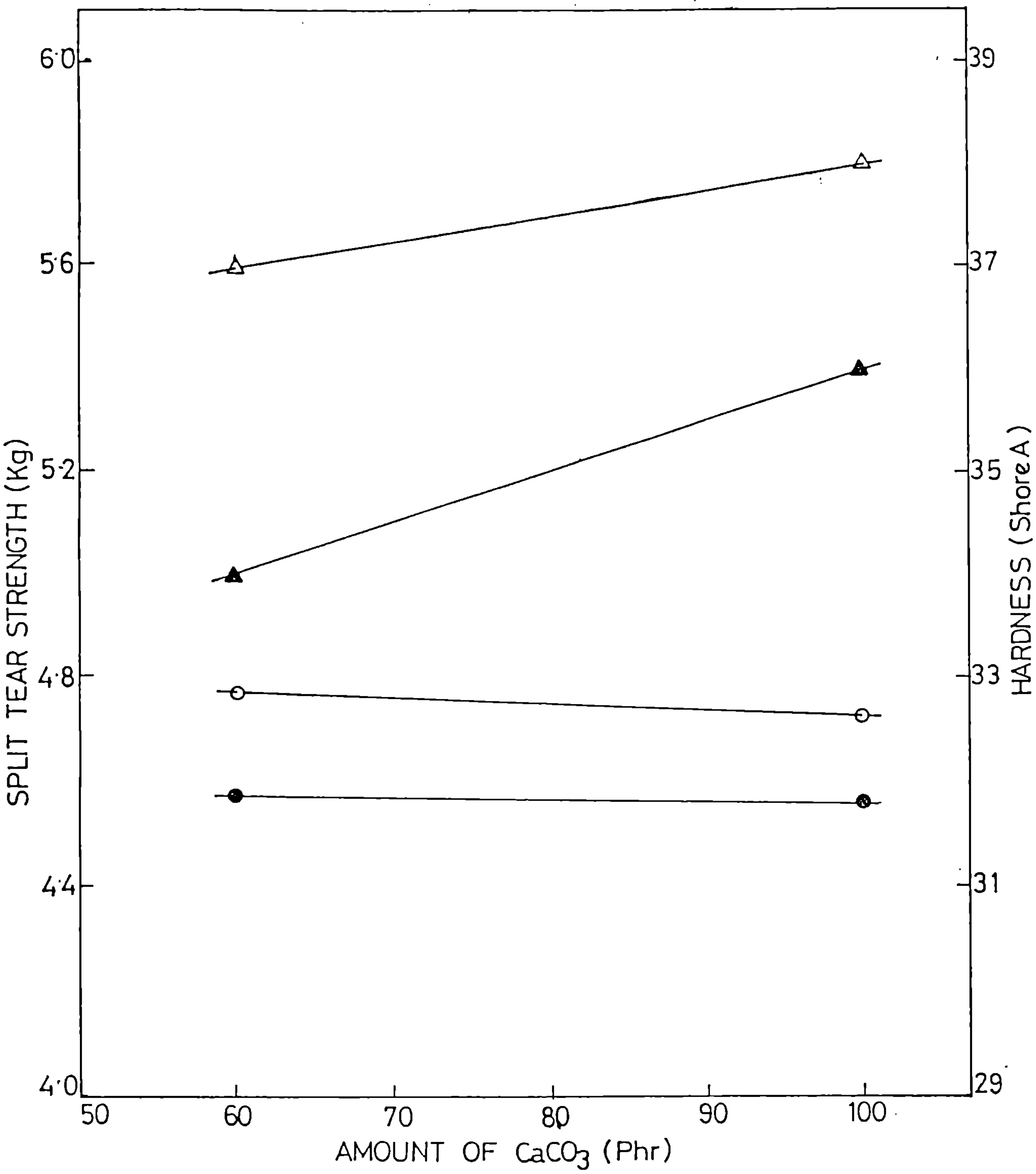

Fig.3.1.30 Variation of split tear strength and hardness with increase in the amount of calcium carbonate. NBR/S-PVC: (○) split tear strength, (△) hardness. NBR/E-PVC: (●) Split tear strength (▲) hardness.

similar behaviour as in the case of other fillers shown in Fig.3.1.31. Water absorption, compression set, relative density, expansion and flex resistance of the MC sheets (shown in Table 3.1.15) show similar behaviour as in the case of other fillers. NBR/E-PVC based MC sheets also show similar behaviour.

Fig.3.1.32 shows the variation of split tear strength and hardness with amount of microcrumb loading in NBR/S-PVC blend based MC sheets. Split tear strength increases as the amount of microcrumb loading increases (upto 100 phr) and then decreases. This increase in split tear strength may be due to an increase in the matrix strength. Above 100 phr the microcrumb may form a continuous phase resulting in decreased split tear strength. Hardness of the MC sheet increases with increasing amount of crumb. This may be attributed to the lower expansion of the MC sheet. Microcrumb improves hardness while split tear strength is equivalent to that of other fillers like china clay, silica etc. This shows that microcrumb produces some reinforcement to the polymer phase. Fig.3.1.33 shows the variation of abrasion loss and heat shrinkage with increase in the amount of microcrumb in NBR/S-PVC based MC sheets. Abrasion loss decreases as the amount of microcrumb increases (upto 100 phr) and then increases. This is due to the thicker cell walls resulting from lower expansion of MC sheets [22]. (When the expansion of the MC sheet is lower the cell walls will be much thicker). The increase in abrasion loss above 100 phr of crumb may be due to the phase change. Heat shrinkage also decreases with the addition of microcrumb as expected.

The water absorption and compression set decrease as the amount of microcrumb increases as shown in Table 3.1.16. Expansion of the MC sheet decreases with an increase in the amount of microcrumb, consequently relative density increases. The density of microcrumb is comparatively low. The decrease in expansion of the MC sheet may be due to

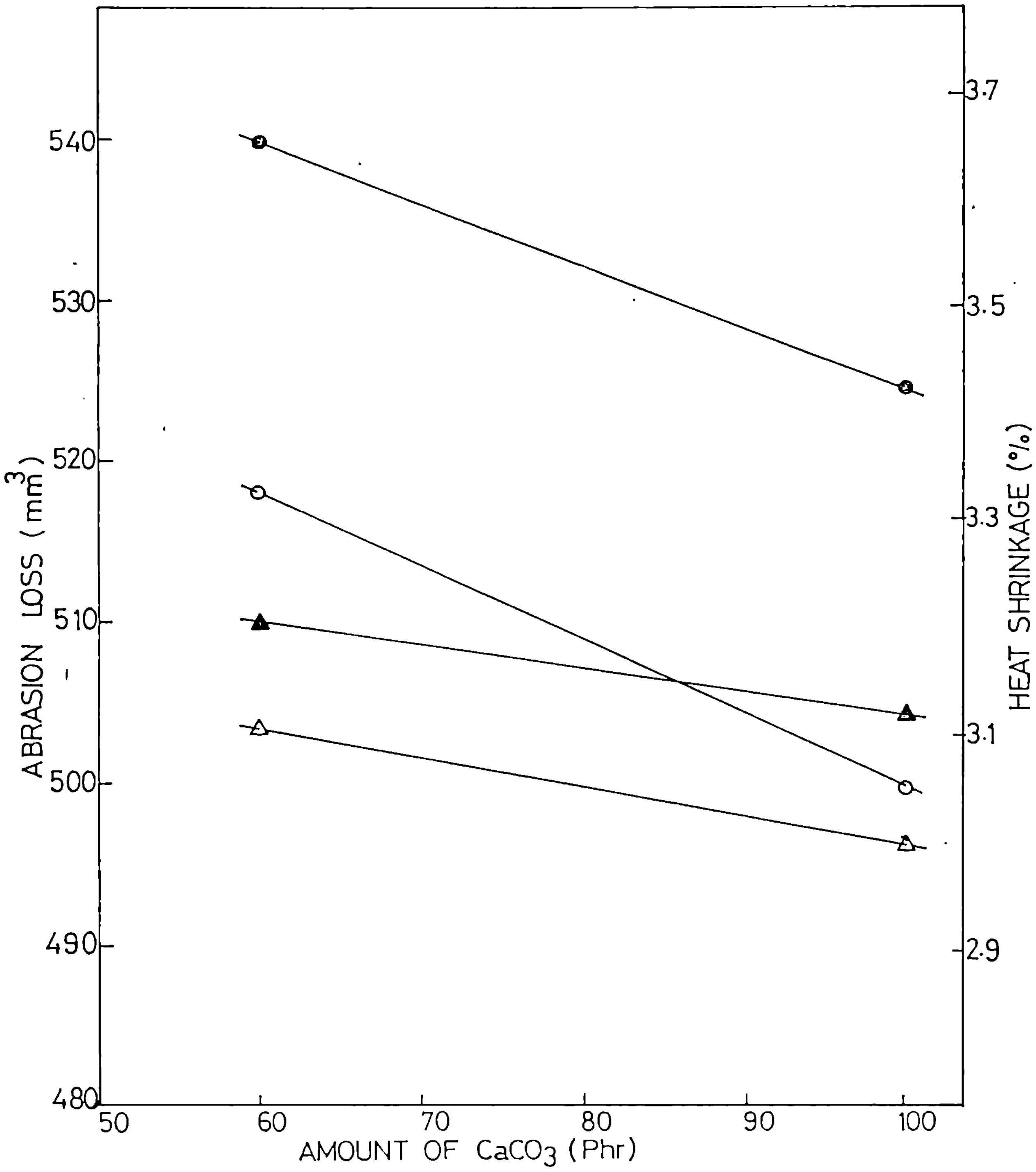

Fig.3.1.31 Variation of abrasion loss and heat shrinkage with increase in the amount of calcium carbonate. NBR/S-PVC: (○) abrasion loss, (△) heat shrinkage. NBR/E-PVC: (●) abrasion loss, (▲) heat shrinkage.

Table 3.1.15

Effect of amount of calcium carbonate on the properties of NBR/PVC

Properties	Amount of calcium carbonate (Phr)			
	NBR/S-PVC		NBR/E-PVC	
	60	100	60	100
Time required for optimum cure 160°C (min)	7.91	7.7	7.5	7.43
Initial expansion (%)	81.25	73.81	89.28	76.78
Final expansion (%)	48.09	45.59	54.76	50.0
Relative density	0.408	0.42	0.37	0.399
Water absorption (percent by mass)	0.159	0.123	0.178	0.154
Compression set (%)	5.6	5.4	5.8	5.4
Flex resistance				
a) Crack initiation in cycles	3,81,476	3,76,000	3,79,950	3,66,750
b) Crack size growth in mm at the end of 100,000 cycles	0.1	0.5	0.1	0.5

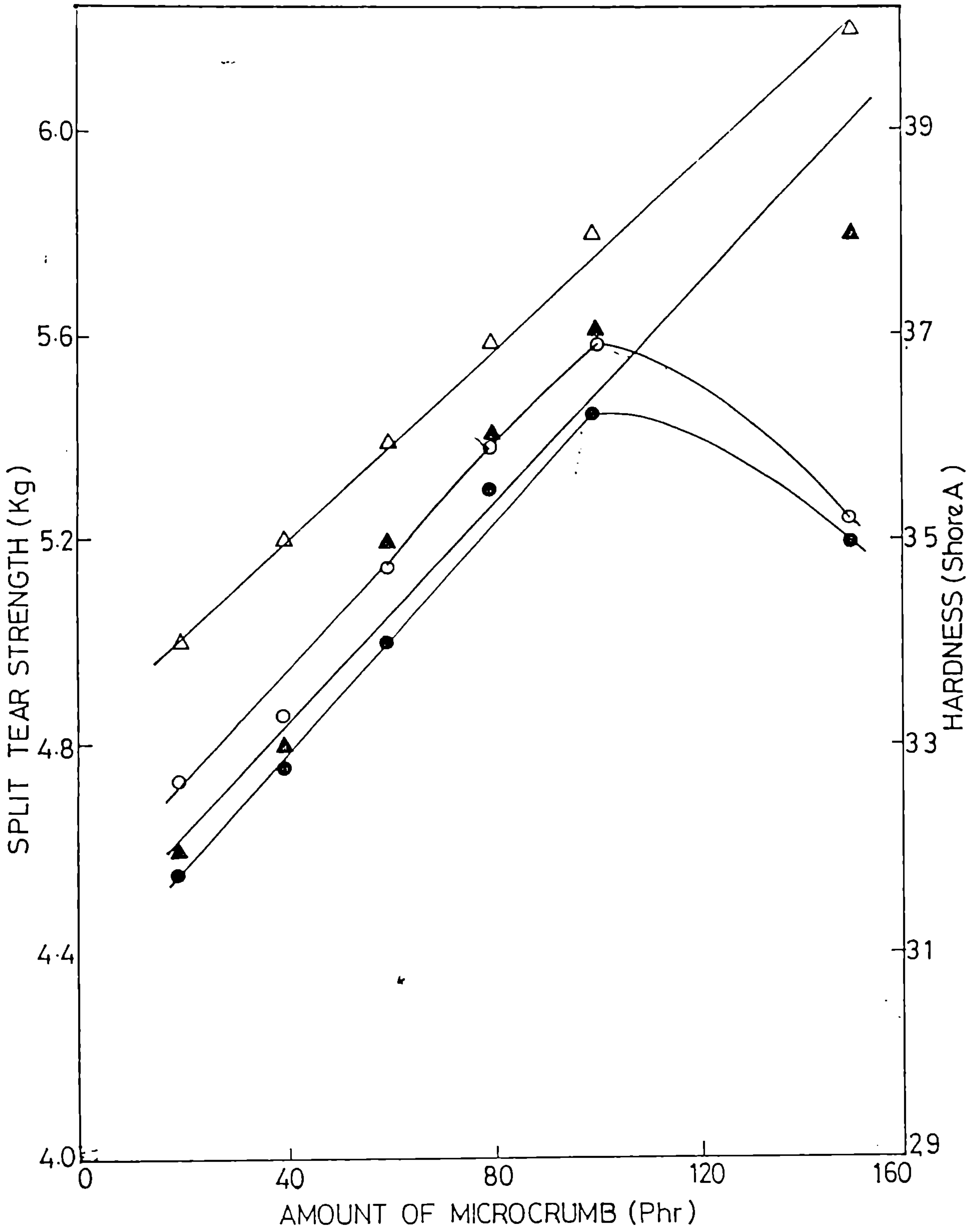

Fig.3.1.32 Variation of split tear strength and hardness with increase in the amount of microcrumb. NBR/S-PVC: (○) split tear strength, (△) hardness. NBR/E-PVC: (●) Split tear strength (▲) hardness.

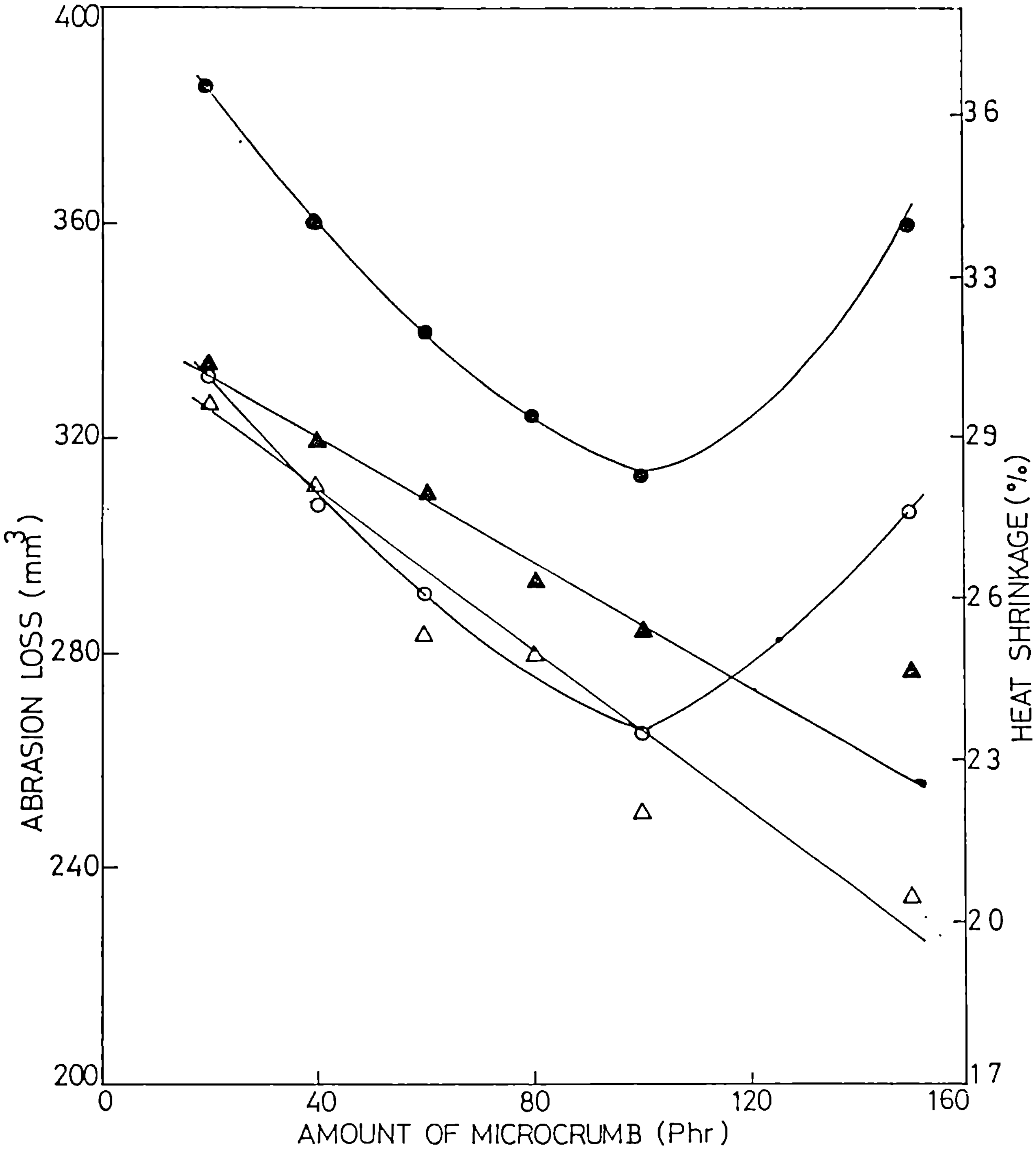

Fig.3.1.33 Variation of abrasion loss and heat shrinkage with increase in the amount of microcrumb. NBR/S-PVC: (○) abrasion loss, (△) heat shrinkage. NBR/E-PVC: (●) abrasion loss, (▲) heat shrinkage.

the presence of already vulcanized crumb, which prevents the expansion of MC sheets as shown in Table 3.1.16. As the crumb level increases the initial crack formation occurs at a lower number of cycles (at 100 phr). The crack growth is almost constant upto 100 phr and then marginally increases. This may be due to the higher size, and poor distribution at higher concentration. NBR/E-PVC based MC sheets also show the similar behaviour.

Figs.3.1.34 and 3.1.35 show the optical microscope photographs of the MC sheet containing same loading of (150 phr) china clay and NBR/PVC microcrumb. It is seen that china clay filled compound gives rise to slightly large cell size compared to microcrumb. But the cell structure is more or less uniform. Hence it may be concluded that in these compounds blowing agent is uniformly dispersed even though it contains high amount of fillers. The large cell size of clay filled MC compounds is obviously the reason for its low split tear strength and low abrasion resistance compared to NBR/PVC microcrumb.

CONCLUSION

1. Addition of clay (upto 150 phr) and silica (upto 60 phr) improves properties like split tear strength, abrasion resistance etc.
2. Part of silica (20 phr) can be replaced by aluminium silicate without much reduction in properties like split tear strength and abrasion resistance.
3. Calcium carbonate does not improve any of the above mentioned properties.
4. Microcrumb can be used as a reinforcing filler in NBR/PVC based microcellular soles upto 100 phr.

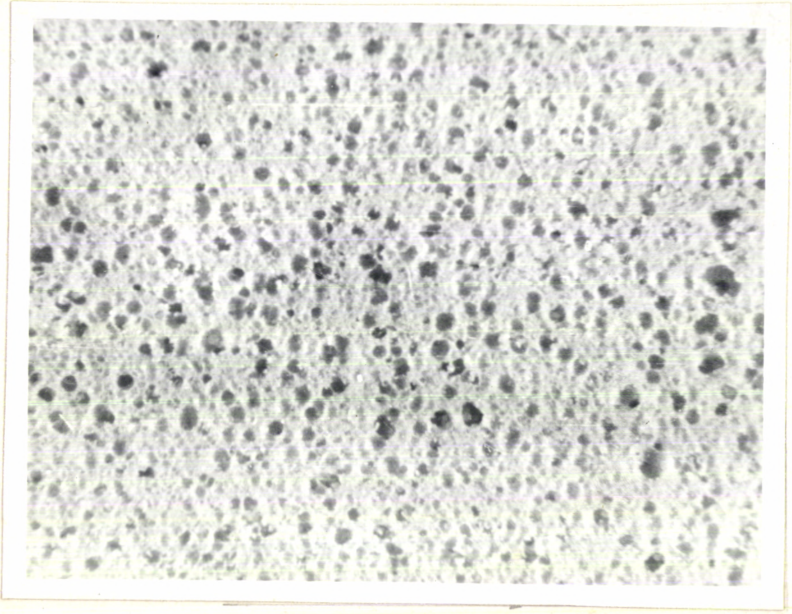

Fig.3.1.34: 150 phr China clay

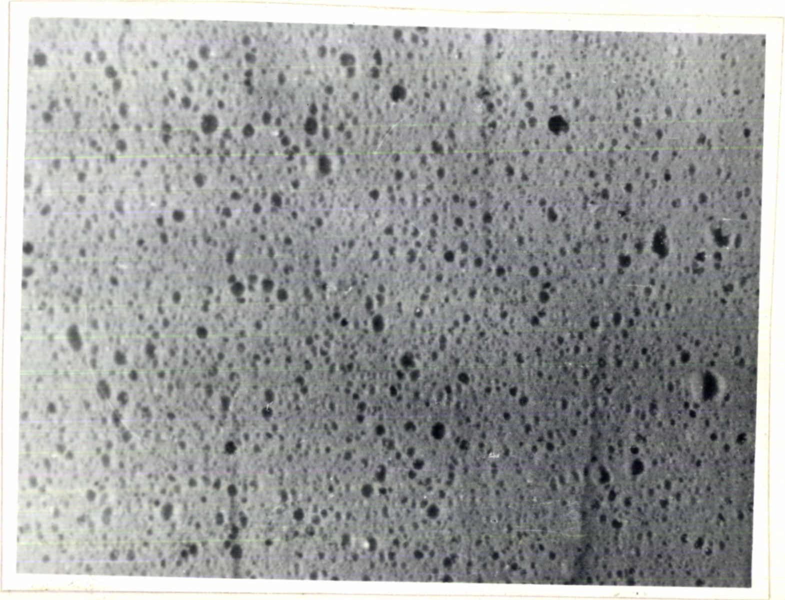

Fig.3.1.35: 150 phr NBR/PVC microcrumb

Optical microscope photographs of NBR/PVC MC sheets

3C. Effect of addition of NR, SBR and HSR as partial replacement for NBR in NBR/PVC blend based microcellular soles

In NBR/PVC blends, incorporation of PVC reduces the elasticity of NBR. In order to increase the elastic properties common rubbers such as natural rubber (NR), Styrene-butadiene rubber (SBR) can be added. This addition also improves tensile properties of the ternary blends. . Varatislav et al.[39] and Zheng et al. [40] attempted the addition of NR, SBR or HSR to make ternary blend for property improvement MC soles based on NBR/PVC blends show excellent technical properties compared to conventional NR/HSR based soles, but cost is comparatively higher. The objective of this study is to improve the properties and reduce the cost of microcellular soles based on NBR/PVC blends.

In this study, part of NBR is replaced by NR, SBR and HSR in a 50/50 NBR/PVC blend while the amount of PVC is kept constant. The properties of the microcellular sheets are compared with 50/50 NBR/PVC based microcellular soles.

Experimental

Blending of the polymers was carried out in a Brabender plasticorder model PL 3S at a rotor speed of 30 rpm and at 150°C. NBR was added initially and homogenized for 1 min, then PVC premixed with stabilizers and plasticizer was added and blending was continued for another 7 min. as before. Addition of NR, SBR and HSR was made on a laboratory model mixing mill. Blends were prepared by replacing parts of NBR (5 to 20 part of the rubber in a 50/50 NBR/PVC blend) by each of these rubbers.

The blend from the plasticorder was homogenized on a two-roll mill and was compounded as per formulations given in Table 3.1.17. The preparation of microcellular

Table 3.1.17

Formulations for NBR/PVC blend based microcellular sole compounds

Ingredients (Phr)	Mix Number			
	1	2	3	4
NBR	45	40	35	30
PVC	50	50	50	50
NR/SBR/HSR	5	10	15	20
Sulphur	1.5	1.5	1.5	1.5
ZnO	3	3	3	3
Stearic acid	1	1	1	1
Zinc stearate	1	1	1	1
TiO_2	4	4	4	4
Precipitated silica	40	40	40	40
China clay	100	100	100	100
DEG	1.5	1.5	1.5	1.5
DOP	5	5	5	5
Wood rosin	2	2	2	2
SP	1	1	1	1
Vulcafor F	1.5	1.5	1.5	1,5
TMTD	0.5	0.5	0.5	0.5
ADC	10	10	10	10

sheets and determination of technical properties were done as per the procedure described in part 3A.

Results and discussion

Table 3.1.18 shows the optimum cure time of the compounds. Addition of NR in NBR/S-PVC blend marginally decreases the cure time. The decrease in cure time is found to be proportional to the amount of NR.

Fig.3.1.36shows the variation of expansion ratio and relative density with increase in the amount of NR in NBR/PVC blends. When a part of NBR is replaced by NR, expansion of the MC sheets marginally increases. As the NR content in the blend further increases (from 5 to 20 parts) expansion marginally decreases. Hence relative density marginally increases with increase in the amount of NR in NBR/S-PVC blend. This decrease in expansion may be due to the degradation of NR phase and poor compatibility.

Fig.3.1.37 shows the variation of split tear strength and abrasion loss with increase in the amount of NR. There is a marginal reduction in split tear strength when the amount of NR increases from 5 to 20 part in NBR/S-PVC blend. The reduction in split tear strength may be due to the poor compatibility of NR and NBR [41]. There is no appreciable change in abrasion loss upto 10 parts of NR, but thereafter abrasion loss increases. This increase in abrasion loss may be due to the increased expansion of the MC sheets.

Fig.3.1.38 shows the variation of hardness and heat shrinkage with increase in the amount of NR. Hardness increases with increase in the amount of NR in the blend. This increase is more significant when 20 parts NBR is replaced by NR. Heat shrinkage

Table 3.1.18 Effect of replacement of NBR by NR, SBR and HSR on properties of NBR/PVC based MC sheets

Blend	Properties	0	Amount of NR				Amount of SBR				Amount of HSR			
			5	10	15	20	5	10	15	20	5	10	15	20
	Time required for optimum cure at 160°C (min.)	10.8	10.6	9.5	8.5	8.5	14	13.7	13.7	13.8	14.8	14.4	15.1	15.5
NBR/	Initial expansion (%)	64.28	69.05	67.87	66.67	64.28	54.96	53.57	52.38	50	58.33	55.95	54.76	50
S-PVC	Final expansion (%)	48.81	59.52	54.76	51.19	48.81	42.86	42.86	40.48	39.28	45.24	44.05	42.86	41.67
	Flex resistance													
	a) Crack initiation in cycles	424412	424000	424000	413750	460000	451000	451740	450000	429000	450000	451010	454000	456800
	b) Crack size growth at the end of 100,000 cycles (mm)	0.05	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Time required for optimum cure at 160°C (min.)	10.7	10.8	9.7	9.6	9.4	14.1	13.6	13.6	13.7	14.4	14	14.95	15
NBR/	Initial expansion (%)	61.93	65k.48	63.09	60.71	60.71	53.54	52.38	50	48.81	52.54	51.19	48.8	48.8
E-PVC	Final expansion (%)	45.24	47.62	46.43	45.24	45.25	42.86	41.67	40.47	38.09	40.48	38.09	35.71	33.33
	Flex resistance													
	a) Crack initiation (cycles)	439400	404750	414777	427811	427811	445750	445750	440000	441000	420000	420950	420950	422000
	b) Crack size growth at the end of 100,000 cycles (mm)	0.05	0.05	0.1	0.1	0.1	0.05	0.05	0.1	0.1	0.05	0.05	0.05	0.1

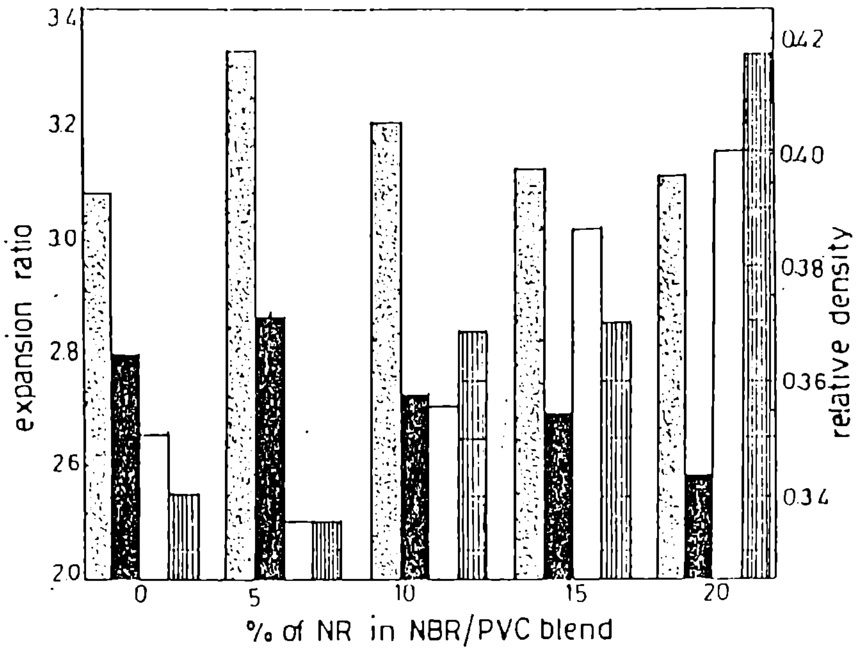

Fig.3.1.36 Variation of expansion ratio and relative density with increase in the amount of NR in NBR/PVC blend. NBR/S-PVC: (▨) expansion ratio, (☐) relative density. NBR/E-PVC: (■) expansion ratio, (▥) relative density.

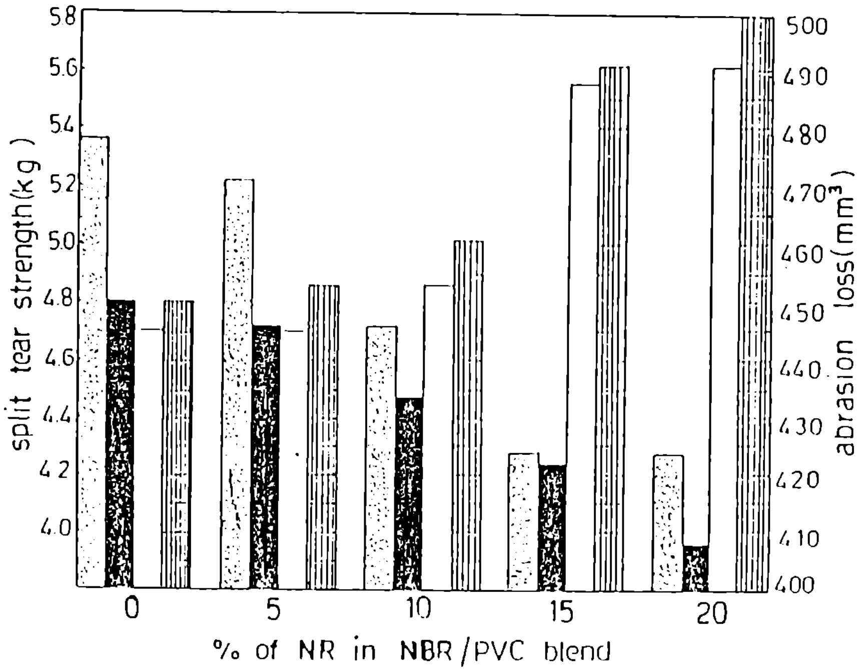

Fig.3.1.37 Variation of split tear strength and abrasion loss with increase in the amount of NR in NBR/PVC blend. NBR/S-PVC: (▨) split tear strength, (☐) abrasion loss. NBR/E-PVC: (■) split tear strength, (▥) abrasion loss.

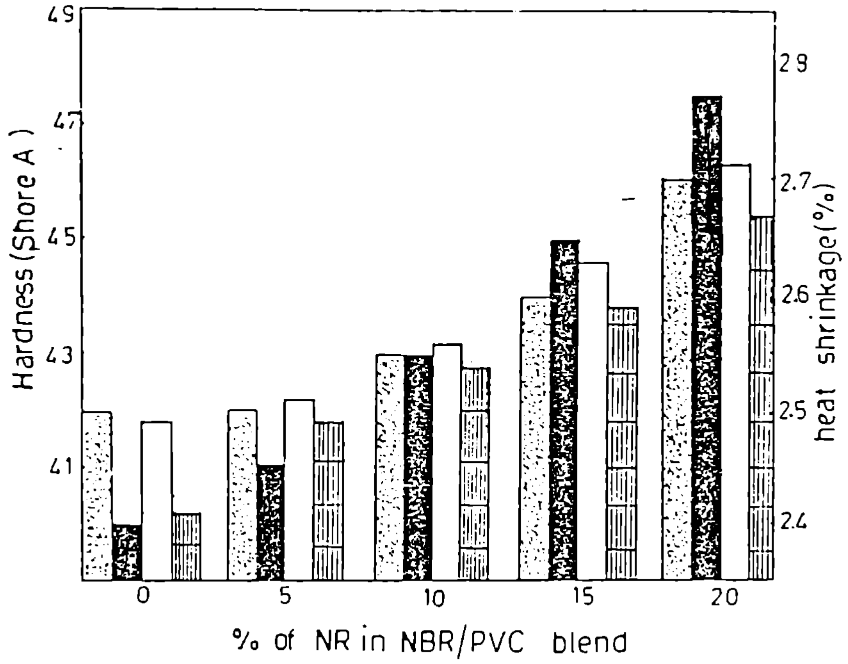

Fig.3.1.38 Variation of hardness and heat shrinkage with increase in the amount of NR in NBR/PVC blend. NBR/S-PVC: (▨) hardness, (□) heat shrinkage. NBR/E-PVC: (■) hardness, (▥) heat shrinkage.

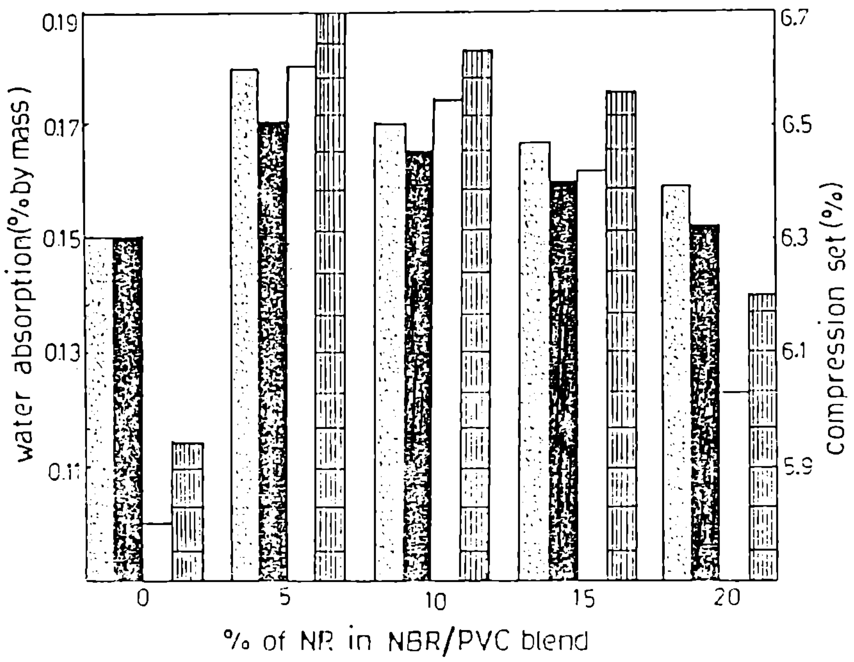

Fig.3.1.39 Variation of water absorption and compression set with increase in the amount of NR in NBR/PVC blend. NBR/S-PVC: (▨) water absorption (□) compression set. NBR/E-PVC: (■) water absorption (▥) compression set.

marginally increases when a part of NBR is replaced by NR. Maximum shrinkage is shown when 20 parts NBR is replaced by NR.

Fig.3.1.39 shows the variation of water absorption and compression set with increase in the amount of NR in the blend. Water absorption of the MC sheets marginally increases with the addition of NR in NBR/S-PVC blend. But as the amount of NR in the blend increases water absorption decreases. Again at higher NR content water absorption is low. Compression set is found to increase when NBR is replaced by NR. As the amount of NR in the blend increases compression set marginally decreases. This decrease in compression set may be due to the decrease in expansion of the MC sheet with increase in the amount of NR addition.

Flex resistance of the samples are shown in Table 3.1.18. Initial crack is formed after a larger number of cycles and crack propagation is slow when part of NBR is replaced by NR as expected. NBR/E-PVC based MC sheets show similar behaviour with NR addition (shown in Figs.3.1.36-3.1.39).

Addition of SBR increases the cure time of the compounds as shown in Table 3.1.18 Expansion of the MC sheets decreases when a part of NBR is replaced by SBR and hence relative density increases. When compared to NR addition of SBR show a significant decrease in expansion as shown in Fig.3.1.40.

Only a marginal reduction in split strength is observed when up to 10 parts NBR is replaced by SBR, but further increase in the amount SBR considerably reduces split tear strength. The reduction in split tear strength is less compared to NR as shown in Fig.3.1.41.

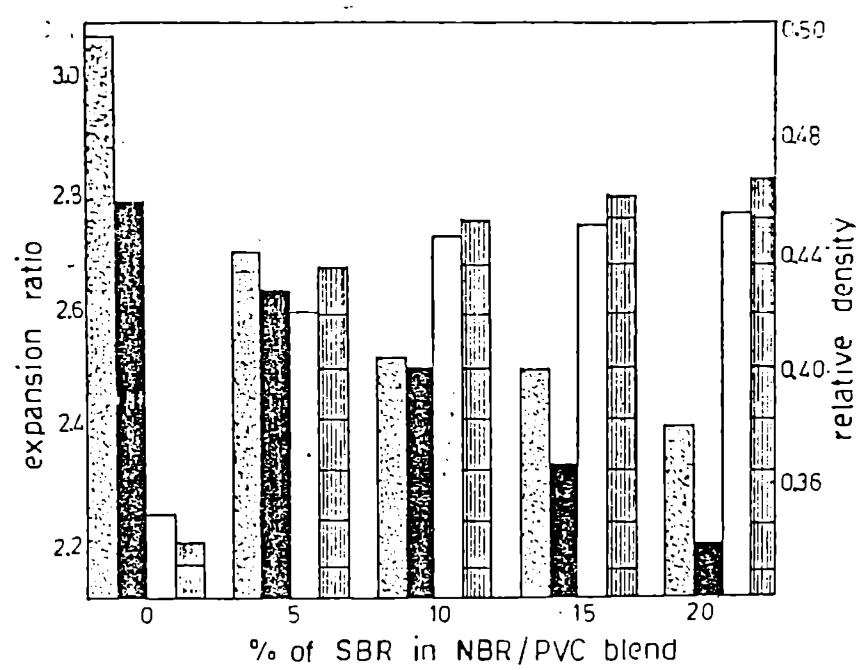

Fig.3.1.40 Variation of expansion ratio and relative density with increase in the amount of SBR in NBR/PVC blend. NBR/S-PVC: (⊡) expansion ratio, (□) relative density. NBR/E-PVC: (■) expansion ratio, (▥) relative density.

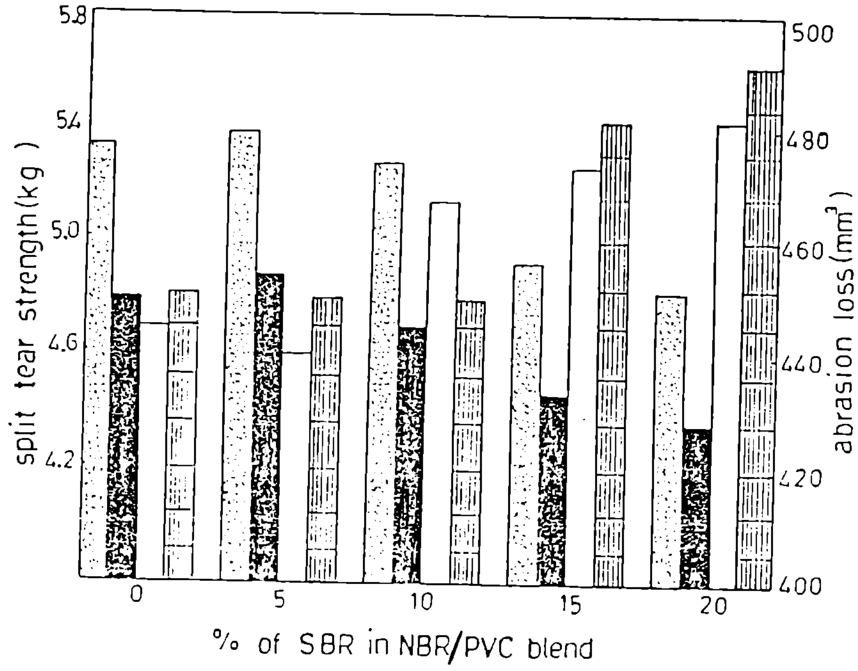

Fig.3.1.41 Variation of split tear strength and abrasion loss with increase in the amount of SBR in NBR/PVC blend. NBR/S-PVC: (⊡) split tear strength, (□) abrasion loss. NBR/E-PVC: (■) split tear strength, (▥) abrasion loss.

Abrasion loss marginally decreases when NBR is replaced upto 5 parts by SBR but further increase in SBR increases abrasion loss.

Fig.3.1.42 shows the variation of hardness and heat shrinkage when part of NBR is replaced by SBR. Significant improvement in hardness is observed when a part of NBR is replaced by SBR and improvement is more significant at higher levels of SBR. Compared to NR, SBR shows higher hardness. Heat shrinkage marginally increases with increase in the amount of SBR in the blend.

Fig.3.1.43 shows the variation of water absorption and compression set with increase in the amount of SBR in the blend. Both water absorption and compression set decrease with increase in SBR content in the blend. This reduction in properties may be due to the lower expansion and higher compatibility of SBR with NBR/PVC blend.

Flex resistance of the MC sheets is shown in Table 3.1.18. Addition of SBR improves flex resistance of the MC sheets compared to NR. Replacement of NBR by SBR in NBR/E-PVC also shows similar behaviour (shown in Figs.3.1.40 to 3.1.43).

Addition of HSR in NBR/S-PVC blends increase the optimum cure time of the compounds as shown in Table 3.1.18.

Fig.3.1.44 shows the variation of expansion ratio and relative density with the amount HSR in NBR/S-PVC blend. Similar to NR and SBR when, a part NBR is replaced by HSR the expansion of MC sheets reduces and consequently relative density increases. Expansion of MC sheets marginally higher for HSR compared to SBR and lower compared to NR.

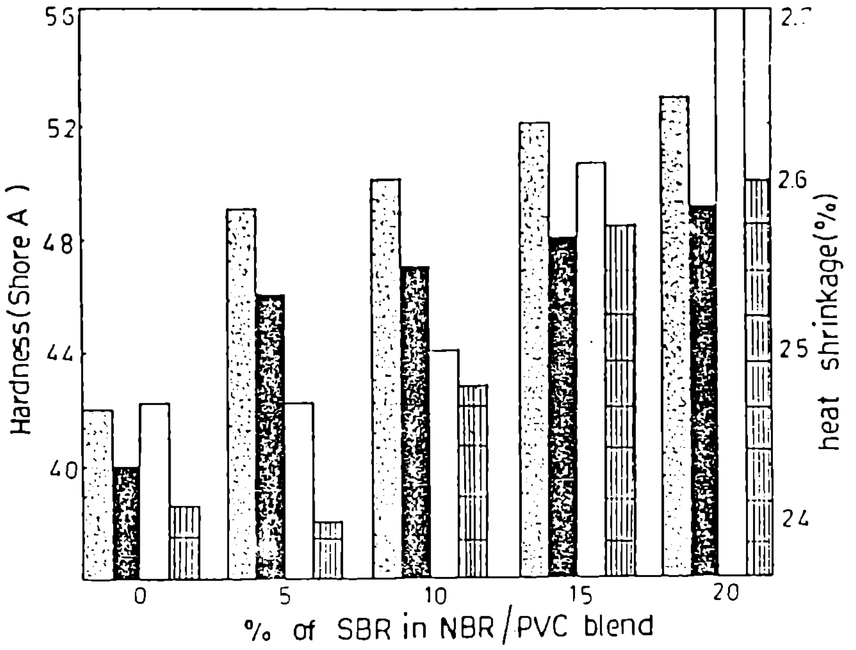

Fig.3.1.42 Variation of hardness and heat shrinkage with increase in the amount of SBR in NBR/PVC blend. NBR/S-PVC: (▨) hardness, (☐) heat shrinkage. NBR/E-PVC: (■) hardness, (▥) heat shrinkage.

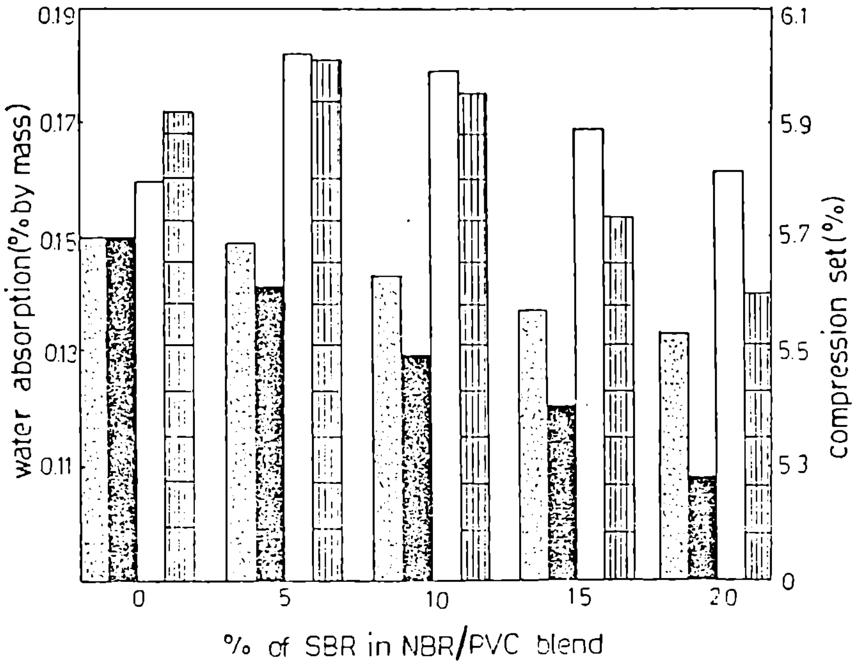

Fig.3.1.43 Variation of water absorption and compression set with increase in the amount of SBR in NBR/PVC blend. NBR/S-PVC: (▨) water absorption (☐) compression set. NBR/E-PVC: (■) water absorption (▥) compression set.

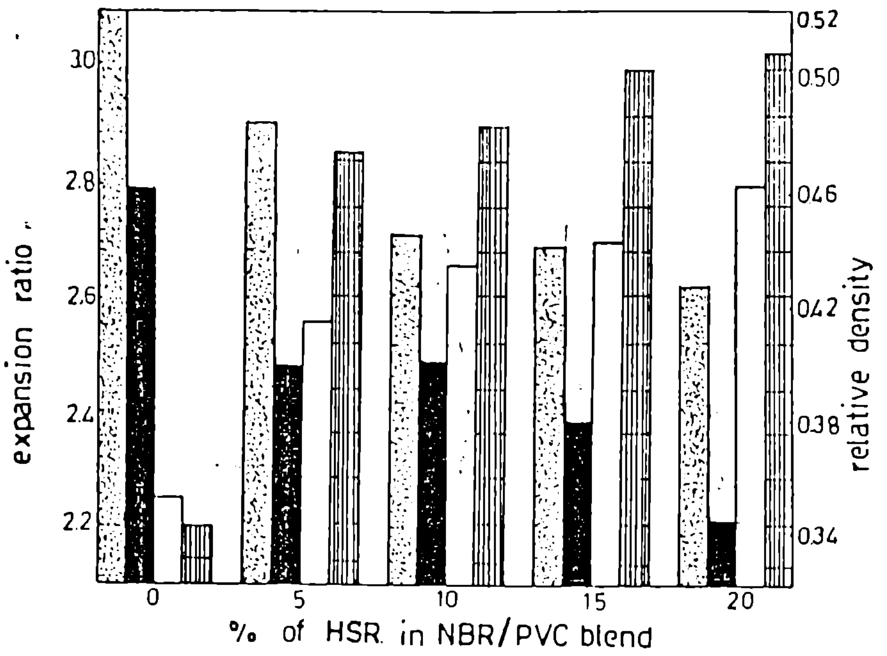

Fig.3.1.44 Variation of expansion ratio and relative density with increase in the amount of HSR in NBR/PVC blend. NBR/S-PVC: (▨) expansion ratio, (☐) relative density. NBR/E-PVC: (■) expansion ratio, (▥) relative density.

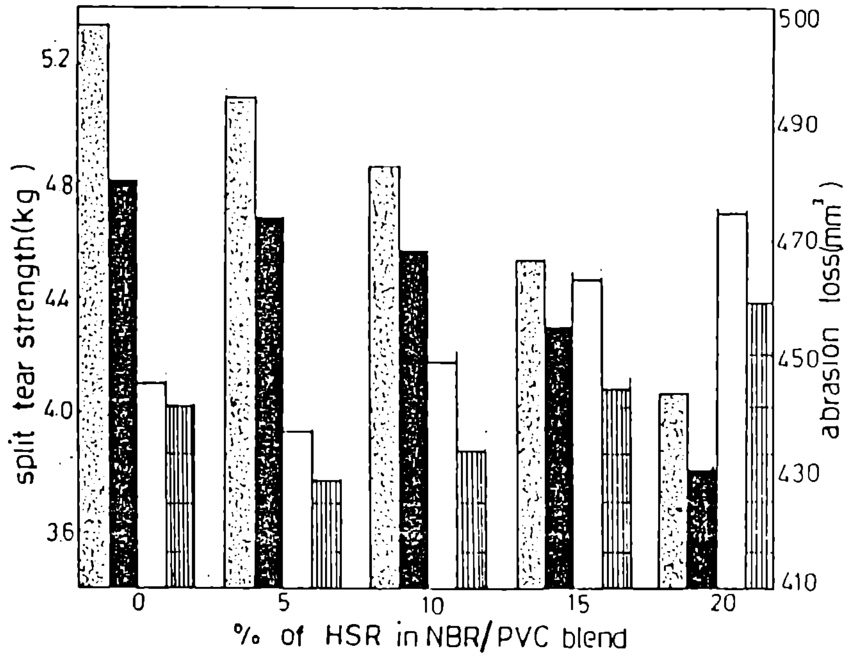

Fig.3.1.45 Variation of split tear strength and abrasion loss with increase in the amount of HSR in NBR/PVC blend. NBR/S-PVC: (▨) split tear strength, (☐) abrasion loss. NBR/E-PVC: (■) split tear strength, (▥) abrasion loss.

Fig.3.1.45 shows the variation of split tear strength and abrasion loss with increase in the amount of HSR in the blend. Split tear strength decreases with increase in HSR content similar to NR and SBR. Split tear strength shows higher values when compared to NR and lower values compared to SBR. Up to 10 parts of replacement of NBR by HSR shows no appreciable change in abrasion loss but further increase in the amount of HSR increases the abrasion loss. This may be due to the poor compatibility of HSR at higher levels with NBR/PVC blend. Replacement of NBR by HSR shows lower abrasion loss compared to NR and SBR.

Fig.3.1.46 shows the variation of hardness and heat shrinkage with increase in the amount of HSR in the blend. Hardness significantly improves by the addition of HSR. Again at higher level of HSR, rate of increase in hardness is high compared to NR and SBR. Heat shrinkage increases with increase in HSR content in the blend. Heat shrinkage shown by the addition of SBR and NR is similar to that in the case of HSR.

Fig.3.1.47 shows the variation of water absorption and compression set with increase in the amount of HSR in the blend. Water absorption and compression set decrease with increase in HSR content in the blend. Replacement of NBR by HSR shows low water absorption and low compression set compared to NR and SBR. The lower water absorption indicates that number of open cells formed is less by the addition of HSR.

Flex resistance of the MC sheets is shown in Table 3.1.18. The initial crack formation occurs at higher number of cycles than NR. The crack propagation is slowest at higher HSR content. Addition of HSR as a partial replacement of NBR in NBR/E-PVC shows similar behaviour (shown in Figs.3.1.44 to 3.1.47).

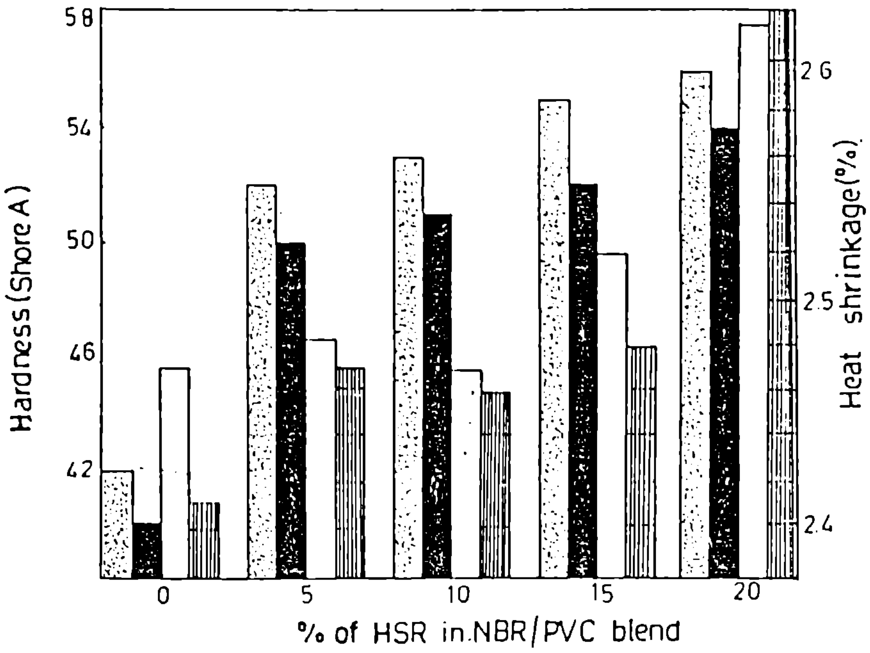

Fig.3.1.46 Variation of hardness and heat shrinkage with increase in the amount of HSR in NBR/PVC blend. NBR/S-PVC: (▨) hardness, (□) heat shrinkage. NBR/E-PVC: (■) hardness, (▥) heat shrinkage.

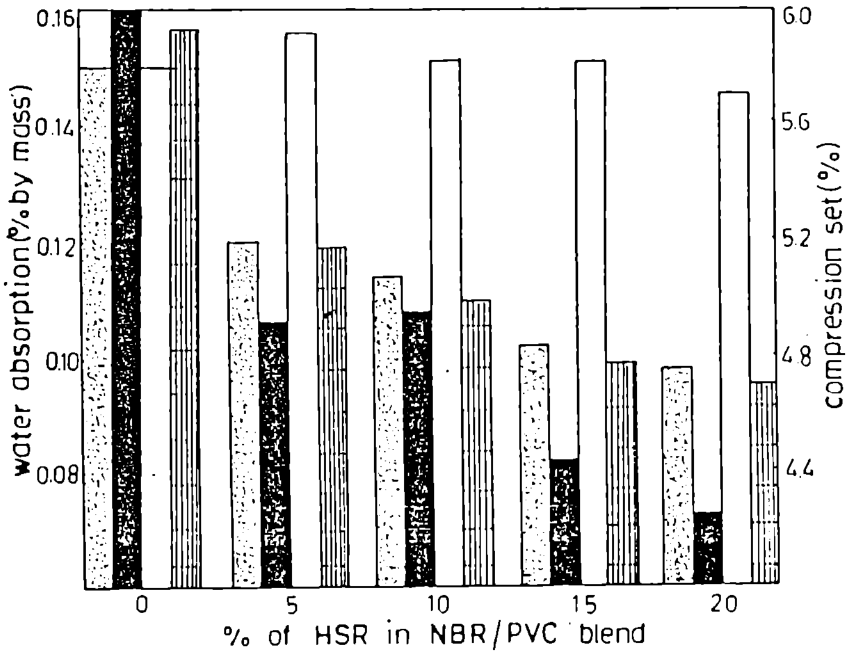

Fig.3.1.47 Variation of water absorption and compression set with increase in the amount of HSR in NBR/PVC blend. NBR/S-PVC: (▨) water absorption (□) compression set. NBR/E-PVC: (■) water absorption (▥) compression set.

Figs.3.1.48 to 3.1.50 show the optical microscope photographs of MC sheets when a part of NBR is replaced by NR, SBR and HSR. Addition of NR, SBR and HSR affects the uniformity of cells and this observation correlates with the lower mechanical properties of such MC sheets.

CONCLUSION

1. NR, SBR and HSR can replace a part of NBR in NBR/S-PVC and NBR/E-PVC based MC soles.
2. Replacement of NBR by SBR increases the split tear strength and hardness while HSR improves hardness and abrasion resistance, up to a lower level and NR shows higher expansion and low density.
3. Upto 15 parts of NBR can be replaced by NR, SBR or HSR for cost reduction without much deterioration in properties.

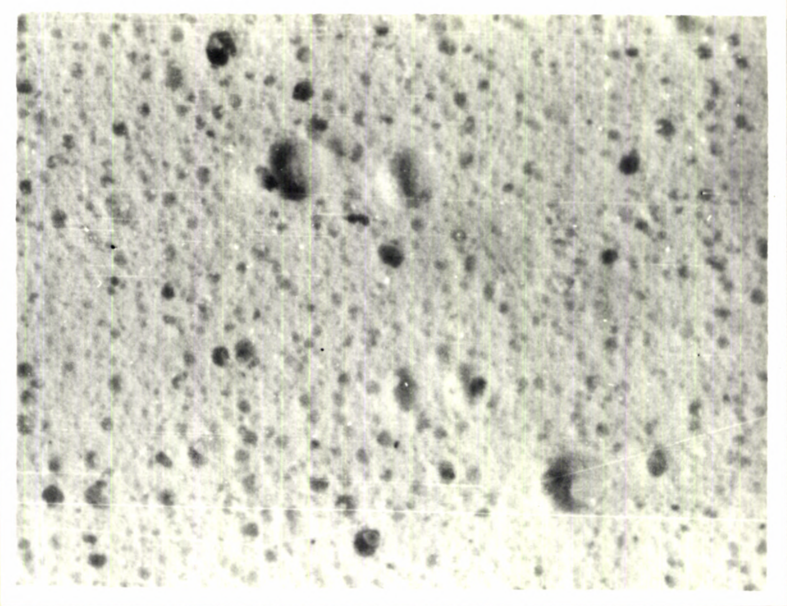

Fig.3.1.48
15% NR

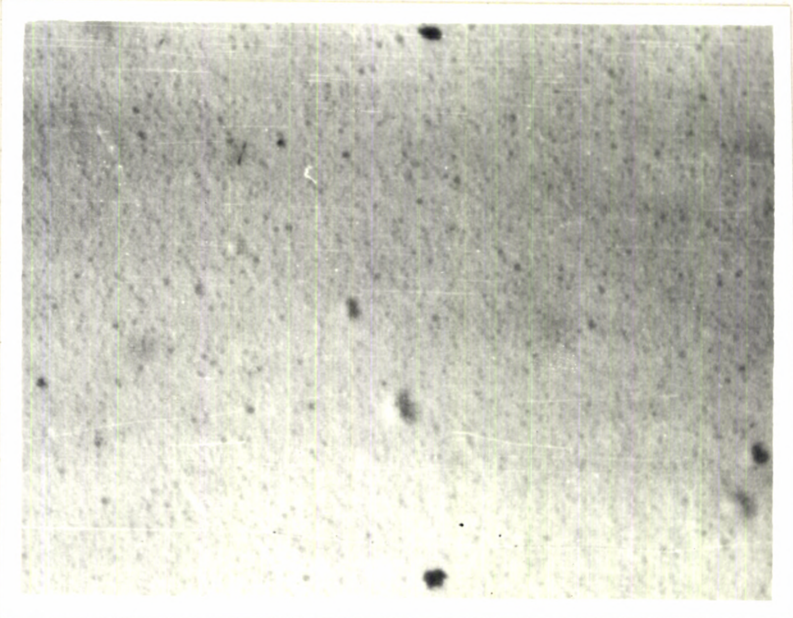

Fig.3.1.49
15% SBR

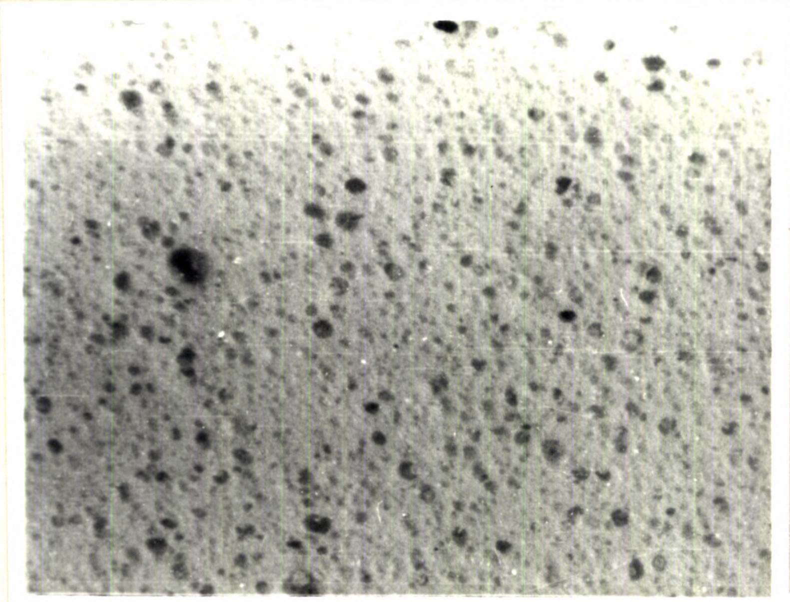

Fig.3.1.50
15% HSR

Optical microscope photographs of NBR/PVC MC sheets

PART II: STUDIES ON THE PROPERTIES OF MICROCELLULAR SOLES BASED ON NR/PVC BLENDS

Blends of several elastomers with PVC have been developed for different applications. Modifying elastomers with PVC is one of the promising methods of improving the solvent, ozone and fire resistance of the vulcanizates [42,43]. Although a large number of blends based on PVC have been proposed for commercial applications many of them do not have the required mechanical properties due to their incompatibility. It has been observed that better tensile properties are obtained when the rubber and plastic have some similarity in chain structure and are compatible. The interaction between the component phases, may however, be brought about either by the addition of agents which interact with both phases and render them mutually compatible or by specific reaction between the two phases [44]. It is now generally accepted that a suitable compatibilizer, which is chemically identical to those in the respective phases should improve interfacial adhesion, and permit a fine dispersion during mixing [45]. It is reported that ENR can act as a compatibilizer in NR/PVC blend [46].

The present study proposes the use of amine terminated liquid natural rubber (ATNR) and ENR as a compatibilizers in the development of NR/PVC based MC soles. Cell structure of a razor cut samples of the MC sheets was investigated using an optical microscope.

Experimental

NR/S-PVC blends were prepared in a Brabender plasticorder model PL 3S at 150°C and at 50 rpm for 6 min. The total mixing time was kept about 6 min. to avoid sticking of the compound. ATNR was added towards the end of blending. Formulations of NR/PVC blend are shown in Table 3.2.1. ATNR and ENR were added as compatibilizers by replacing a part of DOP in the NR/PVC blends. Effect of replacement of NR by ENR in NR/PVC blends was also studied.

The incorporation of other additives was done in a two-roll mixing mill as per the formulations given in Table 3.2.2. The cure characteristics of the compounds were determined using Goettfert Elastograph at 160°C. The NR/PVC blends were then compounded without blowing agent. The compounds were moulded in an electrically heated hydraulic press at 160°C upto their optimum cure times. Tensile properties and tear strength of the vulcanizates were determined as per relevant ASTM Standards from samples punched out of the vulcanizates.

Preparation of microcellular sheets

The NR/S-PVC blends were compounded as per the formulation given in Table 3.2.2. The NR/S-PVC compounds were precured to 80% of their optimum cure time at 160°C. The mould was filled with 3 to 5 per cent excess of the compound on volume basis and expanded sheets were then post cured in an air oven at 70°C for 2h. The technical properties were determined according to relevant Indian standards. Cell structure of the NR/PVC based MC sheets were studied using an optical microscope.

Results and discussion

Cure characteristics of the compounds are given in Table 3.2.1. Cure time of the compounds are marginally reduced when part of DOP is replaced by ATNR.

Table 3.2.2

Formulation for NR/PVC based microcellular sole compound

Ingredients	Phr
NR	100
ZnO	3
Stearic acid	2
Zinc stearate	2
TiO_2	4
Precipitated silica	40
China clay	80
DEG	1.5
SP	1
MBTS	1.5
Sulphur	1.5
ADC	8

Table 3.2.1 shows the effect of incorporation of ATNR and ENR on the mechanical properties of NR/PVC blends. Tensile strength increases with increase in the amount of ATNR. This increase in tensile strength of the NR/PVC blend may be due to the compatibilizing action of ATNR. The tear strength value does not show much increase when the amount of ATNR is increased from 5 to 10. Elongation at break values marginally decrease with the incorporation of ATNR. Incorporation of ENR in NR/PVC blend also marginally improves the tensile strength and tear strength, but the improvement is much lower than that of ATNR. When a part of NR is replaced by ENR in NR/PVC blend, tensile strength decreases considerably.

MC soles based on NR/PVC blends

Table 3.2.3 shows the cure characteristics and technical properties of MC soles based on NR/PVC blends. The optimum cure time marginally decreases with increase in ATNR content. Expansion of the MC sheets shows a marginal decrease with a corresponding increase in relative density. Higher percentage precure results in higher crosslink density which restricts the degree of expansion which may be the reason for the lower expansion [47]. This leads to higher densities. Split tear strength marginally increases with the amount of ATNR in the blend. The incorporation of ATNR shows a marginal increase in strength, for NR/PVC blends. This increase may be due to the compatibilizing action of ATNR. Abrasion loss decreases marginally with ATNR content due to lower expansion. Split tear strength is comparatively low for MC sheets based on NR/PVC blend compared to conventional NR/HSR blend based MC sheets.

Compression set values decrease with increase in ATNR content in the blend whereas hardness marginally increases. Heat shrinkage of the MC sheet decreases with ATNR content

Table 3.2.3 Technical properties of microcellular sheets based on NR/PVC blends

Properties	Mix Number					
	1	2	3	4	5	6
Time for optimum cure at 160°C	12.4	9.76	9.9	8.3	11.5	11.0
Initial expansion (%)	58.33	53.37	51.19	48.21	66.67	65.48
Expansion after 5 mts (%)	35.33	33.33	29.76	29.76	35.33	35.78
Expansion after 24 h (%)	30.95	26.1	21.4	21.4	30.95	30.95
Expansion ratio	2.05	1.9	1.78	1.71	1.97	1.97
Relative density	0.69	0.681	0.694	0.70	0.661	0.676
Split tear strength (kg)	1.9	2.78	2.9	2.90	2.46	2.19
Abrasion loss (mm)	420	342.8	339	328	390	387.6
Compression set (%)	19.4	18.2	15.2	12.6	19.85	18.4
Hardness (Shore A)	28	31	33	35	32	29
Heat shrinkage (%)	1.49	1.29	1.29	1.08	1.44	1.35
Water absorption (percent by mass)	0.074	0.047	0.049	0.069	0.040	0.04
Shrinkage after post curing (%)	2.99	2.87	2.2	1.88	2.48	1.925
Flex resistance						
a) Crack initiation (cycles)	<60,000	>60,000	>60,000	>60,000	>60,000	>60,000
b) Crack growth at the end of 100,000 cycles (%)	>600	>600	>600	< 600	--	--

and water absorption marginally increases as shown in Table 3.2.3. Compared to MC sheets based on other blends, NR/PVC blend based MC sheets show lower shrinkage and water absorption. This shows that the number of open cell present in MC sheet is less.

Shrinkage after post curing decreases with increase in ATNR content and NR/PVC based MC sheet shows considerably lower shrinkage than the conventional NR/HSR blend based MC sheets. Room temperature shrinkage is not observed in this type of MC sheets (kept two weeks in room temperature). The flex resistance of samples are shown in Table 3.2.3. In the case of MC sheets without ATNR, initial crack is observed even below 60,000 cycles. For samples containing higher concentration of ATNR crack initiation occurs after a much larger number of cycles. Crack growth rate is found to be slow at higher concentration of ATNR. The MC soles based on NR/PVC blend shows low crack resistance compared to NBR/PVC based soles.

NR/E- PVC blend was also tried as a base material for MC soles similar results were obtained (not shown).

ENR-50 is tried as a compatibilizer in NR/PVC blends. The MC soles based on ternary blends of 60/30/10 NR/PVC/ENR show lower expansion, low shrinkage and hardness. When ENR is used as compatibilizer crack initiation occurs before 60,000 cycles and crack size growth is also high. Higher relative density, lower hardness, shrinkage and strength are observed for NR/PVC blends with ENR as compatibilizer.

Fig.3.2.1 shows the cell structure of NR/PVC based MC sheets containing DOP alone and Figs.3.2.2 and 3.2.3 when a part of DOP is replaced by ATNR and ENR. The cell structure of the MC sheets containing ATNR is more uniform and the number of cells are smaller. MC sheets containing ENR show comparatively uniform cells (shown in Fig.3.2.3).

CONCLUSION

ATNR and ENR 50 can be used as compatibilizer in NR/PVC blends. The MC soles based on NR/PVC blend show lower shrinkage, hardness, water absorption and split tear strength but higher density when modified withATNR or ENR. The properties of the NR/PVC based MC soles are found to be within the IS specification when ATNR is used as a compatibiliser.

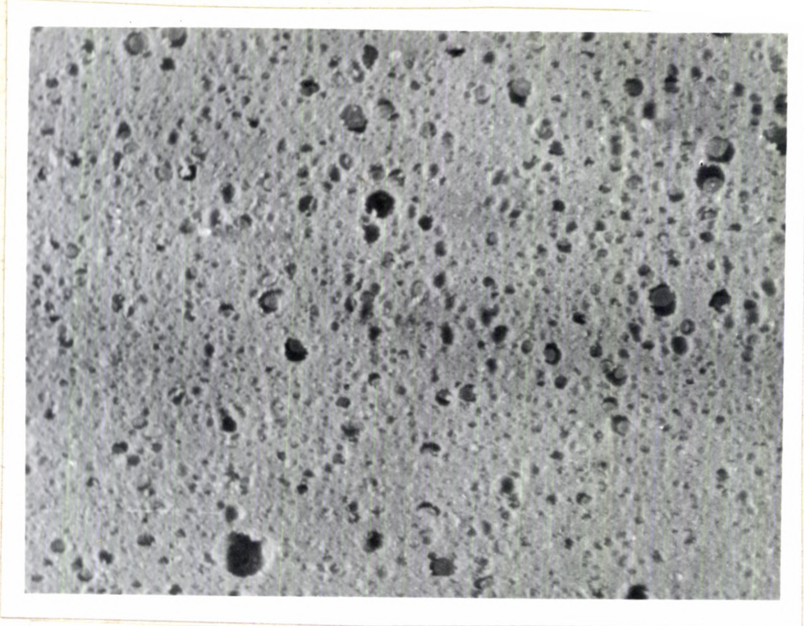

Fig.3.2.1
40 phr DOP

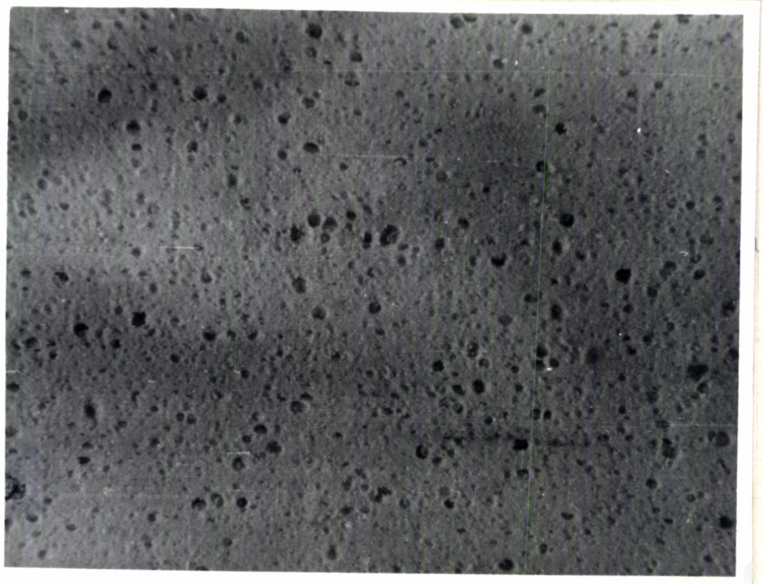

Fig.3.2.2
35 phr DOP/
5 phr ATNR

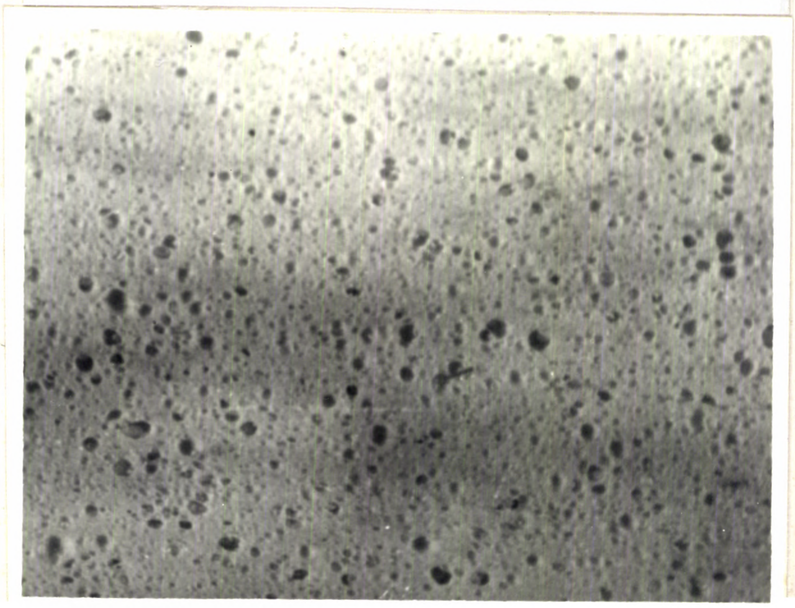

Fig.3.2.3
35 phr DOP/
5 phr ENR

Optical microscope photographs of NR/PVC MC sheets

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CHAPTER 4

PART I: STUDIES ON THE PROPERTIES OF MICROCELLULAR SOLES BASED ON SBS/SBR BLENDS

A wide range of linear and branched styrenic teleblock copolymers have been developed with polydienes or hydrogenated counterparts as centre blocks starting from 1960's. Such materials have good strength, processability and excellent flexibility both at low and room temperatures. These properties, together with the ability of polymer to improve the performance via blending are the reasons for their rapid development [1]. The styrenic blocks at the end of an elastomeric chain immobilise the chain and reduce the cold flow which makes such thermoplastic elastomers as requiring no vulcanization. Compared to other copolymers, the styrene-diene block copolymers are fundamentally different, the styrene molecule form one or two blocks, and the diene molecules form a further block, these blocks are joined to form a single molecule with the general form ABA, where A represents the hard segment of polystyrene and B a soft central segment of polymerised diene or hydrogenated diene molecule respectively [2,3]. So the basic structure of styrenic thermoplastic elastomers are poly(styrene-b-butadiene-b-styrene) (SBS), poly(styrene-b-isoprene-b-styrene) (SIS) or the one with a hydrogenated central ethylene-butylene (EB) block poly-(styrene-b-ethylene-butylene-b-styrene) (SEBS) [4-7].

These polymers have a unique combination of properties of elastomers and thermoplastics. They can be processed like thermoplastics, while retaining the characteristic properties of vulcanisable elastomers. The properties of elastomeric block copolymers such as SBS, are understood to be caused by the presence of isolated glassy domains of styrene blocks in an elastomeric matrix of butadiene. The domains play same role as chemical crosslinks, acting as junctions which create an elastomeric net work structure [8,9]. Due to the thermodynamic incompatibility of the two blocks, the soft diene and hard polystyrene blocks will each segregate in to their own phase to give aggregates or domains. The relative proportions of styrene and diene units in the polymer will determine the properties of these TPEs. As the styrene content is increased the TPE will progress from a soft rubbery material to a hard leather-like material and finally to a hard impact modified thermoplastic approaching PS in properties. The elastomer segment controls many properties such as thermal and oxidative stability, elastic nature etc. and the hard segment determines the tensile strength and upper service temperatures [10]. In styrenic thermoplastic elastomers the two phases are covalently bonded to each other. Thus the hard, rigid polystyrene domains are much more effective in restricting the motion of the mobile polydiene segments, thereby increasing the modulus and elasticity of TPE [3,11-13].

Because of their properties the styrenic thermoplastic elastomers are being used in wide range of important applications such as footwears, adhesives, general moulded parts and for the modification of bitumens and plastics. The single largest application of styrenic thermoplastic rubbers is in footwear applications. The styrenic thermoplastic rubbers that appeared in the shoe sector in the 1970's have now achieved a major share of the market. This is because they are suitable for the production of light weight shoe soles with good grip and elasticity at low temperatures [1]. Currently styrenic TPEs are being used in direct injection molded non canvas and unit sole applications. Even though they are more expensive than conventional vulcanized rubber, they are lower priced compared to the other TPEs. Equally important are the cost savings they bring because of fast processing, scrap recycle etc. [14,15].

The blending of block copolymers with other polymers, either homopolymers or copolymers is an industrially useful technique for the production of new polymeric materials, with desired physical characteristics. Depending on the constituent polymers two phase or multiphase systems can be formed. For such two phase or multiphase polymeric systems, block copolymers have a characteristics role, on the one hand because of their interfacial activity they act as emulsifiers, by means of which it is possible to regulate the particle size of the dispersed phase of the polymer blend, on the other hand as a block copolymer can be located at the interface of a two phase system, an "anchoring" between the phases can be achieved, leading generally to dramatic improvement of the mechanical properties of the material [16-19].

In this part of the study the development and properties of SBS/SBR blend based microcellular soles are proposed to be investigated. The effect of parameters such as blend ratio, percentage precure, post curing temperature and time on the properties of microcellular soles are proposed to be investigated. SBS/SBR MC sole waste is proposed to be added to the virgin material as a filler.

4.1.1 Effect of SBS content on properties of SBS/SBR blends and microcellular soles based on SBS/SBR blends

Experimental

The SBS/SBR blends were prepared on a Brabender plasticorder model PL 3S at 50 rpm at a temperature of 110°C by varying the SBS content from 40 to 80 wt. %. SBS was added first and allowed to melt and homogenise for 2 minutes. Then SBR in the form of a sheet was then added and 3 min. was given for blending. In all the cases torque stabilized to a constant value by this time.

The SBS/SBR blends were compounded for the SBR part on a two roll laboratory mixing mill using formulations given in Table 4.1.1a according to ASTM D 3182. In order to evaluate the properties of the blend, the blowing agent was not added at this stage. The optimum cure time for the compounds were determined on a Goettfert Elastograph 67.85. The compounds were then vulcanized up to their respective optimum cure time in an electrically heated hydraulic press at 160°C. The mould was taken out and cooled in water and then the sheet was taken out of the mould. The tensile and tear properties of the vulcanizates were determined on a Zwick universal testing machine using a crosshead speed of 500 mm/min. according to ASTM standards.

Preparation of microcellular sheets

For preparing microcellular sheets blends having SBS:SBR ratio 40:60, 50:50 and 60:40 were selected. These blends were designated as 1, 2 and 3 respectively. The SBS/SBR blends were compounded according to the formulations given in Table 4.1.1a. The

Table 4.1.1a

Formulations and vulcanizate properties of SBS/SBR blends

Ingredients (Phr)	1	2	3	4	5
SBS	40	50	60	70	80
SBR	60	50	40	30	20
ZnO	4	4	4	4	4
Stearic acid	5	5	5	5	5
China clay	60	60	60	60	60
Precipitated calcium carbonate	40	40	40	40	40
Paraffinic oil	3	3	3	3	3
Styrenated phenol (SP)	1	1	1	1	1
Wood rosin	2	2	2	2	2
Vulcafor F	1.2	1.2	1.2	1.2	1.2
Sulphur	2	2	2	2	2
DNPT	5	5	5	5	5
Cure characteristics					
Optimum cure time T_{90} at 160°C (min.)	10.2	9.8	9.9	10.4	10.1
Properties					
Tensile strength (N/mm^2)	4.23	4.36	5.46	2.38	1.01
Tear strength (N/mm)	22	24.79	29.74	13.99	12.41
Elongation at break (%)	600	580	580	350	350

optimum cure time of the microcellular compounds were determined on the Goettfert Elastograph model 67.85. The compounds were moulded in an electrically heated hydraulic press at 160°C upto 80% of their optimum cure time. The mould was loaded 3 to 5 percent excess of the compound on volume basis. The expanded sheets were then post cured in an air oven at 80°C for 2h. The technical properties of the microcellular sheets were determined as per relevant Indian standards as described in chapter 2.

The cell structure of selected razor cut samples of the microcellular sheets were studied using an optical microscope.

Results and discussion

The cure characteristics and vulcanizate properties of SBS/SBR blends are shown in Table 4.1.1a. The optimum cure times of the SBS/SBR blend based compounds are more or less same. Tensile strength and tear strength of the vulcanizates increase, reach a maximum at 60% SBS content and then decrease. This may be due to the phase change. SBS shows higher strength due to its self reinforcing nature. The elongation at break decreases with increase in SBS content.

Fig.4.1.1 represents the variation of expansion ratio and relative density with increase in the amount of SBS in the blend. Expansion of the MC sheet increases with increase in the amount of SBS, while relative density decreases (percent linear expansion of the MC sheets shown in Table 4.1.1b). The increase in expansion may be due to the comparatively higher expansion of PS domains present in SBS.

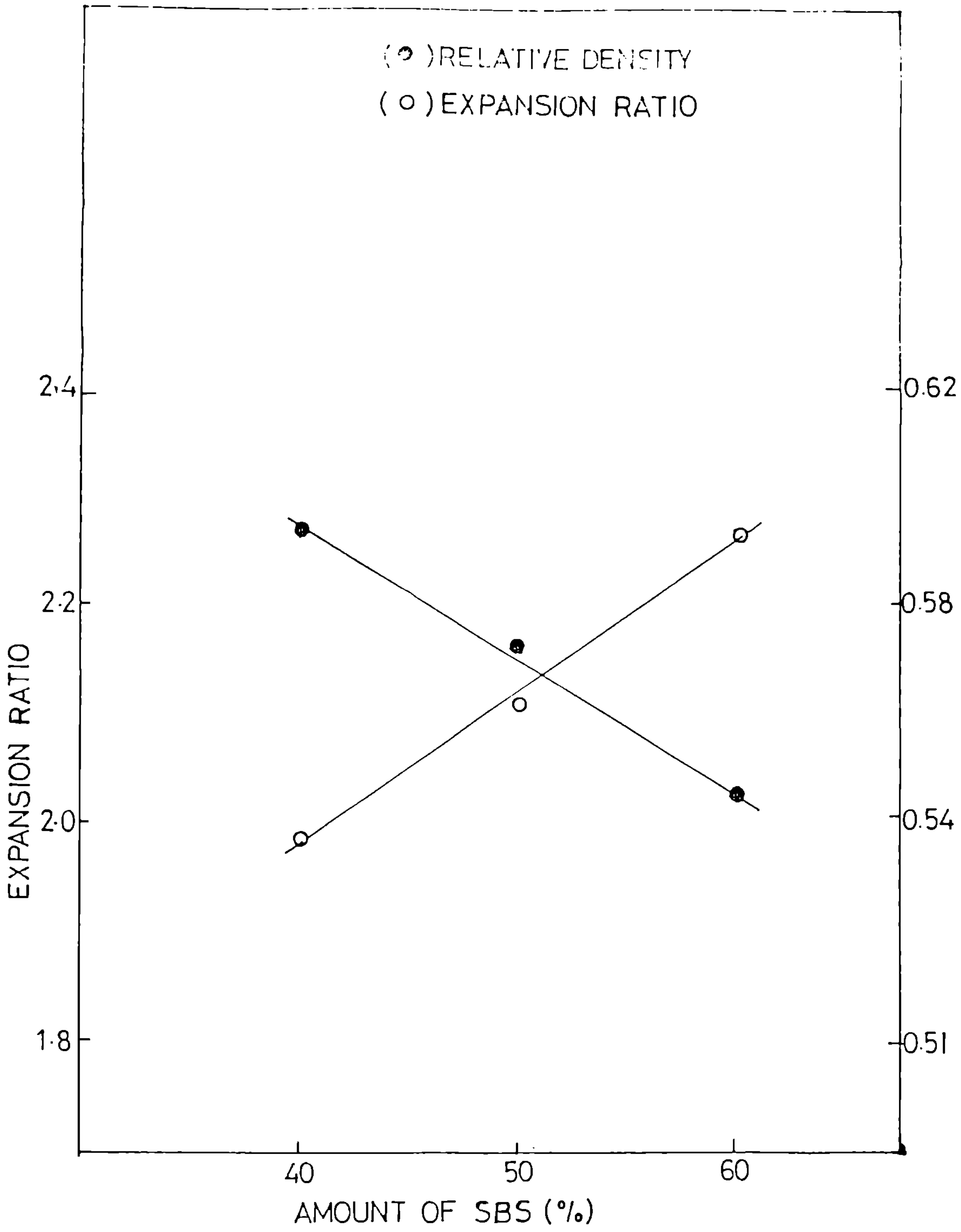

Fig.4.1.1 Variation of expansion ratio and relative density with increase in the amount of SBS.

Table 4.1.1b

Effect of SBS content on the technical properties of microcellular soles based on SBS/SBR blends

Properties	Mix Number		
	1	2	3
Time required for optimum cure at 160°C (min.)	9.9	9.9	10
Initial expansion (%)	58.33	59.52	64.28
Expansion after 5 min. (%)	32.14	35.71	38.09
Expansion after 24h (%)	25	26	28.57
Shrinkage after post curing (%)	4.58	5.3	6.08
Change in hardness after ageing 24h at 100°C	+1	+2	+2
Room temperature shrinkage (%)	1.1	1.5	1.8
Flex resistance			
a) Crack initiation in cycles	346,963	346,963	340,000
b) Crack growth at the end of 100,000 cycles (mm)	0.1	0.1	0.1

Fig.4.1.2 shows the variation of split tear strength and abrasion loss with increase in the amount of SBS in the blend. Split tear strength of the MC sheets marginally increases with increase in SBS content in the blend up to 50 part. Further increase in the amount of SBS in the blend decreases the split tear strength. The observed increase in split tear strength may be due to the presence of polystyrene blocks in SBS. Styrene-butadiene rubber vulcanizates possess low tensile and tear strength under ordinary conditions. As polystyrene and polybutadiene are incompatible, the PS chains aggregate to give submicroscopic domains dispersed in a polybutadiene matrix. These plastic domains of PS provide physical crosslinks and such two phase elastomers have high tensile strength [13]. The observed decrease in split tear strength may be due to the decrease in cell wall thickness with increase in volume of expansion as well as increase in the number of cells per unit volume [20]. Abrasion loss increases with increase in the amount of SBS in the blend. The increase in the expansion of the MC sheet causes an increase in the number of cells which makes the cell walls weak with the chances of breakage of cells resulting in increased abrasion loss.

Fig. 4.1.3 is the variation of water absorption and compression set with increase in the amount of SBS in the blend. As the SBS content in the blend increases, water absorption of the MC sheet increases. This indicates the formation of more open cells, at higher concentration of SBS in the blend. Compression set values are found to be increased with increase in the amount of SBS in the blend. Compared to MC soles based on NR/HSR blends MC soles based on SBS/SBR blend exhibit higher compression set. This may be attributed to the lower crosslinking of SBS in the blend and to the higher expansion of the MC sheet.

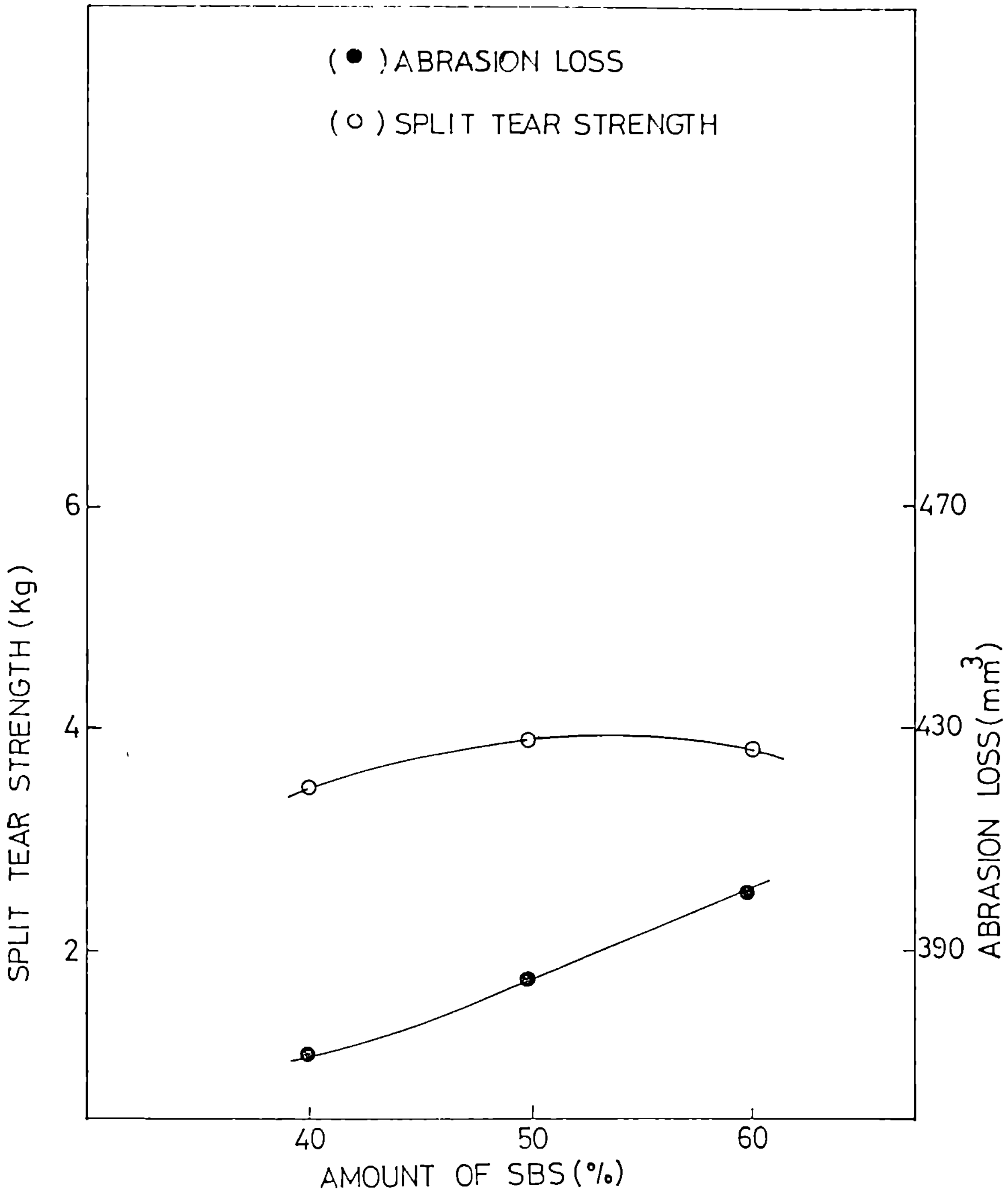

Fig.4.1.2 Variation of split tear strength and abrasion loss with increase in the amount of SBS.

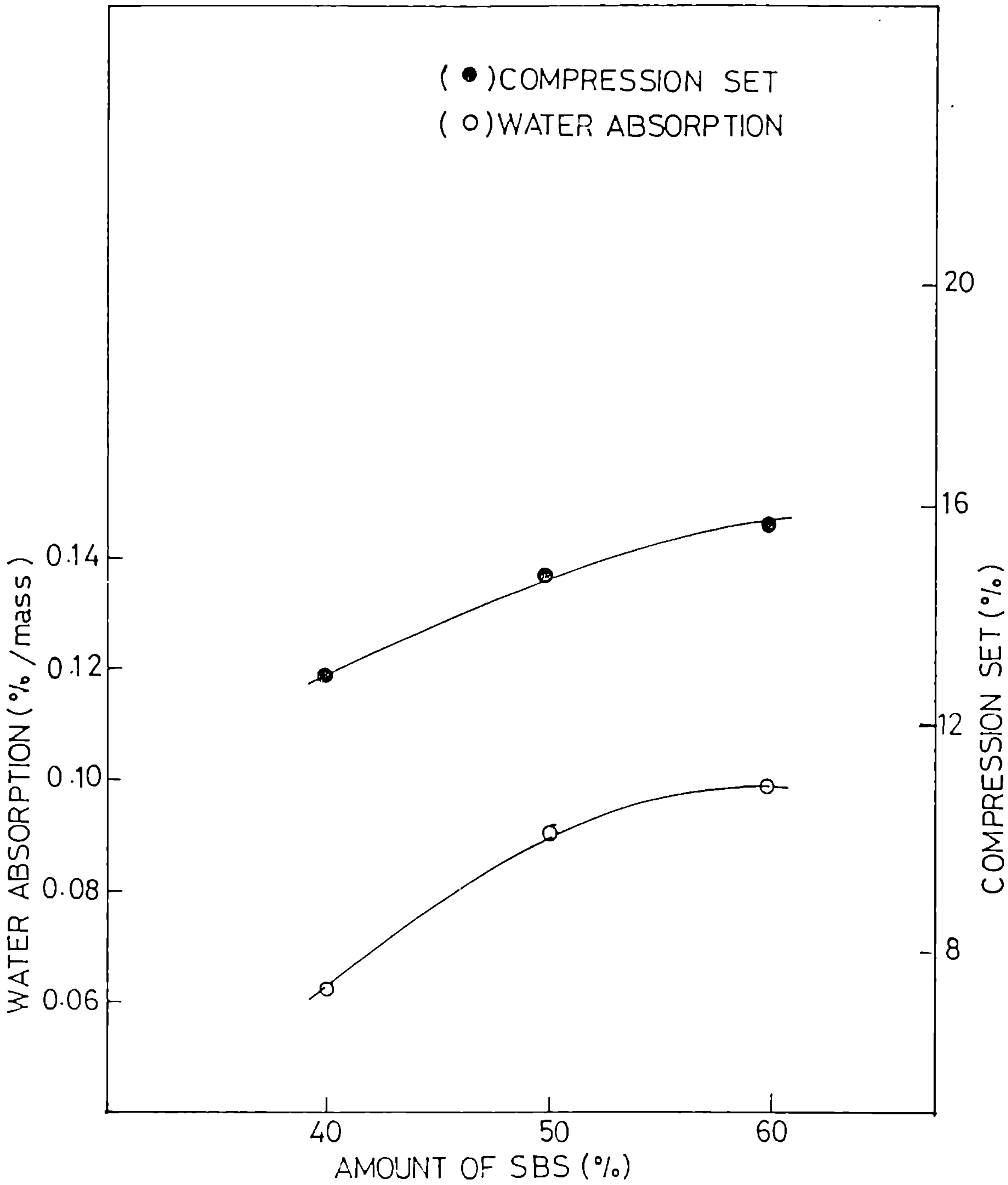

Fig.4.1.3 Variation of water absorption and compression set with increase in the amount of SBS.

Fig.4.1.4 shows the variation of hardness and heat shrinkage with increase in the amount of SBS in the blend. Hardness of the MC sheets decrease with increase in SBS content. This may be due to the lower extent of crosslinking of SBS at higher levels and to the higher expansion of SBS rich blends based MC sheets. Heat shrinkage of the MC sheets marginally increases with SBS content. This is due to higher expansion of the MC sheets.

Shrinkage after post curing of the SBS/SBR based MC sheets increase with increase in the amount of SBS as shown in Table 4.1.1b. This is probably due to the large cell size of the SBS/SBR based MC sheets. The large cell size and higher expansion produce weak cell walls and facilitate diffusion of gases from MC sheets containing higher proportions of SBS.

Flex resistance of SBS/SBR based MC sheets are shown in Table 4.1.1b. Compared to conventional MC soles, the SBS/SBR based MC soles show higher flex crack resistance. Crack growth at the end of 100,000 cycles is also less compared to conventional soles.

Figs.4.1.5 and 4.1.6 are the optical microscope photographs of MC sheets prepared from 40/60 and 50/50 SBS/SBR blends respectively. As the SBS content increases in this range number and size of the cells increase due to higher expansion.

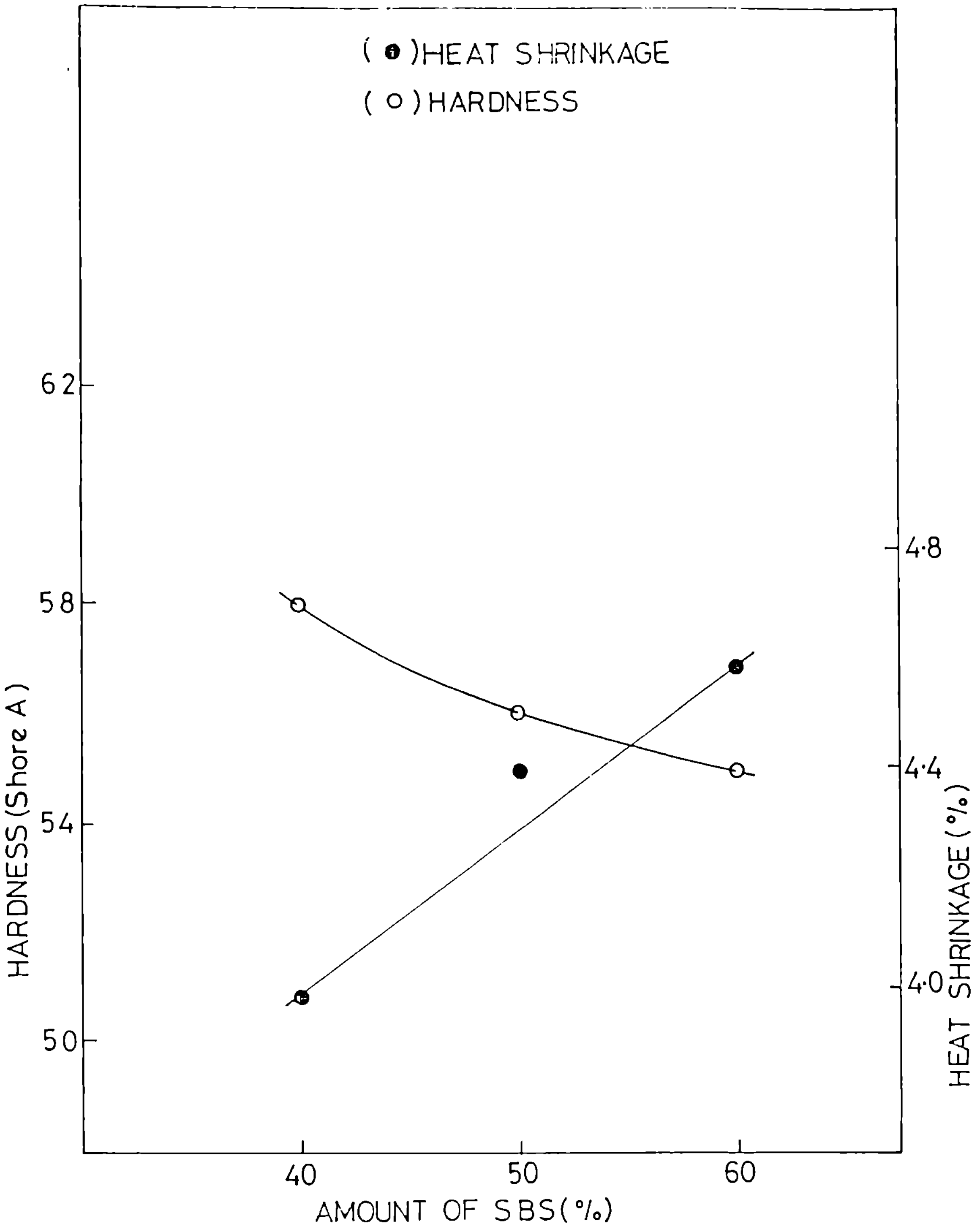

Fig.4.1.4 Variation of hardness and heat shrinkage with increase in the amount of SBS.

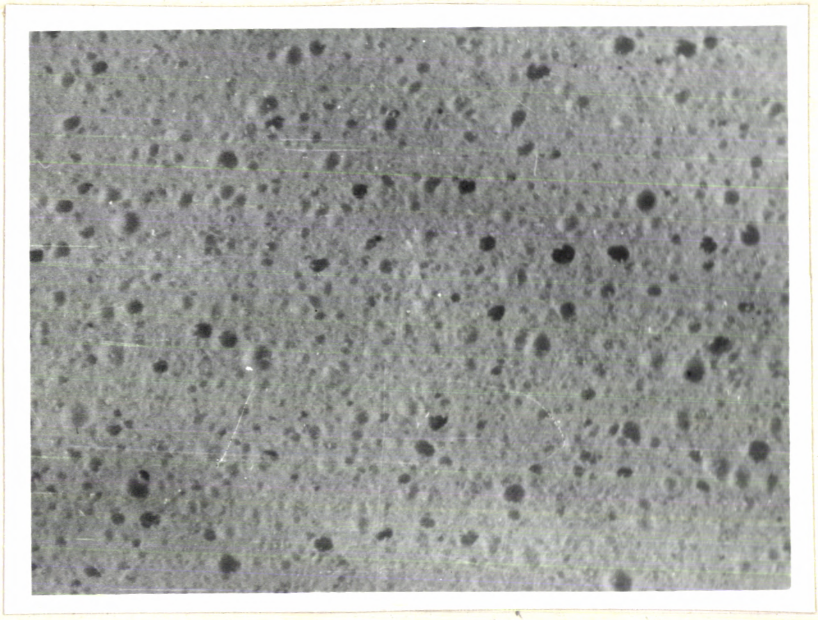

Fig.4.1.5 40/60 SBS/SBR

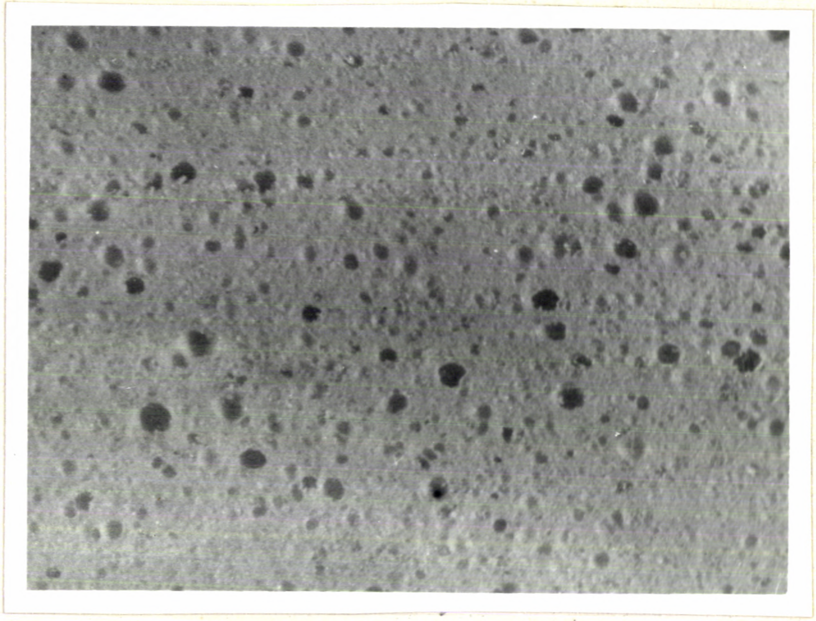

Fig.4.1.6 50/50 SBS/SBR

Optical microscope photographs of MC sheets

4.1.2. Effect of SBS/SBR microcrumb on properties of microcellular soles based on SBS/SBR blends

Experimental

Waste obtained after cutting away the useful product from SBS/SBR blend based MC sheet was passed through the tight nip of a hot two roll mill and homogenised well for 10 min. and sheeted out. This was added to SBS/SBR blend based MC sheets in varying levels from 25 to 100 phr. The levels of all other ingredients were kept the same. The effect of SBS/SBR microcrumb was evaluated in a 50/50 SBS/SBR blend since the 50/50 blend shows optimum technical properties as MC sheets. The different levels of the microcrumb were added and compounded according to the formulations of the mixes (Table 4.1.2a) in a laboratory size two roll mill at room temperature. The compounds were moulded in an electrically heated hydraulic press at 160°C upto 80% of their respective optimum cure times. Expanded microcellular sheets were post cured at 80°C for 2h in an electrically heated air oven. The technical properties of the MC sheets were determined as per the procedure described in chapter 2.

Results and discussion

Fig.4.1.7 shows the variation of expansion ratio and relative density with increase in the amount of SBS/SBR microcrumb in SBS/SBR blend based MC sheets. By the incorporation of SBS/SBR microcrumb expansion of the MC sheet decreases and consequently relative density increases. This decrease in expansion is obviously due to the presence of already vulcanized microcrumb, which does not expand.

Table 4.1.2a

Formulations for MC soles based on SBS/SBR blends

Ingredients (phr)	Mix Number			
	5	6	7	8
SBS	50	50	50	50
SBR	50	50	50	50
ZnO	4	4	4	4
Stearic acid	5	5	5	5
China clay	60	60	60	60
Precipitated calcium carbonate	40	40	40	40
SBS/SBR microcrumb	25	50	75	100
Naphthenic oil	5	5	5	5
Styrenated phenol (Sp)	1	1	1	1
Wood wosin	2	2	2	2
Vulcafor F	1.2	1.2	1.2	1.2
Sulphur	2	2	2	2
DNPT	5	5	5	5

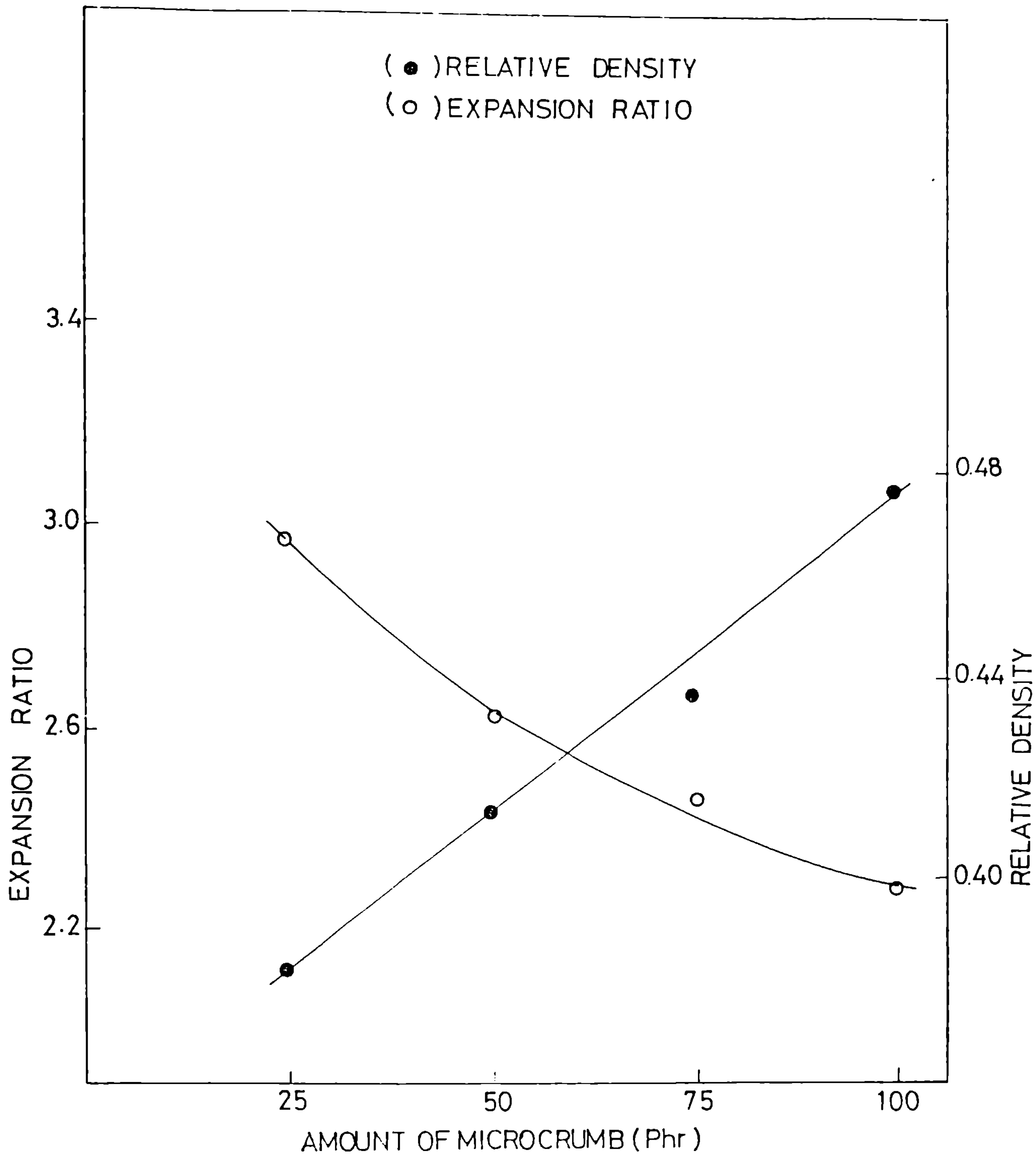

Fig.4.1.7 Variation of expansion ratio and relative density with SBS/SBR microcrumb.

Fig.4.1.8 shows the variation of split tear strength and abrasion loss with increase in the amount of microcrumb. Split tear strength increases with increase in the amount of microcrumb. This is probably due to the reinforcing effect of microcrumb. But above 50 phr level, the split tear strength marginally reduces because the microcrumb probably forms a continuous phase. But abrasion loss decreases with increase in microcrumb content. This is obviously due to the decrease in expansion of the MC sheets which results in increase cell wall thickness as well as decreased number of cells per unit volume.

Fig.4.1.9 shows the variation of water absorption and compression set with increase in the amount of microcrumb. Water absorption decreases with increase in microcrumb concentration. This behaviour is expected since the rate of decrease is more pronounced in MC sheets with higher crumb concentration and the decrease in expansion causes decrease in the number of open cells, resulting in reduced water absorption. Compression set decreases with increasing amount of microcrumb. Decrease in compression set may be attributed to the lower expansion and higher extent of crosslinking in the presence of microcrumb.

Fig.4.1.10 shows the variation of heat shrinkage and hardness. Heat shrinkage of the SBS/SBR blend based MC sheets decrease with increase in the amount of microcrumb as expected. Hardness of the MC sheets increase with increase in the amount of microcrumb. This increase in hardness is the result of lower expansion of the sheets.

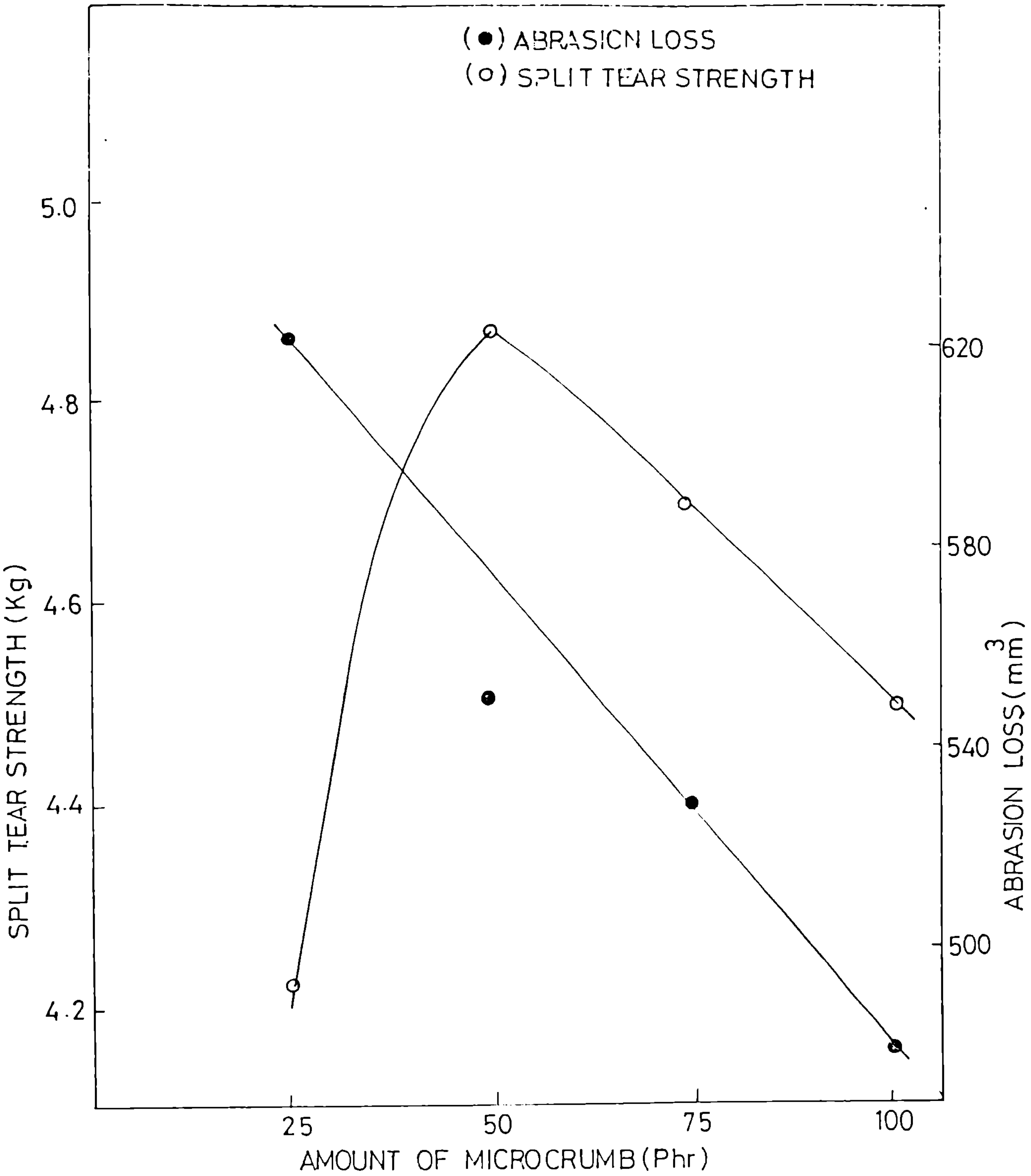

Fig.4.1.8 Variation of split tear strength and abrasion loss with SBS/SBR microcrumb.

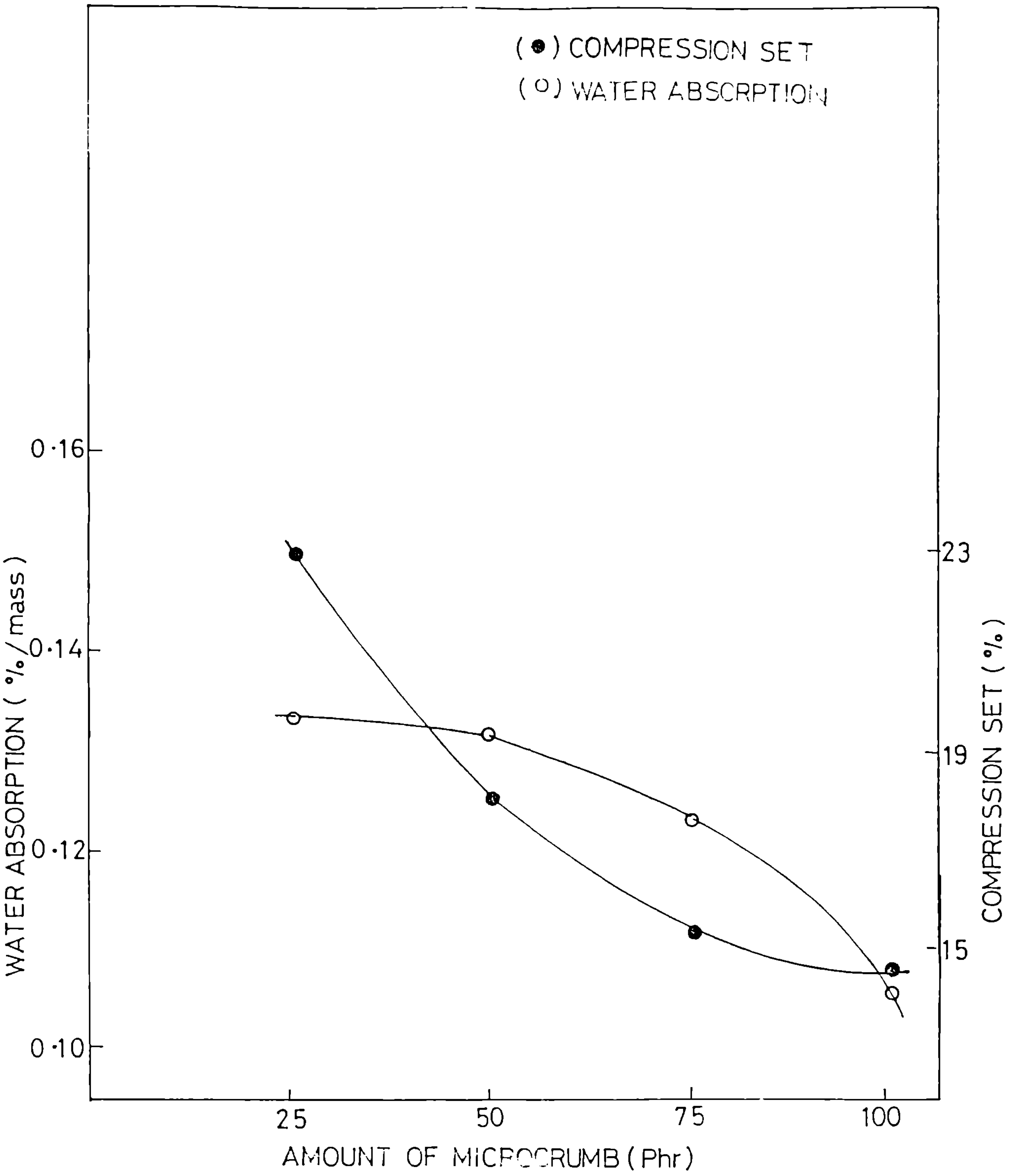

Fig.4.1.9 Variation of water absorption and compression set with SBS/SBR microcrumb.

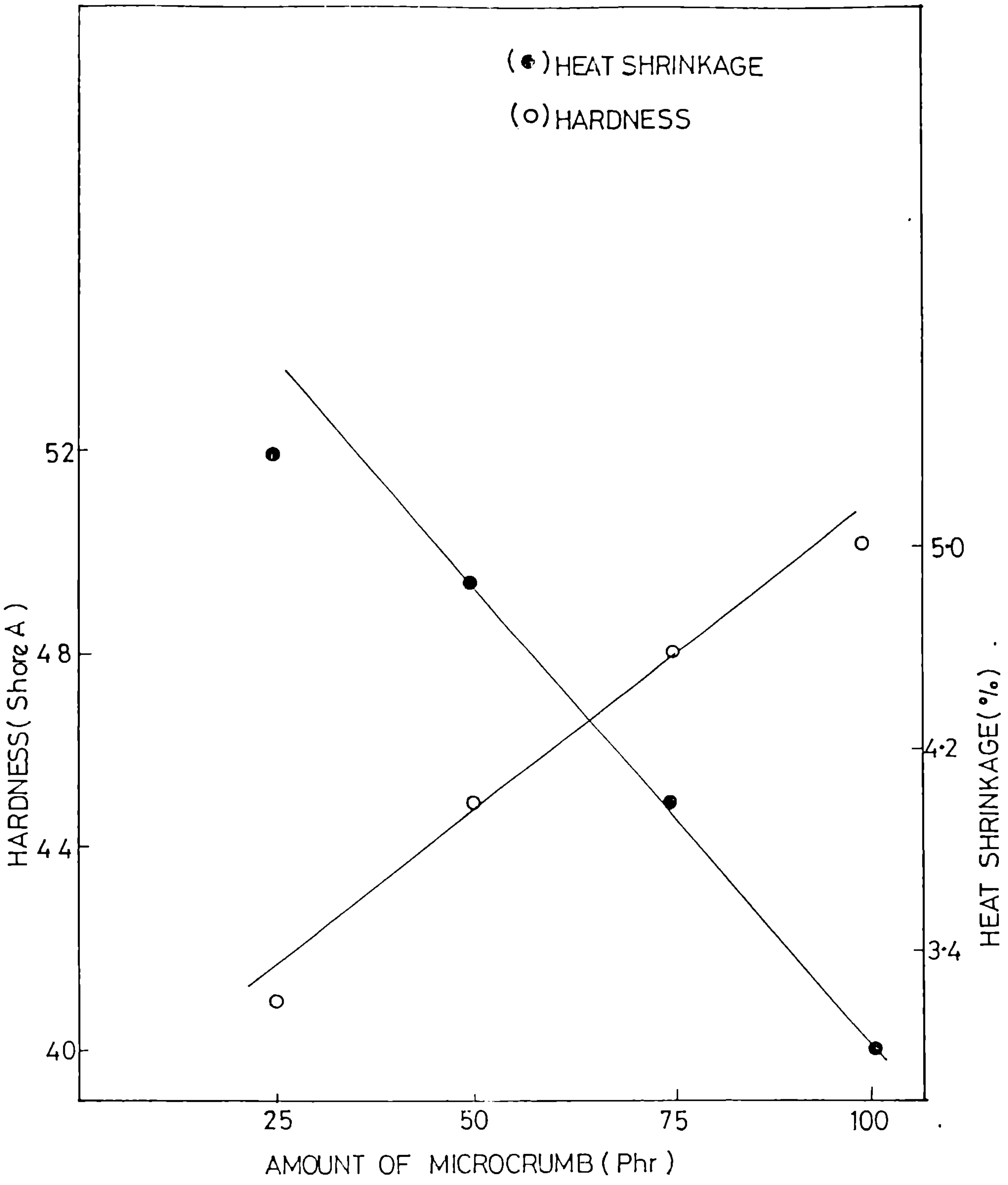

Fig.4.1.10 Variation of heat shrinkage and hardness with SBS/SBR microcrumb.

Flex crack resistance of the MC sheets are shown in Table 4.1.2b, SBS/SBR based MC soling starts cracking after 300,000 cycles. Crack growth is also found to be low after 100,000 cycles with increase in the amount of microcrumb.

It is observed that split tear strength, hardness and abrasion resistance improve by the addition of microcrumb eventhough the expansion of MC sheets is marginally lower.

4.1.3 Effect of percentage precure on properties of SBS/SBR blend based MC sheets

Experimental

A 50:50 SBS/SBR blend was used for this study. Table 4.1.3a gives the formulation used for the MC sole compounds. The compounds were precured to different percentages of their optimum cure times. MC sheets were prepared as per the details outlined in section 4.1.1 and the technical properties of the MC sheets were determined as per the procedure outlined in chapter 2.

Results and discussion

Fig. 4.1.11 shows the variation of expansion ratio and relative density with decrease as in percentage precure. As precure increases expansion of the MC sheets decreases as expected. The resulting size of the sheet is lower and consequently density is higher.

Fig.4.1.12 shows the variation of split tear strength and abrasion loss with decrease in percentage precure. Split tear strength shows an increasing trend with increase in percentage precure. A sharp increase in split tear strength is observed at 80% precure, after which tear strength marginally increases. This indicates that if the degree of precure is too low sufficient

Table 4.1.2b

Effect of SBS/SBR microcrumb on technical properties of microcellular soles based on SBS/SBR blends

Properties	Mix Number			
	A	B	C	D
Time required for optimum cure at 160°C (min.)	9	9	9.1	9.5
Initial expansion (%)	84.52	80.92	79.76	72.62
Expansion after 5 min. (%)	51.19	46.43	45.24	39.29
Expansion after 24h (%)	36.9	35.71	32.48	27.38
Change in hardness after ageing 24h at 100°C	+2	+2	+1	+1
Shrinkage after post curing (%)	7.9	5.3	4.2	3.1
Flex resistance				
a) Crack initiation in cycles	314,574	314,574	314,000	300,000
b) Crack growth at the end of 100,000 cycles (mm)	0.1	0.1	0.1	0.2

Table 4.1.3a

Formulation for SBS/SBR sole compound

Ingredients	Phr
SBS	50
SBR	50
ZnO	4
Stearic acid	5
China clay	60
Precipitated calcium carbonate	40
SBS/SBR microcrumb	50
Paraffinic oil	3
SP	1
Vulcafor F	1.2
Sulphur	2
DNPT	5

Table 4.1.3b

Effect of percentage precure on properties of SBS/SBR blend based MC sheets

Properties	Percentage precure					
	65	70	75	80	85	90
Cure time at 160°C (min.)	6.1	7.5	8.4	9.2	10.8	11.9
Initial expansion (%)	94.05	91.67	89.28	88.09	85.71	83.3
Expansion after 5 min. (%)	58.33	57.14	54.76	54.76	53.57	52.24
Expansion after 24h (%)	38.09	36.9	34.52	33.3	32.14	30.95
Shrinkage after post curing (%)	5.5	6.95	7	7	7.4	8.7

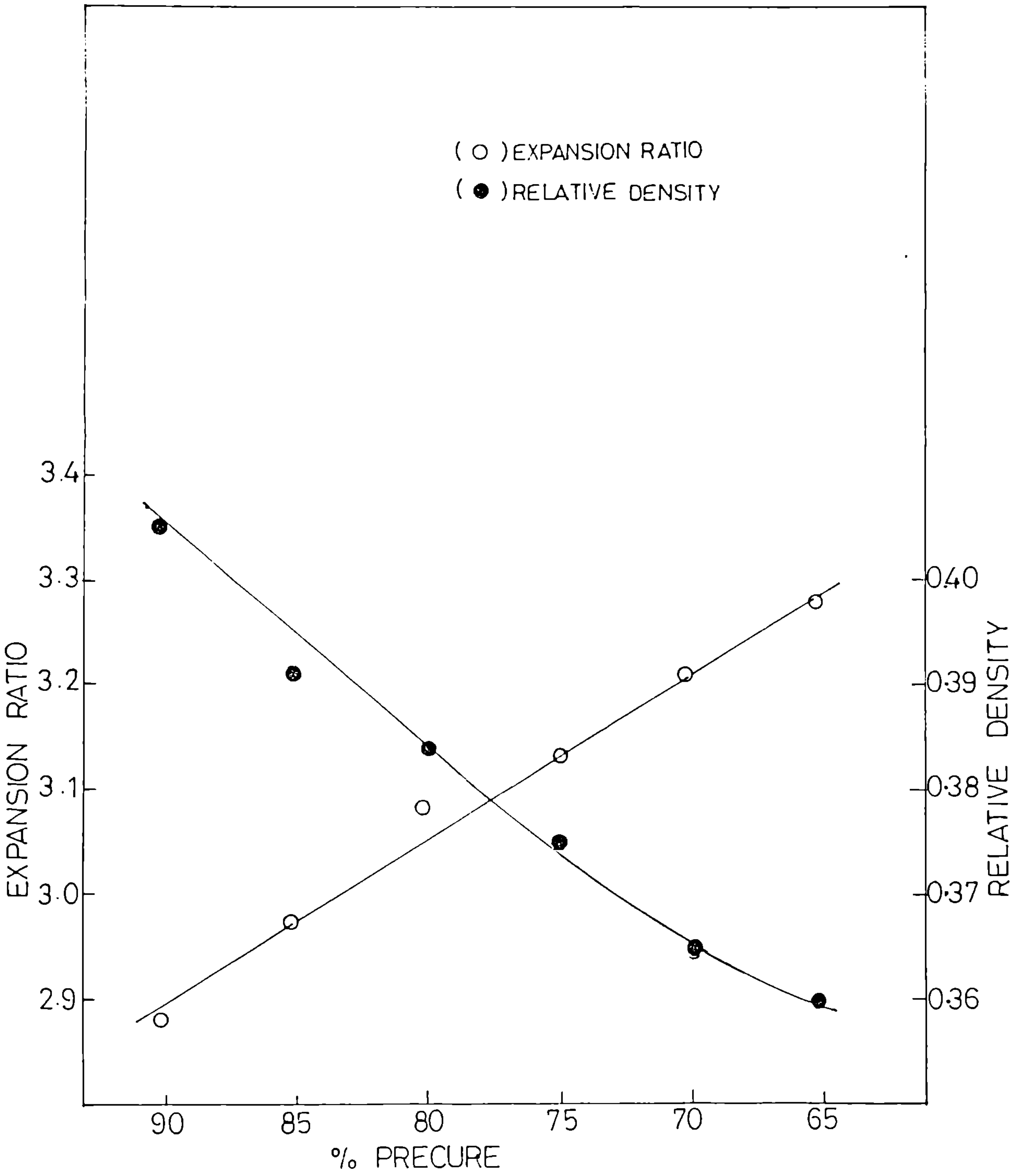

Fig.4.1.11 Variation of expansion ratio and relative density with decrease in percentage precure.

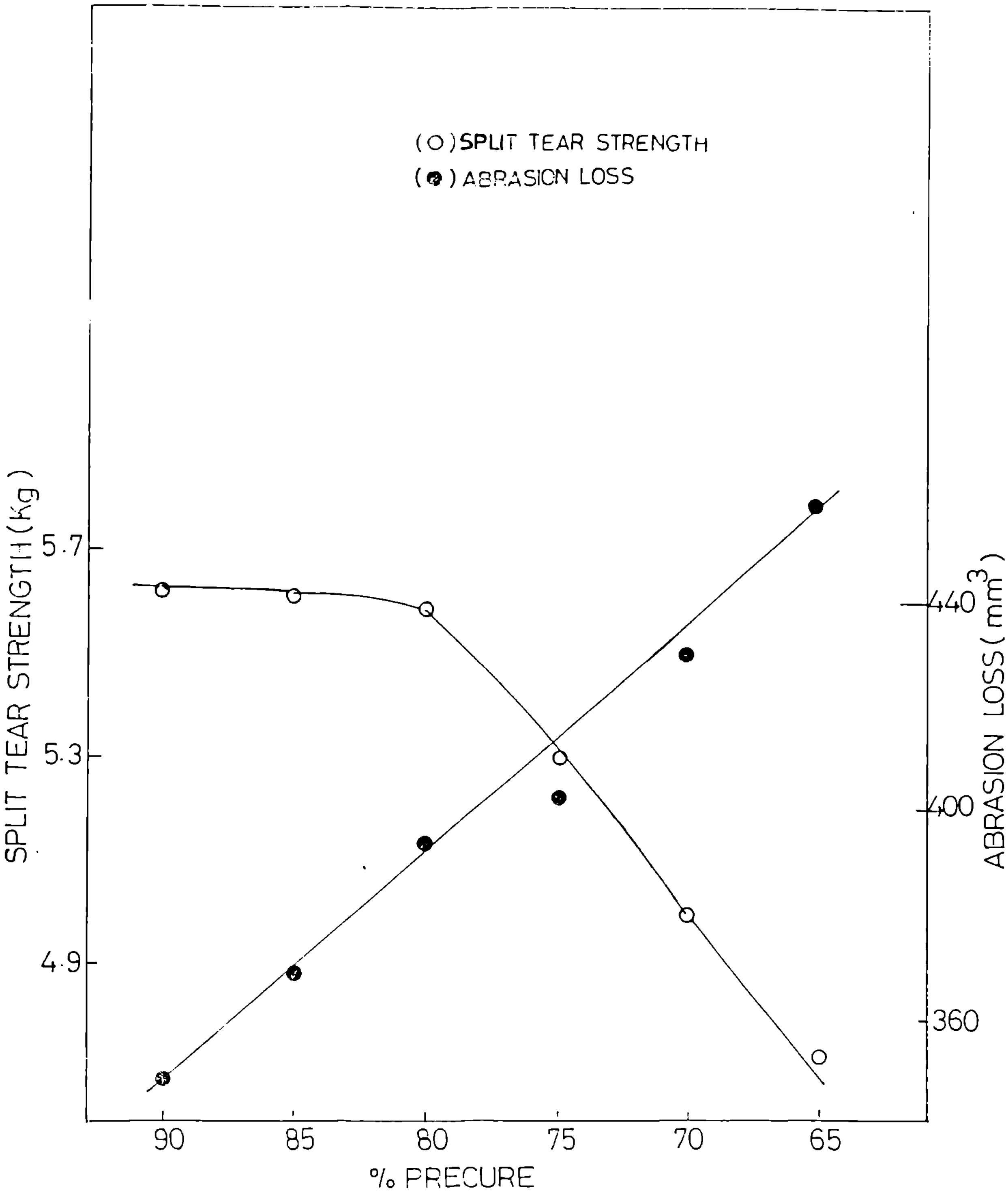

Fig.4.1.12 Variation of split tear strength and abrasion loss with decrease in percentage precure.

strength is not developed in the sheet. But after 80% precure, the increase split tear strength is not pronounced [21]. Abrasion loss decreases with increase in percentage precure. This is also due to the increased strength of the matrix at higher percentage precure.

Fig. 4.1.13 shows the variation of hardness and heat shrinkage with decrease in percentage precure. Hardness of the MC sheets increase with increase in percentage precure while heat shrinkage decreases with increase in percentage precure.

Fig.4.1.14 shows the variation of compression set and water absorption with decrease in percentage precure. Compression set and water absorption decrease with increase in percentage precure. This indicates that when a low percentage precure is given sufficient strength is not developed . So at low percentage precure compression set is high. Water absorption which is a measure of number of open cells, is high at a low percentage precure due to formation of larger number of open cells.

Shrinkage after post cure is high when 90% precure is given as shown in Table 4.1.3b. On post cure and storage the internal pressure of gas comes down due to diffusion of gas and the shrinkage becomes more. To control shrinkage of the final product it is necessary to give as low a degree of precure as possible. But if the precure is too low split tear strength is low and expansion is high. Consequently abrasion loss is high and hardness is low. The study shows that an optimum level of precure is necessary to achieve good technical properties.

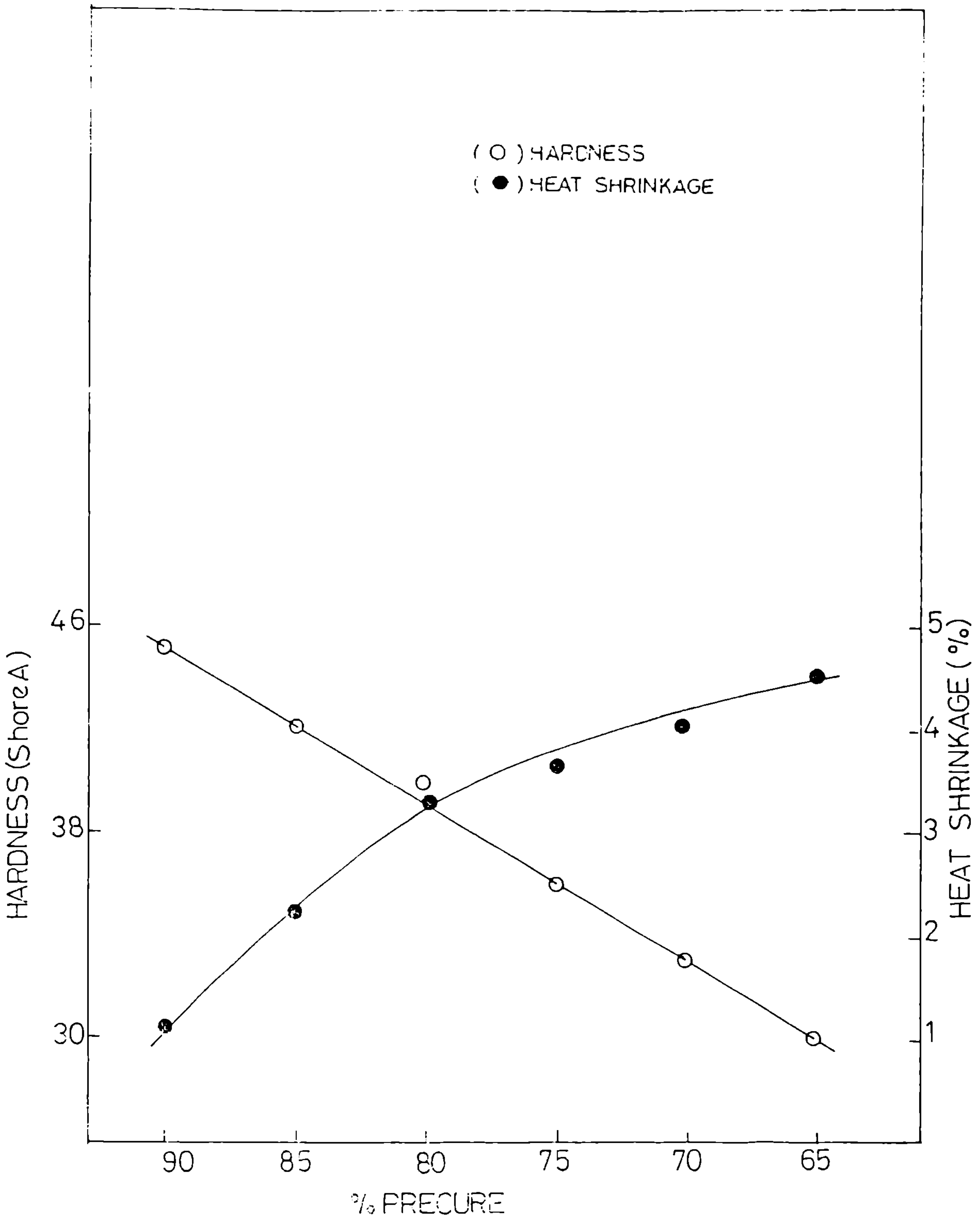

Fig.4.1.13 Variation of hardness and heat shrinkage with decrease in percentage precure.

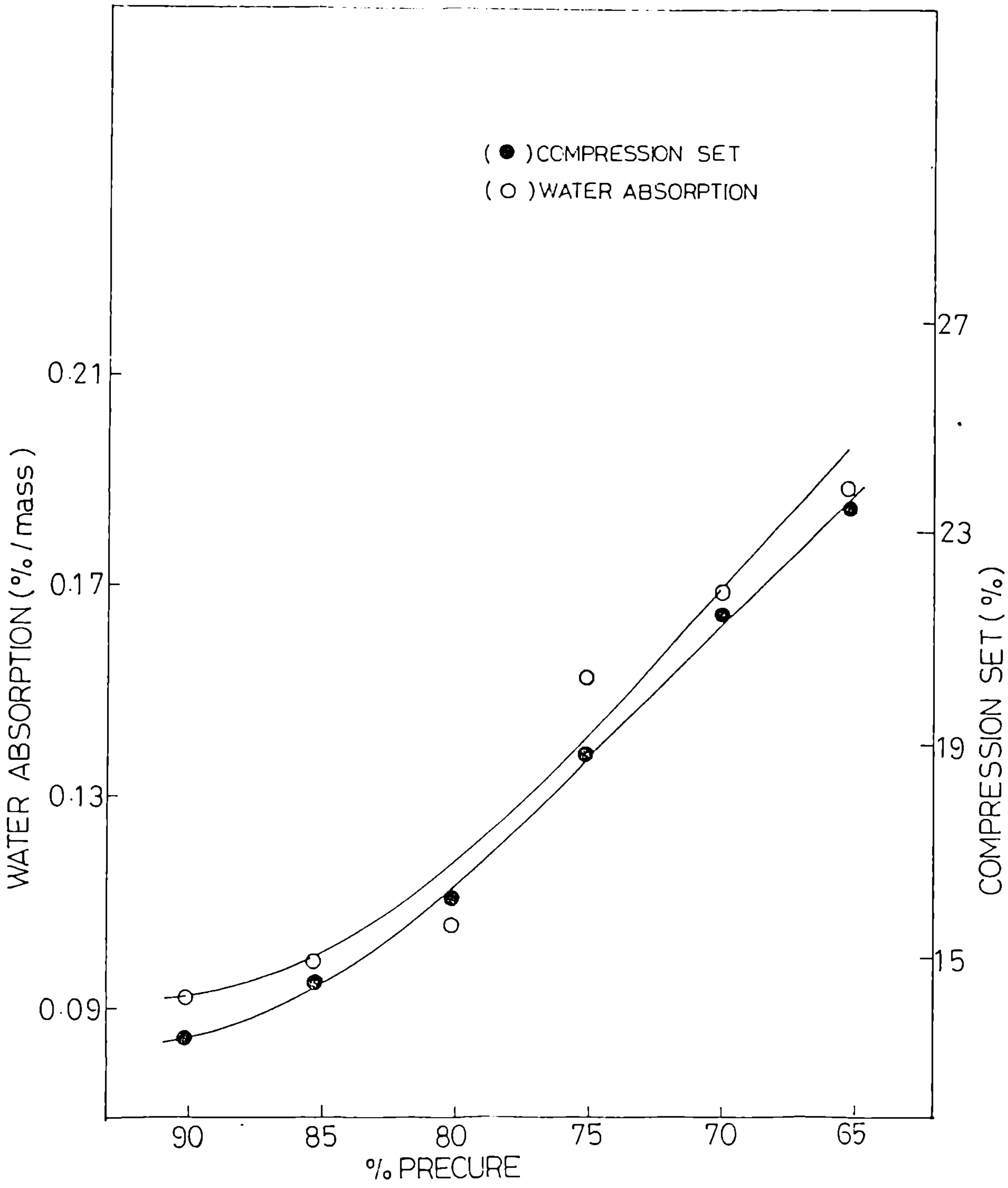

Fig.4.1.14 Variation of water absorption and compression set with decrease in percentage precure.

4.1.4 Effect of post curing time and temperature on technical properties of microcellular soles based on SBS/SBR blends

Experimental

A 50:50 blend of SBS and SBR was used for this study. Compounding moulding and determination of technical properties were done as per the procedure described in section 4.1.1. Formulation used is shown in Table 4.1.3a. In order to find out the effect of post curing temperature on the technical properties the expanded sheets were post cured at different temperatures viz., 70, 80, 90 and 100°C in an air oven for 2 hrs. Post curing time was varied from 1h to 3h at the optimum post curing temperature and its effect on the technical properties was also determined.

Results and discussions

Table 4.1.4a shows the effect of post curing temperature on technical properties of MC soles based on SBS/SBR blends. Expansion of the MC sheets decreases with increase in post cure temperature while the relative density increases. Hardness and split tear strength of the MC sheet also increase with increase in post curing temperature. This is obviously due to the lower expansion of MC sheets. Abrasion loss and heat shrinkage decrease with increase in post curing temperature as shown in table. This further shows that as post curing temperature increases the expansion decreases. Compression set and water absorption decrease with increase in post curing temperature. This shows that curing of the sheets continues and the extent of crosslinking increases as the post curing temperature increases. As the post curing temperature increases technical properties get improved but the size of sheet decreases. So

Table 4.1.4a

Effect of post curing temperature on mechanical properties of SBS/SBR blend based MC sheets

Properties	Post curing temperature °C			
	70	80	90	100
Expansion ratio before post cure	2.24	2.24	2.23	2.26
Expansion ratio after post cure	2.29	2.14	2.0	1.94
Relative density	0.447	0.45	0.474	0.505
Shrinkage after post curing (%)	7.51	4.9	3.44	2.99
Hardness (Shore A)	39	44	45	48
Change in hardness after ageing 24h at 100°C	+2	+1	+1	+1
Abrasion loss (mm^3)	542	460	444	402
Split tear strength (kg)	4.08	4.46	4.51	4.65
Water absorption (percent by mass)	0.204	0.104	0.091	0.084
Compression set (%)	20.4	17.1	14.5	13.2

80°C at which all the technical properties are within the IS limits is selected as the optimum post cure temperature.

Table 4.1.4b shows the effect of post curing time on technical properties of SBS/SBR blend based MC soles. Expansion of the sheets decreases with increase in post curing time. When 3h post curing is given expansion of the MC sheet is found to be lowest. Consequently maximum density is obtained at 3h post curing time. Other technical properties show similar trend as in the case of post curing temperature. Since the size of the sheet gets reduced with post curing time 2h at which properties are optimum is chosen as the post curing time.

CONCLUSION

1. The 50:50 SBS/SBR blend is a potential base material for good quality soles.
2. SBS/SBR microcrumb can be used as an effective low cost filler in SBS/SBR blend based MC soles. Split tear strength, abrasion resistance, hardness, compression set etc. are improved by the addition of microcrumb. About 50 phr SBS/SBR microcrumb can be used without any reduction in technical properties.
3. The optimum percentage of precuring required for microcellular soles is 80% for SBS/SBR blends.
4. The optimum post curing temperature is 80°C and post curing time 2 hours for obtaining good technical properties.

Table 4.1.4b

Effect of post curing time on mechanical properties of SBS/SBR blend based MC sheets

Properties	Post curing time (min.)		
	60	120	180
Expansion ratio before post cure	2.34	2.39	2.39
Expansion ratio after post cure	2.01	1.98	1.84
Relative density	0.451	0.467	0.495
Shrinkage after post curing (%)	8.91	7.51	6.31
Heat shrinkage (%)	3.54	3.14	2.91
Abrasion loss (mm^3)	545	492	420
Split tear strength (kg)	3.95	4.12	4.39
Water absorption (percent by mass)	0.194	0.164	0.124
Hardness (Shore A)	40	42	45
Compression set (%)	21.47	18.48	15.14

PART II: STUDIES ON THE PROPERTIES OF MICROCELLULAR SOLES BASED ON SBS/NR AND SBS/NR/HSR BLENDS

Excellent flex and tear resistance make SBS suitable for shoe soles. SBS has also excellent skid resistance, low shrinkage and flexibility at low temperature. This versatility has enabled SBS to find a major application in footwears [22]. Styrenic block copolymers are technologically compatible with a wide range of materials and hence they can be blended with other elastomers to give useful products [23]. Conventional NR/HSR based MC soles show fungal growth on storage, but SBS based MC soles do not absorb moisture and hence are resistant to fungal growth.

Butadiene-styrene copolymers with a high proportion of styrene (about 50-90) weight percentage have a hardening effect on rubber vulcanizates and have the desirable characteristics of a good soling material [24]. The addition of HSR increases the hardness of products without much change in density. The hardening is more for HSR having higher styrene content. It gives a leathery flexibility desirable in soling material and about four times wear resistance compared to leather [25,26]. High styrene resins (HSR) are primarily used with NR and SBR for hard and light soles since the styrene resins when incorporated into the rubber network, severely soften the vulcanizates at high temperatures [24]. To obtain necessary hardness and flexibility which are the characteristics of microcellular soles, high-styrene resin can be blended with SBS and NR.

This study reports the development of microcellular soles based on SBS/NR and SBS/NR/HSR blends. The mechanical properties of SBS/NR and SBS/NR/HSR blends and the microcellular soles based on them are proposed to be investigated.

4.2.1 Effect of SBS content on properties of SBS/NR blends and microcellular soles based on SBS/NR blends

Experimental

SBS/NR blend was prepared using a Brabender plasticorder model PL 3S at a temperature of 110°C for 6 min. at a rotor speed of 50 rpm. The SBS content was varied from 40 to 70 weight percent. For preparing SBS/NR/HSR ternary blends, HSR was passed through the tight nip of a laboratory mixing mill and sheeted out and then added to SBS/NR blend at different percentages.

The above blends were compounded (without blowing agent) as per formulations given in Tables 4.2.1 and 4.2.2 respectively. Mixing was carried out on a laboratory size two roll mill. The compounds were vulcanized to their respective optimum cure times at 160°C in an electrically heated hydraulic press. The mould was clamped under pressure when it was in the press and then water cooled after taking out.

The tensile properties and tear strength of the vulcanizates were measured on a Zwick universal testing machine 1445, using a crosshead speed of 500 mm/min.

Table 4.2.1

Formulations and vulcanizate properties of SBS/NR blends

Ingredients (phr)	Mix Number				
	1	2	3	4	5
SBS	40	50	60	70	80
NR	60	50	40	30	20
ZnO	4	4	4	4	4
Stearic acid	5	5	5	5	5
China clay	60	60	60	60	60
Precipitated calcium carbonate	40	40	40	40	40
Naphthenic oil	5	5	5	5	5
SP	1	1	1	1	1
Wood rosin	2	2	2	2	2
Vulcafor F	1.2	1.2	1.2	1.2	1.2
Sulphur	2	2	2	2	2
DNPT	5	5	5	5	5
Cure characteristics					
Optimum cure time T_{90} at 160°C (min.)	9	9.2	9.4	9.4	9.5
Properties					
Tensile strength (N/mm^2)	7.5	7.8	7.6	5.7	3.2
Tear strength (N/mm)	29.17	30.1	30.97	27.93	26.53
Elongation at break (%)	500	480	400	270	280

Table 4.2.2

Formulations and vulcanizate properties of SBS/NR/HSR blends

Ingredients (phr)	Mix Number			
	A	B	C	D
SBS	50	50	50	50
NR	50	35	30	25
HSR	--	15	20	25
ZnO	4	4	4	4
Stearic acid	5	5	5	5
China clay	60	60	60	60
Precipitated calcium carbonate	40	40	40	40
NR/HSR microcrumb	50	50	50	50
Naphthenic oil	5	5	5	5
SP	1	1	1	1
Wood rosin	2	2	2	2
Vulcafor F	1.2	1.2	1.2	1.2
Sulphur	2	2	2	2
DNPT	5	5	5	5
Cure characteristics				
Optimum cure time T_{90}(min.)at 160°C	10	11.1	10.9	10.5
Properties				
Tensile strength (N/mm2)	7.8	6.8	6.9	7.1
Tear strength (N/mm)	26.64	26.53	27.93	28.75
Elongation at break (%)	480	430	390	380
Hardness (Shore A)	48	50	52	55

Preparation of microcellular sheets

SBS/NR and SBS/NR/HSR blends were compounded as per formulations given in Tables 4.2.1 and 4.2.2 respectively. The mixing was carried out on a laboratory size two roll mixing mill and curatives and blowing agent were added on a cold mill. The microcellular sole was moulded in an electrically heated hydraulic press at 160°C up to 80% upto of their optimum cure time. The mould was loaded with 3 to 5 percent excess of the compound on volume basis. The expanded sheets were then post cured in an air oven at 80°C for 2h.

The technical properties of MC sheets were measured as per relevant Indian standards as described in chapter 2. The cell structure of selected samples were observed using an optical microscope.

Results and discussion

A. Studies on SBS/NR blends

Table 4.2.1 shows the cure characteristics and vulcanizate properties of SBS/NR blends. The optimum cure time of the compounds increase marginally with SBS content. Tensile strength of the vulcanizates increase with increase in SBS content in the blend up to 60% similar to the behaviour of SBS/SBR blends. Further increase in the amount of SBS produces a decrease in tensile strength. Tear strength of the vulcanizates also show a similar behaviour. The elongation at break decreases with increase in SBS content in the blend. Compared to SBS/SBR blend, SBS/NR blend shows higher tensile strength. This may be due to the higher gum strength of NR compared to SBR.

Figure 4.2.1 is the variation of expansion ratio and relative density with increase in the amount of SBS in the blend. Expansion of SBS/NR based MC sheets increase with amount of SBS, while the relative density decrease. The increase in expansion may be due to the thermoplastic nature of SBS.

Figure 4.2.2 shows the variation of split tear strength and abrasion loss with increase in the amount of SBS in the blend. Split tear strength marginally increases with SBS content in the blend up to 50%. This may be due to the presence of PS domains in SBS and also due to the presence of NR which can undergo stress induced crystallisation [26,27]. Compared to SBS/SBR blend based MC sheets SBS/NR based MC sheets show higher split tear strength. Abrasion loss of the MC sheet increases with increase in SBS content in the blend. This increase in abrasion loss is probably due to the decrease in cell wall thickness, as the cell wall thickness decreases with increasing expansion of MC sheets as shown in Table 4.2.3.

Figure 4.2.3 shows the variation of water absorption and compression set with increase in the amount of SBS in the blend. Water absorption increases with increase in the amount of SBS. This is obviously due to the increase in the percentage of open cells. Compression set values increase with increasing amount of SBS in the blend. The increase is more pronounced at higher concentration of SBS in the blend. This may be due to the higher expansion of the MC sheets and also due to lower extent of crosslinking of the SBS phase at higher concentration of SBS.

Figure 4.2.4 shows the variation of hardness and heat shrinkage with SBS content in the blend. Hardness of the MC sheets decrease with increasing amount of SBS in the blend.

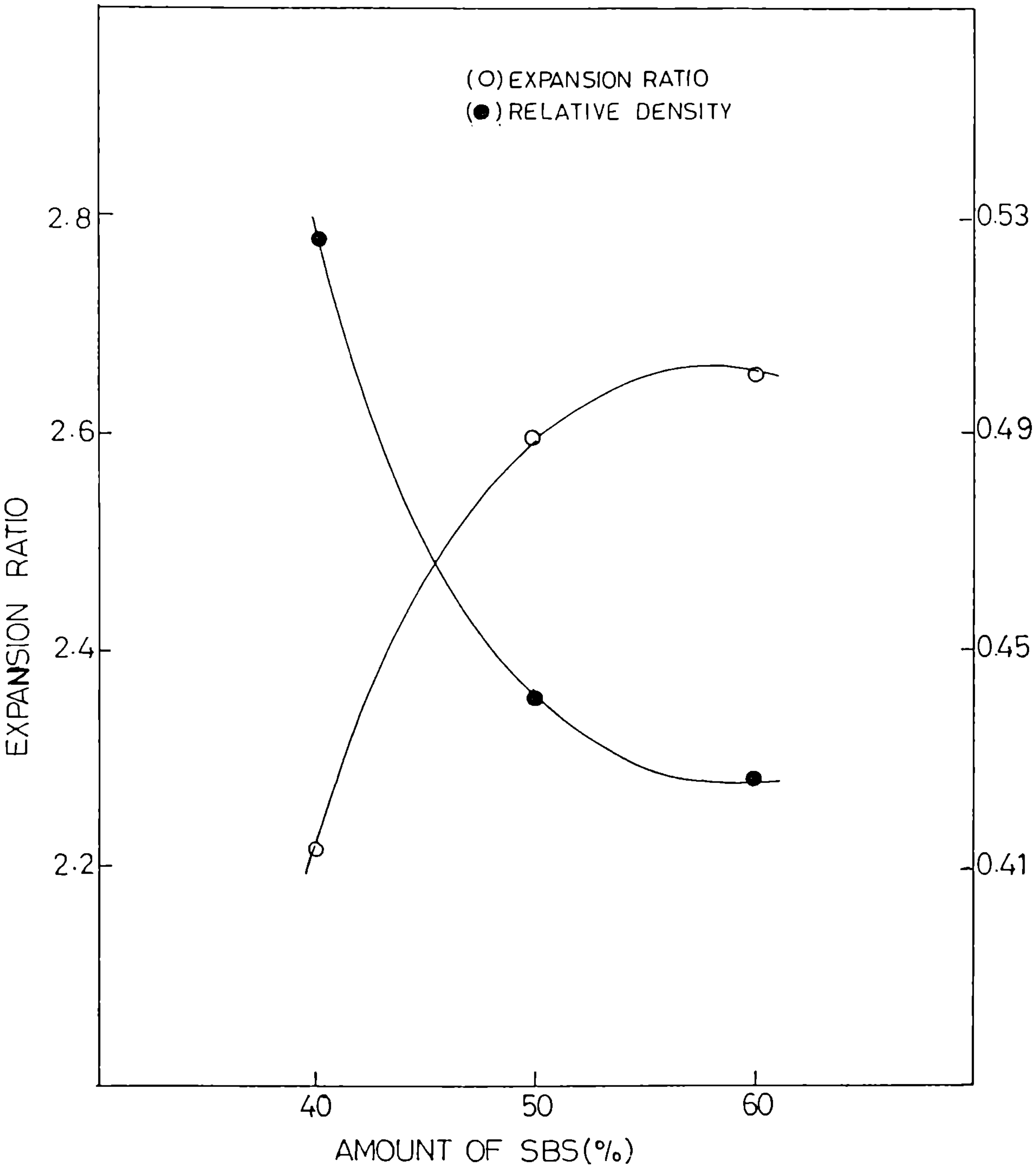

Fig.4.2.1 Variation of expansion ratio and relative density with increase in the amount of SBS.

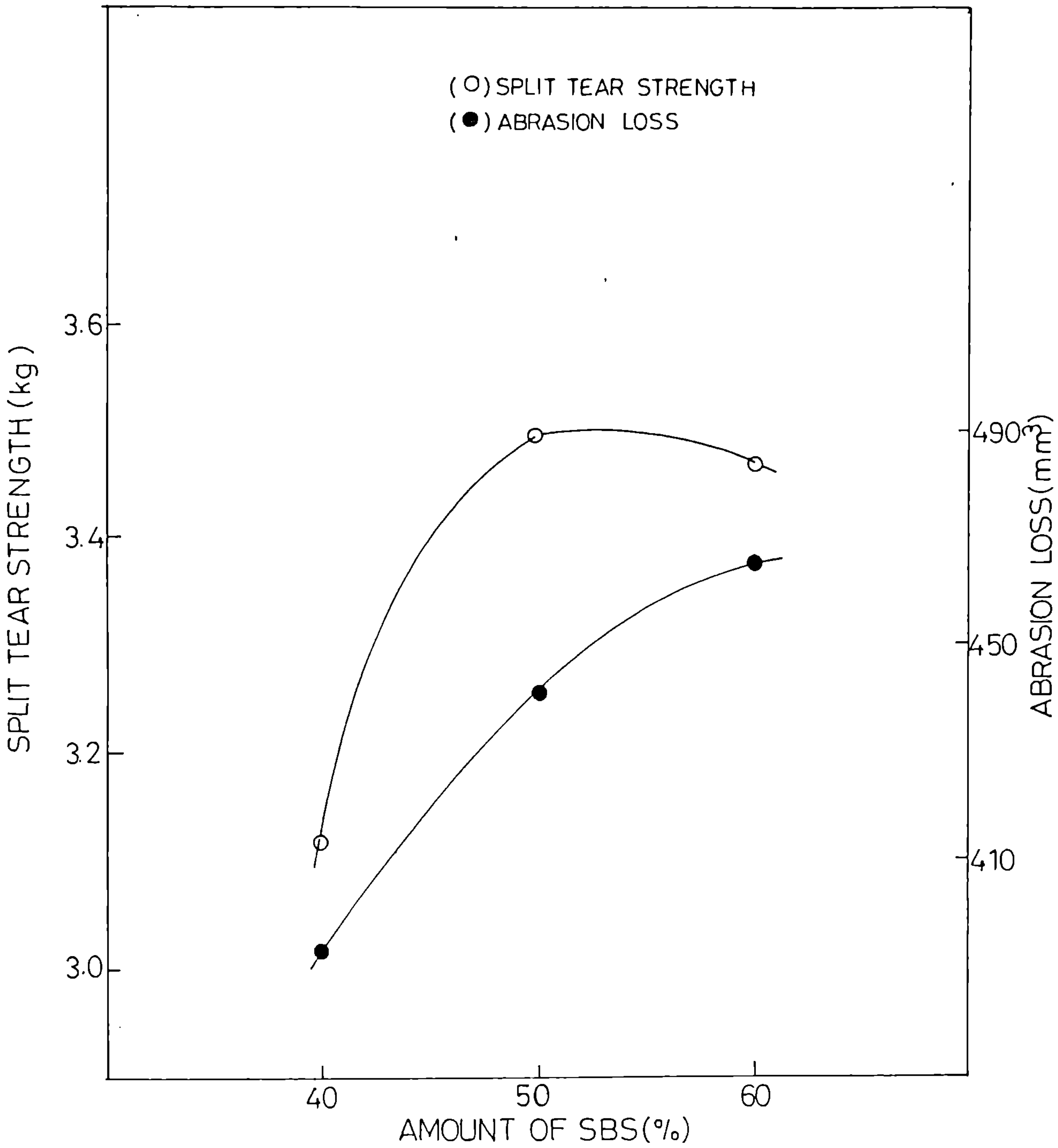

Fig.4.2.2 Variation of split tear strength and abrasion loss with increase in the amount of SBS.

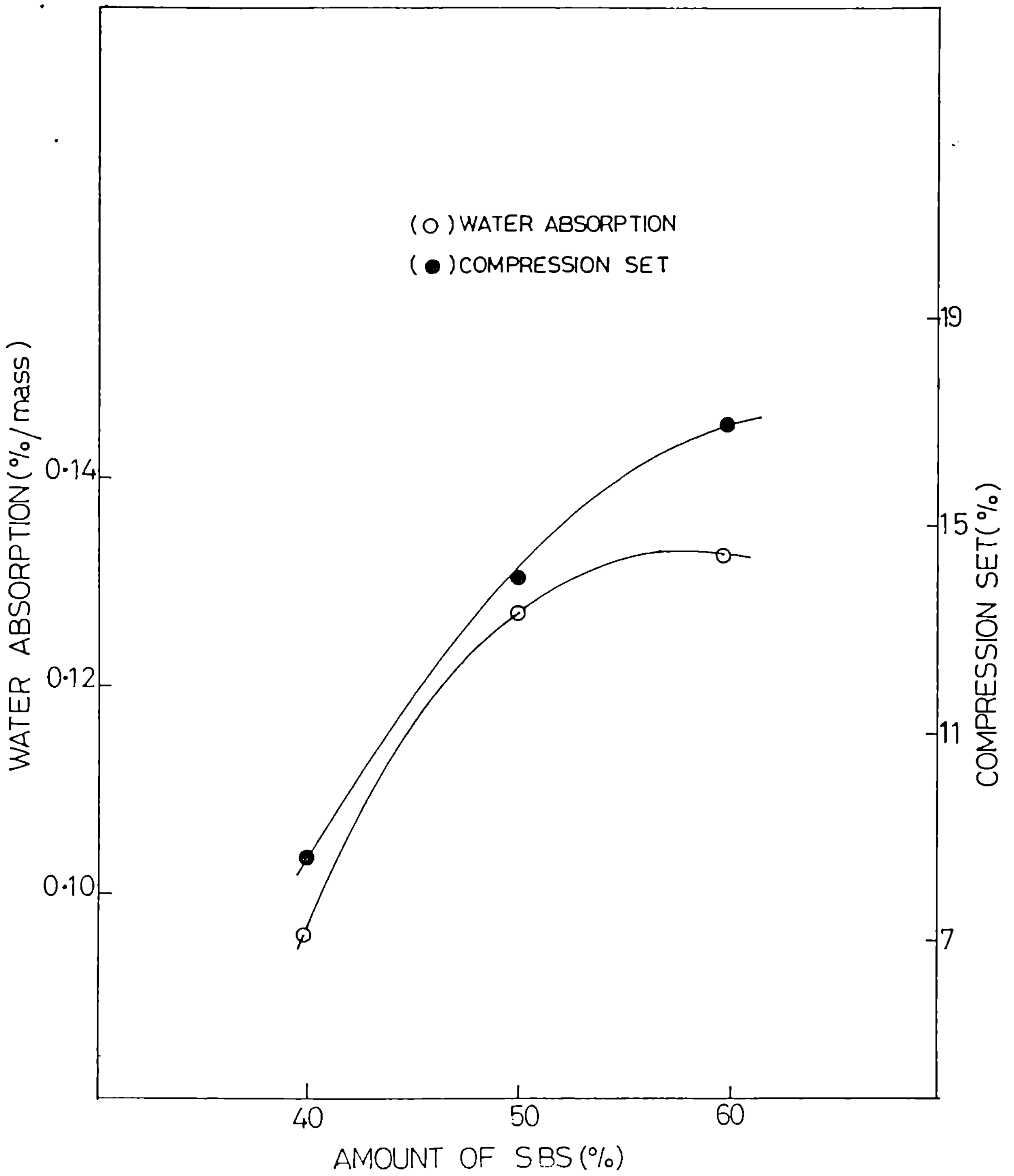

Fig.4.2.3 Variation of water absorption and compression set with increase in the amount of SBS.

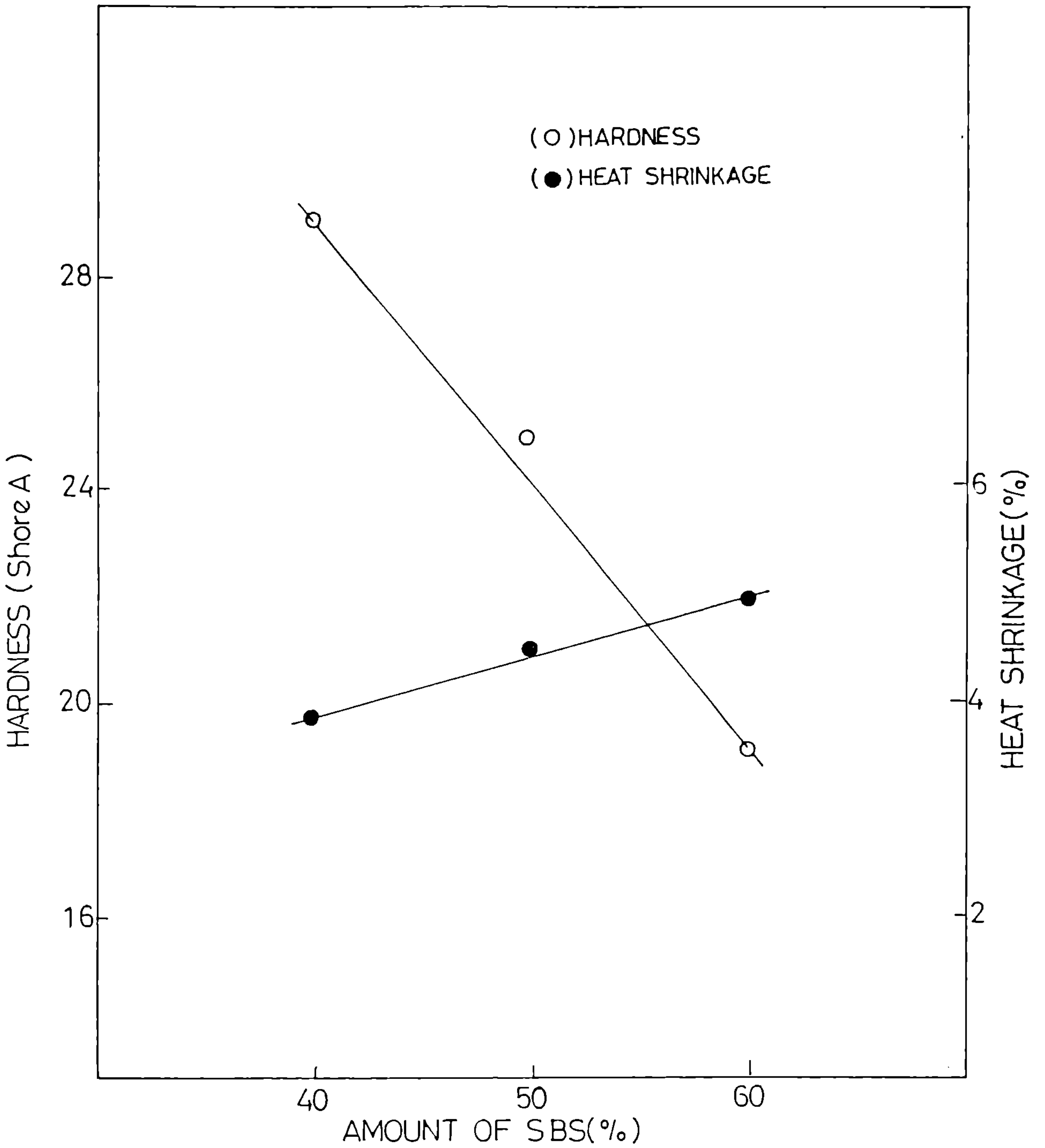

Fig.4.2.4 Variation of hardness and heat shrinkage with increase in the amount of SBS.

This is due to the increase in expansion of the MC sheet. Heat shrinkage increases with increasing amount of SBS and this increase may be due to the increased number of open cells produced at higher expansion. This observation is further proven from the increased water absorption of MC sheets. The larger cell size and lower wall thickness permit more diffusion of gas.

Flex crack resistance of samples are shown in Table 4.2.3. Compared to SBS/SBR based MC soles, SBS/NR based MC soles show less flex crack resistance. However, crack growth at the end of 100,000 cycles is more or less the same as that of SBS/SBR based MC soles. Shrinkage after post curing also increases with increase in SBS content as shown in table.

4.2.2 Use of NR/HSR microcrumb as filler in microcellular soles based on SBS/NR blends

Experimental

A 50:50 SBS/NR blend was selected for this study. The blend was compounded as per formulation given in Table 4.2.4a on a laboratory mixing mill. The microcellular sheets were prepared as per the procedure outlined in section 4.2.1. The technical properties were determined according to the relevant Indian standards.

Results and discussion

Table 4.2.4b shows the technical properties of MC soles based on SBS/NR blends. Expansion of the MC sheets marginally decrease by the addition of NR/HSR microcrumb. Consequently relative density increases. Because of the increase in density, properties like

Table 4.2.3

Effect of SBS content on technical properties of microcellular Soles based on SBS/NR blends

Properties	Mix Number		
	1	2	3
Time required for optimum cure T_{90} (min) at 160° C	8.5	9.0	9.2
Initial expansion (%)	73.81	88.1	89.28
Expansion after 5 min. (%)	41.66	47.62	47.62
Expansion after 24h (%)	28.57	32.14	33.2
Shrinkage after post curing (%)	5.1	5.5	6.1
Change in hardness after ageing 24h at 100°C	+1	+2	+3
Flex resistance			
a) Crack initiation in cycles	301,496	300,000	300,058
b) Crack growth at the end of 100,000 cycles (mm)	No crack growth	0.1	0.1

Table 4.2.4a

Formulation of SBS/NR based microcellular sole compound

Ingredients (Phr)	Mix Number	
	6	7
SBS	50	50
NR	50	50
ZnO	4	4
Stearic acid	5	5
China clay	60	60
Precipitated calcium carbonate	40	40
NR/HSR microcrumb	- -	50
Wood rosin	2	2
Naphthenic oil	5	5
Styrenated phenol (SP)	1	1
Vulcafor F	1.2	1.2
Sulphur	2	2
DNPT	5	5

Table 4.2.4b

Effect of addition of NR/HSR microcrumb on properties of SBS/NR blend based microcellular soles

Properties	Mix Number	
	6	7
Time required for optimum cure at 160°C (min.)	8	8
Initial expansion (%)	86.9	84.52
Expansion after 5 min. (%)	62.09	51.19
Expansion after 24h (%)	46.43	33.33
Expansion ratio	3.32	2.82
Relative density	0.389	0.406
Split tear strength (kg)	2.99	3.3
Hardness (Shore A)	25	30
Change in hardness after ageing 24h at 100°C	+2	+4
Abrasion loss (mm3)	388	350
Heat shrinkage (%)	4.2	2.2
Compression set (%)	17.3	16.4
Shrinkage after post curing at 80°C 2h (%)	6.06	5.83
Water absorption (% by mass)	0.128	0.119
Flex resistance		
a) Crack initiation in cycles	285,460	286,000
b) Crack growth at the end of 100,000 cycles (mm)	0.1	0.1

hardness and split tear strength increase with the addition of NR/HSR microcrumb. Heat shrinkage, abrasion loss and water absorption decrease with the addition of NR/HSR microcrumb. Shrinkage after post curing also get reduced by the addition of NR/HSR microcrumb. Flex resistance of MC sheet shows no change with the addition of microcrumb.

The study shows that addition of NR/HSR microcrumb improve the technical properties of SBR/NR blend like split tear strength, hardness, abrasion resistance etc. and it can be loaded upto about 50 phr.

4.2.3 Effect of percentage precuring on properties of SBS/NR based MC soles

Experimental

A 50:50 SBS/NR blend was used for this study also. The blend was compounded as per the formulation given in Table 4.2.5a. In order to study the effect of percentage precure of MC sheets based on SBS/NR blends, the MC sheets were precured in the mould to different percentages of their optimum cure times The MC sheets were prepared as per the procedure outlined in section 4.2.1. and the technical properties were determined as per the procedure given in chapter 2.

Results and discussion

Fig. 4.2.5 shows the variation of expansion ratio and relative density with decrease in percentage precure. Expansion of the sheets decreases with increase in precure as in the case of SBS/SBR based MC sheets and consequently relative density increases with decrease in precure. Figure 4.2.6 shows the variation of split tear strength and abrasion loss with decrease in percentage precure. Split tear strength shows an increasing trend with increase in percentage

Table 4.2.5a

Formulation for SBS/NR based microcellular sole compounds

Ingredients (Phr)	Mix Number
	8
SBS	50
NR	50
ZnO	4
Stearic acid	5
China clay	60
Precipitated calcium carbonate	40
Naphthenic oil	5
SP	1
Wood rosin	2
Vulcafor F	1.2
Sulphur	2
DNPT	5

Table 4.2.5b

Effect of percentage precure on properties of microcellular soles based on SBS/NR blends

Properties	Percentage precure			
	75	80	85	90
Cure time at 160° C (min.)	8.2	8.8	9.3	10
Initial expansion (%)	90.48	88.1	86.9	80.92
Expansion after 5 min. (%)	48.8	47.62	46.43	46.43
Expansion after 24h (%)	36.7	35.71	34.52	30.95
Shrinkage after post curing (%)	8.7	8.7	8.9	9.0

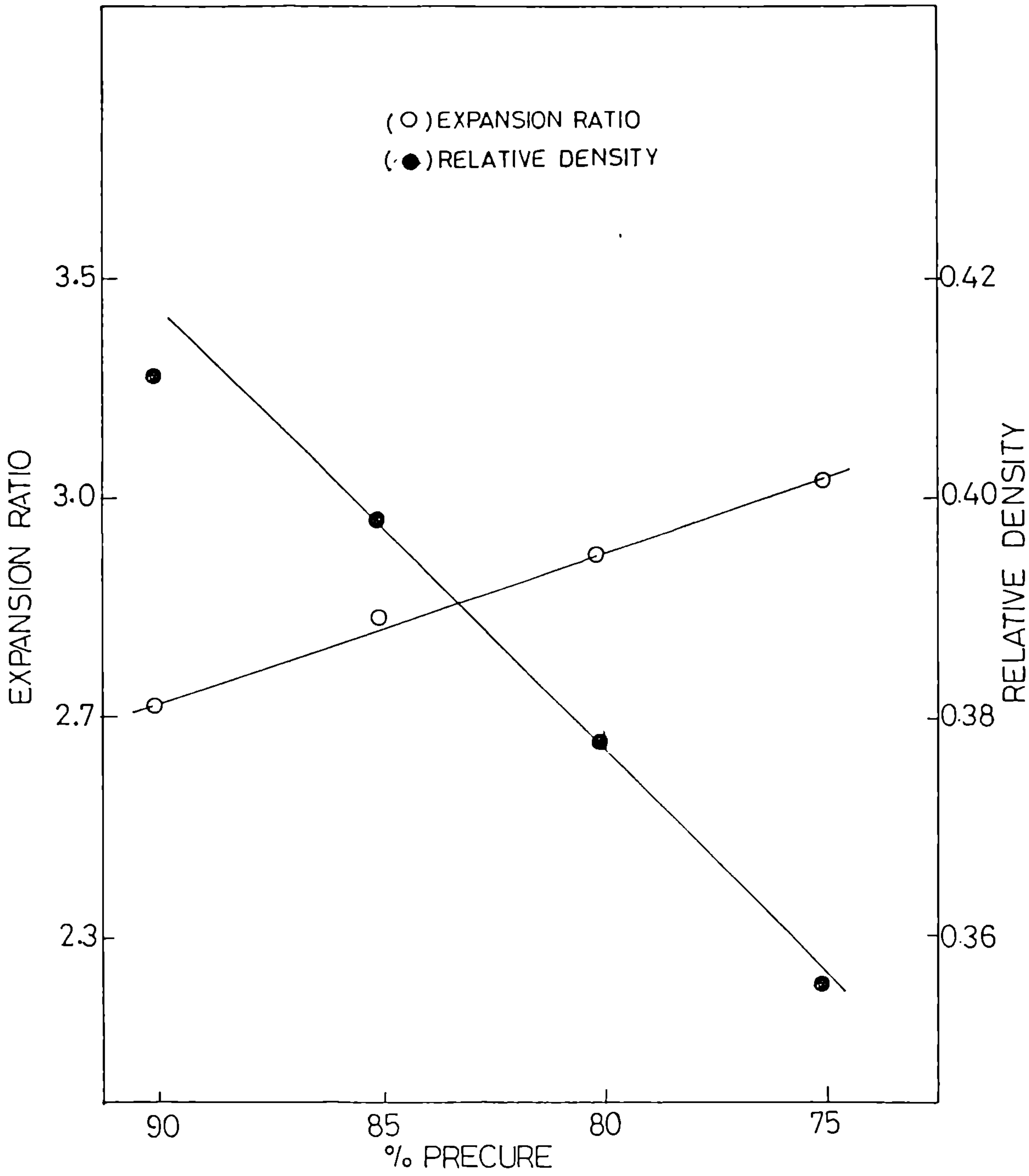

Fig.4.2.5 Variation of expansion ratio and relative density with decrease in percentage precure.

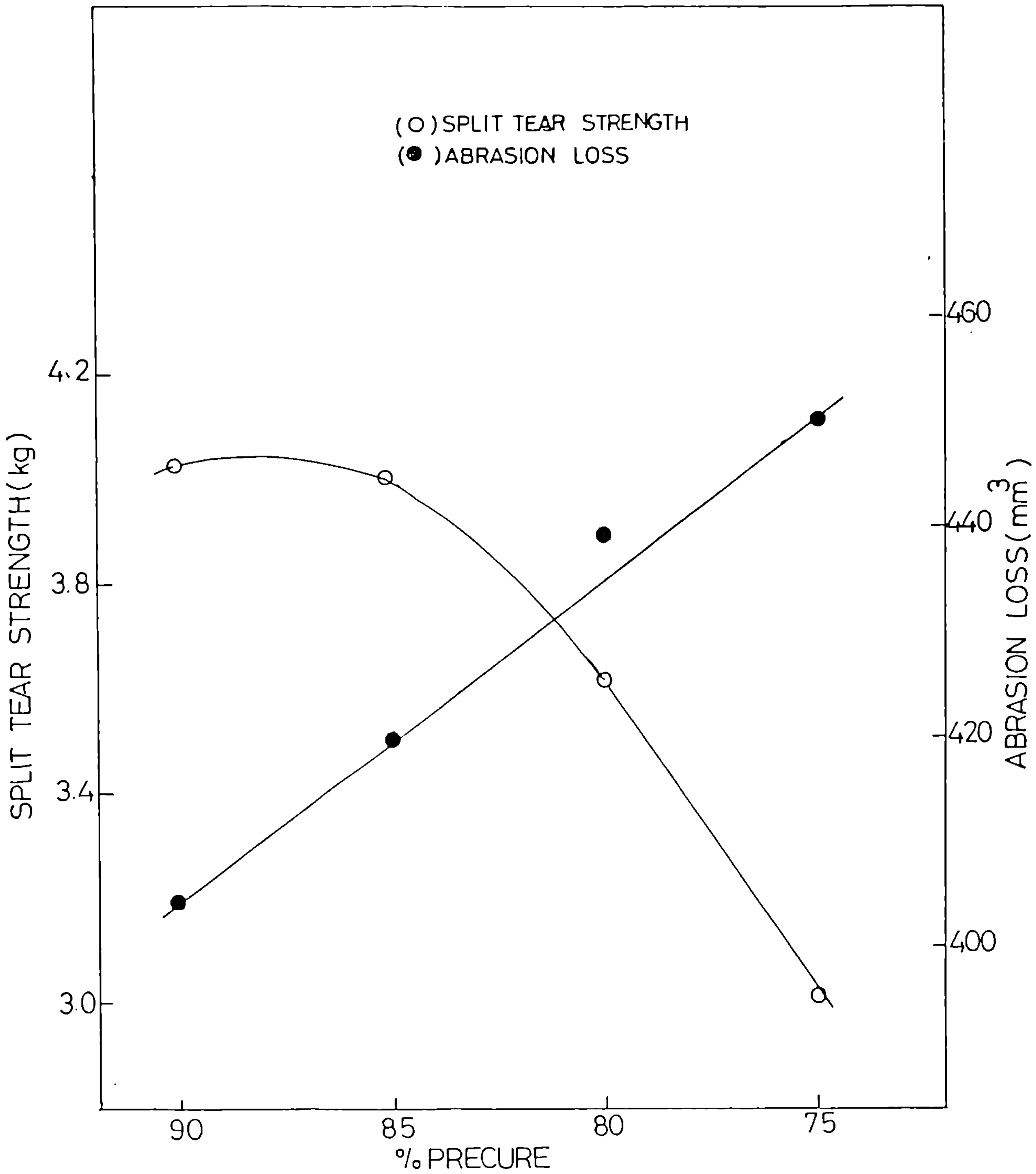

Fig.4.2.6 Variation of split tear strength and abrasion loss with decrease in percentage precure.

precure. At 75% precure the strength is too low. Maximum strength is attained when the percentage precure is 90%. Abrasion loss decreases with increase in percentage precure and it is minimum at 90% precure. This shows that an optimum level of precure is necessary for developing sufficient strength in the MC soles.

Variation of water absorption and compression set with decrease in percentage precure is shown in Fig.4.2.7. Water absorption and compression set decrease with increase in percentage precure. At high percentage precure water absorption and compression are found to be low. Variation of hardness and heat shrinkage with decrease in percentage precure is shown in Fig.4.2.8. Hardness of the MC sheet increases with increase in precure as expected. Heat shrinkage remains unchanged with increase in percentage precure.

Shrinkage after post curing becomes higher when high degree of precure is given as shown in Table 4.2.5b. When a low degree of precure is given high expansion is obtained and consequently the hardness and the split tear strength come down. This further shows that an optimum percentage of precure has to be given for getting best technical properties.

Effect of post curing time and temperature on technical properties of MC soles based on SBS/NR blends were also evaluated. Results are similar to those of SBS/SBR blend based MC soles.

B. Studies on SBS/NR/HSR blends

Cure characteristics and vulcanizate properties of SBS/NR/HSR blends are shown in Table 4.2.2. Addition of HSR as partial replacement of NR marginally reduces the optimum

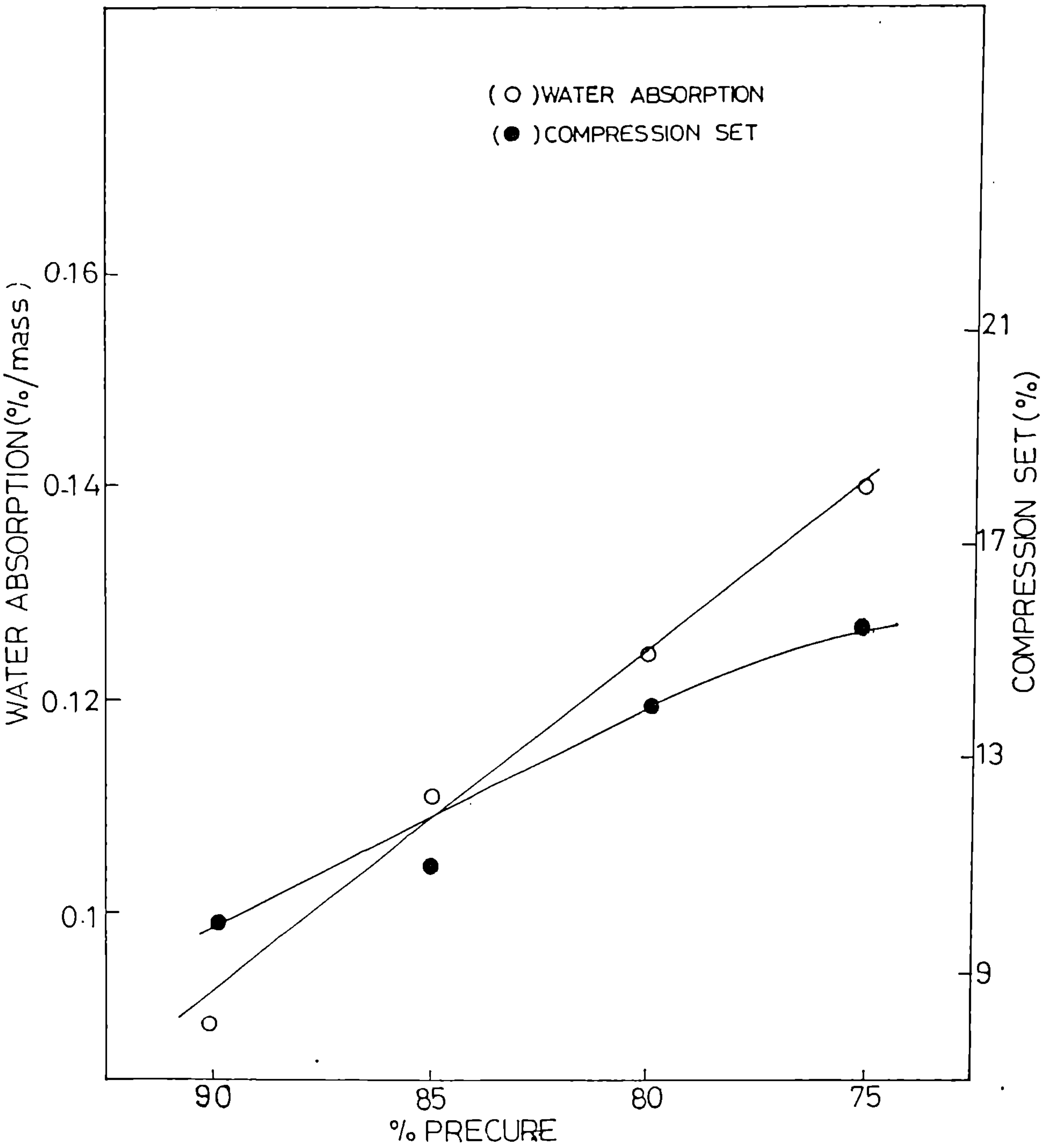

Fig.4.2.7 Variation of water absorption and compression set with decrease in percentage precure.

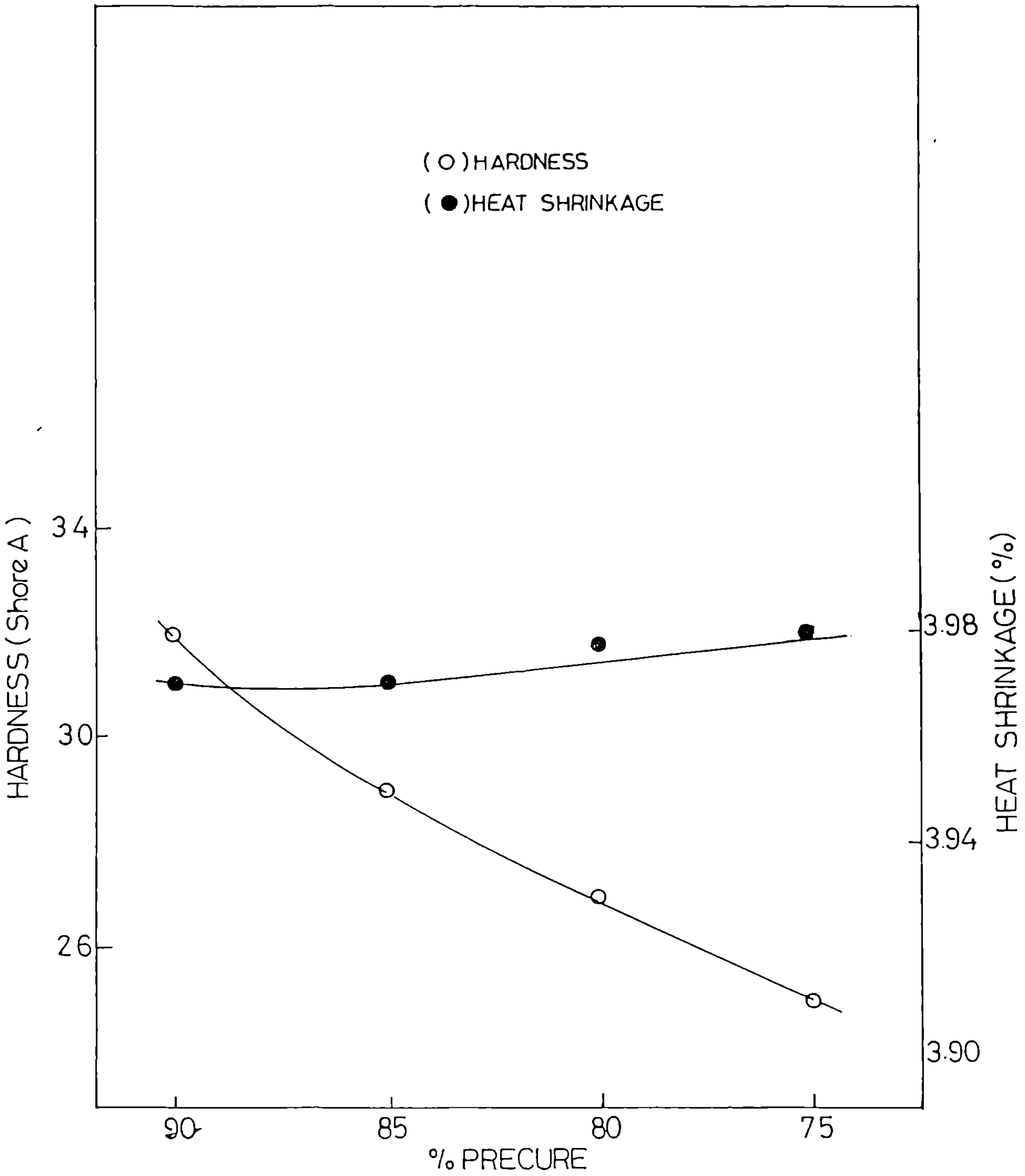

Fig.4.2.8 Variation of hardness and heat shrinkage with decrease in percentage precure.

cure time of the vulcanizates (Mixes B to D). The tensile strength increases with HSR addition while elongation at break decreases. The increase in the strength may be due to the reinforcing effect of HSR. Hardness of the vulcanizates increase with HSR content in the blend. Tear strength also increases with increase in HSR content in the blend. The improvement in hardness and tear strength is also due to the presence of HSR in the blend, which is a self reinforcing resin.

SBS/NR based microcellular sheet shows increased expansion and low density. But properties like hardness and split tear strength get marginally lowered due to the higher expansion of the MC sheets. So to improve the technical properties like hardness, and split tear strength a part of NR in SBS/NR blend is replaced by HSR.

Table 4.2.6 shows the technical properties of MC soles based on SBS/NR/HSR blends. Relative density of the microcellular sheets increase marginally when a part of NR is replaced by HSR while expansion ratio decreases marginally. Addition of HSR, increases the crosslinking between NR and HSR and prevents the expansion of the MC sheet. It may also be noticed that heat shrinkage of the MC sheets decrease with increase in the amount of HSR as shown in Table 4.2.6. Shrinkage after post curing also decreases with increase in the amount of HSR in the blend. Compression set and split tear strength increase with increase in HSR content. This may be again due to the thermoplastic nature of HSR and decreased expansion of MC sheets. Solid vulcanizates also show an increasing trend in tensile properties with the addition of HSR.

Table 4.2.6

Technical properties of microcellular soles based on SBS/NR/HSR blends

Properties	Mix No.			
	A	B	C	D
Optimum cure time T_{90} at 160° C (min)	10.5	11.1	10.9	10.8
Initial expansion (%)	98.8	85.70	84.52	81.53
Expansion after 5 min. (%)	48.8	48.8	47.62	47.62
Expansion after 24h (%)	34.52	33.3	32.14	32.14
Expansion ratio	2.89	2.74	2.73	2.78
Relative density	0.423	0.449	0.45	0.469
Hardness (Shore A)	32	38	40	46
Split tear strength (kg)	3.89	3.97	4.31	4.46
Abrasion loss (mm^3)	479.5	450.2	434	394.7
Heat shrinkage (%)	5.55	4.76	3.29	2.91
Compression set (%)	7.92	7.32	8.38	9.03
Water absorption (% by mass)	0.123	0.113	0.108	0.105
Change in hardness after ageing 24h at 100°C	+2	+2	+1	+1
Room temperature shrinkage (%)	1.67	1.11	1.05	1.05
Shrinkage after post curing (%)	8.9	8.87	8.8	7.2
Flex resistance .				
a) Crack initiation in cycles	270,712	260,000	260,000	260,000
b) Crack growth at the end of 100,000 cycles (min.)	0.05	0.1	0.1	0.1

Hardness of the microcellular sheets increase with increase in the amount of HSR as shown in Table 4.2.6. There is a large improvement in hardness when a part of the NR is replaced by HSR. This may be due to the reinforcing effect of HSR [25].

Abrasion loss of the microcellular sheets decrease with the addition of HSR due to the reinforcing effect of HSR. Water absorption shows a marginal decrease with increase in the amount of HSR in the blend. The flex resistance of the samples are shown in Table 4.2.6. The flex resistance of all the samples are found to be within the specification limit given in Indian Standards [IS: 3400 (part 16) 1974]. Crack growth after 100,000 cycles increases with the addition of HSR.

Figs.4.2.9 to 4.2.10 show the optical microscope photographs of MC sheets prepared from 60/40 SBS/NR and 50/30/20 SBS/NR/HSR blends. SBS/NR blends show a more uniform cell structure than that of the ternary blends.

CONCLUSION

1. SBS/NR blend is a potential base material for producing MC soles. The 50/50 SBS/NR blend is an ideal combination for getting good quality MC soles.
2. NR/HSR microcrumb can be used as a filler in NR/SBS blend based MC soles up to 50 phr, for cost reduction and improving the properties like hardness, split tear strength and abrasion resistance.

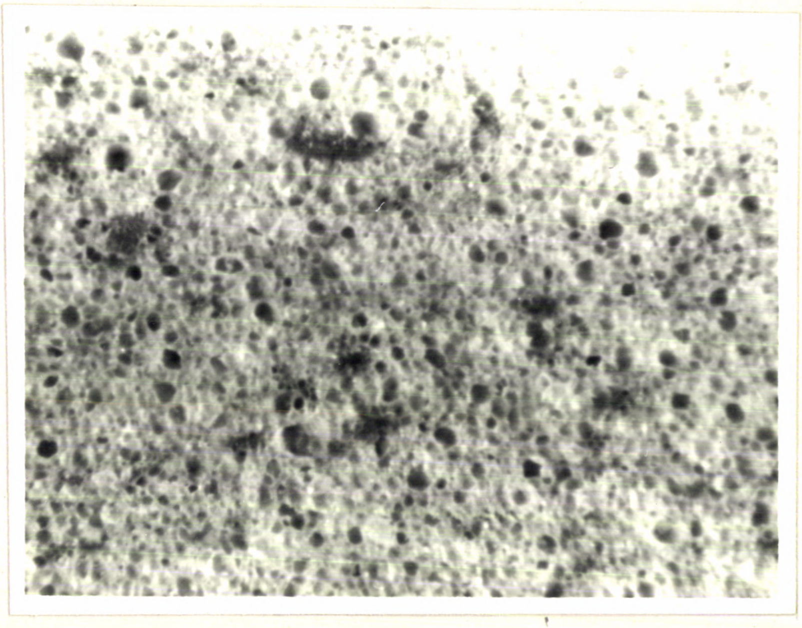

Fig.4.1.9 60/40 SBS/NR

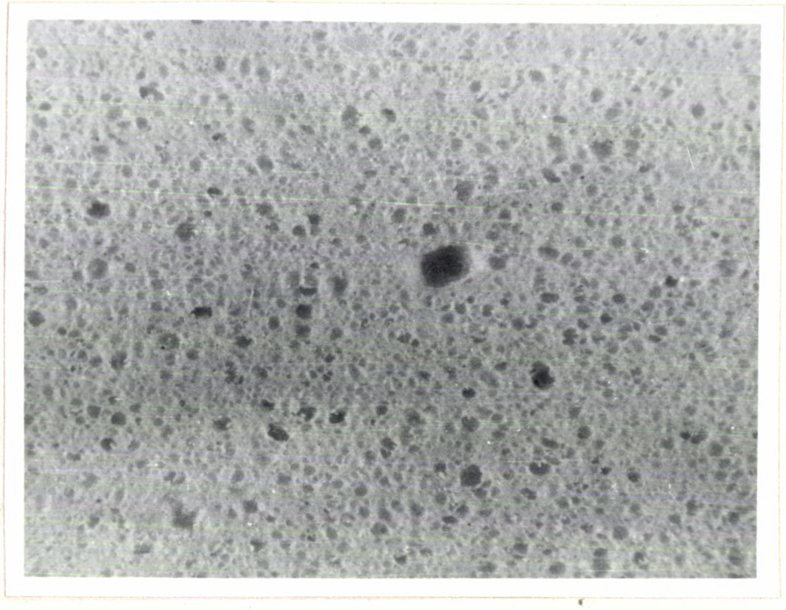

Fig.4.1.10 50/30/20 SBS/NR/HSR

Optical microscope photographs of MC sheets

3. The optimum percentage precure required for MC soles based on SBS/NR blend is about 80.
4. The technical properties like hardness, split tear strength and abrasion resistance improve while the shrinkage reduces when part of NR is replaced by HSR.

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CHAPTER 5

PART I: USE OF NR/EVA AND NR/HSR/EVA BLENDS AS NOVEL BASE MATERIALS FOR MICROCELLULAR SOLES

Ethylene vinyl acetate (EVA) copolymers are thermoplastic materials formed by the copolymersation of ethylene and vinyl acetate. Their properties are in between those of low density polyethylene, that is those possessed by semi-rigid translucent products, and those corresponding to materials of a transparent and rubbery appearance similar in many properties to plasticized PVC and certain rubbers [1]. A wide range of EVA copolymers with varying VA content and melt flow index are available.

The properties of EVA copolymers can be varied depending on the comonomer ratio, molecular weight and other structural features. EVA copolymers having 5 to 50% vinyl acetate content are classified as thermoplastic elastomers. As the vinyl acetate content increases, the polarity of the copolymer increases. This gives rise to a number of interesting properties such as compatibility with polar polymers and dielectric loss factor. The suitability for crosslinking, expansion on blowing, low temperature flexibility etc. are also improved with VA content. EVA copolymers have intrinsically good processability, can be readily pigmented to provide a range of colours and can be extended to a high level with suitable fillers [1,2].

The semicrystalline nature and polarity enable EVA copolymers to form compatible blends with many other polymers [1]. Kinetics of vulcanization and mechanical properties of NR/EVA blends have been reported [3]. Blends of EVA-PE are used in very low density microcellular soling [4].

EVA possess an overall balance of properties and hence it may be a promising alternative for HSR in microcellular soles. The aim of this study is to assess the suitability of NR/EVA blends in microcellular soling. The effect of blend ratio, blending temperature, postcuring time and temperature, amount of blowing agent and effect of addition of NR/EVA microcrumb and NR/HSR microcrumb etc. on the properties of MC soles based on NR/EVA blends are proposed to be evaluated. It is also proposed to investigate the effect of addition of EVA as a partial replacement of HSR or as a separate ingredient in microcellular soles based on NR/HSR blends.

A. NR/EVA blend based MC sheets

5.1.1 Effect of EVA content on properties of microcellular soles based on NR/EVA blends

Experimental

Blends of NR and EVA were prepared on a Brabender plasticorder model PL 3S at a rotor speed of 50 rpm at 120°C. NR was added initially and homogenized for 2 min. and then EVA was added and blended for another 4 min.

For preparing microcellular sheets, NR/EVA blends in the ratios 40:60, 30:70, 20:80, 10:90 and 0:100 were used. The blends were compounded according to the formulation given in Table 5.1.1 on a laboratory mixing mill. The ingredients were thoroughly blended and the batch was sheeted out as very thin smooth sheets. The optimum cure time of the compounds were determined using Goettfert Elastograph model 67.85. The compoundswere precured in the mould upto 80% of their optimum cure times [5] at 170°C. The mould was filled with 3-5% excess of the compound on volume basis. Hard chromium plated mould was used for

Table 5.1.1: Formulations for NR/EVA blend based microcellular sole compounds

Ingredients (Phr)	Mix Number				
	1	2	3	4	5
NR	40	30	20	10	0
EVA	60	70	80	90	100
Zinc stearate	2	2	2	2	2
Stearic acid	2	2	2	2	2
China clay	40	40	40	40	40
Precipitated calcium carbonate	40	40	40	40	40
Paraffinic oil	3	3	3	3	3
Dicumyl peroxide (40% active)	4	4	4	4	4
SP	1	1	1	1	1
ADC	4	4	4	4	4

Table 5.1.2: Effect of EVA content on technical properties of NR/EVA based microcellular soles

Properties	Mix Number				
	1	2	3	4	5
Time for optimum cure 160°C min	13.5	12.4	13.0	12.8	14.5
Initial expansion (%)	86.9	88.1	96.42	102	108.3
Expansion after 5 min. (%)	57.14	63.1	70.24	72.62	79.76
Exapnsion after 24h (%)	38.09	41.66	42.86	46.43	53.57
Change in hardness after ageing 24h at 100°C	+1	+2	+2	+1	+3
Shrinkage after post curing at 80°C for 2h (%)	13.8	14	14.5	15.0	16.02
Room temperature shrinkage (%)	1.1	1.05	1.78	1.9	2.2
Flex resistance					
a) Crack initiation in cycles	397,960	397,960	400,000	442,925	443,000
b) Crack size growth in mm at the end of 100,000 cycles (%)	<600	<600	<600	<600	<600

producing good quality MC sheets. Since the expansion in this case is more than that of NR/HSR soles the mould was made gas tight to prevent leakage of gas.

The sheets were taken from the mould immediately after the release of pressure. They were placed on a plane surface and the excess material was trimmed, quickly so as to avoid bending of sheet and cracking of the sides of the sheets due to the higher expansion. The expanded sheets were then post cured in an air oven at 80°C for 2h. The technical properties of NR/EVA sheets were evaluated according to the relevant Indian standards. The cell structure of razor cut samples of MC sheets were studied using an optical microscope.

Results and discussion

Since blends with high proportions of EVA are highly thermoplastic the product had to be handled carefully to avoid tearing. Also the tendency to stick to the mould is high. It is found that a very dilute silicone emulsion or soap solution works satisfactory as a mould release agent for these products. It may be noted that for conventional MC soles based on NR/HSR blends, the hot tear strength is quite high and conventional mould releasing agents like silicon emulsion are sufficient [5].

Fig.5.1.1 shows the variation of expansion ratio and relative density with increase in the amount of EVA in the blend. The expansion of the microcellular sheets increases with increase in EVA content. The linear expansion of the MC sheets are shown in Table 5.1.2. This increase in expansion may be due to the lower melt viscosity and polar nature of EVA [4,5]. Due to the high expansion, relative density decreases with increase in the EVA content in the blend.

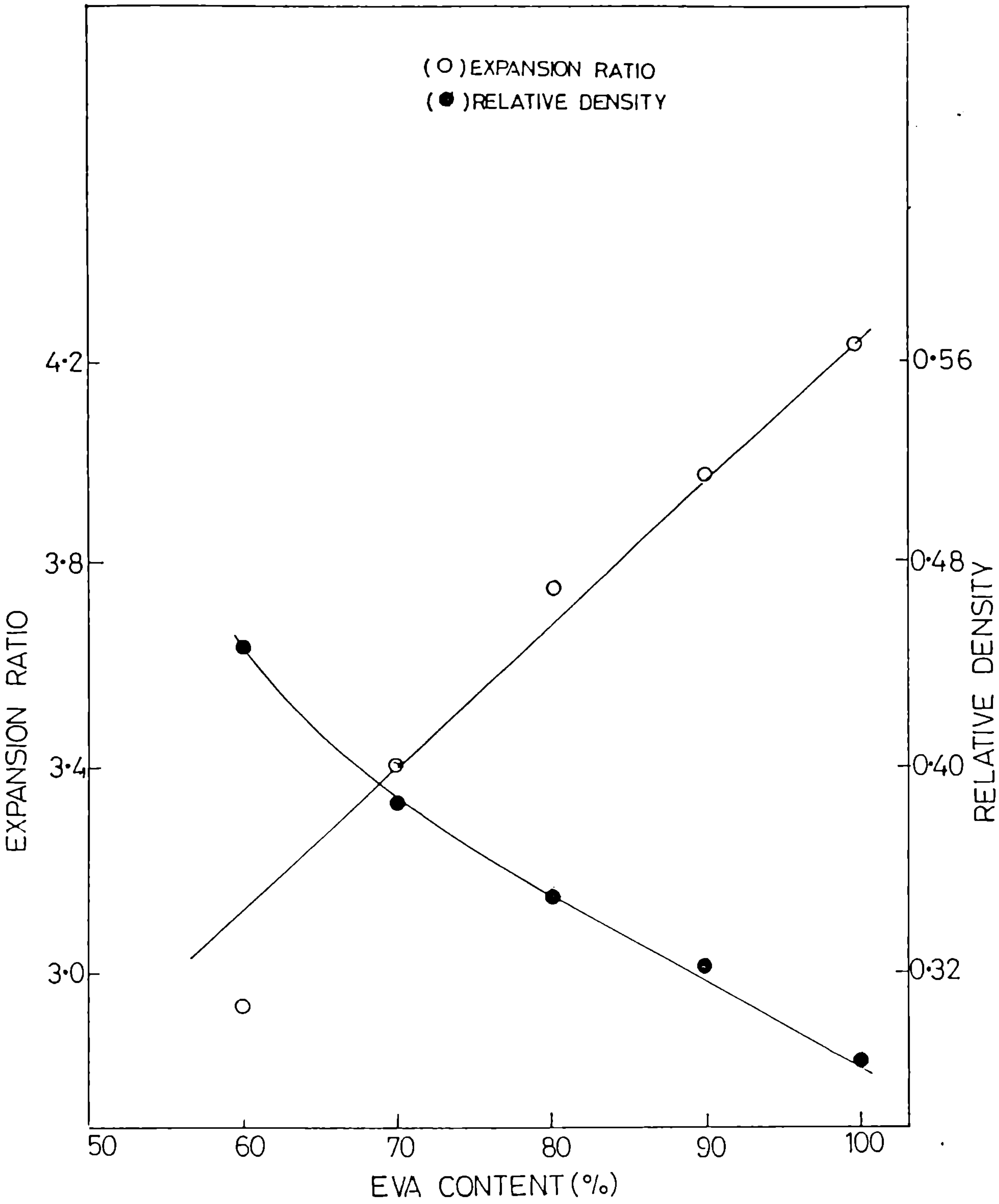

Fig.5.1.1 Variation of expansion ratio and relative density with increase in the amount of EVA.

Fig.5.1.2 shows the variation of split tear strength and abrasion loss with increase in the amount of EVA in the blend. Split tear strength of the MC sheets increases sharply as the EVA content in the blend increases, even though the expansion of the MC sheet increases. This may be due to the crystalline nature of EVA [1]. Abrasion loss of the MC sheets increases with increase in the amount of EVA in the blend. This is obviously due to the higher expansion of MC sheets, which helps easy wearing of the product.

Fig.5.1.3 shows the variation of hardness and heat shrinkage with increase in the amount of EVA. Hardness of the MC sheets decrease with increase in EVA content while heat shrinkage increases with increase in EVA content as expected [4].

Fig.5.1.4 shows the variation of compression set and water absorption with increase in the amount EVA in the blend. Compression set and water absorption increase with increase in EVA content in the blend. The increase in compression set is due to the thermoplastic nature of EVA [4]. Water absorption increases due to the presence of large number of open cells produced during the expansion.

Shrinkage after post curing of NR/EVA based microcellular soles increase with increase in the amount of EVA as shown in Table 5.1.2. Flex resistance of the samples increase with EVA content in the blend. This may also be due to the thermoplastic nature of EVA. EVA rich MC sheets show higher flex resistance.

Figs.5.1.5 and 5.1.6 show the optical microscope photographs of MC sheets prepared from 40/60 and 20/80 NR/EVA blends. As the EVA content increases the size of the cells becomes larger and the structure becomes more uniform. NR/EVA blend has a fine and

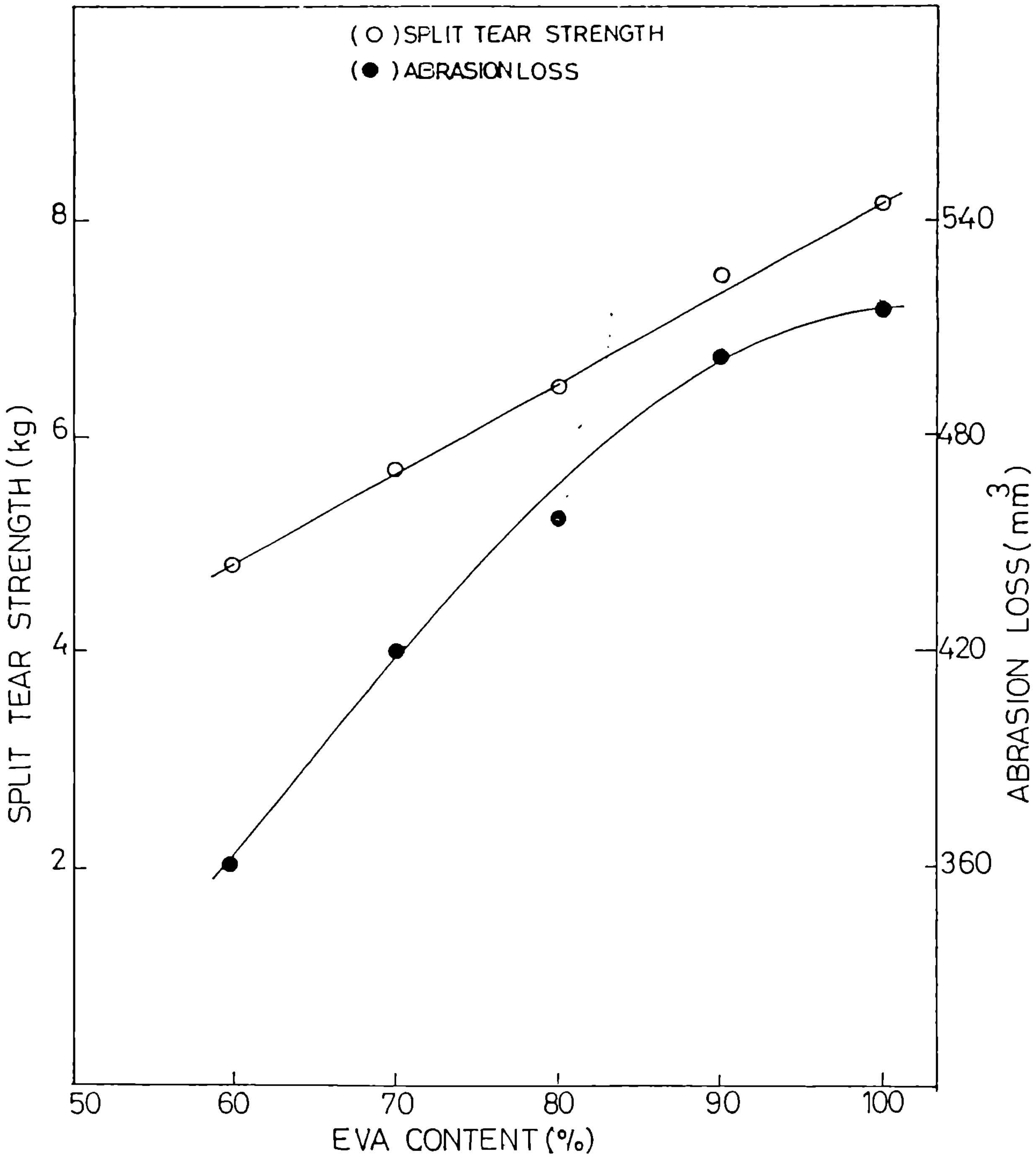

Fig.5.1.2 Variation of split tear strength and abrasion loss with increase in the amount of EVA.

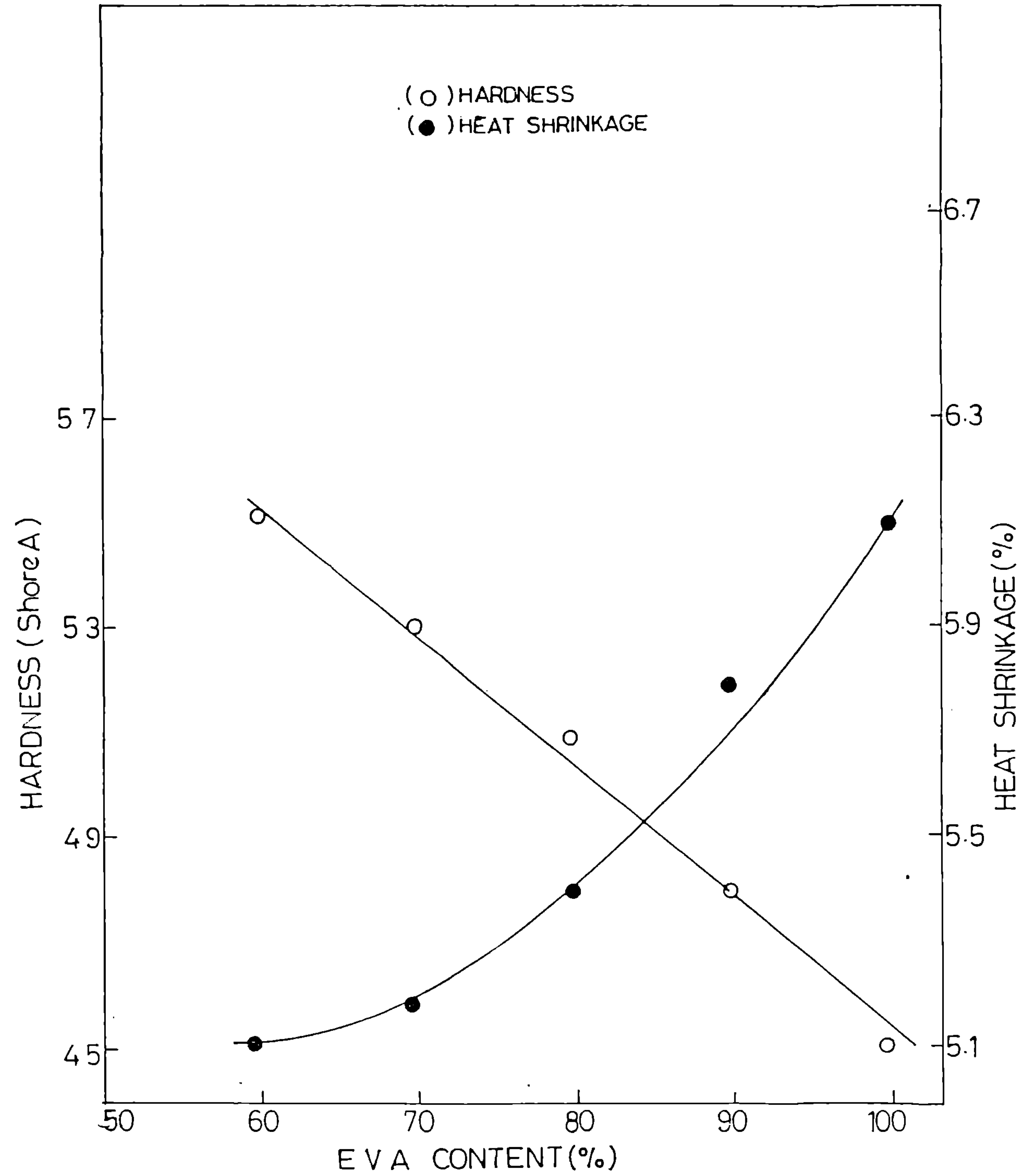

Fig.5.1.3 Variation of hardness and heat shrinkage with increase in the amount of EVA.

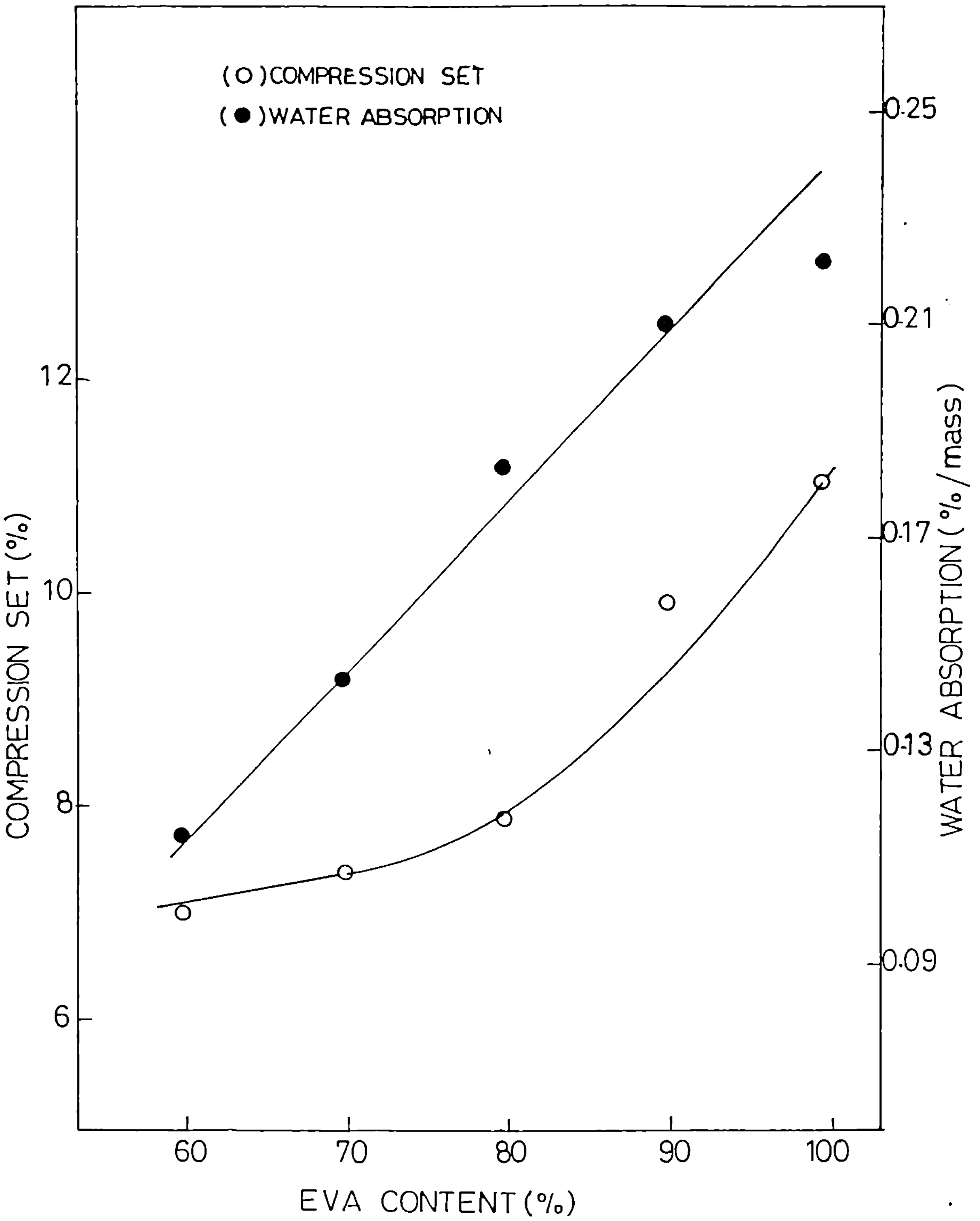

Fig.5.1.4 Variation of water absorption and compression set with increase in the amount of EVA.

Fig.5.1.5 40/60 NR/EVA

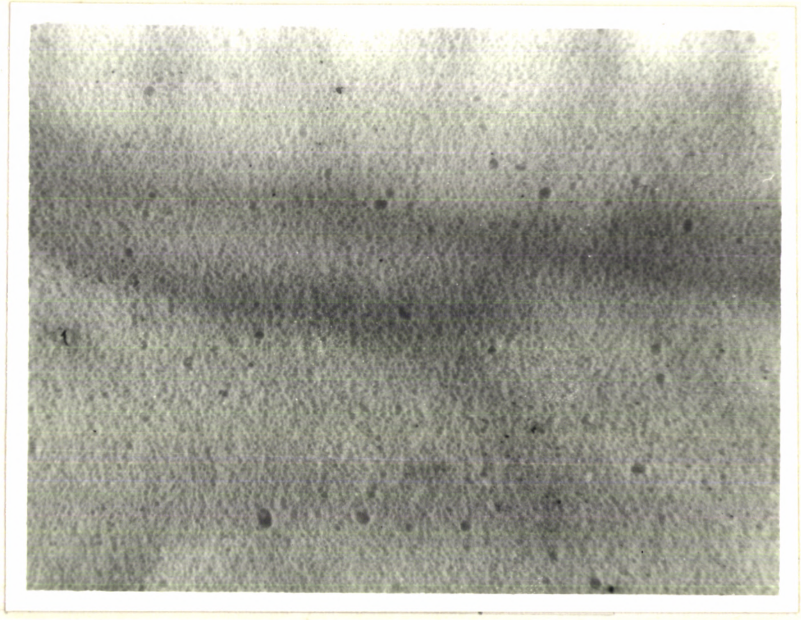

Fig.5.1.6 20/80 NR/EVA

Optical microscope photographs of MC sheets

uniform cell structure compared to all the other blends. Consequently these blends show the best technical properties.

5.1.2 Optimisation of blending temperature

Experimental

A 40/60 NR/EVA blend was prepared at different temperatures viz., 110, 120, 130, 140 and 150°C using a Brabender plasticorder and compounded as per the formulation given in Table 5.1.3 keeping all other parameters constant. The compounding, moulding and determination of technical properties were done as per the procedure described in section 5.1.1.

Results and Discussion

Table 5.1.4 shows the cure characteristics of the MC sole compounds. The cure time decreases with increase in blending temperature. Fig.5.1.7 shows the variation of expansion ratio and relative density with increase in blending temperature. Expansion of the MC sheet decreases with increase in the blending temperature thereby increasing the relative density.

Fig.5.1.8 shows the variation of split tear strength and abrasion loss with increase in blending temperature. Split tear strength of the MC sheets remain almost same up to 130°C. Further increase in blending temperature produces a decrease in split tear strength. This decrease in split tear strength may be due to the degradation of rubber phase at higher temperature. Abrasion loss is found to decrease with increase in blending temperature. This may be due to the lower expansion of the MC sheets.

Fig.5.1.9 shows the variation of hardness and heat shrinkage with increase in blending temperature. Hardness shows a marginal increase with blending temperature, while heat

Table 5.1.3: Formulation for NR/EVA microcellular sole compound

Ingredients	Phr
Polymer (60/40 EVA/NR blend)	100
Zinc stearate	2
Stearic acid	2
China clay	40
Precipitated calcium carbonate	40
Paraffinic oil	3
SP	1
DCP (40% active)	4
ADC	4

Table 5.1.4

Effect of blending temperature on the technical properties of microcellular soles based on NR/EVA blends

Properties	Blending temperature °C				
	110	120	130	140	150
Time for optimum cure 170°C min	11·5	11·0	9·2	9.9	10.5
Initial expansion (%)	92.38	90.19	85.71	84.52	83.33
Expansion after 5 min. (%)	76.19	76.19	59.52	59.52	52.38
Expansion after 24h (%)	40.48	39.28	25.0	24.19	22.62
Shrinkage after post curing (%)	15.11	14.1	13.8	13.3	13.1
Flex resistance					
a) Crack initiation in cycles	390,400	390.400	385,400	385.400	385,000
b) Crack size growth in mm at the end of 100,000 cycles	<600	<600	<600	<600	<600

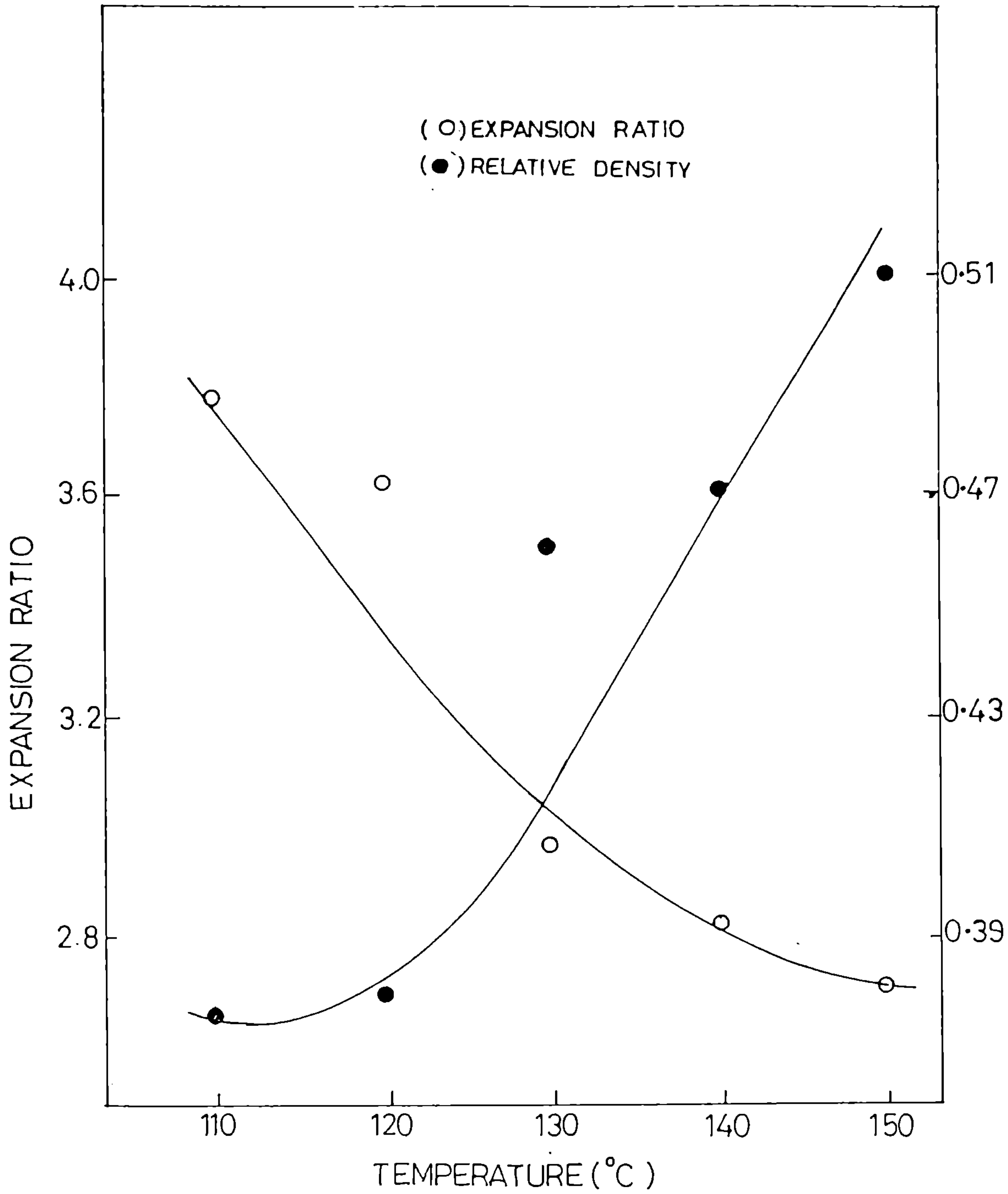

Fig.5.1.7 Variation of expansion ratio and relative density with blending temperature.

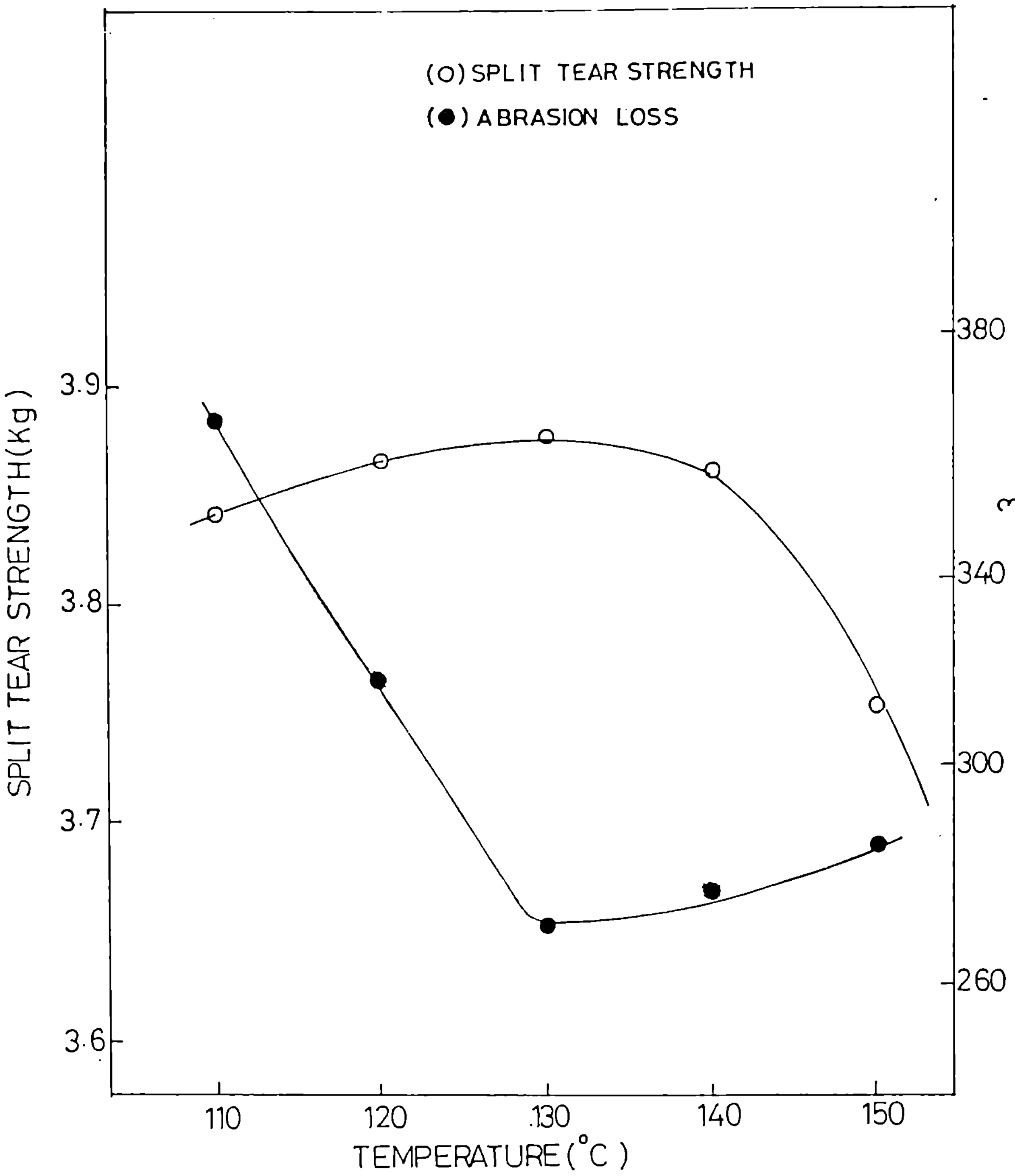

Fig.5.1.8 Variation of split tear strength and abrasion loss with blending temperature.

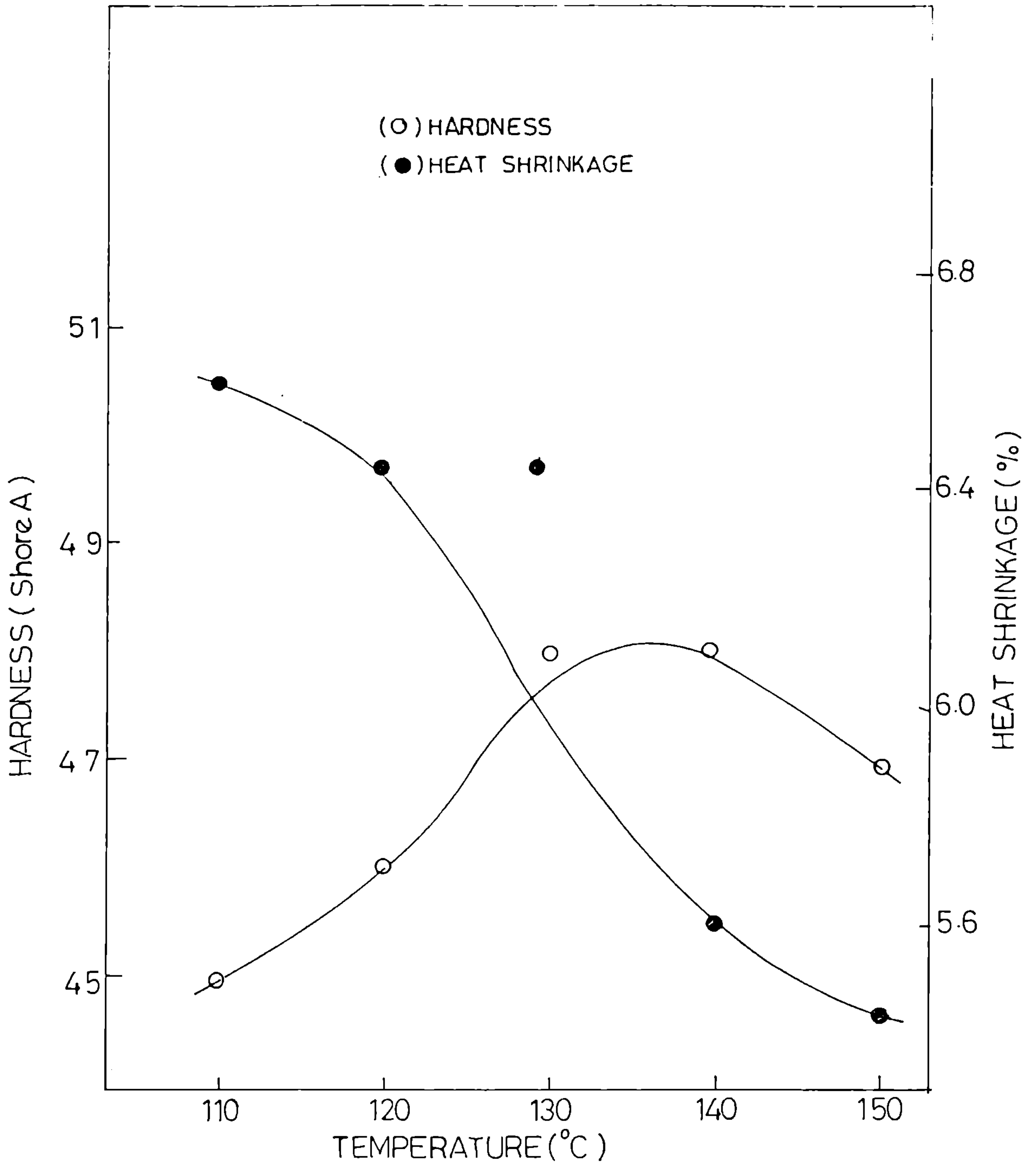

Fig.5.1.9 Variation of hardness and heat shrinkage with blending temperature.

shrinkage decreases with increase in blending temperature. This may be due to the lower expansion of MC sheets.

Fig.5.1.10 shows the variation of water absorption and compression set with increase in blending temperature. Water absorption and compression set are found to decrease with blending temperature.

Shrinkage after post curing marginally reduces with increase in blending temperature as shown in Table 5.1.4. Flex resistance marginally decreases with increase in blending temperature. For blends prepared at 110°C initial crack formation occurs after 390,400 while crack initiation occurs at 385,000 cycles for the blends prepared at 150°C. Considering all the technical propertiess 120°C is taken as the optimum temperature for preparing the blends.

5.1.3 Effect of postcuring temperature and time on properties of microcellular soles based on NR/EVA blends

Experimental

A 30/70 NR/EVA blend was prepared in a Brabender plasticorder model PL 3S at a rotor speed of 50 rpm and at 120°C temperature, and compounded as per the formulations given in Table 5.1.5. Compounding and moulding were done as per the procedure described in section 5.1.1. MC sheets having the same size were post cured at different temperatures 70, 80, 90 and 100°C for 2 hours in an air oven. To study the effect of post curing time, the MC sheets were post cured at 80°C for 60, 90, 120, 150, and 180 minutes. Technical properties of microcellular sheets were determined according to relevant Indian standards.

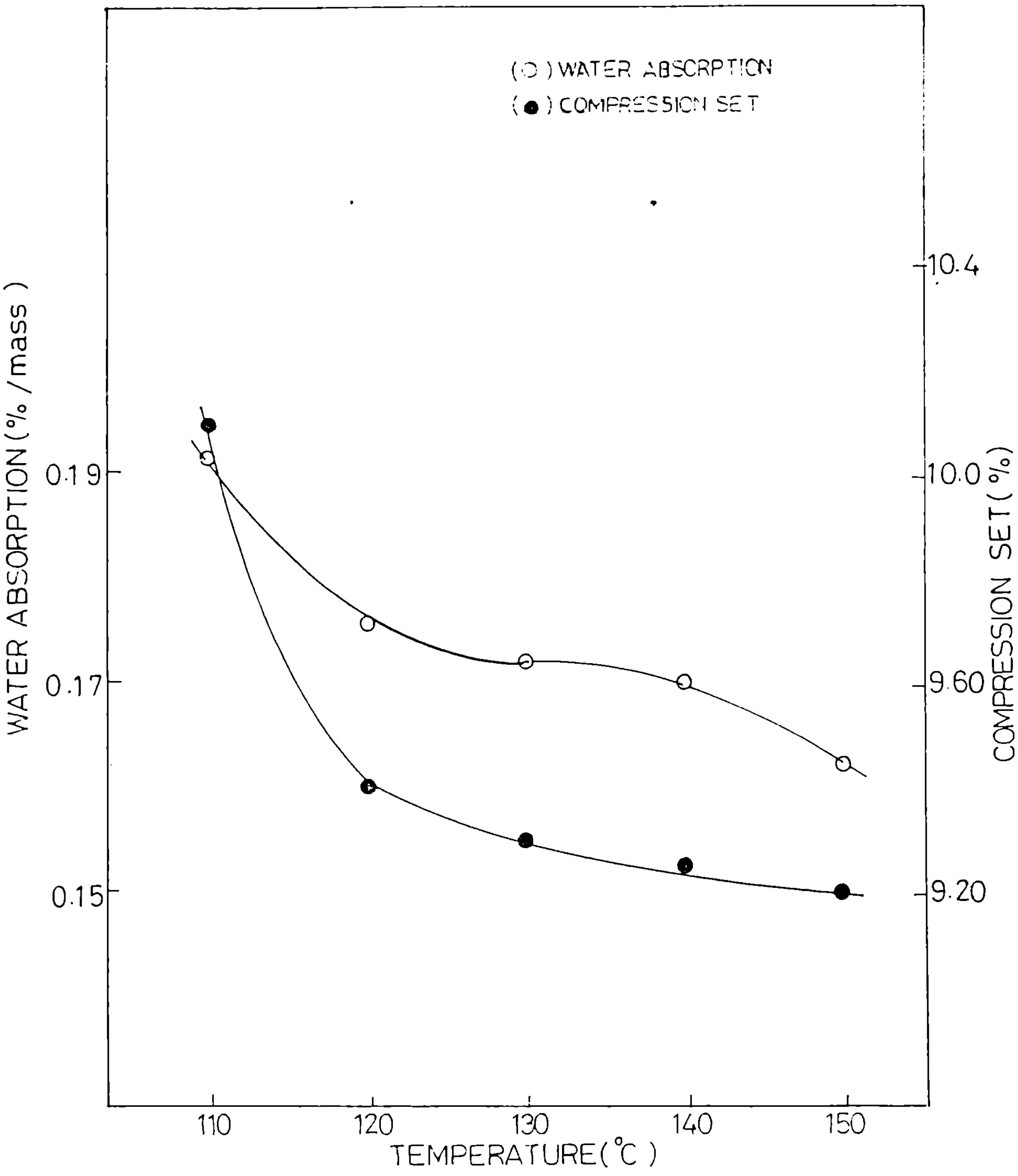

Fig.5.1.10 Variation of water absorption and compression set with blending temperature.

Table 5.1.5 Formulation for NR/EVA microcellular sole compound

Ingredients	Phr
Polymer (70/30 EVA/NR blend)	100
Zinc stearate	2
Stearic acid	2
China clay	40
Precipitated calcium carbonate	40
Paraffinic oil	3
SP	1
DCP (40% active)	4
ADC	4

Results and discussion

(i) Effect of post curing temperature on properties of microcellular soles based on NR/EVA blends

Table 5.1.6 shows the effect of post curing temperature on the technical properties of microcellular soles based on NR/EVA blends. As the post curing temperature increases the relative density of the MC sheet increases since the expansion of the MC sheet decreases. This decrease in expansion of the MC sheet at higher temperature may be due to the increased diffusion of gases, during post curing at higher temperature [6]. Shrinkage after post curing is also found to be increase with increase in temperature of post curing.This increase in shrinkage is more pronounced when the post curing temperature is changed from 90 to 100°C due to the size reduction of the sheet which in turn results in higher density.

Abrasion loss and water absorption decrease with increase in post curing temperature. This may be due to the lower expansion of the MC sheet. Hardness and split tear strength increase with post curing temperature as expected. Compression set and heat shrinkage marginally decrease with post curing temperature.

(ii) Effect of post curing time on properties of microcellular soles based on NR/EVA blends

Table 5.1.7 shows the effect of post curing time on properties of MC sheets based on NR/EVA blends. Expansion of the MC sheets marginally decrease as post curing time increases, consequently relative density increases. Shrinkage after post curing increases with post curing time as shown in the table.

Table 5.1.6

Effect of post curing temperature on the technical properties of microcellular Soles based NR/EVA blends

Properties	Post curing temperature °C.			
	70	80	90	100
Optimum cure time at 170°C min.	10.5	10.5	10.5	10.5
Initial expansion (%)	88.1	84.5	80.92	78.57
Expansion after 5 min. (%)	63.1	60.71	58.33	55.95
Expansion after 24 h (%)	60.71	57.14	54.76	54.76
Expansion ratio	3.23	3.28	3.10	3.2
Relative density	0.329	0.35	0.379	0.399
Split tear strength (kg)	3.88	4.56	4.90	4.95
Abrasion loss (mm^3)	649.5	557.1	500.5.	450.4
Hardness (Shore A)	45	46	48	50
Water absorption (percent by mass)	0.236	0.215	0.169	0.131
Compression set (%)	7.6	7.47	7.845	8.27
Heat shrinkage (%)	5.14	5.03	4.9	4.47
Shrinkage after 2h post curing (%)	7.42	8.82	11.54	12.9

Table 5.1.7

Effect of post curing time on the technical properties of microcellular soles based on NR/EVA blends

Properties	Post curing time in min.				
	60	90	120	150	180
Optimum cure time at 170°C min.	10.5	10.4	10.5	10.5	10.5
Initial expansion (%)	78.57	77.38	76.19	75	72.62
Expansion after 5 min. (%)	57.14	52.38	54.76	53.57	51.19
Expansion after 24 h (%)	54.76	40.48	38.09	36.9	35.71
Expansion ratio	2.94	2.91	2.73	2.71	2.6
Relative density	0.386	0.434	0.442	0.481	0.510
Split tear strength (kg)	5.15	5.53	5.84	5.99	5.9
Abrasion loss (mm^3)	421.9	388.2	360	289.4	280
Hardness (Shore A)	51	52	54	55	57
Water absorption (percent by mass)	0.162	0.118	0.115	0.105	0.095
Compression set (%)	13.2	13.49	13.33	13.1	12.5
Heat shrinkage (%)	4.32	4.41	4.40	4.39	3.9
Shrinkage after post curing at 80°C 2 h (%)	7.7	8.4	9.0	11.8	16.0

Abrasion loss and water absorption decrease, while hardness and split tear strength increase, with increase in the post curing time. Compression set remains almost the same. Heat shrinkage marginally decreases with post curing time. From the studies 80°C is chosen as the optimum post curing temperature and 2h as the post curing time.

5.1.4 Effect of concentration of blowing agent on properties of microcellular soles based on NR/EVA blends

Experimental

A 30:70 NR/EVA blend was used for this study. The amount of blowing agent was varied from 3-5 phr, keeping all other ingredients at the same level. Formulation of the mixes were shown in Table 5.1.8. Compounding, moulding and determination of technical properties were done as described in section 5.1.1.

Results and Discussion

Table 5.1.9 shows the cure characteristics and technical properties of microcellular sheets with different levels of the blowing agent (ADC). The optimum cure time increases with increase in concentration of blowing agent. The blowing efficiency depends on the type of vulcanization system used [7]. Percent volume expansion of the MC sheets increase with increase in concentration of blowing agent, while relative density decreases [8]. This is due to the comparatively higher decomposition of blowing agent ADC and entrapment of the decomposed inert gases [9]. Hardness of the MC sheets decrease with increase in blowing agent concentration. While there is only a marginal decrease upto 4 phr, there is a large decrease in hardness above 4 phr. Split tear strength decreases with decrease in relative density due to the decrease in the volume percentage of rubber [9].

Table 5.1.8

Formulation for NR/EVA microcellular sole compounds

Ingredients (Phr)	Mix Number		
	1	2	3
Polymer (70 EVA/30 NR)	100	100	100
Stearic acid	2	2	2
Zinc stearate	2	2	2
China clay	40	40	40
Precipitated calcium carbonate	40	40	40
Paraffinic oil	3	3	3
SP	1	1	1
DCP (40% active)	4	4	4
ADC	3	4	5

Table 5.1.9

Effect of concentration of blowing agent on the technical properties of microcellular soles based NR/EVA blends

Properties	Amount of blowing agent (Phr)		
	3	4	5
Optimum cure time at 170°C min.	15	15.4	15.5
Initial expansion (%)	73.81	80.92	96.43
Expansion after 5 min. (%)	46.43	53.57	69.05
Expansion after 24 h (%)	26.19	32.14	40.47
Expansion ratio	2.58	2.85	3.46
Relative density	0.468	0.422	0.364
Hardness (Shore A)	55	53	49
Split tear strength (kg)	6.49	5.7	4.59
Abrasion loss (mm^3)	366.9	382.7	400
Heat shrinkage (%	4.1	5.12	6.276
Compression set (%)	11.14	13.34	14.88
Water absorption (percent by mass)	0.145	0.181	0.214
Shrinkage after post curing at 80°C 2 h (%)	13.11	13.38	14.18
Flex resistance			
a) Crack initiation in cycles	305,000	305,175	305,000
b) Crack growth at the end of 100,000 cycles (%)	<600	<600	<600

Abrasion loss increases with increase in blowing agent concentration as shown in table. This may be due to the increase in expansion of the MC sheets. Cell wall thickness decreases with increase in the volume of expansion and the number of cells per unit volume increases which results in higher abrasion loss [9]. With increase in blowing agent from 3 to 5 phr heat shrinkage and water absorption are found to be increased. This increase in heat shrinkage is due to the increase in cell size due to the higher expansion. The number of cells per unit volume increases with increase in the concentration of blowing agent, which results in increased water absorption [10]. Compression set is also found to increase with increase in the amount of blowing agent. This may be due to the higher expansion. Shrinkage after post curing marginally increases with increase in the concentration of blowing agent. Flex resistance of samples are also shown in table: no crack is developed even after 305,000 cycles.

It may be concluded that the increased amount of blowing agent does not affect the flex resistance of the sample, but it adversely affects some of the critical properties like split tear strength, abrasion loss and hardness.

5.1.5 Effect of NR/HSR and NR/EVA microcrumb on properties of microcellular soles based on NR/EVA blends

Experimental

Waste obtained after cutting away the useful product from NR/HSR and NR/EVA based MC soles was passed through the tight nip of a hot two roll mill (50-60°C) and homogenised. Milling was continued for 15-20 minutes to get a soft sheet. This was used as a filler in this part of the study.

A 30/70 NR/EVA blend was used as the control for this study. The amount of NR/HSR crumb was varied from 30-60 phr and the amount of NR/EVA crumb was varied from 15 to 50 phr. Formulations of the mixes are shown in Table 5.1.10. Compounding, moulding and determination of technical properties were done as per the standard procedures described in section 5.1.1.

Results and Discussion

i) NR/HSR microcrumb

Table 5.1.11 shows the cure characteristics and technical properties of MC sheets containing NR/HSR crumb. The optimum cure time marginally decreases due to the presence of already vulcanized crumb. Expansion of the MC sheet is also slightly reduced by the presence of already crosslinked crumb which results in higher relative density [11]. With the incorporation of NR/HSR microcrumb split tear strength increases upto 45 phr crumb loading followed by a gradual decrease upto 60 phr. This increase in split tear strength may be attributed to the reinforcement imparted by the microcrumb. The drop in split tear strength at higher crumb loading may be due to the non-homogeneity and the larger size of microcrumb [12]. Hardness of the MC sheets increase with increase in microcrumb loading as expected. This is obviously due to the increased crosslinking of microcrumb and lower expansion of MC sheets. Abrasion loss decreases with increase in the amount of crumb loading. This is probably due to the thicker cell walls resulting from lower expansion of MC sheets as shown in the table.

Heat shrinkage decreases with increase in the amount of crumb. The decrease is fairly large from 30 to 45 phr crumb loading, while it is marginal from 45 to 60 phr. Shrinkage after post curing also reduces with crumb loading. Water absorption decreases with increase in

Table 5.1.10

Formulations of NR/EVA microcellular sole compounds

Ingredients (phr)	Mix Number				
	6	7	8	9	10
Polymer (70/30, EVA/NR blend)	100	100	100	100	100
Zinc stearate	2	2	2	2	2
Stearic acid	2	2	2	2	2
Precipitated calcium carbonate	80	80	80	80	80
NR/HSR crumb	30	45	60	-	-
NR/EVA crumb	-	-	-	15	50
SP	1	1	1	1	1
paraffinic oil	3	3	3	3	3
DCP (40% active)	4	4	4	4	4
ADC	4	4	4	4	4

Table 5.1.11

Effect of amount of NR/HSR and NR/EVA crumb on the technical properties of MC soles based on NR/EVA blends

Properties	NR/HSR crumb			NR/EVA crumb	
	30	45	60	15	50
Optimum cure time at 170°C (min.)	10.4	9.9	9.2	12.5	11.4
Initial expansion (%)	90.48	89	87.09	108.3	84
Expansion after 5 min. (%)	58.33	57.14	55.95	83.33	57.95
Expansion after 24 h (%)	35.71	33.4	31.0	54.76	41.66
Expansion ratio	3.208	3.063	2.946	2.819	2.8
Relative density	0.410	0.421	0.443	0.41	0.428
Split tear strength (kg)	4.126	4.4	3.9	5.9	5.6
Abrasion loss (mm^3)	455.43	356.29	338.6	463	390
Hardness (Shore A)	53	56	57	49	55
Water absorption (percent by mass)	0.122	0.112	0.105	0.114	0.1
Compression set (%)	23.95	24	23.1	18.9	19.4
Heat shrinkage (%	4.348	2.5	2.128	3.297	2.22
Shrinkage after post curing at 80°C 2 h (%)	16.81	14.28	13.39	13.33	12
Flex resistance					
a) Crack initiation in cycles	280,175	280,000	265,000	292,590	291,575
b) Crack growth at the end of 100,000 cycles (%)	<600	<600	<600	<600	<600

crumb loading and compression set values do not show any noticeable change. The decrease in water absorption may be due to the lower percentage of open cells as shown in the table. At higher levels of microcrumb crack initiation occurs after 265,000 cycles while at lower levels of crumb (30 phr) crack initiation occurs after 280,175 cycles. This shows that as the microcrumb level increases flex resistance decreases.

(ii) NR/EVA microcrumb

Table 5.1.11 shows the cure characteristics and the technical properties of NR/EVA based microcellular soles containing NR/EVA crumb. Since it was found that upto about 50 phr of NR/HSR microcrumb could be used as filler in NR/EVA based MC soles, so the effect of 15 and 50 phr crumb loading on properties of MC sheets were studied. NR/EVA crumb containing MC sheets show similar behaviour and properties as in the case of NR/HSR crumb containing MC sheets. As in the case of NR/HSR crumb, expansion of the MC sheets decrease with the addition of NR/EVA crumb, resulting in increased relative density. Split tear strength of the MC sheets increase with increase in crumb upto a certain level and then shows a marginal reduction. The increase in split tear strength is more in the case of NR/EVA crumb compared to NR/HSR crumb. This may be due to the higher reinforcement of NR/EVA crumb. Hardness of the MC sheets also show considerable increase with the addition of NR/EVA crumb. Abrasion loss, heat shrinkage and water absorption decrease with increase in crumb loading. On the other hand compression set shows a marginal increase. Shrinkage after post curing also decreases with increase in crumb loading as shown in the table. Flex resistance is also good.

B. NR/HSR/EVA blend based MC sheets

Experimental

NR/EVA blends were prepared first as per the procedure described in 5.1.1 and HSR in the form of a sheet was then added on the mixing mill. To study the effect of incorporation of EVA in NR/HSR blends, a part of HSR was replaced by EVA. NR/HSR/EVA blend was compounded as per the formulation given in Table 5.1.12 and moulded at 160°C. The moulding of the MC sheets and determination of technical properties were done as per the procedure described in 5.1.1. The optical photograph of selected samples were taken using an optical microscope.

Results and Discussion

Table 5.1.13 shows the technical properties and cure characteristics of the MC sheets based on NR/HSR/EVA blends. When a part of HSR is replaced by EVA in NR/HSR blend, the expansion of MC sheets increases and, consequently relative density decreases. There is a considerable reduction in relative density when EVA is added. This is due to the higher expansion of NR/HSR blend in the presence of EVA thereby reducing density resulting in increased wearing comfort. Addition of EVA as a separate ingredient also improves the expansion of the MC sheets.

Split tear strength of MC sheets marginally reduce by the replacement of HSR by EVA. This may be due to the increased volume of expansion of the MC sheets, which renders the cell walls thinner and weaker [5]. Abrasion loss of the MC sheets marginally increase as the amount of EVA in the blend increases as expected. Addition of EVA as a separate ingredient also reduces the split tear strength but increases the abrasion loss.

Table 5.1.12

Formulations for NR/HSR/EVA microcellular sole compounds

Ingredients (Phr)	Mix Number			
	A	B	C	D
Natural rubber	60	60	60	60
High styrene resin	40	25	20	40
Ethylene vinyl acetate	0	15	20	10
ZnO	4	4	4	4
Stearic acid	6	6	6	6
Clay	80	80	80	80
Precipitated silica	20	20	20	20
NR/HSR microcrumb	50	50	50	50
Naphthenic oil	5	5	5	5
DEG	1.5	1.5	1.5	1.5
SP	1	1	1	1
Vulcafor F	1.2	1.2	1.2	1.2
Sulphur	2.25	2.25	2.25	2.25
DNPT	6	6	6	6

Table 5.1.13

Technical properties of microcellular soles based NR/HSR/EVA blends

Properties	A	B	C	D
Optimum cure time at 160°C min.	5	4.5	5.6	4.5
Initial expansion (%)	68.45	75	79.74	72.22
Expansion after 5 min. (%)	47.02	52.24	54.76	46.43
Expansion after 24 h (%)	39.28	40.48	41.66	41.66
Expansion ratio	2.35	2.60	2.91	2.68
Relative density	0.502	0.448	0.384	0.441
Split tear strength (kg)	4.59	4.1	3.79	4.04
Abrasion loss (mm^3)	344	352	380.3	340
Hardness (Shore A)	55	49	46	54
Change in hardness after ageing 100°C 24 h	+1	+1	+2	+1
Compression set (%)	15.54	14.20	11.99	15.1
Water absorption (percent by mass)	0.115	0.147	0.152	0.122
Heat shrinkage (%	5.208	4.808	4.648	4.17
Room temperature shrinkage (%)	1.47	1.2	1.4	1.47
Shrinkage after post curing (%)	7.143	4.902	4.803	6.299
Flex resistance				
a) Crack initiation in cycles	210,450	298,000	300,000	298,910
b) Crack growth at the end of 100,000 cycles (%)	<600	<600	<600	<600

Hardness and compression set of the microcellular sheets decrease with increase in EVA content, the extent of decrease being higher when 20 part of HSR is replaced by EVA. Compression set is also found to decrease with increase in EVA content. Addition of EVA as a separate ingredient gives almost similar effect with MC soles based on NR/HSR blends.

Water absorption of microcellular sheets increase when a part HSR is replaced by EVA. This may be due to the presence of larger number of cells. Heat shrinkage is more for NR/HSR based microcellular sheets. The addition of EVA decreases the heat shrinkage. Because EVA is an excellent anti-shrinkage material [13] shrinkage after post curing of the microcellular sheets decrease, by the inclusion of EVA as shown in Table 5.1.13. The reduction in shrinkage after post curing helps to reduce the sheet size stabilisation time to a great extent [13].

Flex resistance of samples are shown in the table. When 10 parts of EVA is present, crack initiation occurs only after 298,000 cycles. This means that EVA increases flex resistance. This may be due to its thermoplastic nature.

Figs.5.1.11 and 5.1.12 show the optical microscope photographs of MC sheets prepared from 60/40 NR/HSR and 60/20/20 NR/HSR/EVA blends. Replacement of HSR by EVA improves the cell structure of the MC sheets significantly.

CONCLUSION

1. Microcellular soles prepared from 30/70 NR/EVA blend show excellent technical properties.

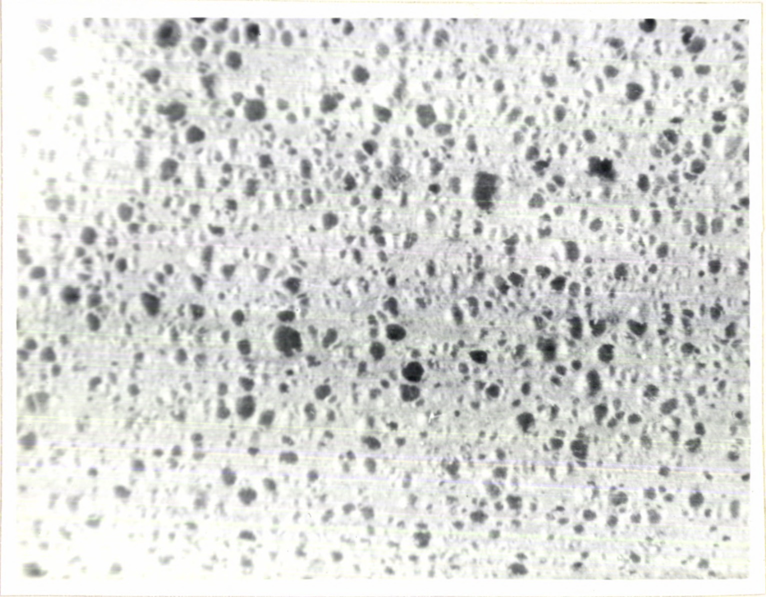

Fig.5.1.11 60/40 NR/HSR

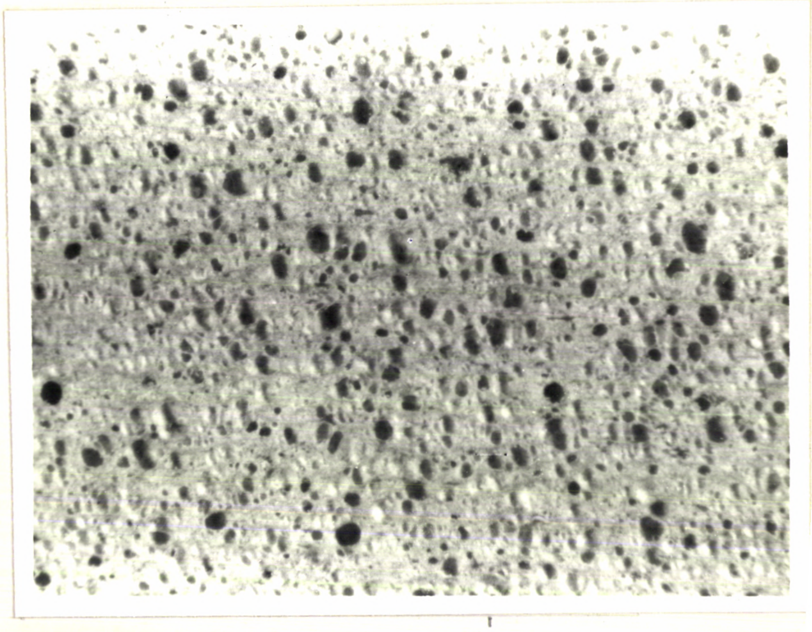

Fig.5.1.12 60/20/20 NR/HSR/EVA

Optical microscope photographs of MC sheets

2. The blending temperature required for getting optimum properties is 120°C and post curing required is 2h at 80°C.
3. The optimum level of addition of blowing agent is 4 phr.
4. The optimum level of addition of NR/HSR crumb is 45 phr while that of NR/EVA crumb is 50 phr without reduction in properties.
5. Addition of EVA either as a separate ingredient or as a partial replacement can increase the expansion of NR/HSR based microcellular soles and thereby reduce the density.
6. Inclusion of EVA prevents shrinkage of the expanded sheets on storage and provides the MC sheets excellent colour qualities.
7. MC soles based on EVA have the advantages of higher expansion, light weight for higher thickness, good flexibility and thermoformability with uniform cell structure.

PART II : STUDIES ON THE PROPERTIES OF MICROCELLULAR SOLES BASED ON NR/POLYETHYLENE BLENDS

In recent years, rubber-plastic blends have become technologically important for use as thermoplastic elastomers [14,15]. They are gaining industrial importance as they combine the ease and economy of processing as thermoplastic resins with the mechanical properties of vulcanized rubbers [16-18]. In recent years some of the polyethylene blends have become commercially important and certain properties of the blends are better than those of parent polymers. The NR polyolefin thermoplastic elastomers have advantages like good low temperature flexibility, low density, elastic recovery, heat resistance, low processing cost with reusable scrap, low material cost etc [18].

In the present study, we propose to investigate the suitability of sulphur cured and DCP cured NR/LDPE and NR/HDPE blends for the production of microcellular soles. The effect of partial replacement of LDPE by HSR is also proposed to be investigated. The properties of microcellular sheets based on NR/LDPE, NR/HDPE and NR/LDPE/HSR are proposed to be evaluated and compared with NR/HSR based microcellular soles. The mechanical properties of above blends are also proposed to be studied.

Experimental

NR/LDPE blend was prepared on a Brabender plasticorder model PL 3S employing a rotor speed of 60 rpm at 150°C. LDPE was melted for one min. and then masticated NR was added and the mix was allowed to blend for 3 min. and then taken out [18]. HSR in the form of a sheet was then added on a mixing mill.

The blends were prepared in the weight ratio 80/20 NR/LDPE, NR/HDPE and 70/30 and 60/40 NR/HSR blends. A part of HSR in NR/HSR blend was replaced by LDPE. These blends were compounded as per formulation given in tables 5.2.1 and 5.2.2 without blowing agent, to study the mechanical properties of blends.

Optimum cure time of the compounds were determined using a Goettfert Elastograph model 67.85. Sheets of 120x120x2 mm size were prepared at 160°C by compression moulding. Test specimens for tensile tests were punched out from the moulded sheets with dimensions according to the standard specifications. Tensile properties were determined at 25° C and 50% relative humidity as per ASTM Standards on a Zwick UTM at a crosshead speed of 500 mm/min.

Preparation of microcellular sheets

The blends were compounded with blowing agent according to the formulations given in tables 5.2.1 and 5.2.2 respectively. The NR/LDPE and NR/LDPE/HSR blends based MC sheets were moulded in an electrically heated hydraulic press at 160°C. The moulding of MC sheets were described in 5.1.1.

The technical properties of the microcellular sheets were evaluated according to relevant Indian standards. The cell structure of razor cut samples of MC sheets were studied using an optical microscope.

Results and discussion

Table 5.2.1 shows the cure characteristics and mechanical properties of sulphur cured blends. Optimum cure time of the compounds marginally increase with the addition of LDPE.

Table 5.2.1: Formulation and mechanical properties of sulphur cured NR/PE and NR/LDPE/HSR blends

Ingredients (Phr)	Mix Number							
	A	B	C	D	E	F	G	H
NR	80	80	80	70	70	70	60	60
LDPE	-	20	-	-	15	10	-	20
HDPE	-	-	20	-	-	-	-	-
HSR	20	-	-	30	15	20	40	20
ZnO	3	3	3	3	3	3	3	3
Stearic acid	6	6	6	6	6	6	6	6
Precipitated silica	20	20	20	20	20	20	20	20
China clay	80	80	80	80	80	80	80	80
NR/HSR microcrumb	25	25	25	25	25	25	25	25
Wood rosin	2	2	2	2	2	2	2	2
Diethylene glycol	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Naphthenic oil	3	3	3	3	3	3	3	3
SP	1	1	1	1	1	1	1	1
Vulcafor F	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
DNPT	6	6	6	6	6	6	6	6
Cure characteristics								
Optimum cure time (T_{90}) at 160°C (min.)	5.9	6.5	6.3	9	7	7.8	5.7	7.3
Vulcanizate properties								
Tensile strength (N/mm^2)	7.97	8.92	9.11	10.3	11.28	10.69	9.80	7.1
Tear strength (N/mm)	32.22	37.14	37.91	39.37	40.85	36.62	35.67	39.37
Elongation at break (%)	400	390	400	460	420	420	450	370

Table 5.2.2: Formulations and mechanical properties of DCP cured NR/PE and NR/HSR/LDPE blends

Ingredients (Phr)	Mix Number							
	I	J	K	L	M	N	O	P
NR	80	80	80	70	70	70	60	60
LDPE	-	20	-	-	15	20	-	20
HDPE	-	-	20	-	-	-	-	-
HSR	20	-	-	30	15	10	40	20
ZnO	3	3	3	3	3	3	3	3
Stearic acid	4	4	4	4	4	4	4	4
China clay	80	80	80	80	80	80	80	80
Precipitated silica	20	20	20	20	20	20	20	20
Wood rosin	2	2	2	2	2	2	2	2
Diethylene glycol	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Naphthenic oil	5	5	5	5	5	5	5	5
SP	1	1	1	1	1	1	1	1
DCP (40% active)	5	5	5	5	5	5	5	5
DNPT	6	6	6	6	6	6	6	6
Cure characteristics								
Optimum cure time (T_{90}) at 160°C min.	10.8	10.8	11.8	11.9	11.4	11.8	11.9	11.1
Vulcanizate properties								
Tensile strength (N/mm^2)	6.66	7.2	8.1	9.8	11	10.6	9	9.1
Tear strength (N/mm)	35.2	35.67	38.82	37.05	33.75	32.1	36.77	36
Elongation at break (%)	390	380	390	360	300	325	380	345

The tensile strength of the vulcanizate increase with the addition of LDPE. When a part of HSR in a 70/30 or 60/40 NR/HSR blend is replaced by LDPE, the tensile strength increases upto 15 part LDPE but decreases thereafter. The decrease in tensile strength above 15 phr may be due to incompatibility of NR and LDPE. Tear strength also shows a similar behaviour. Elongation at break reduces sharply by the addition of LDPE.

Cure characteristics and mechanical properties of DCP-cured blends are shown in Table 5.2.2. There is a gradual increase in cure time when DCP is used as a curing agent. The tensile strength and tear strength show marginal reduction when DCP is used as crosslinking agent. The study shows that in NR-PE blends the properties can be changed with the nature of crosslinking agent. The degree of crosslinking and related properties depend on the curatives used [18]. Compared to sulphur cured blends, the DCP cured has lower crosslink density. Tensile strength of the vulcanizates increase with the addition of LDPE in DCP cured blend upto 15 parts, but further addition brings down the tensile strength. Tear strength of the vulcanizates show similar behaviour as tensile strength. Elongation at break reduces when HSR is replaced by LDPE, probably due to the crystalline nature of LDPE.

(i) Microcellular soles prepared with sulphur as curing agent

Table 5.2.3 shows the properties of MC sheets prepared using sulphur as curing agent. When 80/20 NR/LDPE blend is compared with a 80/20 NR/HSR blend the expansion of the MC sheet is higher in the former and consequently relative density is lower. This may be due to the thermoplastic nature of LDPE. The degree of crystallinity in sulphur cured NR/LDPE systems is lower than that of pure LDPE as sulphur crosslinks in NR retards the crystallisation of LDPE [18]. Hardness and split tear strength marginally decrease in 80/20 NR/LDPE based MC sheet. This decrease in properties may be due to the presence of uncured LDPE phase,

Table 5.2.3

Technical properties of sulphur cured microcellular soles based on NR/PE and NR/LDPE/HSR blends

Properties	Mix Number							
	A	B	C	D	E	F	G	H
Optimum cure time at 160°C (min.)	8.9	8	9.8	8	8.1	8	8	9
Initial expansion (%)	73.81	78.57	90.47	76.19	77.38	78.57	71.43	72.62
Expansion after 5 min. (%)	41.66	50	63.07	47.69	48.8	48.8	35.71	47.2
Expansion after 24 h (%)	33.3	41.60	52.38	35.71	38.09	38.09	29.76	38.09
Expansion ratio	2.139	2.634	3.133	2.39	2.505	2.546	2.259	2.579
Relative density	0.4711	0.4452	0.3255	0.4589	0.3676	0.4182	0.4523	0.4431
Split tear strength (kg)	3.698	3.079	2.6	4.01	2.767	2.375	4.592	2.486
Abrasion loss (mm^3)	426.7	470	556.07	446.7	440.69	461.5	420	451.36
Hardness (Shore A)	48	37	30	49	45	44	51	44
Compression set (%)	7.9	13.07	18.94	8.403	12	14.57	10.49	13.94
Heat shrinkage (%)	3.541	3.867	3.99	3.593	3.678	3.601	6.23	3.714
Water absorption (percentage by mass)	0.1	0.1286	0.1159	0.1065	0.0964	0.095	0.1024	0.1147
Shrinkage after post curing (%)	4.5	3.89	4.44	7.2	5.645	5.7	6.67	5.646
Flex resistance								
a) Initiation crack in cycles	156,000	290.975	288.549	248.547	281,950	297,185	229.590	240.000
b) Crack growth at the end of 100,000 cycles (%)	<600	<600	<600	<600	<600	<600	<600	<600

since LDPE phase does not get cured in presence of sulphur and vulcafor F. Compression set and abrasion loss show an increase in the case of the NR/LDPE based MC sheets. This increase in set values may be due to the higher expansion of the MC sheets. Water absorption and heat shrinkage are found to be higher for NR/LDPE based MC sheets. This increase in water absorption is due to the presence of more open cells, resulting from higher expansion [12]. This is also confirmed from increased heat shrinkage of NR/LDPE based MC sheets. NR/HDPE based MC sheet also shows similar behaviour.

When a part of HSR in 70/30 and 60/40 NR/HSR blends is replaced by LDPE, the expansion of the MC sheets increase resulting in lower density. Maximum expansion is obtained for 70/20/10 NR/LDPE/HSR blend. But the addition of LDPE in the blend reduces the split tear strength and hardness. Compared to NR/LDPE or NR/HDPE blend hardness and split tear strength show higher values for NR/LDPE/HSR blends. The reduction of the properties with the addition of LDPE may be attributed to the increased expansion of the MC sheets in presence of LDPE. Abrasion loss increases with LDPE content in the blend. Heat shrinkage also increases with the addition of LDPE. This may also be due to the increased expansion of the MC sheet. Water absorption decreases marginally in 70/15/15 NR/LDPE/HSR blend. This shows that number of open cell is less. But a 60/20/20 blend based MC sheets show increase in water absorption. This is due to the presence of more open cells. A 60/20/20 NR/HSR/LDPE based MC sheet shows improvement in abrasion resistance compared to a 70/20/10 NR/LDPE/HSR blend based MC sheet. Compression set increases with increase in the amount of LDPE. This is due to the presence of uncured LDPE which decreases the total crosslink density. Flex resistance of all the samples are found to be within the specification limits given in Indian Standards as shown in table.

NR/PE blend based MC sheet shows excellent flex resistance compared to NR/HSR blends. Shrinkage after post curing is minimum for NR/LDPE and NR/HDPE based MC sheets as shown in Table 5.2.3.

(ii) Microcellular soles prepared with DCP as curing agent

Table 5.2.4 shows the cure characteristics and technical properties of MC sheets prepared with DCP as curing agent. Optimum cure time increases when DCP is used as curing agent. As the amount of LDPE increases expansion of the MC sheet increases, resulting in lower relative density. Compared S-cured MC sheets DCP cured sheet show higher expansion. There is a slight improvement in split tear strength of 80/20 NR/LDPE based MC sheets whereas there is a reduction in the split tear strength of NR/HSR based MC sheets when DCP is used as the curing agent. This may be due to curing of LDPE phase in presence of DCP. Abrasion loss and water absorption are also high for DCP cured MC sheets. This may be attributed to the higher expansion of MC sheet, resulting in weaker cell walls of the product [12]. Heat shrinkage of DCP cured MC sheet is higher when compared to sulphur cured MC sheets. This may be due to the higher expansion. Hardness of the MC sheets are found to be lower and water absorption high. The number of open cells obviously increase in DCP cured MC sheets due to higher expansion resulting in higher shrinkage after post curing.

Table 5.2.4 shows the properties of DCP cured MC sheets based on NR/HSR/LDPE blend. Expansion of MC sheets is higher compared to sulphur cured NR/HSR/LDPE based MC sheets. Split tear strength of MC sheets prepared using DCP as curing agent is found to be higher, especially in 70/15/15 and 70/20/10 NR/LDPE/HSR blends. This suggest that LDPE phase also gets cured in presence of DCP. Compression set is slightly lower in DCP cured NR/LDPE/HSR blend based MC sheets. But heat shrinkage and water absorption are

Table 5.2.4: Technical properties of DCP cured microcellular soles based on NR/PE and NR/LDPE/HSR blends

Properties	Mix Number							
	I	J	K	L	M	N	O	P
Optimum cure time at 160°C min.	9	9	7.9	8	9	8.6	8	7
Initial expansion (%)	67.86	82.14	94.05	69.05	90.48	96.43	71.43	96.43
Expansion after 5 min. (%)	36.9	48.8	66.7	38.09	55.95	61.9	39.28	63.1
Expansion after 24 h (%)	29.76	41.66	54.76	30.95	45.24	53.57	32.14	57.14
Expansion ratio	2.35	2.78	3.51	2.9	3.31	3.57	2.566	3.479
Relative density	0.49	0.379	0.306	0.486	0.346	0.320	0.475	0.30
Split tear strength (kg)	3.67	3.35	2.99	3.59	2.89	2.95	4.08	3.302
Abrasion loss (mm^3)	510	623	570.9	523.8	553.47	586.9	495	545
Hardness (Shore A)	34	22	25	34	32	30	38	28
Compression set (%)	7.1	9.42	15.94	10.4	12.96	14.35	13.13	14.39
Heat shrinkage (%)	6.41	8.6	8.8	8.1	7.44	8.45	7.9	7.68
Water absorption (percent by mass)	0.112	0.141	0.138	0.112	0.169	0.175	0.0714	0.1969
Shrinkage after post curing (%)	5.6	5.69	5.75	4.51	5.26	5.48	6.08	6.14
Flex resistance								
a) Crack initiation in cycles	201,915	350,000	300,500	250,125	248,547	248,547	248,547	251,000
b) Crack growth at the end of 100,000 cycles (%)	<600	<600	<600	<600	<600	<600	<600	<600

higher compared to sulphur cured MC sheets. Abrasion loss shows marginal increase compared to sulphur cured MC sheets. Hardness shows a slight decrease. This may be due to the matrix getting slightly damaged at the indentation [19].

Flex resistance of all the samples are found to be within the specification limit given in Indian Standards. DCP cured 80/20 NR/LDPE or NR/HDPE blend based sheets show excellent flex resistance. Flex resistance of MC sheets based on NR/LDPE/HSR blend is superior compared to NR/HSR based MC sheets.

Figs.5.2.1 and 5.2.2 show the cell structure of the S-cured 70/30 NR/HSR and 70/20/10 NR/LDPE/HSR blend based MC sheets. A fine and uniform cell structure is formed when a part of HSR is replaced by LDPE. Fig.5.2.3 shows the cell structure of DCP cured 70/20/10 NR/LDPE/HSR based MC sheet. DCP cured MC sheet has a non-uniform cell structure. The study shows that curing agent affects the cell structure of the MC sheets.

CONCLUSION

1. 80/20 NR/LDPE or NR/HDPE blend can be used for making light weight, low cost microcellular soles.
2. A part of HSR in the 70/30 NR/HSR and 60/40 NR/HSR blend can be replaced by LDPE without much reduction in technical properties.
3. 70/15/15 NR/LDPE/HSR or 60/20/20 NR/LDPE/HSR blend can be used for making light weight and good quality MC soles.

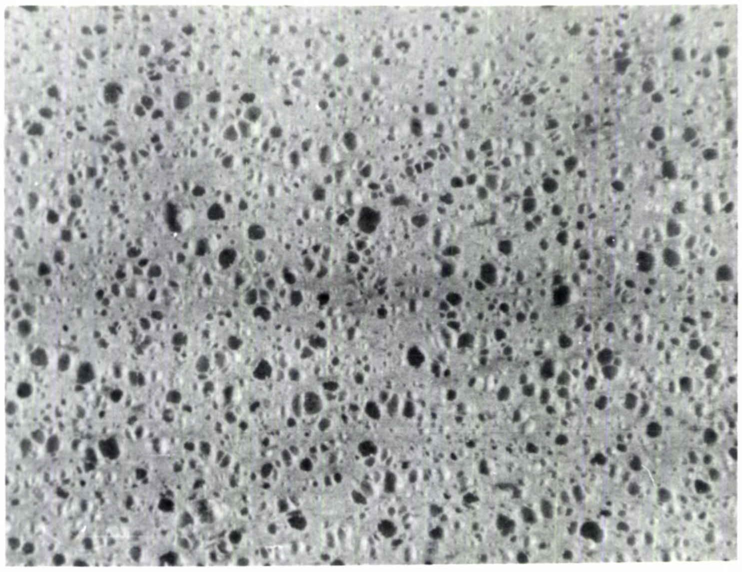

Fig.5.2.1
70/30 NR/HSR
(S-cured)

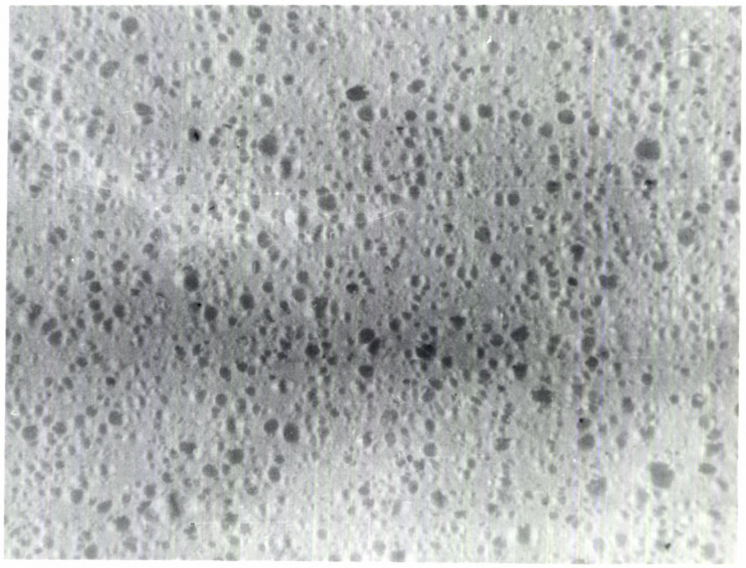

Fig.5.2.2
70/20/10
NR/LDPE/HSR
(S-cured)

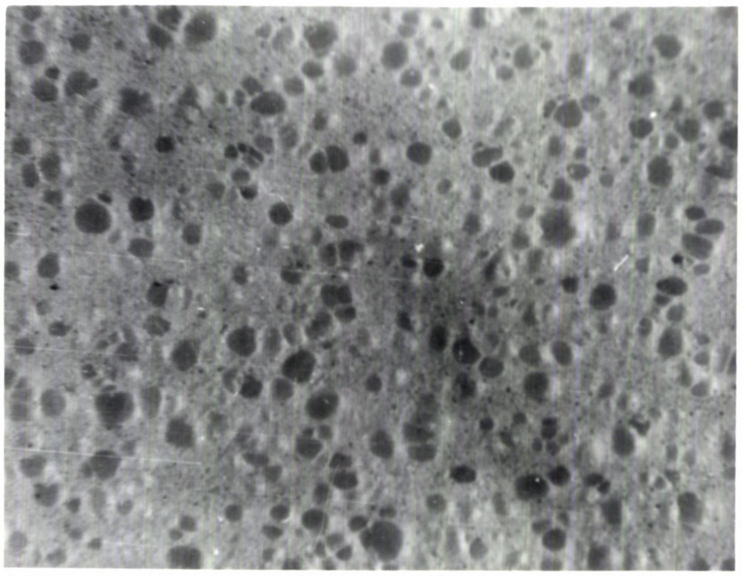

Fig.5.2.3
70/20/10 NR/LDPE/HSR
(DCP cured)

Optical microscope photographs of MC sheets

PART III: DEVELOPMENT OF MICROCELLULAR SOLES BASED ON BR/PE BLENDS FOR LOW TEMPERATURE APPLICATIONS

The elastic properties of rubber change as the temperature is changed. The term 'low temperature stability of rubber' refers to the retention of its elastic properties when cooled below 0°C [20-22]. The problem of low temperature flexibility of vulcanized rubber arises from the fact that its high elastic properties are evident only within a limited temperature range because of the relaxation characteristics. This temperature range depends, not only on the nature of rubber, but also on the conditions of deformations, especially on the time of application of the force. On cooling a rubber loses its rubberiness as the polymer passes through its glass transition temperature (T_g), or by crystallization [22]. As the temperature is reduced toward the T_g the specimen becomes increasingly stiff or "logy", loses resilience and increases modulus and hardness. The low temperature properties depend on the T_g of a polymer. The molecular factors controlling T_g are chain stiffness, interchain attraction, molecular symmetry, copolymerization, branching and crosslinking and finally solvents and plasticizers. So for optimum low temperature properties a low T_g is required [22].

In this part of the study microcellular soles for low temperature application are proposed to be developed using a blend of polybutadiene with T_g (-100°C) and polyethylene with T_g (-25°C). These polymers also possesses excellent flex resistance at room temperature and have a low cost. MC sheets based on NR/BR/PE the ternary blends are also proposed to be developed and technical properties evaluated The mechanical properties of BR/PE and NR/BR/PE blends are also proposed to be evaluated.

Experimental

Preparation of BR/LDPE blends

Blends of polybutadiene rubber (BR) and low density polyethylene (LDPE) were prepared by melt mixing the polymers in a Brabender plasticorder model PL 3S with a rotor speed of 50 rpm at 150°C. LDPE was added and 1 min. was given for its melting, then BR in the form of a sheet was added and 4 more min were given for blending.

The blends obtained from the Brabender plasticorder were sheeted out under hot condition through the open mill at a tight nip gap, NR was masticated, BR/LDPE blend was added and mixed well for 3 min.

To study the mechanical properties of blends, both S-cured and DCP cured blends were prepared (without the blowing agent). Formulations of BR/PE and NR/PE/BR blends are shown in Tables 5.3.1 and 5.3.2. The blends were compounded on a two roll mill and the optimum cure time was determined at 150°C on a Goettfert Elastograph Model 67.85. The sheets were compression moulded at 150°C upto their respective optimum cure times at a pressure of 180 kg/cm^2 in an electrically heated hydraulic press. The mouldings were then cooled by dipping the mould in water.

The tensile and tear properties were measured on a Zwick universal testing machine using a crosshead speed of 500 mm/min. according to ASTM standards.

Table 5.3.1: Formulations and mechanical properties of sulphur cured BR/LDPE and NR/BR/LDPE blends

Ingredients (Phr)	Mix Number						
	A	B	C	D	E	F	G
NR	-	-	30	30	-	30	30
BR	90	80	60	50	90	60	50
LDPE	10	20	10	20	10	10	20
ZnO	4	4	4	4	4	4	4
Stearic acid	6	6	6	6	6	6	6
China clay	60	60	60	60	70	70	70
Precipitated calcium carbonate	40	40	40	40	-	-	-
Microcrumb	25	25	25	25	-	-	-
HAF black	-	-	-	-	30	30	30
Naphthenic oil	5	5	5	5	5	5	5
SP	1	1	1	1	1	1	1
Wood rosin	2	2	2	2	2	2	2
Vulcafor F	1.2	1.2	1.2	1.2	1.2	1.2	1.2
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Sulphur	2	2	2	2	2	2	2
DNPT	6	6	6	6	7	7	7
Cure characteristics							
Optimum cure time (T_{90}) at 150°C min.	7.9	8.1	6.7	6.7	6	5.9	6.8
Vulcanizate properties							
Tensile strength (N/mm^2)	3.9	4.47	6.7	6.9	11.2	12.87	12
Tear strength (N/mm)	13.72	14.1	20.1	23.42	35.62	32.37	31.34
Elongation at break (%)	280	240	290	270	296	310	298

Table 5.3.2: Formulation and mechanical properties of DCP and BR/LDPE and NR/BR/LDPE blends

Ingredients (Phr)	Mix Number						
	H	I	J	K	L	M	N
NR	-	-	30	30	-	30	30
BR	90	80	60	50	90	60	50
LDPE	10	20	10	20	10	10	20
ZnO	4	4	4	4	4	4	4
Stearic acid	5	5	5	5	5	5	5
China clay	60	60	60	60	70	70	70
Precipitated calcium carbonate	40	40	40	40	-	-	-
NR/HSR microcrumb	25	25	25	25	-	-	-
HAF black	-	-	-	-	30	30	30
Dicumyl peroxide (DCP) (40% active)	3	3	3	3	3	3	3
SP	1	1	1	I	1	1	1
Wood rosin	2	2	2	2	2	2	2
Naphthenic oil	4	4	4	4	4	4	4
DNPT	5	5	5	5	5	5	5
<u>Cure characteristics</u>							
Optimum cure time (T_{90}) at 150°C (min.)	24.3	27.3	22.8	23	23.4	20.7	20
<u>Vulcanizate properties</u>							
Tensile strength (N/mm^2)	3.48	4.17	4.92	5.01	9.19	9.69	9.69
Tear strength (N/mm)	14.29	18.2	22.86	23.78	28.01	30.34	30.9
Elongation at break (%)	330	280	320	315	374	370	330

Preparation of microcellular sheets based on BR/PE and NR/BR/PE blends

For the preparation of microcellular soles mixes with blowing agent were compounded according to the formulation given in Table 5.3.1 (S-cured) and Table 5.3.2 (DCP cured). MC sheets were moulded at 150°C upto 80% of their optimum cure time . The expanded sheets were then post cured at 80°C for 2h. Low temperature flexibility of selected samples (90/10 BR/PE and 60/30/10 BR/NR/PE blends) were evaluated according to SATRA PM 60-1992. Procedure is described in chapter 2.

Results and Discussion

The mechanical properties of sulphur cured blends are given in Table 5.3.1. Tensile strength of BR/PE blends increase as the PE content in the blend increases while elongation at break decrease. Replacement of a part of BR by NR improves the tensile strength. 30/50/20 NR/BR/PE blend shows increase in tensile strength compared to 30/60/10 NR/BR/PE blend. But elongation decreases with increase in the quantity of PE obviously due to the crystalline nature of PE [18]. On addition of HAF black there is an improvement in tensile strength as expected . In blends with a higher content of rubber the effect of carbon blacks on the mechanical properties is more pronounced, is due to the interaction of carbon black and rubber which leads to an increase in tensile strength [23]. The tensile properties get marginally reduced by using DCP as curing agent as shown in Table 5.3.2. The optimum cure time of compounds are increased when DCP is used as curing agent. On addition of HAF black there is an improvement in tensile strength as observed in sulphur cured sample. Tear strength also shows a similar behaviour.

i) Properties of microcellular soles based on sulphur cured BR/PE and NR/BR/PE blends

Table 5.3.3 shows the technical properties of S-cured microcellular sheets. The cure characteristics of the compounds show that, this type of blend based compound has lowest cure time, which can lead to higher expansion of MC sheets. Highest expansion is obtained with the 80/20 BR/PE blend leading to low density and hardness.

The split tear strength of the microcellular sheets based on BR/PE blend is low while abrasion loss is high. Compression set and heat shrinkage are found to increase with PE content in the blend. This may be due to the lower extent of crosslinking and higher expansion of the MC sheets. Water absorption decreases with increase in the amount of PE in the blend due to the increase in the number of open cells.

When a part of BR is replaced by NR, there is reduction in the expansion of the MC sheet with a corresponding increase in the relative density. Higher expansion is obtained for 30/50/20 NR/BR/PE blend with low density. Split tear strength of the MC sheet improves marginally with addition of NR. A 30/50/20 NR/BR/PE shows marginal decrease in strength, which may be due to presence of higher amount of PE, which produces higher expansion. Hardness and heat shrinkage decrease with PE content in NR/BR/PE blends. When compared to BR/PE blends hardness and abrasion resistance of these ternary blends are marginally superior. Shrinkage after post curing also decreases in NR/BR/PE blends. However, BR/PE blends show excellent flex resistance compared to NR/BR/PE blends.

Table 5.3.3 shows the effect of addition of HAF black as filler in NR/BR/PE and BR/PE blends (Mixes E, F, G) based microcellular soles. Addition of HAF black improves

Table 5.3.3: Technical properties of sulphur cured microcellular soles based on BR/LDPE and NR/BR/LDPE blends

Properties	Mix Number						
	A	B	C	D	E	F	G
Optimum cure time at 150°C min.	7.5	8	5.5	6	6.6	5.9	6.8
Initial expansion (%)	65.48	67.86	47.62	48.8	50	42.86	47.62
Expansion after 5 min. (%)	38.09	39.28	34.52	34.52	36.6	26.9	34.52
Expansion after 24 h (%)	28.57	30.95	25.57	28.57	29.76	27.43	23.81
Expansion ratio	2.3	2.58	1.87	1.9	1.77	1.41	1.65
Relative density	0.519	0.481	0.62	0.604	0.551	0.72	0.709
Split tear strength (kg)	2.68	2.73	2.75	2.69	2.7	2.9	2.99
Abrasion loss (mm^3)	317.7	379.5	304.5	340	363	294.8	296
Hardness (Shore A)	28	27	32	30	38	45	42
Heat shrinkage (%)	2.89	2.84	2.04	2.19	1.79	1.03	1.13
Compression set (%)	11.01	12	9.2	10.3	7.2	7.19	8.2
Water absorption (percent by mass)	0.114	0.129	0.107	0.114	0.098	0.087	0.090
Shrinkage after post curing (%)	4.04	4.762	3.85	3.92	2.912	2.88	3.0
Flex resistance							
a) Crack initiation in cycles	297,970	297,970	275,100	275,100	299,500	290,500	290,500
b) Crack growth at the end of 100,000 cycles (%)	<600	<600	<600	<600	<600	<600	<600
Low temperature flexibility at –5°C, KC	1.5		1.5		1.5	1.5	

split tear strength and hardness. Heat shrinkage and expansion of MC sheets decrease with the addition of HAF black. Water absorption and compression set also decrease with the addition of HAF black. This may be due to the lower expansion of MC sheets. Relative density of MC sheets increase with the addition of HAF black as shown in Table 5.3.3. Blends with higher content of rubber show a higher strength on addition of black as expected [24].

Flex resistance of all the samples are within the IS specification. Cracks develop after 297970, and 275100 cycles for BR/PE and NR/BR/PE blend respectively. Crack size growth after 100,000 cycles is also found to low for these blends based MC sheets. 90/10 BR/PE and 60/30/10 BR/NR/PE blend based MC sheets show excellent low temperature flexibility.

(ii) Properties of microcellular soles based on DCP cured BR/PE and NR/BR/PE blends

Table 5.3.4 shows the technical properties of DCP cured microcellular sheets DCP cured microcellular sheets based on BR/PE blend achieve a higher degree of expansion and hence lower densities. As the amount of PE increases expansion further increases and this leads to very low densities. There is a marginal increase in split tear strength for the DCP cured MC sheets compared to sulphur cured MC sheets. Abrasion loss and water absorption are comparatively higher for DCP cured MC sheets due to the higher expansion. Lower hardness is obtained for DCP cured MC sheets. Heat shrinkage decreases with increase in PE content in BR/PE blend and compression set marginally increases. This increase in compression set may be due to the lower extent of crosslinking due to higher expansion.

When a part of BR is replaced by NR expansion reduces and relative density increases. Properties like hardness, compression set, split tear strength and abrasion resistance are

Table 5.3.4: Technical properties of DCP cured microcellular soles based on BR/PE and NR/BR/PE blends

Properties	Mix Number						
	H	I	J	K	L	M	N
Optimum cure time at 150°C min.	8	8.1	9.9	9.5	10	10.4	11
Initial expansion (%)	80.92	84.52	59.52	72.62	76.19	50	51.19
Expansion after 5 min. (%)	41.66	55.95	40.48	48.8	44.05	30.95	33.3
Expansion after 24 h (%)	36.9	40.48	35.71	39.28	38.69	28.57	28.57
Expansion ratio	2.386	2.39	2.10	2.295	2.1	1.745	1.898
Relative density	0.4338	0.3785	0.4458	0.4223	0.5188	0.607	0.59
Split tear strength (kg)	2.9	2.957	3.01	2.6	3.2	3.81	3.95
Abrasion loss (mm^3)	392	412	311.7	360	328.7	301.4	318.6
Hardness (Shore A)	25	23	27	24	28	32	31
Heat shrinkage (%)	5.494	4.44	2.22	2.896	4.237	3.226	3.34
Compression set (%)	18.67	19.14	17.66	18.65	16.49	15.1	15.95
Water absorption (percent by mass)	0.127	0.1386	0.1185	0.121	0.11	0.098	0.0989
Shrinkage after post curing (%)	6.307	6.71	5.39	6.01	5.185	4.396	3.614
Flex resistance							
a) Initiation crack in cycles	267.500	267.500	250.500	250.500	250.170	250.170	246.516
b) Crack growth at the end of 100.000 cycles (%)	<600	<600	<600	<600	<600	<600	<600
Low temperature flexibility –5°C, KC	1.5		1.5		1.5	1.5	

improved. Heat shrinkage and water absorption decrease. Shrinkage after post curing is also found to decrease with the partial replacement of BR by NR. Addition of HAF black in DCP cured compounds shows improvement in technical properties as shown in Table 5.3.4.

Flex resistance of DCP cured MC sheets also show comparable values. Here crack initiation starts after 267,500 cycles for BR/PE blends and 250,170 cycles for NR/BR/PE blend as shown in Table 5.3.4. Low temperature flexibility values of the samples show that a 90/10 BR/PE and 60/30/10 BR/NR/PE blend based MC sheets are suitable for low temperature application.

Fig.5.3.1 shows the cell structure of 90/10 BR/PE (S-cured) MC sheets and Fig.5.3.2 that of 30/60/10 NR/BR/PE (S-cured) MC sheet. BR/PE blend based MC sheet shows smaller and uniform cells. When part of BR is replaced by NR, there is not much change in the cell structure.

CONCLUSION

1. Very low density microcellular soles can be obtained from BR/PE and NR/BR/PE DCP cured blends with excellent flex resistance.
2. Sulphur cured MC sheets show improvement in technical properties like hardness, split tear strength, abrasion resistance etc. compared to DCP cured MC sheets.
3. 90/10 BR/PE and 60/30/10 BR/NR/PE blend based microcellular soles are suitable for low temperature applications.

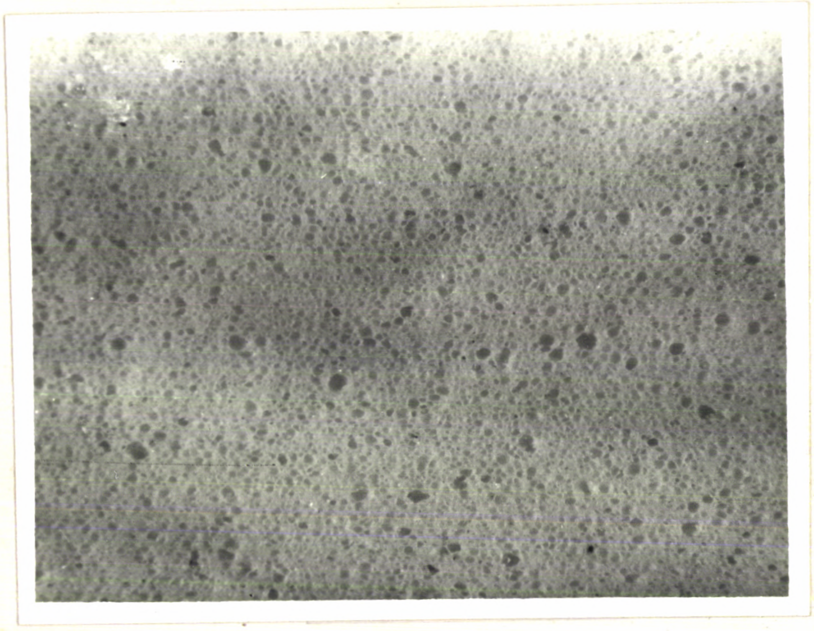

Fig.5.3.1 90/10 BR/PE
(S-cured)

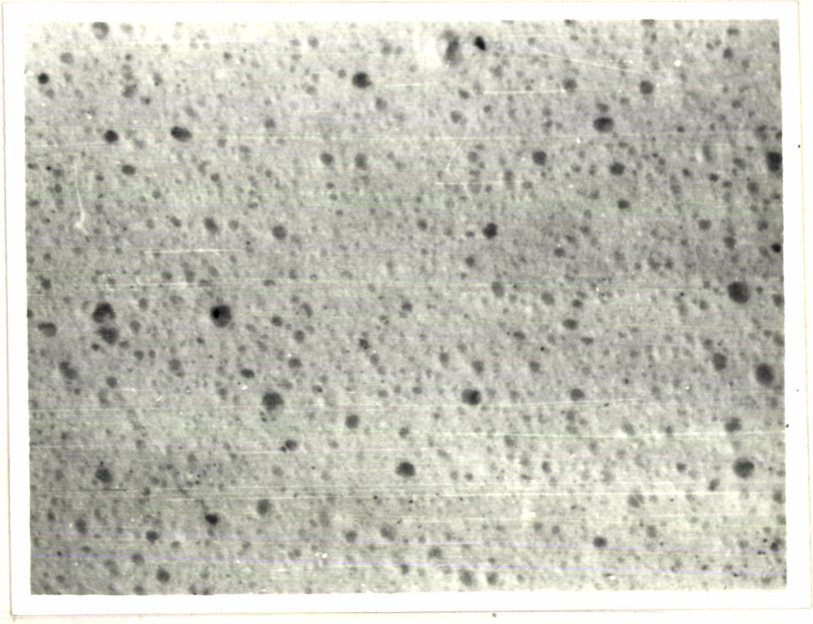

Fig.5.3.2 60/30/10 BR/NR/PE
(S-cured)

Optical microscope photographs of MC sheets

PART IV: DEVELOPMENT OF MICROCELLULAR SOLES BASED ON BR/HSR BLENDS

Polybutadiene rubber is used in footwears due to their excellent abrasion resistance, good resistance to crack initiation and high resilience [25]. Indian Petrochemical Corporation Limited has footwear grade polybutadiene, having the properties, superior tensile strength, elongation, flex cracking properties, abrasion resistance and excellent low temperature flexibility.

The high-styrene resins are used primarily to increase vulcanizate hardness with very little increase in density [26,27]. The present study investigates the suitability of BR/HSR blends for making light weight microcellular soles. Complete replacements of NR may be necessary in some cases due to the protein allergy caused by the extractable protein present in natural rubber. The mechanical properties of BR/HSR blends are also proposed to be evaluated.

Experimental

The polybutadiene rubber was masticated at a temperature of 45-50°C until a good band was formed on the roll. Then HSR in the form of a sheet was added and mixed well.

In order to determine the tensile properties of the blends, the blends were compounded without blowing agent as per formulation given in Table 5.4.1. The optimum cure time of the compounds were determined using a Goettfert Elastograph 67.85. The compound was moulded in an electrically heated hydraulic press upto their optimum cure times at 150°C and the mechanical properties were tested according to the relevant ASTM standards.

Table 5.4.1

Formulation and mechanical properties of BR/HSR blends

Ingredients (Phr)	Mix Number		
	1	2	3
Polybutadiene rubber	60	70	80
High Styrene Resin	40	30	20
Zinc oxide	4	4	4
Stearic acid	7	7	7
China clay	60	60	60
Precipitated calcium carbonate	40	40	40
NR/HSR crumb	25	25	25
Naphthenic oil	3	3	3
SP	1	1	1
Vulcafor F	1.2	1.2	1.2
Sulphur	2	2	2
DNPT (100% active)	6	6	6
<u>Cure characteristics</u>			
Optimum cure time at 150°C min	5.5	6.9	6.3
<u>Properties</u>			
Tensile strength (N/mm^2)	4.1	4.9	5.5
Tear strength (N/mm)	14.5	16.5	16.54
Elongation at break (%)	550	500	480
Modulus (at 300% elongation) N/mm^2	6.53	6.8	7.8

Preparation of microcellular sheets.

The blends were compounded with blowing agents (formulations shown in Table 5.4.1). The MC sheets were moulded in an electrically heated hydraulic press at 150°C. The mould was filled with three to five percent excess of the compound on volume basis. The compounds were precured in the mould up to 80% of their respective optimum cure times. The expanded sheets were then post cured in an air oven for 2 hrs at 80°C.

The technical properties of microcellular sheets were evaluated according to the relevant Indian Standards. The cell structure of razor cut samples of MC sheets were studied using an optical microscope.

Results and Discussion

Table 5.4.1 shows the cure characteristics and mechanical properties of BR/HSR blends. The BR/HSR blends show a lower cure time compared to the NR/HSR blends. Tensile strength and tear strength increase with BR content in the blend while elongation at break decreases. The increase in tensile strength only at lower levels of HSR shows that the blends containing higher levels of HSR is incompatible.

Fig.5.4.1 shows the variation of expansion ratio and relative density with increase in BR content in the blend. Volume of expansion of the MC sheets increases with increase in BR content, while relative density decreases.

Fig.5.4.2 shows the variation of split tear strength and abrasion loss sheets with increase in BR content in the blend. Split tear strength marginally decreases with increase in

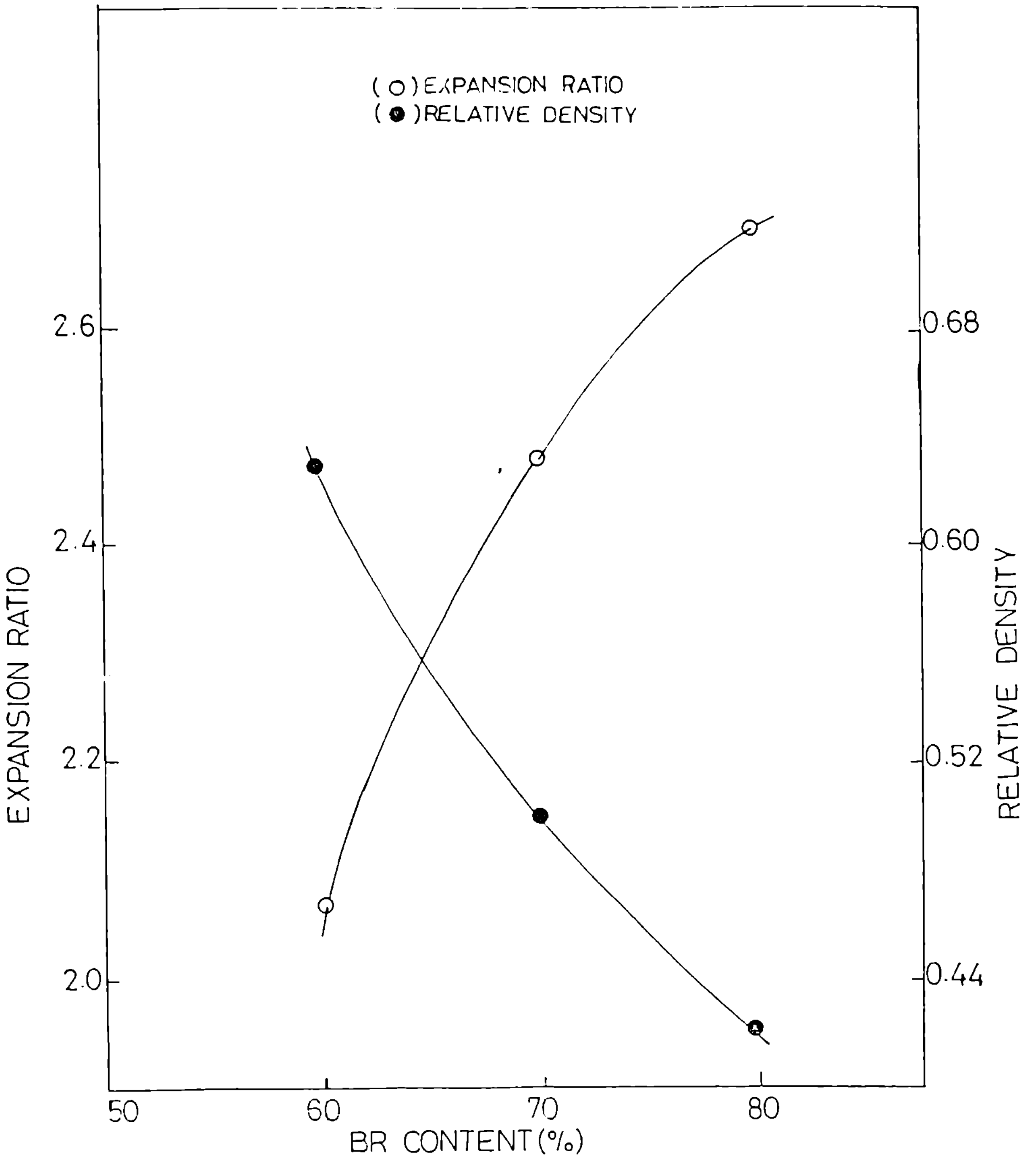

Fig.5.4.1 Variation of expansion ratio and relative density with increase in the amount of BR.

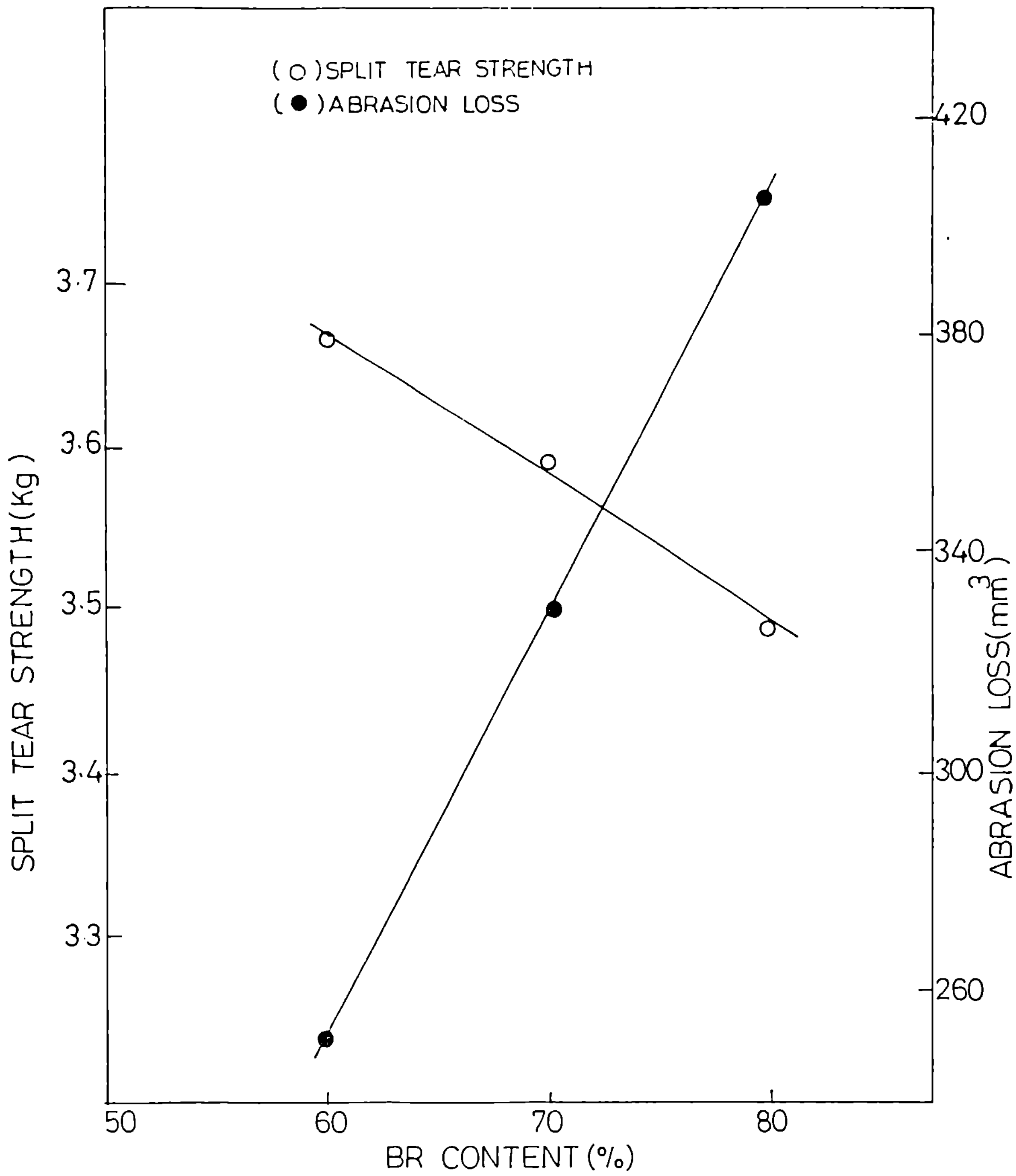

Fig.5.4.2 Variation of split tear strength and abrasion loss with increase in the amount of BR.

BR content in the blend. This decrease may be due to the increase in expansion, which decreases as the rubber content increases [9]. Tensile properties (Table 5.4.1) increase with increase in rubber content. Abrasion loss of the MC sheet increases with increase in BR content in the blend. The 60/40 BR/HSR blend based MC sheets show higher abrasion resistance compared to conventional NR/HSR blend based MC sheets.

Fig.5.4.3 shows the variation of hardness and heat shrinkage with increase in the amount of BR in the blend. Hardness of the MC sheet decreases with increase in BR content. Heat shrinkage marginally reduces with BR content in the blend. This may be due to the lower percentage of open cells present in the MC sheets.

Fig.5.4.4 shows the variation of water absorption and compression set with increase in amount of BR in the blend. Water absorption shows a marginal increase with BR content in the blend. The water absorption is found to be lower compared to conventional soles which shows that the MC sheets contain only a small percentage of open cells which is also evident from the lower shrinkage of the MC sheets. Compression set values decrease with increase in BR content in BR/HSR blend.

Shrinkage after post curing marginally increases with increase in BR content. This may be due to the higher expansion of the MC sheets, at high BR levels. Flex resistance of samples are shown in Table 5.4.2. Compared to conventional NR/HSR based MC soles, BR/HSR blend based MC sheets show higher flex resistance. Crack growth is also found to be lower for BR/HSR blend based MC sheets.

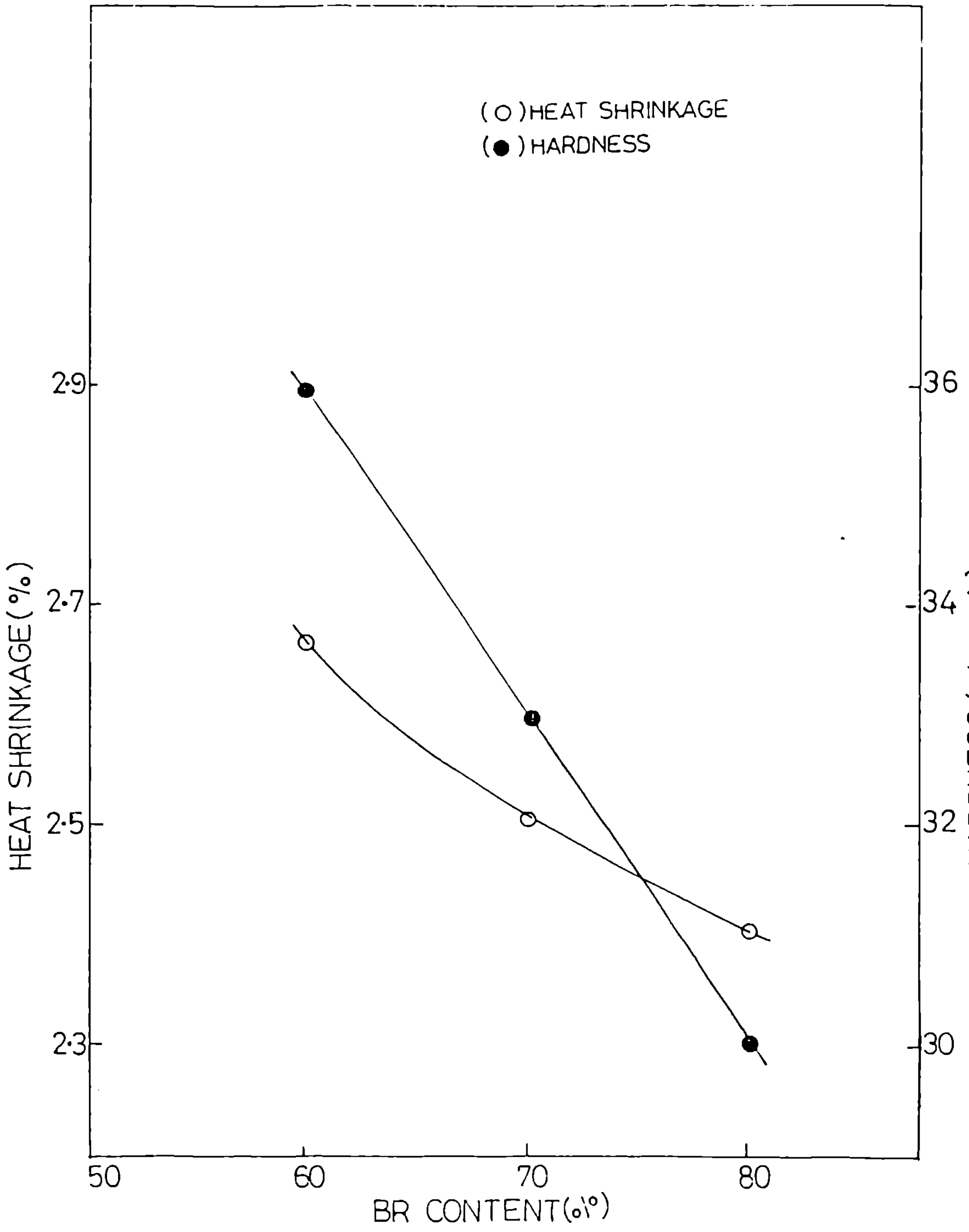

Fig.5.4.3 Variation of heat shrinkage and hardness with increase in the amount of BR.

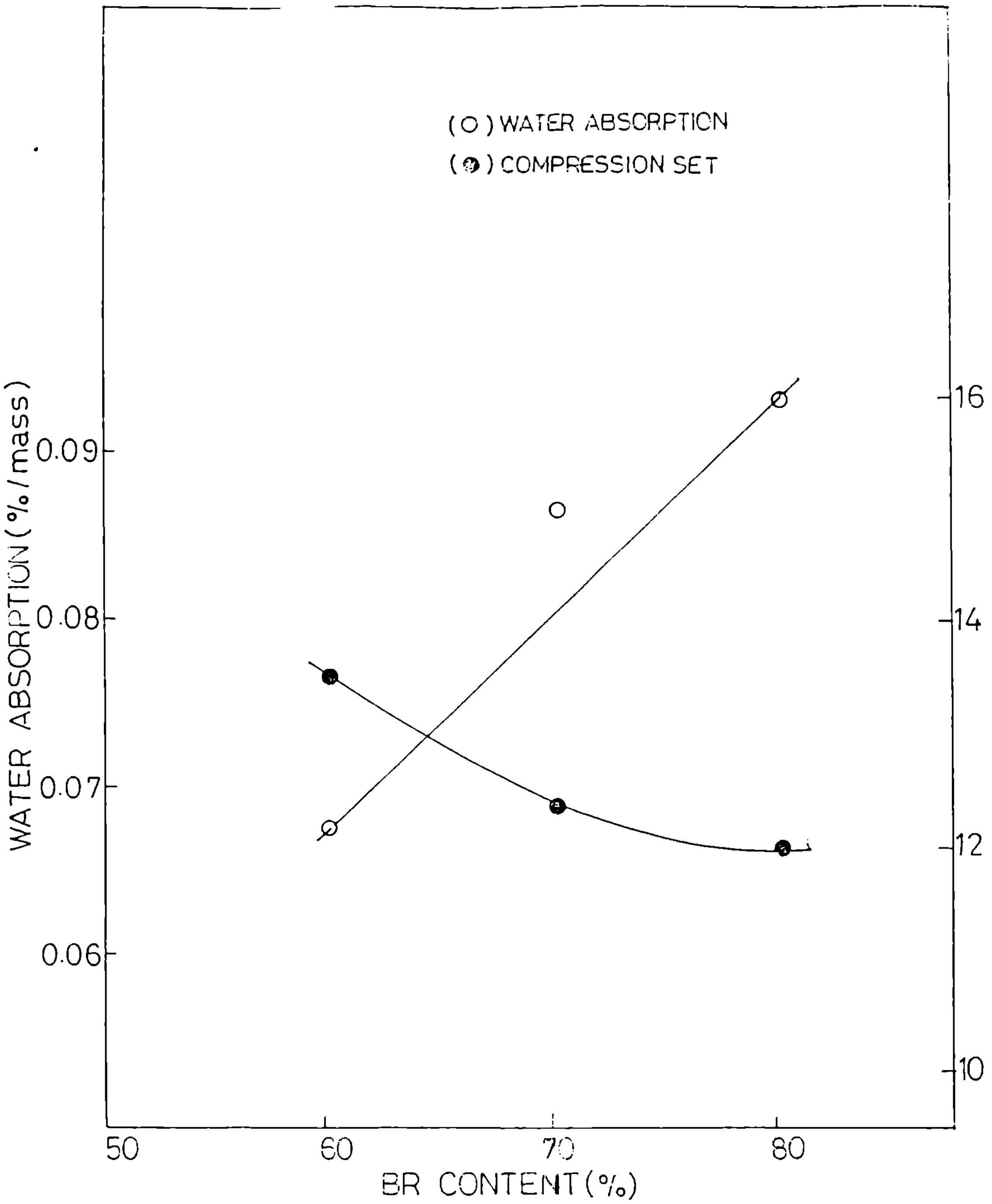

Fig.5.4.4 Variation of water absorption and compression set with increase in the amount of BR.

Table 5.4.2

Technical properties of microcellular soles based on BR/HSR blends

Properties	Mix Number		
	1	2	3
Optimum cure time at 150°C (min.)	5	5	5.5
Initial expansion (%)	60.11	69.05	71.43
Expansion after 5 min. (%)	42.26	47.62	51.78
Expansion after 24 h (%)	27.38	33.93	35.71
Change in hardness after ageing 100°C for 24 hrs	+2	+1	+2
Shrinkage after post curing (%)	5.67	5.78	5.99
Room temperature shrinkage (%)	0.834	0.869	0.934
Flex resistance			
a) Crack initiation in cycles	319,000	329,000	329,000
b) Crack growth at end of 100,000 cycles (%)	<600	<600	<600

Figs.5.4.5 and 5.4.6 show the optical microscope photographs of 70/30 and 80/20 BR/HSR MC sheets. As the amount of BR increases number of cells increases but at the expense of the uniformity. This supports the earlier observation of higher water absorption and lower technical properties.

CONCLUSION

1. A 60/40 BR/HSR blend can be used for making light weight microcellular soles.
2. BR/HSR is a fast curing blend and hence is more economical compared to conventional soles.
3. BR/HSR blend based MC soles show good abrasion resistance, flex resistance, low shrinkage and water absorption.

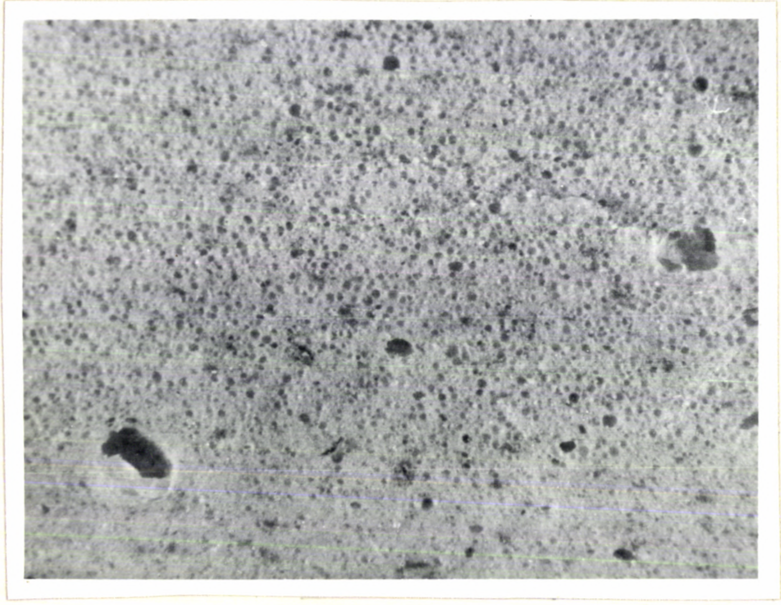

Fig.5.4.5 70/30 BR/HSR

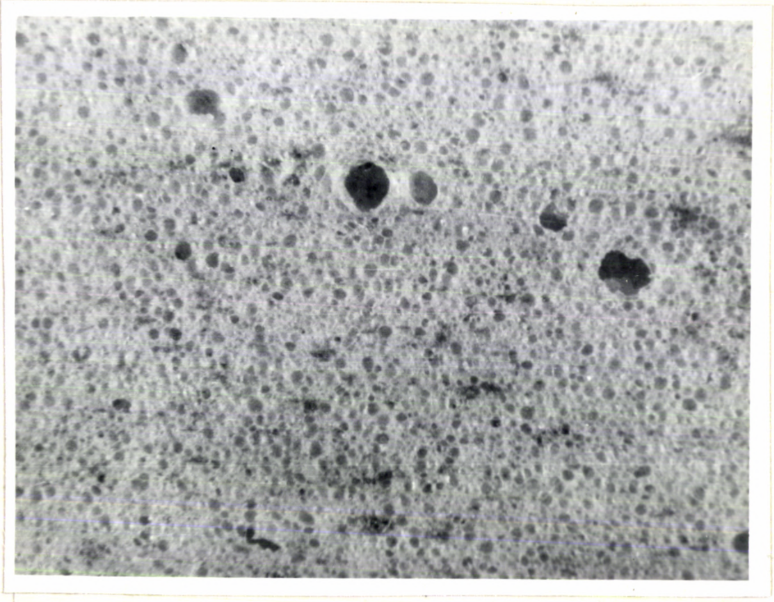

Fig.5.4.6 80/20 BR/HSR

Optical microscope photographs of MC sheets

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CHAPTER 6

PART I: MODIFICATION OF NR/HSR MC SOLE WASTE AND LATEX FOAM WASTE FOR UTILISATION IN MICROCELLULAR SOLES BASED ON NR/HSR BLENDS

Protection of the environment has become a strategic issue for the industrial and business sectors in recent times. Because of this recycling of polymeric materials has recently attracted increasing interest and activity [1]. The utilisation of dry rubber reclaim in rubber industry is widely practised to reduce the compound cost and to conserve energy and raw materials [2-5]. But due to the deterioration in properties the use of dry rubber reclaim constitutes only a very low percentage of total rubber consumption [6-8]. Recycling of materials from discarded products is intended to reduce the amount of waste and the use of virgin raw material and conserve energy [9-12].

Rubber footwear industry has a very significant position among the other footwear industries. Rubber footwears are usually cut from, the microcellular sheets, and the rejects constitute large amount of waste materials. Only small amount of waste thus generated is reused in the MC sheet manufacture and the rest goes as dumped waste.

The waste obtained from latex foam manufacture is the compound squeezed out of the moulds during the moulding and is called "flash" [13]. Latex foam waste represents a source of high quality rubber hydrocarbon and, it is a potential material for reclaimed rubber.

In this study different chemical modifications are proposed to be done on MC sole waste and foam waste to further improve its quality as reclaimed rubber. This modified MC sole waste and foam is proposed to be added in NR/HSR based MC soles. We also wish to study the effect of addition of modified MC sole waste and foam waste as fillers and as partial replacement of NR in NR/HSR blend based microcellular soles. Properties of these MC soles are proposed to be compared with the commercial ones.

Experimental

Preparation of modified NR/HSR microcrumb

The MC sole waste was passed through the tight nip of a two roll mill for 15 minutes and sheeted out. About 20 g natural rubber was masticated on the two roll mill and 0.5 g Z-MBT and 3 g parafinic oil were added and 200 g MC sheet waste was then added. This was then autoclaved at 125°C for 2 hours at 25 kg/cm^2 pressure.

Preparation of modified foam waste

The foam waste was dried properly after passing through the tight nip of a mixing mill. Then 20 g natural rubber was masticated on the mixing mill, 0.5 g MBT and 3 g naphthenic oil were added and then 100 g of foam waste was added and the homogenization was done for another 5 minutes. The properties of this modified latex foam waste are shown in Table 6.1.1.

Preparation of NR/HSR blend based MC sheets

NR/HSR blend was prepared on a laboratory mixing mill. NR was masticated on a two roll mill and HSR in the form of a sheet was then added. The blends were then compounded in a laboratory mixing mill (150x300 mm) at a friction ratio 1:1.25 according to the formulations given in Tables 6.1.2 to 6.1.4. Modified and unmodified microcrumb and the unmodified foam waste were used as fillers, while the modified foam waste was used to replace NR. The optimum cure time of the compounds were determined using Goettfert

Table 6.1.1: Properties of modified latex foam waste

Properties	
Mooney viscosity (ML 1+4)100°C	64
Initial plasticity Po	46
Ash content % by mass	48.42
Rubber hydrocarbon (%)	49.37
Free sulphur (% by mass)	1.54
Volatile matter % by mass	0.67

Table 6.1.2

Formulations and properties of NR/HSR based microcellular soles containing NR/HSR microcrumb

Ingredients	(Phr)	Properties	Unmodified micro-crumb	Modified microcrumb	Autoclaved microcrumb
Natural rubber	70	Optimum cure time (T_{90}) 150°C (min.)	10.2	9.76	9.7
High Styrene Resin	30	Scorch time (T_{10}) 150°C (min.)	2.7	2.3	2.2
Zinc oxide	5	Initial expansion (%)	79.76	80.95	64.28
Stearic acid	6	Expansion after 5 min. (%)	38.09	40.47	32.14
Precipitated silica	20	Expansion after 24 h (%)	28.57	28.57	27.38
China clay	80	Expansion ratio	2.04	2.1	1.96
Diethylene glycol	1.5	Relative density	0.495	0.483	0.567
Naphthenic oil	5	Split tear strength (kg)	4.49	5.14	5.24
Unmodified/modified/autoclaved microcrumb	50	Abrasion loss (mm^3)	302	259.3	247.2
		Heat shrinkage (%)	4.76	4.01	3.72
Vulcafor F	1.2	Hardness (Shore A)	51	54	59
Styrenated phenol (SP)	1	Change in hardness after ageing 24 h at 100°C	+2	+3	+2
Wood rosin	2	Water absorption (% by mass)	0.118	0.117	0.119
Sulphur	2.25	Compression set (%)	8.42	8.21	8.28
DNPT	6	Shrinkage after post curing (%)	5.95	4.76	3.57
		Room temperature shrinkage (%)	1.9	1.5	0.98
		Flex resistance			
		a) Crack initiation in cycles	85,750	86,000	87,760
		b) Crack growth at the end of 100,000 cycles (%)	<600	<600	<600

Table 6.1.3: Formulations for NR/HSR based MC sole compounds containing latex foam waste

Ingredients (Phr)	Mix Number				
	1	2	3	4	5
NR	70	60	55	50	45
HSR	30	30	30	30	30
Latex foam waste	0	20	30	40	50
Zinc oxide	5	5	5	5	5
Stearic acid	6	6	6	6	6
Precipitated silica	20	20	20	20	20
China clay	80	80	80	80	80
Diethylene glycol	1.5	1.5	1.5	1.5	1.5
Naphthenic oil	5	5	5	5	5
Vulcafor F	1.2	1.2	1.2	1.2	1.2
SP	1	1	1	1	1
Wood rosin	2	2	2	2	2
Sulphur	2.25	2.25	2.25	2.25	2.25
DNPT	6	6	6	6	6

Table 6.1.4

Formulations for NR/HSR based MC sole compounds containing vulcanized foam waste

Ingredients (Phr)	Mix Number			
	6	7	8	9
NR	70	70	70	70
HSR	30	30	30	30
Zinc oxide	5	5	5	5
Stearic acid	6	6	6	6
Vulcanized latex foam waste	20	30	40	50
Precipitated silica	20	20	20	20
China clay	80	80	80	80
Diethylene glycol	1.5	1.5	1.5	1.5
Naphthenic oil	5	5	5	5
Vulcafor F	1.2	1.2	1.2	1.2
SP	1	1	1	1
Wood rosin	2	2	2	2
Sulphur	2.25	2.25	2.25	2.25
DNPT	6	6	6	6

Elastograph model 67.85. The MC sheets containing NR/HSR microcrumb were then moulded in an electrically heated hydraulic press at 150°C upto 80% of their optimum cure time while the sheets containing foam waste were moulded at 160°C. The mould was loaded with 3 to 5 percent excess of the compound on volume basis. The expanded sheets were then post cured in an air oven for 1 hour at 100°C.

The technical properties of the MC sheets were evaluated according to the relevant Indian Standards and described in chapter 2. The cell structure of the selected razor cut samples of microcellular sheets were studied using an optical microscope.

Results and discussion

A. Effect of addition of NR/HSR sole waste on NR/HSR based MC soles

Optimum cure time and scorch time are marginally reduced when unmodified and modified microcrumb are used as fillers in NR/HSR based microcellular soles. Similar trend is observed for the compound containing autoclaved sample also as shown in Table 6.1.2. This is possibly due to the presence of crosslinking precursors and/or unreacted curatives in the micro crumb [6,12].

Expansion of the MC sheet is marginally higher and relative density lower when modified crumb is added to it as compared to unmodified microcrumb. With the addition of autoclaved microcrumb expansion of the MC sheet marginally decreases and consequently, the relative density of the MC sheet increases. MC sheets containing autoclaved microcrumb show higher relative density compared to modified and unmodified microcrumb as shown in Table 6.1.2. Hardness and split tear strength of the MC sheets increase with the addition of unmodified, modified and autoclaved microcrumb. The sheets containing modified and autoclaved crumb show higher split tear strength and hardness. This may be due to the presence of already vulcanized crumb [14]. Abrasion loss is found to be lower for MC sheet containing autoclaved microcrumb. Heat shrinkage of the MC sheets decrease with the addition of modified and autoclaved microcrumb. This is due to the presence of already vulcanized crumb. Water absorption remains the same with modified and autoclaved microcrumb. Compression set is marginally reduced with modified and autoclaved microcrumb.

By the addition of modified and autoclaved crumb shrinkage after postcuring is considerably reduced as shown in Table 6.1.2. Flex resistance of the samples are shown in Table 6.1.2. For the samples containing unmodified microcrumb, crack initiation occurs at a lower number of cycles compared to sheets containing modified and autoclaved microcrumb. Flex resistance of NR/HSR based MC soles is less than other MC soles, eg. SBS/SBR, SBS/NR etc. Modified microcrumb improves the flex resistance of the NR/HSR MC soles.

B. Effect of addition of latex foam waste in NR/HSR blend based microcellular soles

(i) Effect of replacement of NR by latex foam waste in NR/HSR blend based microcellular soles

Table 6.1.5 shows the cure characteristics of the compound containing latex foam waste. The optimum cure time (T_{90}) and the scorch time (T_{10}) are found to decrease with the addition of latex foam waste. This may be due to the unreacted curatives present in latex foam waste [6].

Relative density marginally increases with the addition of latex foam waste. Consequently expansion of MC sheet marginally decreases. This is because the addition of

Table 6.1.5: Cure characteristics and technical properties of MC soles based on NR/HSR blends

Properties	Mix Number				
	1	2	3	4	5
Scorch Time T_{10} at 160°C (min.)	2.2	2.0	1.9	1.8	1.5
Optimum cure time T_{90} at 160°C (min.)	8.1	7.4	7	6.4	5.3
Initial expansion (%)	70.24	61.9	60.7	58.33	57.14
Expansion after 5 min. (%)	45.24	40.47	38.09	35.71	33.33
Expansion after 24 h (%)	36.9	33.33	32.14	30.95	28.57
Expansion ratio	2.69	2.60	2.59	2.35	2.27
Relative density	0.361	0.366	0.371	0.407	0.412
Split tear strength (kg)	4.6	4.66	4.74	4.7	4.2
Compression set (%)	11.98	11.89	11.1	10.61	9.94
Abrasion loss (mm^3)	462	457.1	386.1	371	368.2
Hardness (Shore A)	49	50	52	54	56
Change in hardness after ageing 100°C for 24 h	+2	+1	+2	+1	0
Heat shrinkage (%)	2.51	2.45	2.22	2.21	2.08
Water absorption (% by mass)	0.225	0.19	0.162	0.148	0.127
Shrinkage after post curing (%)	3.91	3.54	2.84	2.5	2.1
Flex resistance					
a) Crack initiation in cycles	71.475	71.475	70.541	70.100	65.000
b) Crack growth at the end of 100.000 cycles (%)	<600	<600	<600	<600	<600

already crosslinked latex foam waste restricts the expansion of the MC sheets as shown in table. Split tear strength of the MC sheets marginally increase with the addition of latex foam waste up to 15 phr and then decrease with further addition of latex foam waste. This may be due to the poor distribution of latex foam waste at higher concentration. Compression set of the MC sheets decrease with the addition of latex foam waste. This may also be due to the lower expansion of MC sheets as shown in table. Abrasion loss is found to decrease with the addition of latex foam waste. This may be due to the decrease in expansion of the MC sheets and also due to the higher crosslink density of the vulcanizates containing latex foam waste. Hardness of the MC sheets increase with the addition of latex foam waste. This is due to the higher density of MC sheets containing latex foam waste.

Table 6.1.5 shows the variation of heat shrinkage and water absorption with increase in the amount of latex foam waste. Heat shrinkage marginally decreases with the addition of latex foam waste. This is due to the lower expansion in presence of latex foam waste and due to the higher crosslink density of vulcanizates containing latex foam waste. Water absorption decreases as the amount of latex foam waste increases. This may be due to the lower expansion of MC sheets. Flex resistance of the samples are shown in table. Flex resistance of the MC sheets are within the IS specifications. Shrinkage after postcuring is found to decrease with increase in the amount of latex foam waste as expected.

(ii) Effect of vulcanized latex foam waste as filler in MC soles based on NR/HSR blends

The cure characteristics of the compounds are shown in Table 6.1.6. The optimum cure time is found to decrease with increase in the amount of latex foam waste.

Table 6.1.6

Effect of amount of vulcanized latex foam waste on technical properties of microcellular soles based on NR/HSR blends

Properties	Mix Number			
	6	7	8	9
Optimum cure time at 160°C (T_{90}) min.	6.5	6	5.8	5.3
Scorch time (T_{10}) at 160°C min.	2.9	2.5	2.3	1.9
Initial expansion (%)	71.43	65.48	60.71	59.52
Expansion after 5 min. (%)	38.09	34.52	33.33	32.14
Expansion after 24 h (%)	33.33	29.79	28.57	28.57
Shrinkage after post curing (%)	4.31	3.53	2.67	1.73
Flex resistance				
a) Crack initiation in cycles	90.475	90.157	90,157	89.875
b) Crack growth at the end of 100.000 cycles (%)	<600	<600	<600	<600

Fig.6.1.1 shows the variation of expansion ratio and relative density with increase in the amount of latex foam waste in MC soles based on NR/HSR blends. This is similar to the case of modified latex foam waste, where the expansion decreases with the addition of latex foam waste and consequently relative density marginally increases.

Fig.6.1.2 shows the variation of split tear strength and abrasion loss with increase in the amount of latex foam waste. Split tear strength marginally reduces with the addition of latex foam waste. This may be due to the poor distribution of latex foam waste at higher concentration. Abrasion loss decreases up to 40 phr but, on further addition abrasion loss increases. This may be due to the large size of latex foam waste. This also explains the deterioration in properties at higher concentration of latex foam waste.

Figure 6.1.3 shows the variation of hardness and heat shrinkage with increase in the amount of latex foam waste. Hardness of the MC sheet increases with the addition of latex foam waste while heat shrinkage decreases with the addition of latex foam wastes as expected.

Fig.6.1.4 shows the variation of water absorption and compression set with increase in the amount of latex foam waste. Water absorption and compression set decrease with the addition of latex foam waste. This may be due to the lower expansion and higher crosslink density of the vulcanizates containing latex foam waste.

The flex resistance of the MC sheets are shown in Table 6.1.6. The flex resistance of all the MC sheets are within the specification limits of Indian standards.

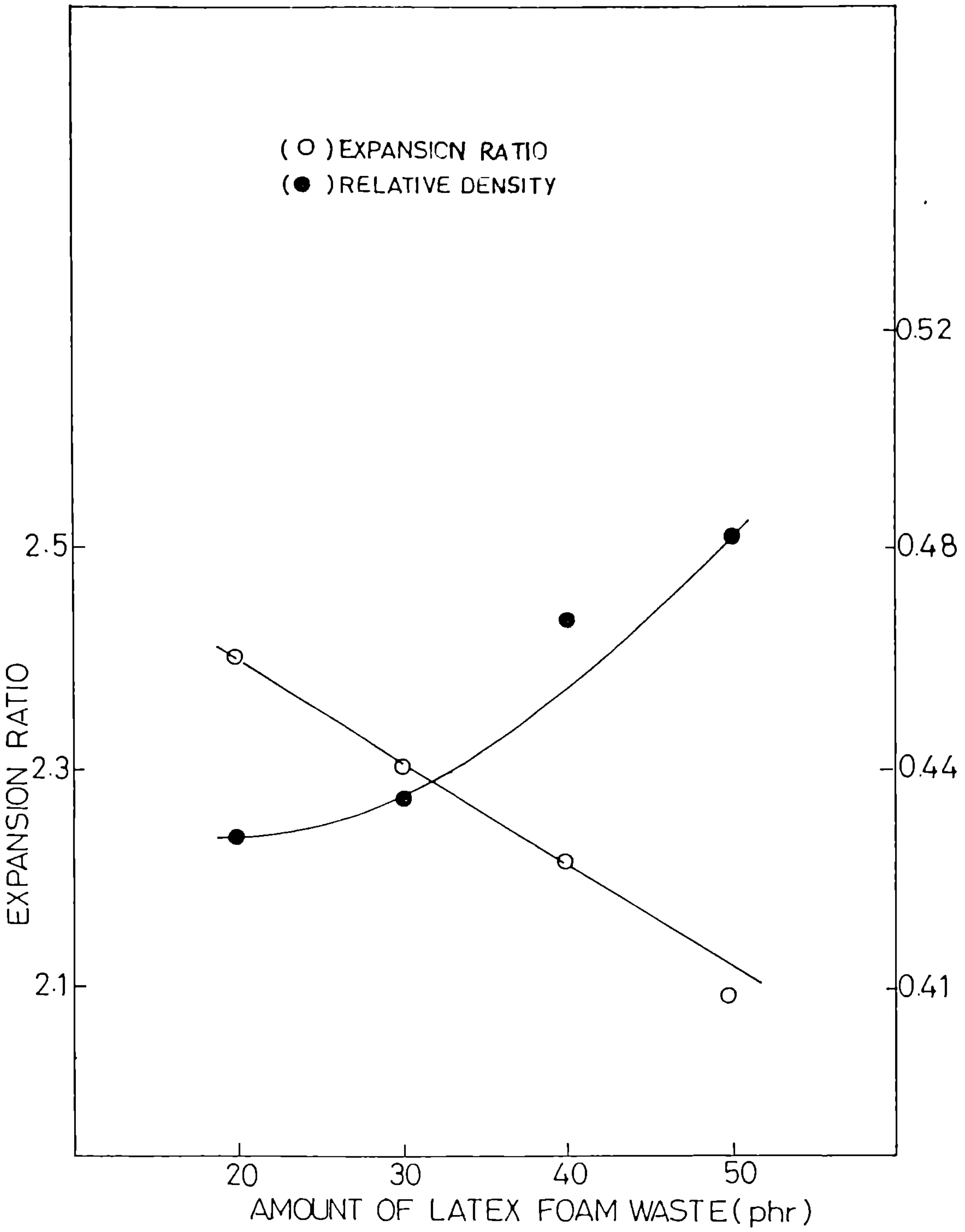


Fig.6.1.1 Variation of expansion ratio and relative density with increase in the amount of latex foam waste.

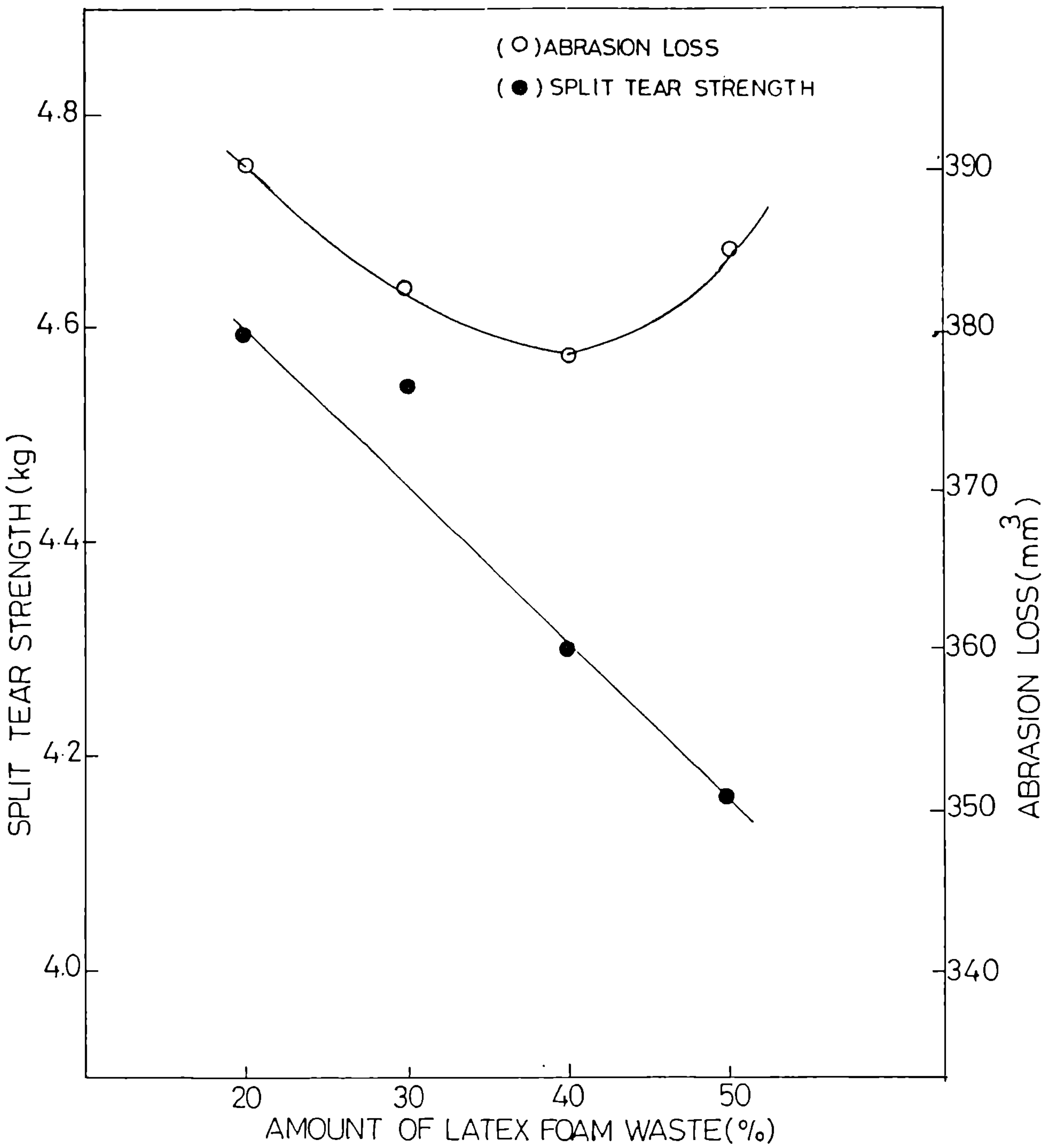


Fig.6.1.2 Variation of split tear strength and abrasion loss with increase in the amount of latex foam waste.

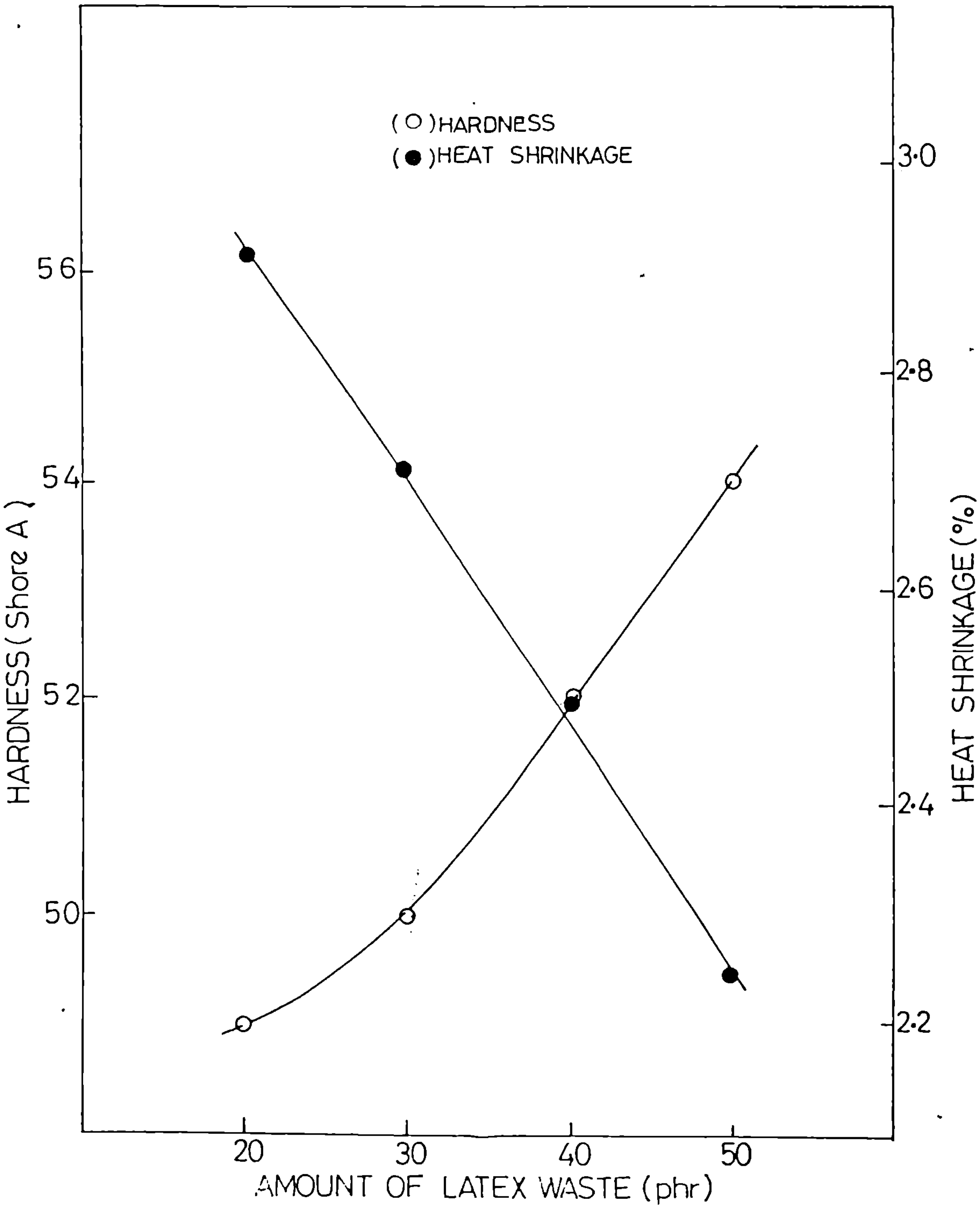


Fig.6.1.3 Variation of hardness and heat shrinkage with increase in the amount of latex foam waste.

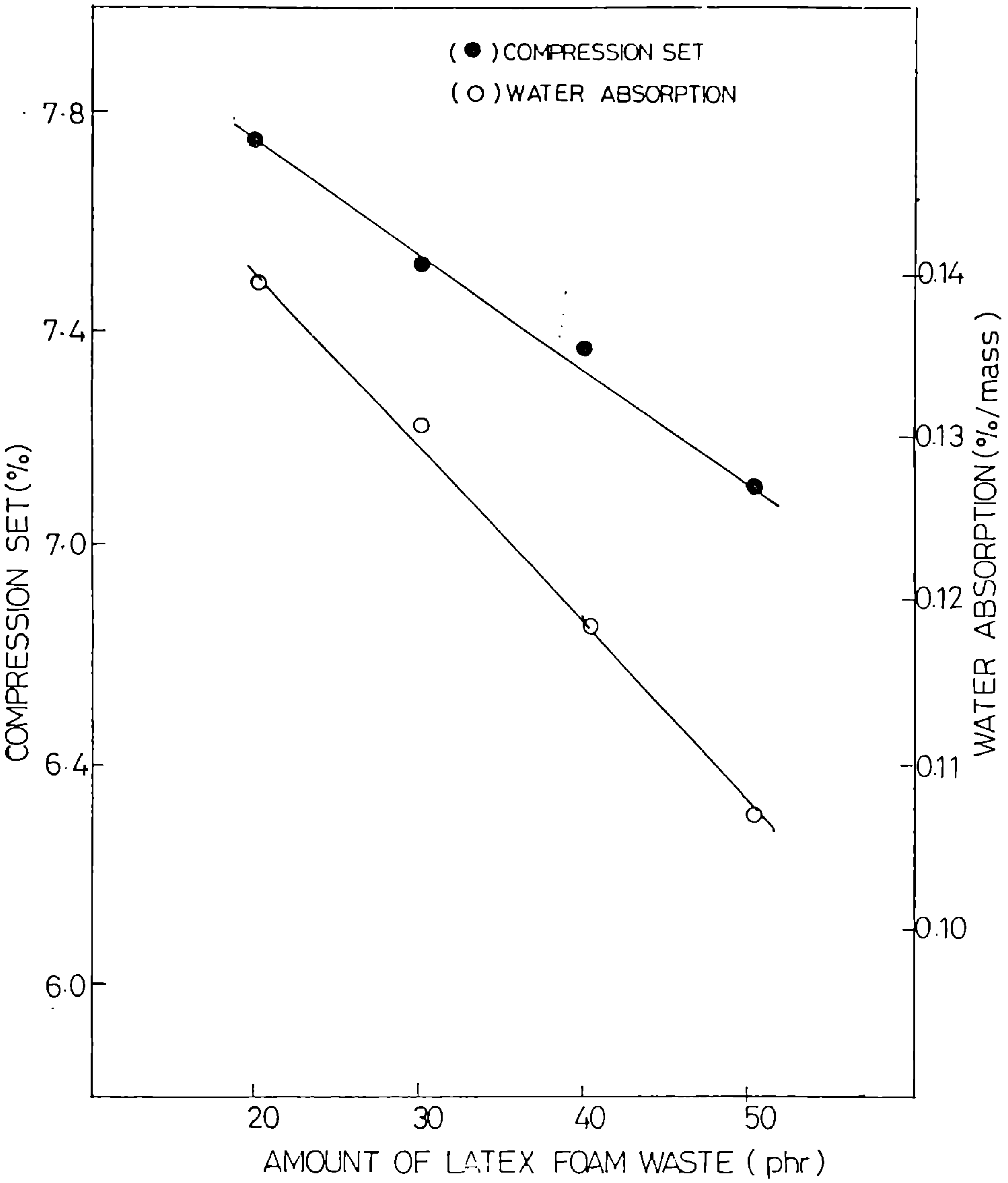


Fig.6.1.4 Variation of compression set and water absorption with increase in the amount of latex foam waste.

Figs.6.1.5 and 6.1.6 show the cell structure of MC sheets containing unmodified and modified NR/HSR microcrumb. Addition of microcrumb affects the uniformity of cells obviously due to the large size of the microcrumb. MC sheets containing modified microcrumb has a comparatively more uniform cell structure which support the higher technical properties observed in this case.

Figs.6.1.7 shows the optical microscope photographs of MC sheets containing 30 phr unmodified latex foam waste. As in the case of the microcrumb addition of unmodified latex foam waste affects the cell structure: cells become large and non-uniform. When part of NR is replaced by modified latex foam waste (15 phr) cells become more uniform and small in size (Fig.6.1.8).

CONCLUSION

1. The modification of microcrumb makes its incorporation easy in NR compound.
2. The addition of the microcrumb marginally decreases the cure time.
3. NR/HSR microcrumb can be used as a reinforcing filler in NR/HSR based microcellular soles. MC soles modified with autoclaved microcrumb show superior technical properties compared to those modified with microcrumb and modified microcrumb.
4. Modified latex foam waste can replace natural rubber up to 15 parts in NR/HSR based microcellular soles. The cure time of the compounds decrease with the increasing amount of latex foam waste.
5. Vulcanized latex foam waste without modification can be used as a low cost filler in NR/HSR based microcellular soles up to 50 phr without much reduction in properties.

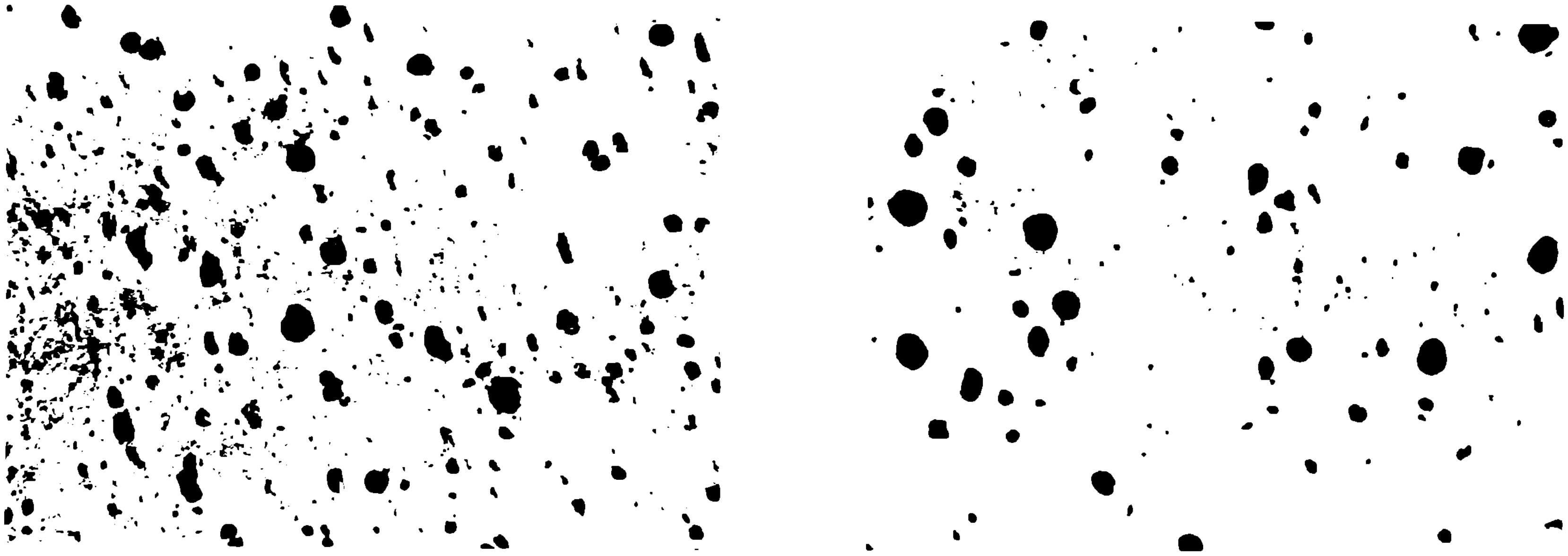


Fig.6.1.5: Unmodified microcrumb Fig.6.1.6: Modified microcrumb

Optical microscope photographs of NR/HSR MC sheets

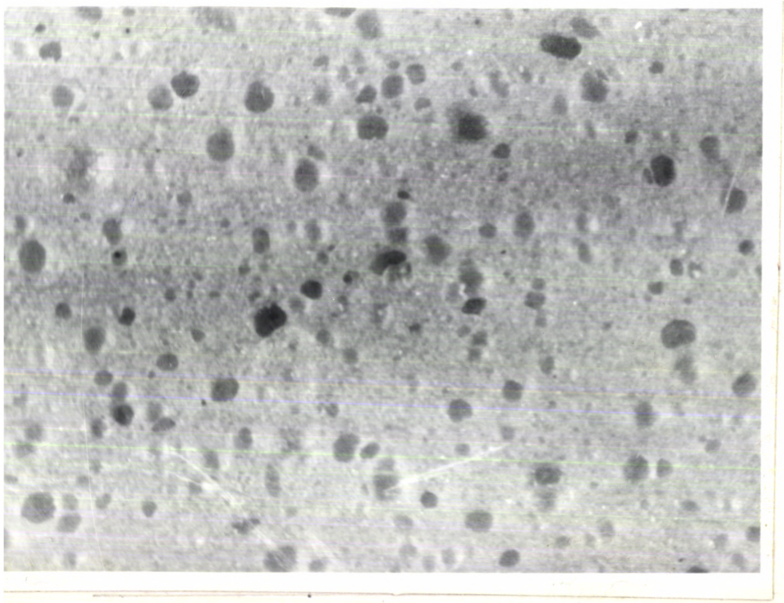


Fig.6.1.7: Unmodified latex foam waste

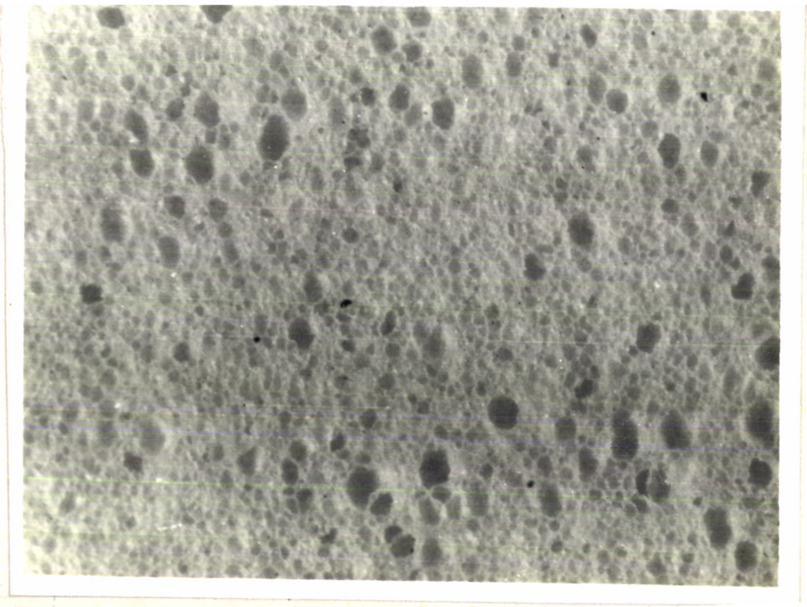


Fig.6.1.8: Modified latex foam waste

Optical microscope photographs of NR/HSR MC sheets

PART II: RICE HULL ASH AND COIR PITH AS FILLERS IN MICRO-CELLULAR SOLES BASED ON NR/HSR BLENDS

The production of rice which is one of the major food crops of the world generates major wastes like rice hull and straw. Disposal of the hulls is a serious problem, due to the high resistance to degradation, low bulk density and high ash content of the rice hulls prevent their effective utilization. Usually large amounts of rice hulls accumulate in the vicinity of rice mills. The use of agricultural waste like rice hull ash is increasingly urgent. Several years ago, efforts have been made to use rice hull ash (RHA) as a filler for rubbers [15-17] and for plastics such as polypropylene [18]. Mehta and Pitt described a new process of rice hull disposal which promises not only to utilize the energy content of the hulls but also to provide an ash which is used for a variety of applications [19]. Rice hull when burnt in open air yields two types of ashes that have good potential to serve as fillers. The upper layer of RHA mount is subjected to open burning in air and yields black carbonized ash. The inner layer of the mount, being subjected to a higher temperature, results in the oxidation of the carbonized ash to yield white ash that consists predominantly of silica. Black RHA on the other hand has a lower silica content and a substantial carbon content [20]. In NR/HSR soles silicas are used as reinforcing fillers to provide adequate resistance to abrasion and tear resistance.

Coir pith constitutes about 70% of the coconut husk and it is estimated that 5,00,000 tonnes of coconut pith is produced per annum in India [21]. Coconut production in Kerala is estimated at 4000 million nuts per annum and an equal amount of the agro-waste "coconut husk is available for the extraction of "golden coir" [22]. Coir pith is a very low density material and it is classified based on the mode of extraction of coir fiber into the following: (a) pith from retted husk which is subjected to retting in backwaters for a period of 6-8 months.

(b) Pith from the unretted husk which involves direct mechanical extraction of fiber [21]. Coir waste is found to contain a good amount of very short fibers also. Recently short fiber reinforcement of rubber matrices has gained importance due to the processing advantages and improvements in mechanical properties of the product [23-29]. The use of coconut fiber and coir pith as reinforcing fillers for plastics as well as rubbers has also been reported [30,31].

In this part of the study rice hull ash and coir pith are proposed to be used as fillers in conventional NR/HSR based MC soles. The modification of coir pith is also proposed to be done to improve its reinforcing nature.

Experimental

(i) White ash

Chemical analysis of the ash shows that it contains mostly acid soluble silicious material. It contains about 85% silica. Properties of white ash are shown in Table 6.2.1. The acid soluble portions contain metal oxides of calcium, magnesium, iron etc. It also contains oxides of phosphorous and aluminium. Silica in a hydrated amorphous form, as hulls are a natural product, their composition varies with the location where the rice is harvested. The major ingredients of the rice hulls are ash about 40%, cellulose, legnin and moisture. The white ash was dried in an oven at 120°C for at least 5h prior to mixing.

(ii) Coir pith

Analysis of raw coir pith indicates that it contains cellulose and legnin as the major constituents [21]. It is a very low density material of brown in colour and its physical and chemical properties [31] are shown in Table 6.2.2.

Table 6.2.1: Properties of White ash

Properties	
SiO_2 (silica) (%)	85.5
Colour	Grey powder
Particle size (um)	<2
pH	11.9
Sieve analysis (%) through 325 mesh	95
Density (g/cm^3)	2.8

Table 6.2.2: Physical and chemical properties of raw coconut coir pith

Physical properties	
Bulk density (g/cm^3) Particle density (g/cm^3) Porosity (%)	0.1525 0.4916 76.77
Chemical properties	
pH	5.8
Nitrogen (%)	0.68
Phosphorus (%)	0.09
Calcium (%)	0.84
Lignin (%)	30.0
Iron (%)	0.07
Manganese (ppm)	64.5
Zinc (ppm)	80.0
Total phenols (mg/g)	50

Modification of coir pith

The coir pith powder (this contains short fiber) was steam heated in an autoclave at 125°C under pressure for 2h. The autoclaved coir pith was dried and used as filler in microcellular soles.

Preparation of microcellular sheets

NR/HSR blend was prepared on a laboratory mixing mill. NR was masticated on a mixing mill and HSR in the form of a sheet was then added and mixed well. The blends were then compounded in a laboratory mixing mill (150x300 mm) at a friction ratio 1:1.25 according to the formulations given in Table 6.2.3 and 6.2.4 respectively. The amount of white ash was varied from 30 to 60 phr and the DNPT was varied from 5.75 to 5 with increase in the amount of white ash (Table 6.2.3). Both modified and unmodified coir pith were used as fillers in NR/HSR based MC soles.

The MC sheet was moulded in an electrically heated hydraulic press to 80% of their optimum cure time at 150°C. The mould was loaded with 3 to 5 percent excess of the compound on volume basis. The expanded sheets were then post cured in an air oven for 1 hour at 100°C.

The technical properties of the MC sheets were evaluated according to the relevant Indian Standards as per the procedure described in chapter 2. The cell structure of the razor cut samples were taken using an optical microscope.

Table 6.2.3

Formulation for NR/HSR sole compounds containing white ash and precipitated silica

Ingredients (Phr)	1	2	3	4	5	6	7	8
NR	70	70	70	70	70	70	70	70
HSR	30	30	30	30	30	30	30	30
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	6	6	6	6	6	6	6	6
Precipitated silica	30	40	50	60	--	--	--	--
China clay	80	80	80	80	80	80	80	80
White ash	--	--	--	--	30	40	50	60
Naphthenic oil	5	5	5	5	5	5	5	5
Diethylene glycol	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
SP	1	1	1	1	1	1	1	1
Wood rosin	2	2	2	2	2	2	2	2
Vulcafor F	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
DNPT	6	6	6	6	5.75	5.5	5.25	5

Table 6.2.4

Formulations for NR/HSR sole compounds containing coir pith

Ingredients (phr)	1	2	3	4
NR	70	70	70	70
HSR	30	30	30	30
ZnO	5	5	5	5
Stearic acid	6	6	6	6
Titanium dioxide	4	4	4	4
Wood rosin	2	2	2	2
Precipitated silica	20	20	20	20
China clay	80	80	80	80
Unmodified/modified coir pith	10	20	30	40
Naphthenic oil	6	6	6	6
SP	1	1	1	1
Vulcafor F	1.2	1.2	1.2	1.2
Sulphur	2.25	2.25	2.25	2.25
DNPT	6	6	6	6

Results and Discussion

(i) Effect of replacement of silica by rice hull ash in NR/HSR blend based microcellular soles

Table 6.2.5 shows the cure characteristics of the compounds containing silica and white ash in NR/HSR based MC sheets. There is a marginal decrease in cure time of the mixes containing white ash. This slight reduction in cure time may be due to the decreased adsorption of accelerator on the surface of white ash compared to silica.

Fig.6.2.1 shows the variation of expansion ratio and relative density with increase in the amount of filler loading in NR/HSR based MC sheets. Expansion of MC sheets is found to be marginally lower when silica is replaced by white ash, expansion of the MC sheets increases with increase in white ash content. So the concentration of blowing agent is varied so as to get almost same trend in expansion for the microcellular sheets prepared from white ash.

Fig.6.2.2 shows the variation of split tear strength and abrasion loss with increase in the amount of filler loading in NR/HSR based MC sheets, split tear strength is marginally improved when silica is replaced by white ash. This indicates that white ash can bring about equivalent reinforcement as that of silica. According to H.E.Haxo and P.K.Mehta, RHA in SBR 1502 gives equivalent reinforcement as that of silica [15]. The abrasion loss of the MC sheets decreases when silica is replaced by white ash. This may be due to the stronger cell walls resulting from the lower expansion [32].

Fig.6.2.3 shows the variation of hardness and heat shrinkage with increase in the amount of filler in NR/HSR based MC sheets. Hardness of the MC sheets increase with the addition of white ash. This increase in hardness is also due to the reinforcement of white ash.

Table 6.2.5: Cure characteristics and technical properties of the compounds containing silica and white ash

Properties	Silica				White ash			
	1	2	3	4	5	6	7	8
Optimum cure time at 150°C min.	14.5	14.2	14.0	13.9	12.5	12.3	12.1	11.9
Initial expansion (%)	95.24	94.05	83.33	77.38	54.76	52.38	50	48.81
Expansion after 5 min. (%)	39.29	38.09	35.71	34.52	36.9	27.38	26.19	25
Expansion after 24 h (%)	34.52	34.52	30.95	29.7	22.62	22.62	21.43	21.43
Shrinkage after post curing (%)	3.57	2.83	2.58	2.38	2.83	2.80	2.30	1.88
Flex resistance								
a) Crack initiation in cycles	100.125	100.125	100.125	99.009	101.110	101.000	100.060	99.975
b) Crack size growth at the end of 100.000 cycles (%)	<600	<600	<600	<600	<600	<600	<600	<600

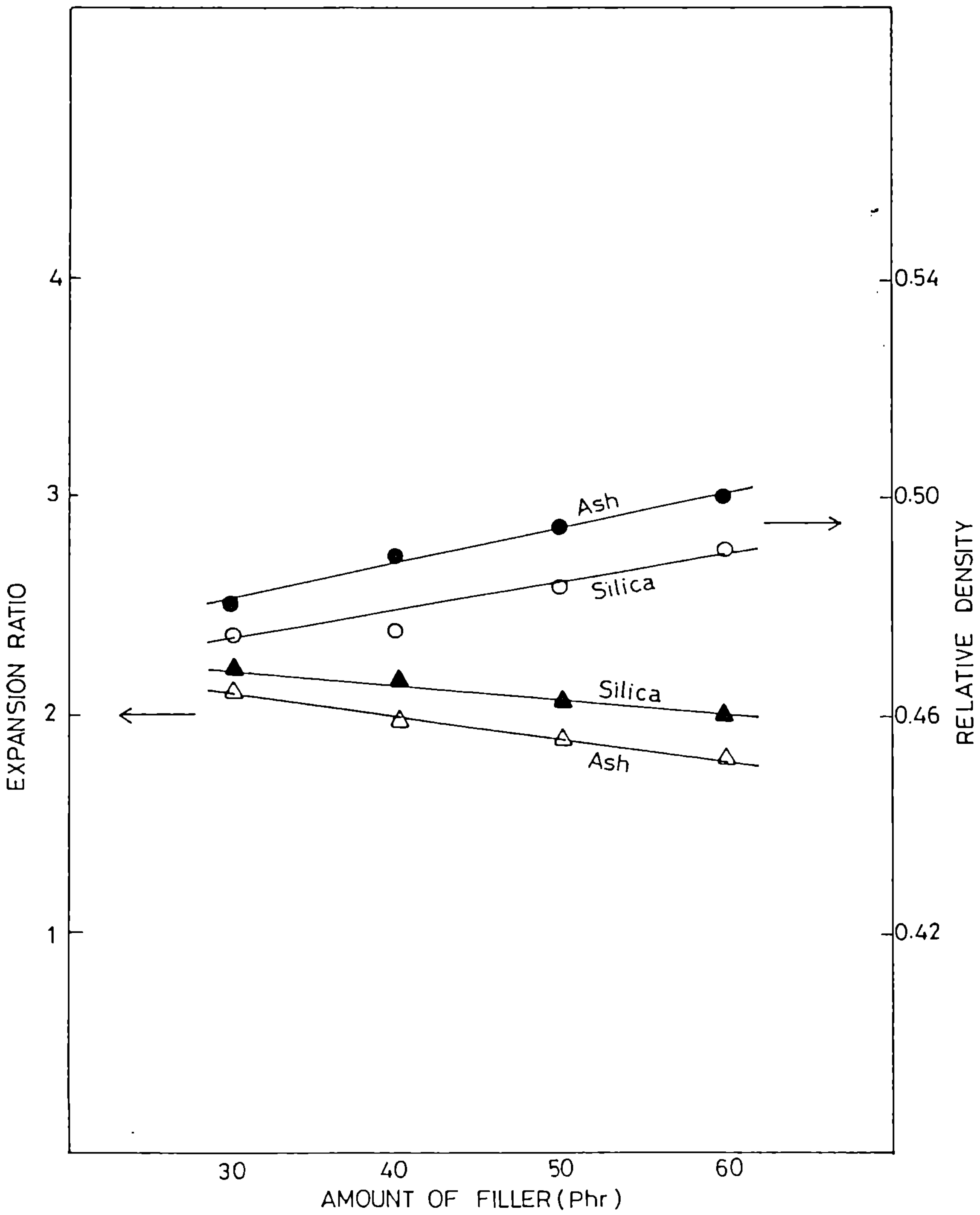


Fig.6.2.1 Variation of expansion ratio and relative density with increase in the amount of filler loading.

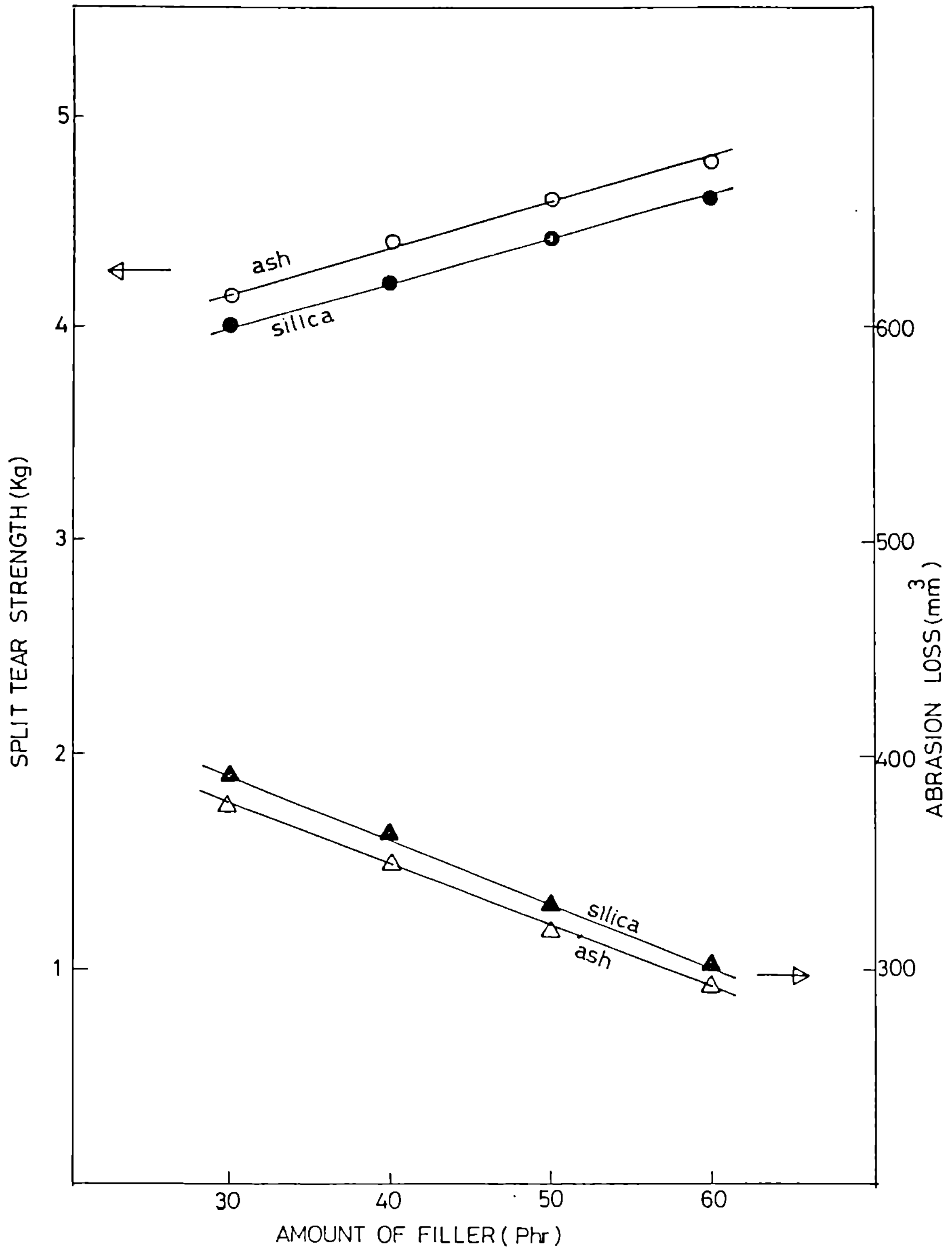


Fig.6.2.2 Variation of split tear strength and abrasion loss with increase in the amount of filler loading.

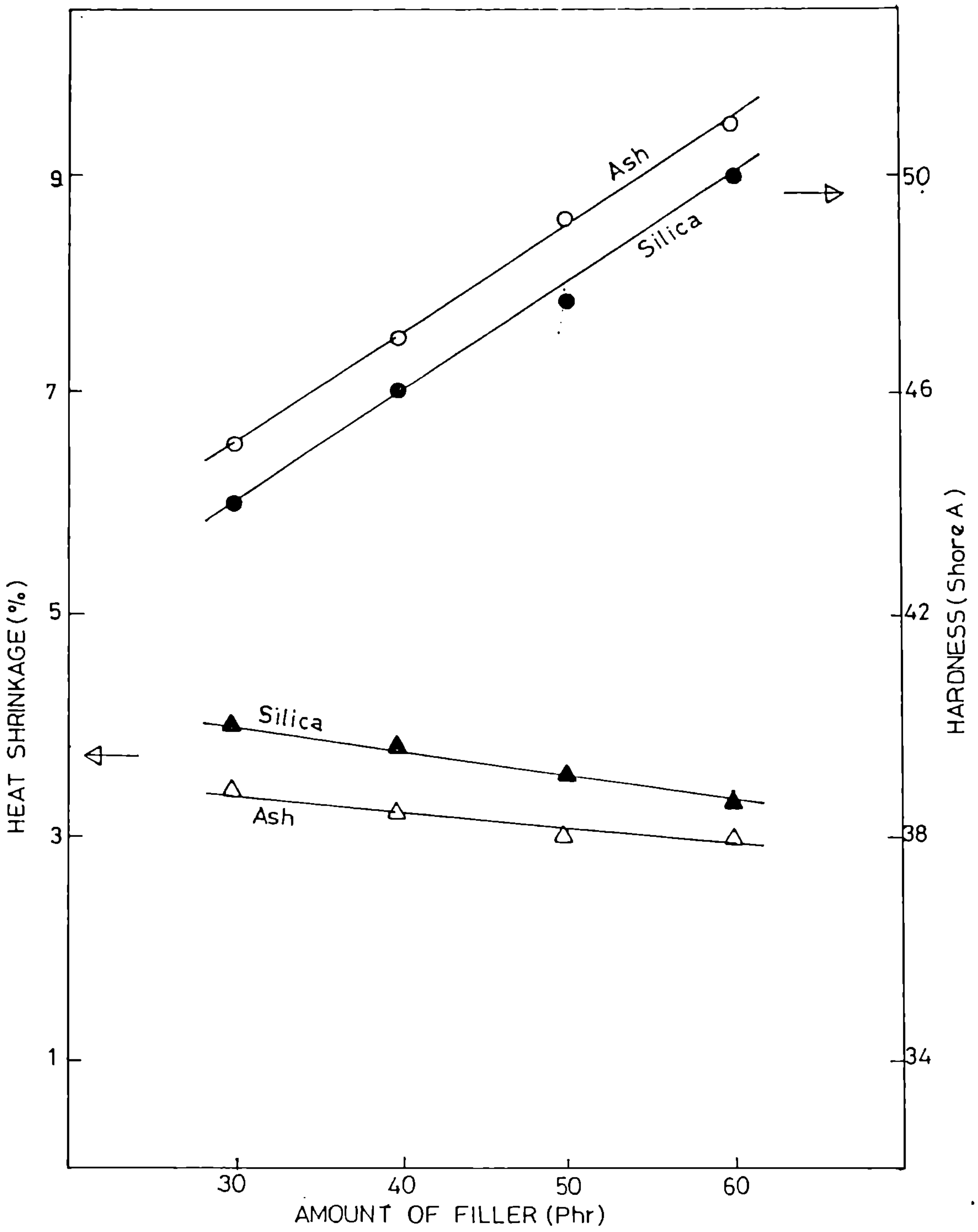


Fig.6.2.3 Variation of heat shrinkage and hardness with increase in the amount of filler loading.

Heat shrinkage of the MC sheet is marginally reduced when white ash is used in place of silica. This is due to the lower expansion of the MC sheet.

Fig.6.2.4 shows the compression set and water absorption in NR/HSR based MC sheets. Compression set decreases when silica is replaced by white ash. This is also due to the stronger cell walls resulting from lower expansion of the MC sheets. There is a reduction in water absorption when silica is replaced by white ash. This may be due to the lower percentage of open cells.

Table 6.2.5 shows the flex resistance of MC sheets, crack initiation occurs at 100,125 cycles for both silica and white ash filled MC sheets. After 100,000 cycles crack growth is small. Shrinkage after post curing is less for white ash filled MC sheets.

(ii) Effect of addition of coir pith as a filler in microcellular soles

Table 6.2.6 shows the optimum cure time of the compounds containing coir pith. As the amount of coir pith increases the optimum cure time decreases. This decrease in cure time is probably due to the lignin present in coir pith since lignin retards vulcanization [31]. The modified coir pith shows a lower cure time. This may be due to the lower percentage of lignin in it.

Fig.6.2.5 shows the variation of expansion ratio and relative density with increase in the amount of unmodified/modified coir pith in NR/HSR based MC soles. Expansion of the MC sheets (as shown in Table 6.2.6) decreases with increase in the amount of coir pith. Consequently relative density increases with coir pith content. But modified coir pith shows further decrease in expansion compared to unmodified coir pith.

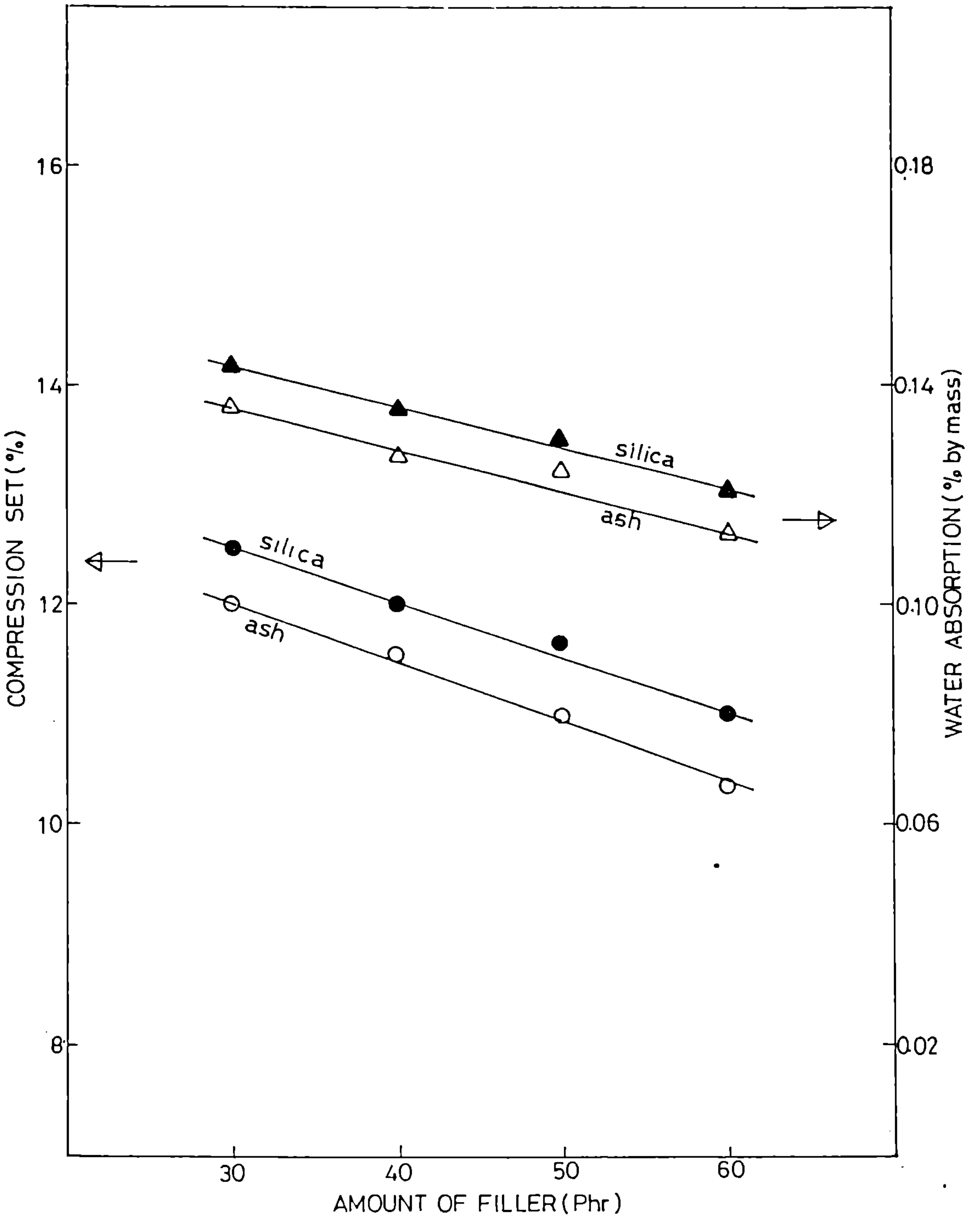


Fig.6.2.4 Variation of compression set and water absorption with increase in the amount of filler loading.

Table 6.2.6

Effect of coir pith loading on technical properties of microcellular soles based on NR/HSR blend

Properties	Unmodified coir pith (phr)				Modified coir pith (phr)			
	10	20	30	40	10	20	30	40
Optimum cure time at 150°C min.	8.4	8	7.3	7.2	7.6	6.4	6.4	6.3
Initial expansion (%)	75	67.46	60.71	60.9	65.47	64.28	63.09	61.9
Expansion after 5 min. (%)	40.47	38.09	36.9	36.9	35.71	34.52	33.3	32.14
Expansion after 24 h (%)	33.3	30.95	28.57	28.57	32.14	32.14	30.95	30.95
Shrinkage after post curing (%)	4.27	3.50	3.57	3.42	2.65	2.67	2.65	2.21
Flex resistance								
a) Crack initiation in cycles	91,000	91,000	85,000	81,246	93,462	92,950	86,000	80,009
b) Crack growth at the end of 100,000 cycles (%)	<600	<600	<600	<600	<600	<600	<600	<600

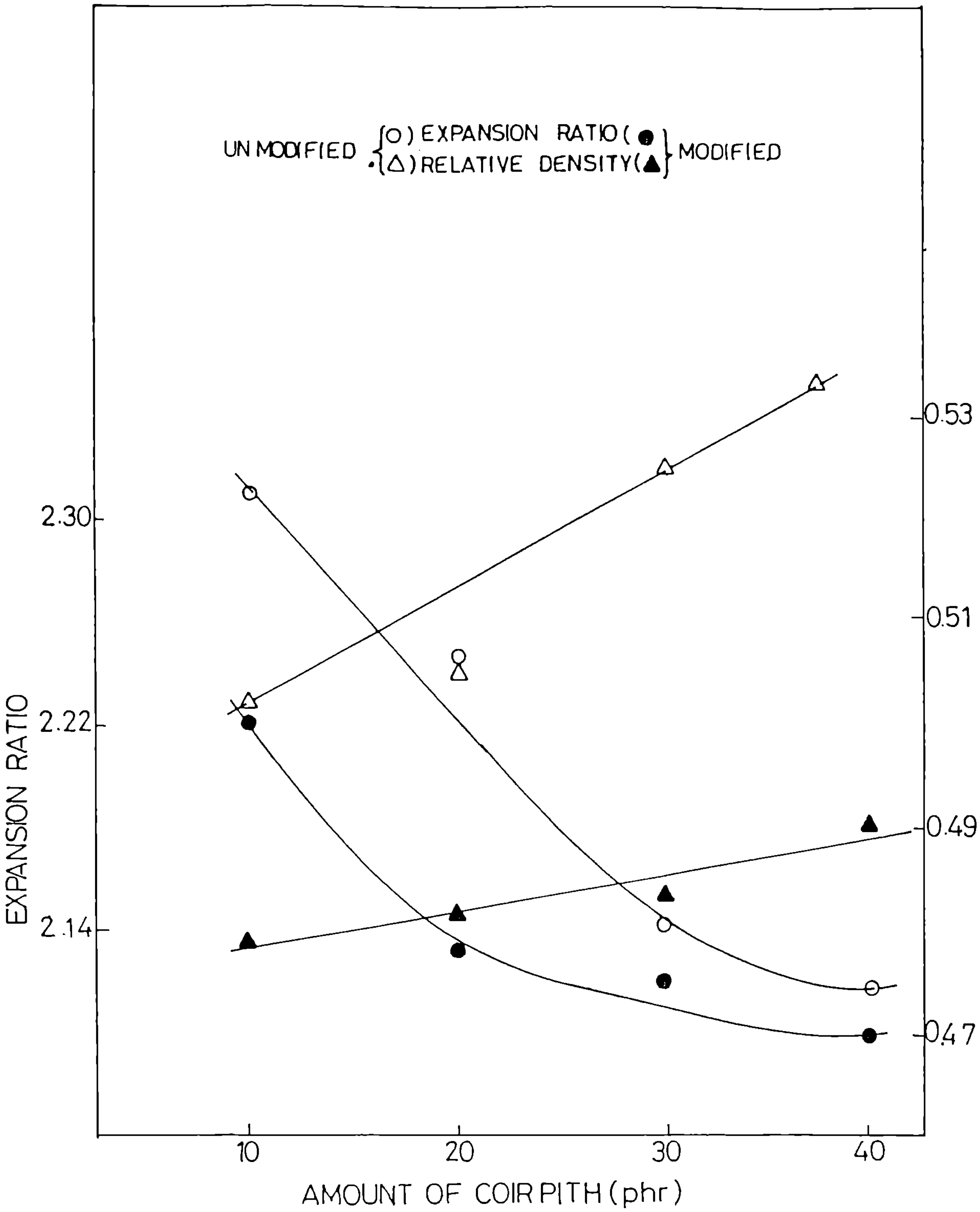


Fig.6.2.5 Variation of expansion ratio and relative density with increase in the amount of coir pith.

Fig.6.2.6 shows the variation of split tear strength and abrasion loss with increase in the amount of unmodified/modified coir pith. Split tear strength is found to decrease when coir pith loading is increased. It is evident that coir pith does not have a reinforcing action eventhough they can cheapen the products to a considerable extent. Abrasion loss increases with increase in coir pith loading. This may be due to the formation of more open cell structure which produces weakness in cell walls, so easy wearing of the product is possible. This is also evident from increased water absorption of the MC sheet with increase in coir pith content. But modified coir pith shows improved split tear strength and low abrasion loss. This may be due to the improved dispersion of modified coir pith, and lower expansion of the MC sheets.

Water absorption and compression set increase on increasing coir pith content. This shows that as the coir pith content increases number of open cells increase, which is the result of higher water absorption as shown in Fig.6.2.7. The increase in compression set may be due to the lower extent of crosslinking. Modified pith shows decreased water absorption and compression set.

Fig.6.2.8 shows the variation of hardness and heat shrinkage with increase in the amount of coir pith. Hardness of the MC sheets increase on increasing coir pith while heat shrinkage marginally reduces with coir pith content. This may be due to the lower expansion of the MC sheet. Modified coir pith gives higher hardness and lower shrinkage compared to unmodified pith containing MC sheets.

Shrinkage after postcuring of the MC sheets decreases with increased coir pith content. Modified coir pith shows further decrease in shrinkage. Crack initiation and development are

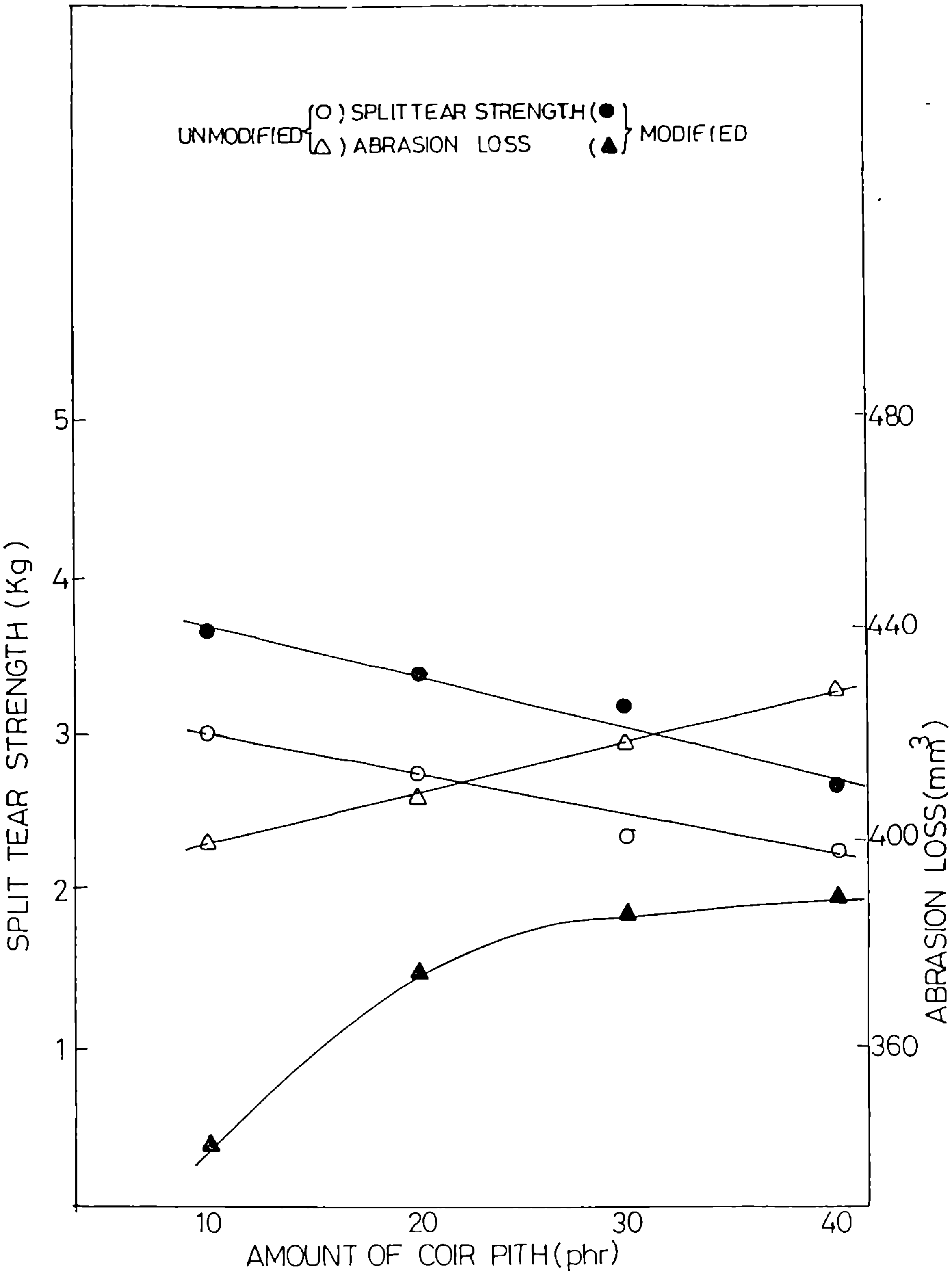


Fig.6.2.6 Variation of split tear strength and abrasion loss with increase in the amount of coir pith.

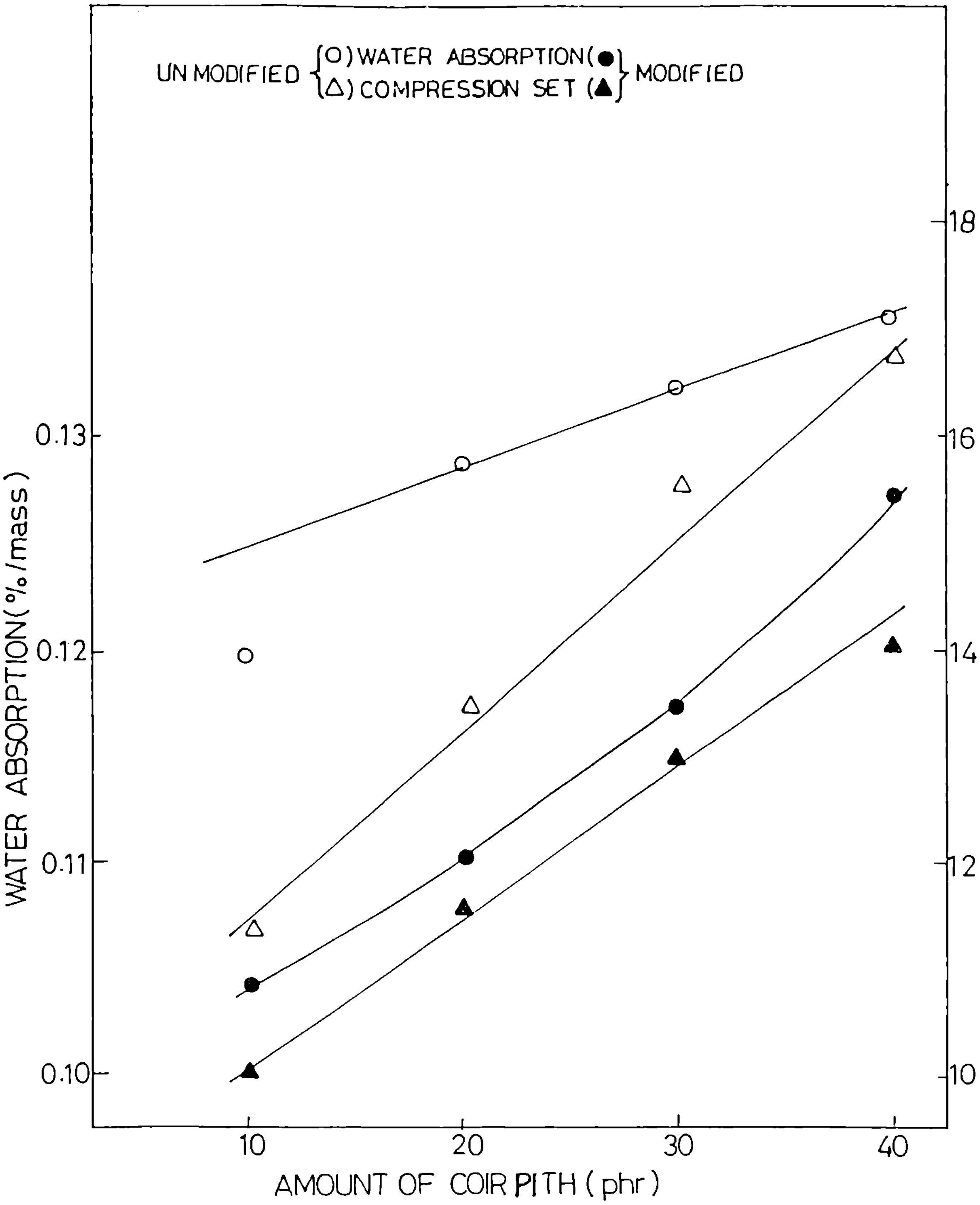


Fig.6.2.7 Variation of water absorption and compression set with increase in the amount of coir pith.

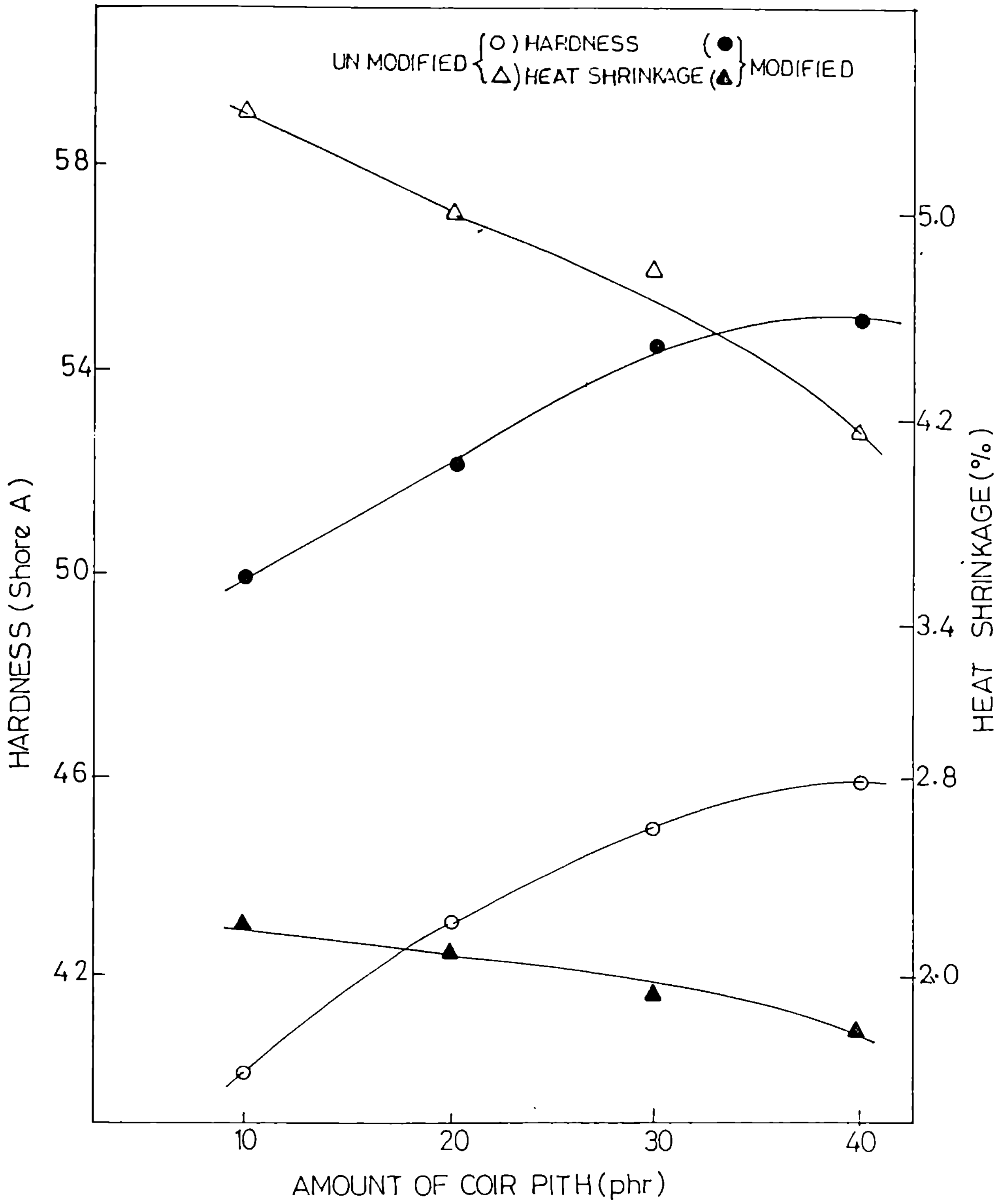


Fig.6.2.8 Variation of hardness and heat shrinkage with increase in the amount of coir pith.

followed by the higher dosage of coir pith in the mix. Flex resistance values of MC sheets is found to be within the specification limit. This may be due to the higher particle size of coir pith and poor distribution of coir pith in the matrix. But modified pith shows higher flex resistance. This may be due to the improved distribution of modified pith.

Figs.6.2.9 and 6.2.10 show the optical microscope photographs of MC sheets containing silica and rice hull ash. Cell structure of the MC sheets remain unchanged when silica is replaced by rice hull ash.

Figs.6.2.11 and 6.2.12 show the optical microscope photographs of MC sheets containing unmodified and modified coir pith. Addition of coir pith affects the cell structure of MC sheets. Cells become larger and non-uniform. But modified coir pith containing MC sheets show smaller and uniform cells. This also supports the improved technical properties of MC sheets containing modified coir pith.

CONCLUSION

1. There is a marginal decrease in the cure time when silica is replaced by white ash.
2. Compounds containing white ash show a higher expansion compared to compounds containing silica.
3. Properties like split tear strength, abrasion resistance, hardness etc. are improved by the addition of white ash.
4. White ash can be used as a low cost filler in place of silica in microcellular soles.
5. Unmodified coir pith reduces the cure rate of NR/HSR compounds while modified coir pith does not affect the cure rate.

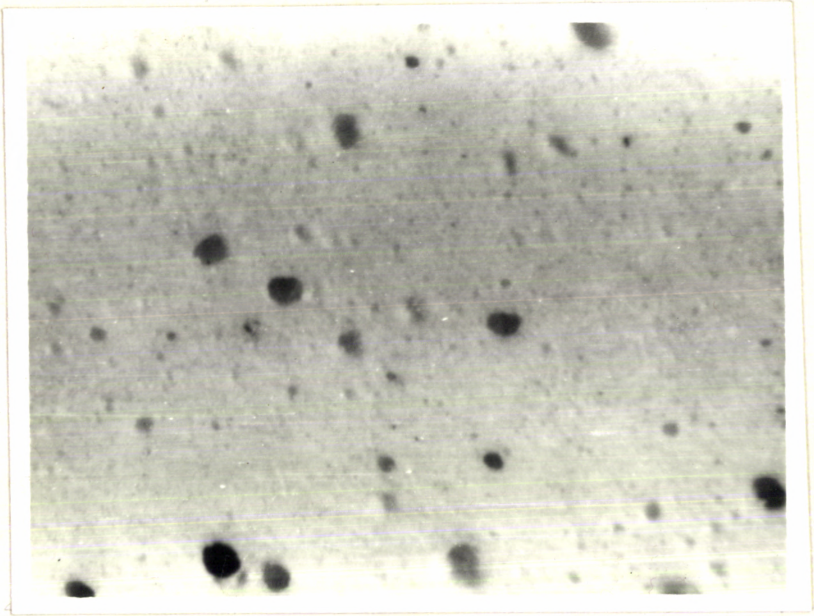


Fig.6.2.9: Silica

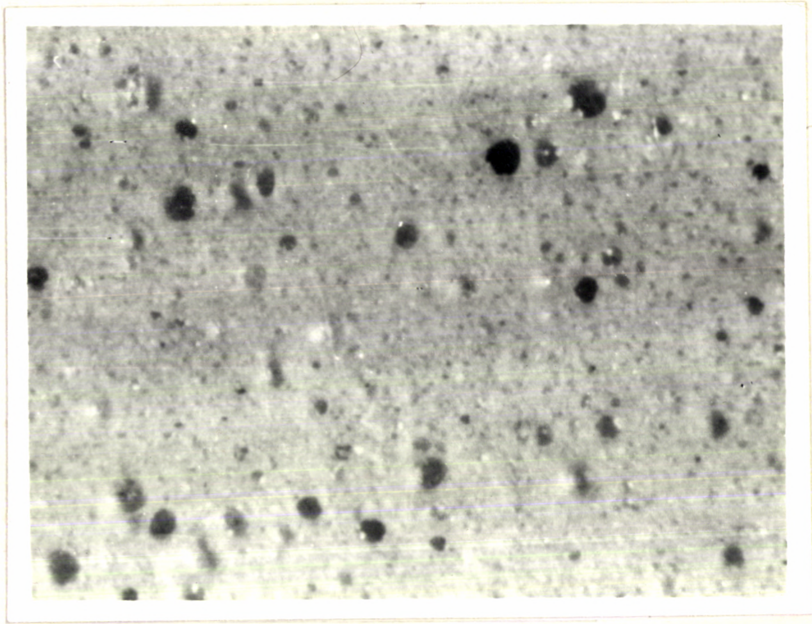


Fig.6.2.10: Rice hull ash

Optical microscope photographs of NR/HSR MC sheets

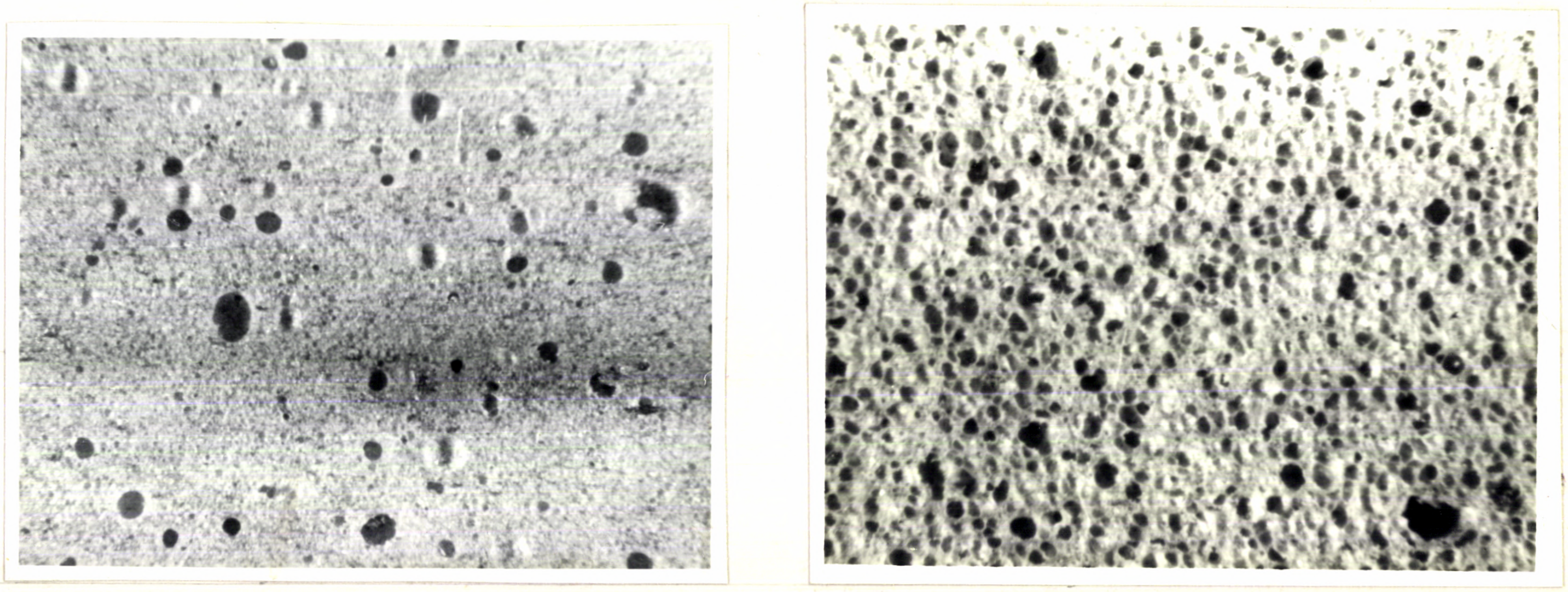


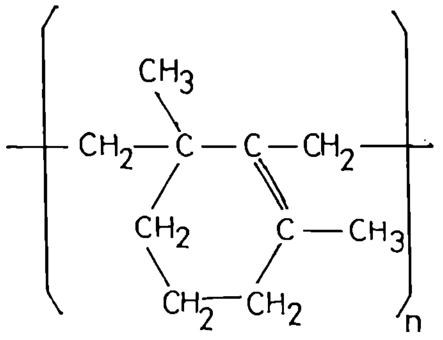
Fig.6.2.11: Unmodified coir pith Fig.6.2.12: Modified coir pith

Optical microscope photographs of NR/HSR MC sheets

6. Properties like split tear strength and abrasion resistance decrease with increase in coir pith loading while compression set, hardness and water absorption increase with coir pith loading.
7. Modified coir pith shows improved properties compared to unmodified coir pith and can be effectively added up to 40 phr level as a filler in microcellular soles without sacrificing much of the required properties.

PART III: PREPARATION AND USE OF CYCLIZED RUBBER IN MICROCELLULAR SOLES

The resinification of natural rubber by acid catalyst has been investigated since 1937 [33]. Under the action of heat, especially in the presence of acidic catalyst, rubber is transformed in to isomeric resinous substances with greatly reduced unsaturation with same empirical composition as rubber [34]. This modification of rubber is assumed to be due to the isomerization, which takes place especially under the influence of electrophilic agents [35,36] or heat with the formation of internal rings and the process is accompanied by a loss of double bonds. This phenomenon is termed as cyclization and the products are referred to as cyclized or cyclorubbers. Cyclized rubber formed is nonpolar, non crystallizing polymer [37,38] and is brittle and hard. Marsh, and Zamey [39] have suggested the generally favoured structure, formed by reaction between pairs of adjacent isoprene units of the rubber chain as shown below:



In the present study the cyclised natural rubber is proposed to be prepared in the laboratory and is added in microcellular soles. The properties of NR/cyclized rubber blend based MC soles are compared with those of conventional NR/HSR blend based MC soles.

Experimental

Preparation of cyclized rubber

Concentrated sulphuric acid (161g) was added to 200 g of latex containing 60 percent of dry rubber and stabilized with 2g of Dispersol-VL, where the serum of the latex contained 75 per cent by weight of the acid. After heating for 6 hours at 90°C, the reaction mixture was poured in to three times its volume of water. The dispersion thus obtained was filtered and washed with 1% ammonia solution till all the sulphuric acid was removed, which tested with the help of a litmus paper. The completely cyclized polymer formed a powdery precipitate instead of an elastic substance. Then the precipitate was washed with water and dried. The product was analyzed with IR, TGA and by determining melting point [37]. The IR spectrum of the cyclized rubber was taken by using a Perkin Elmer model 983. The thermogravimetric analysis of the cyclized rubber was also done using a Shimadzu-50 Thermogravimetric analyser.

Preparation of NR/cyclized rubber blends

Natural rubber was masticated on a laboratory mixing mill and cyclized rubber in powder form was added at different percentages. In order to prevent agglomeration, cyclized rubber was added together with silica filler and the blends were compounded according to the formulation given in Table 6.3.1.

Table 6.3.1

Formulations for NR/cyclized rubber or HSR based microcellular sole compounds

Ingredients (phr)	Mix Number		
	1	2	3
NR	80	70	60
HSR/Cyclized rubber	20	30	40
ZnO	5	5	5
Stearic acid	6	6	6
Precipitated silica	20	20	20
China clay	80	80	80
NR/HSR microcrumb	50	50	50
DEG	1.5	1.5	1.5
Naphthenic oil	5	5	5
SP	1	1	1
Vulcafor F	1.2	1.2	1.2
Sulphur	2.25	2.25	2.25
DNPT	6	6	6

NR/HSR blend was also prepared on a laboratory mixing mill. NR was masticated on a laboratory mixing mill and HSR in the form of a sheet was then added. The blends were compounded as per formulation given in Table 6.3.1.

The optimum cure time of the compounds were determined using Goettfert Elastograph 67.85. The microcellular sheets were moulded in an electrically heated hydraulic press at 150° C. The mould was loaded with three to five percent excess of the compound on volume basis. The compounds were precured in the mould to 80 percent of their respective optimum cure times and the expanded sheets were then postcured in an air oven at 100°C for one hour.

The technical properties of the MC sheets were evaluated according to the relevant Indian standards as per the procedure described in chapter 2. The cell structure studies of the MC sheets were done on a cut portion of microcellular sheets using an optical microscope.

Results and discussion

i) Infrared spectroscopic study of cyclized rubber

Fig. 6.3.1 shows the spectrographs obtained. Intense bands in the region of 2700-3000 cm^{-1} and also in the 1440cm^{-1} regions indicate the presence of methyl groups in cyclized rubber. Bands at the 830-840 cm^{-1} region, present in the IR spectrum of natural rubber is absent in the spectrum of cyclorubber. This complete disappearance of 830cm^{-1} band from the spectrum of cyclized rubber indicates formation of tetra-alkyl type of double bond. Two different absorption bands in the 880-1800 cm^{-1} region do not have sufficiently clear resolution. Similar observations were made by D'Ianni et al [39] for cyclized polyisoprene and Shelton and Lee for cyclized polybutadiene. These results suggest that the double bonds formed in the

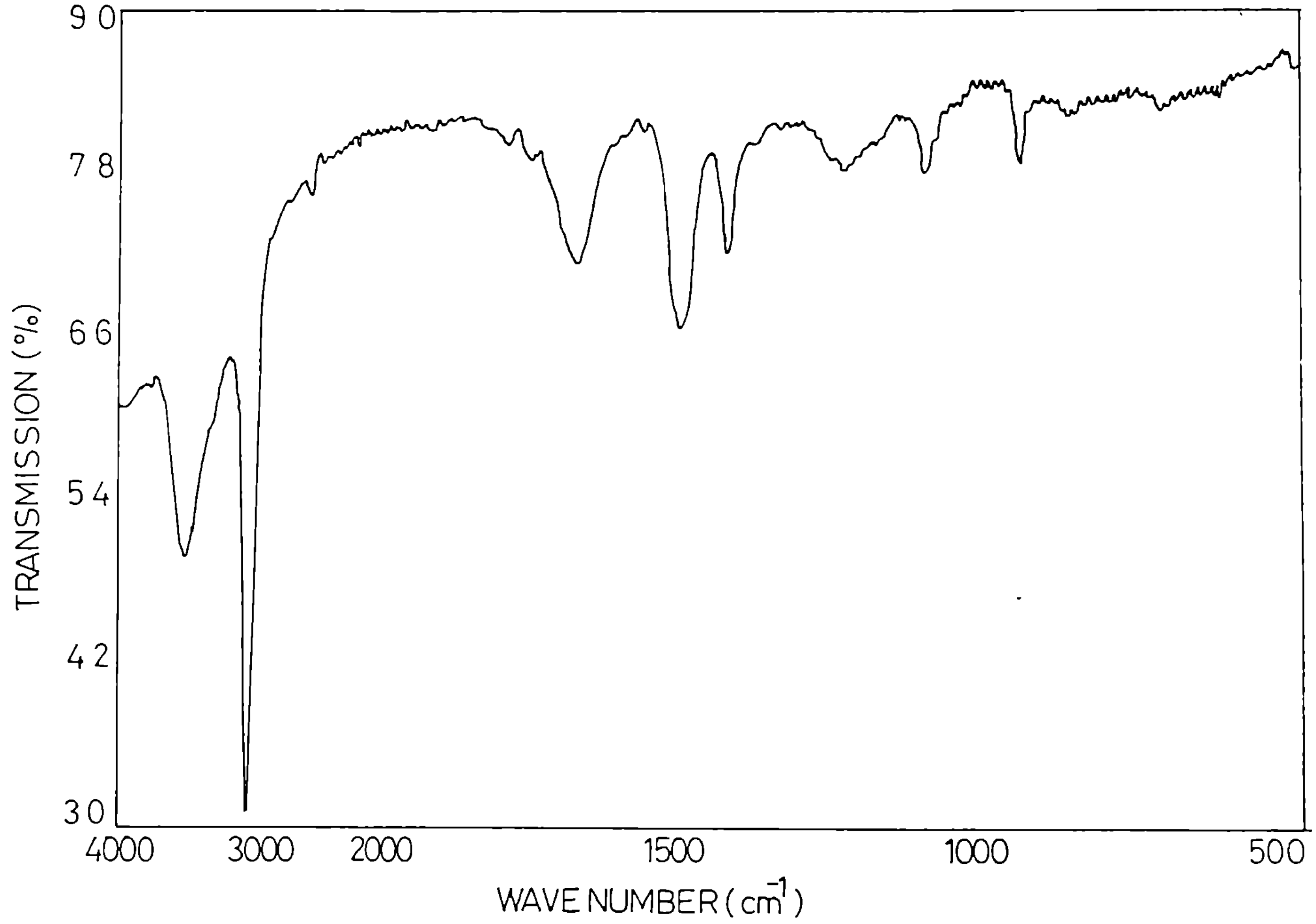


Fig.6.3.1 IR spectrograph of cyclized rubber

termination reaction are eventually reactivated and cyclized with any adjacent unreacted units [33,40-42].

ii) Thermogravimetric analysis

Fig.6.3.2 shows the TGA graph of the cyclized rubber sample. The figure shows that weight loss occurs at a temperature of 450°C. This shows that the cyclized rubber is stable upto 450°C. As it is stable at the processing and service temperature of MC soles it can be used in this product.

The softening point of the cyclized rubber is in between 130-140°C.

Effect of addition of cyclized rubber in microcellular soles

Fig.6.3.3 shows the variation of expansion ratio and relative density with increase in the amount of cyclized rubber/HSR content in the blend. Expansion of the microcellular sheet decreases with increase in the cyclized rubber/HSR content in the blend; consequently relative density increases marginally. This behaviour may be due to the addition of cyclized rubber or HSR which makes the compound hard because it reduces the expansion of MC sheets. Compared to cyclized rubber HSR produces more expansion due to the more thermoplastic nature of HSR [43].

Fig.6.3.4 shows the variation of split tear strength and abrasion loss with increase in the amount of cyclized rubber/HSR. Split tear strength of the MC sheets marginally increase with increase in cyclized rubber/HSR in the blend. NR/cyclized rubber based MC sheets show marginal reduction in split strength compared to NR/HSR based MC sheets. This may be due to the agglomerates formed during mixing which produces holes after expansion. The sheet

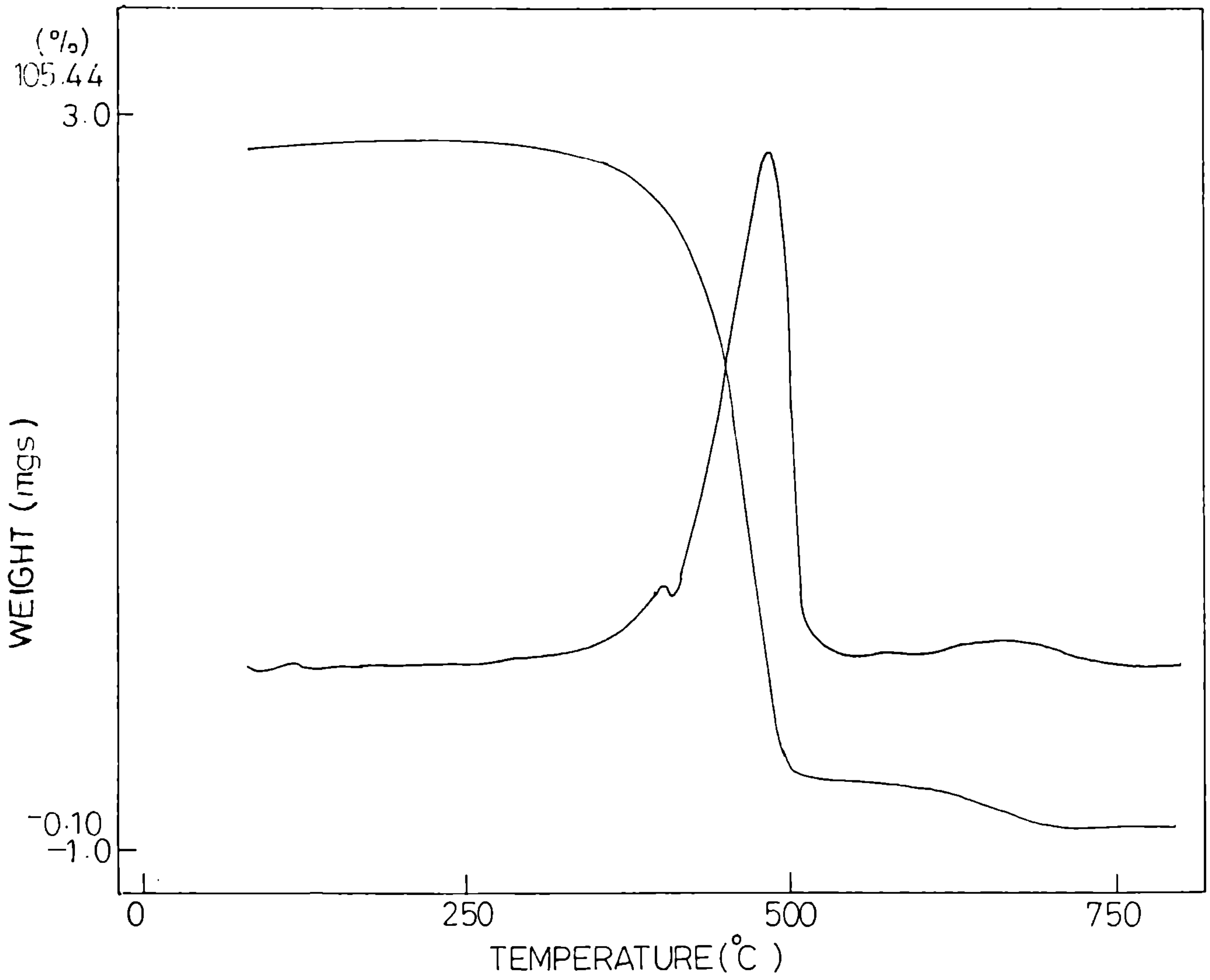


Fig.6.3.2 TGA graph of cyclized rubber

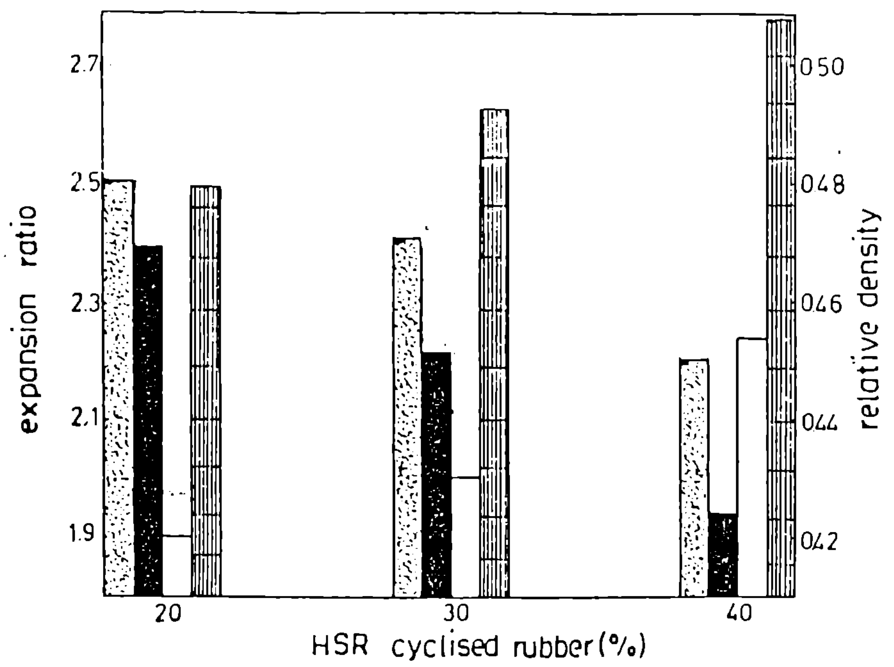


Fig.6.3.3 Variation of expansion ratio and relative density with increase in the amount of cyclized rubber/HSR. For cyclized rubber: (■) expansion ratio, (▥) relative density. For HSR: (▨) expansion ratio, (☐) relative density.

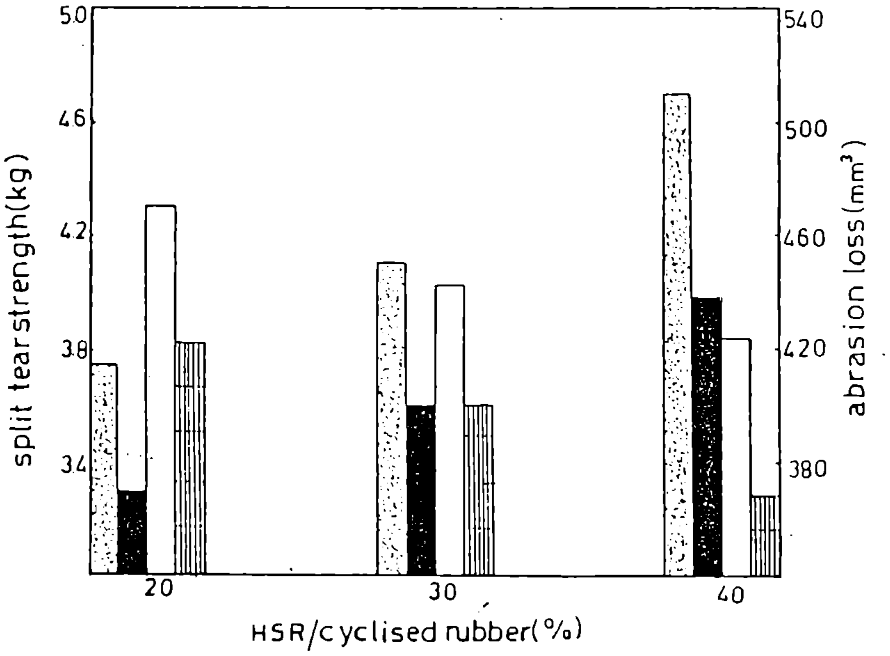


Fig.6.3.4 Variation of split tear strength and abrasion loss with increase in the amount of cyclized rubber/HSR. For cyclized rubber: (■) split tear strength (▥), abrasion loss. For HSR: (▨) split tear strength, (☐) abrasion loss.

tear that position, so strength is less. Abrasion loss decreases with increase in the amount of cyclized rubber/HSR in the blend. But NR/cyclized rubber based MC sheets show low abrasion loss compared NR/HSR based MC sheets. This may be due to the lower expansion of MC sheets by the addition of cyclized rubber.

Fig.6.3.5 shows the variation of water absorption and compression set with increase in the amount of cyclized rubber/HSR. Water absorption and compression set decrease with increase in the amount of cyclized rubber/HSR. The decrease in both the properties may be due to the lower expansion of the MC sheets, which produces stronger cell walls and low percentage of open cells. Cyclized rubber based MC sheet shows high compression set values and low water absorption. But HSR based MC sheet shows low compression set this may be due to the residual thermoplastic nature of HSR.

Fig.6.3.6 shows the variation of heat shrinkage and hardness with increase in the amount of cyclized rubber/HSR. Heat shrinkage decreases with increase in the amount of cyclized rubber/HSR. This may be due to the lower expansion of MC sheets. The small cell size and high cell wall thickness decrease the diffusion of gases. This may be the reason for low shrinkage of MC sheets based on such blends. Hardness of the MC sheet increases with increase in the amount of cyclized rubber/HSR. Cyclized rubber based MC sheet shows tremendous improvement in hardness compared to HSR based MC sheets. Cyclized rubber is a reinforcing resin, so it increases the hardness of the MC sheet. In cyclized rubber the molecular chains have been stiffened by ring formation.

Flex resistance of MC sheets are shown in Table 6.3.2 MC soling with HSR starts cracking after 129,965 cycles and crack growth is not pronounced compared to cyclized rubber. This is because HSR covulcanize with the rubber network. But cyclized rubber based

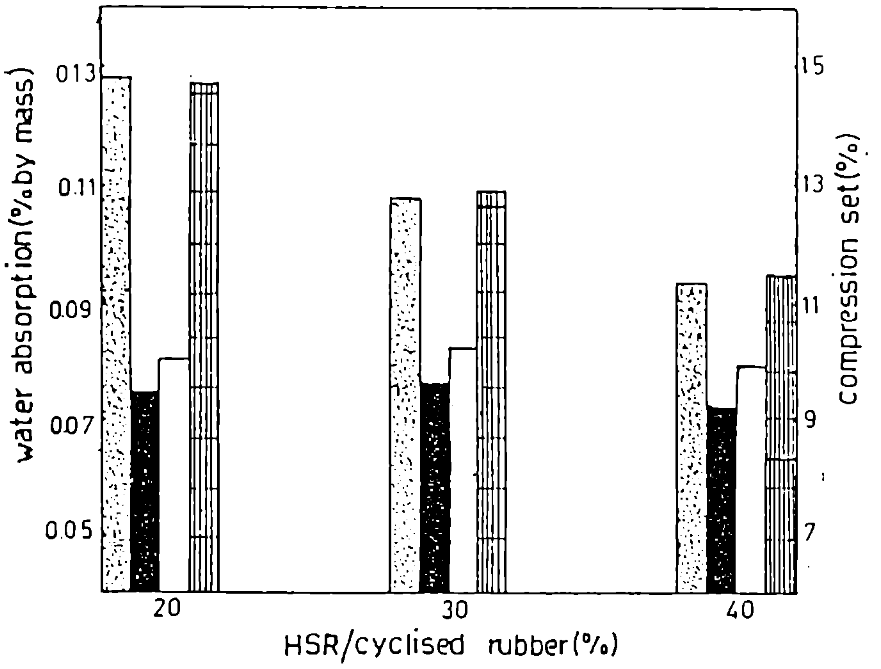


Fig.6.3.5 Variation of water absorption and compression set with increase in the amount of cyclized rubber/HSR. For cyclized rubber: (■) water absorption, (▥) compression set. For HSR:(▨) water absorption, (□) compression set.

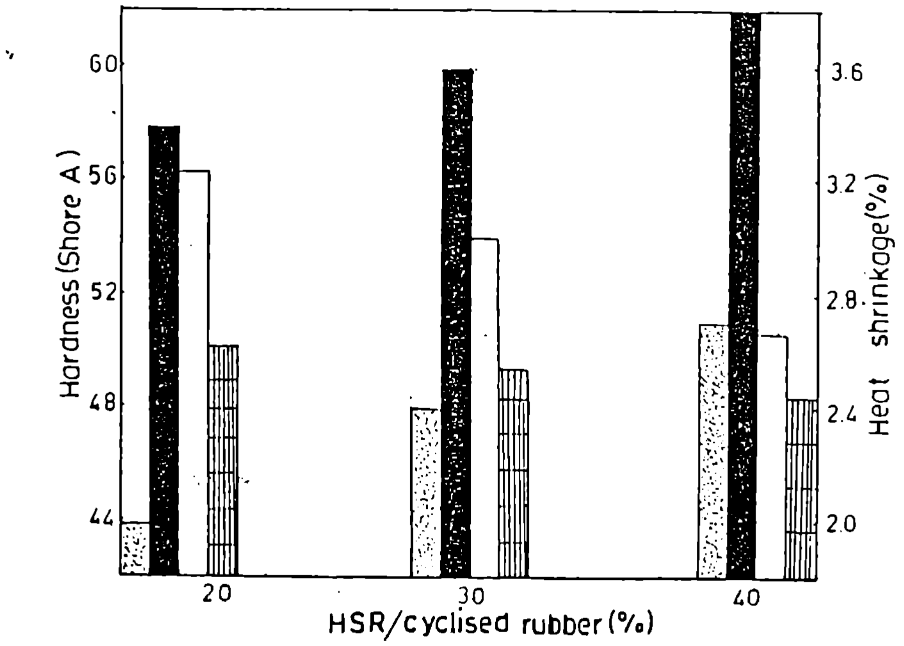


Fig.6.3.6 Variation of heat shrinkage and hardness with increase in the amount of cyclized rubber/HSR. For cyclized rubber: (▥) heat shrinkage, (■) hardness. For HSR: (□) heat shrinkage, (▨) hardness.

Table 6.3.2

Technical properties of MC soles based on NR/cyclized rubber or HSR blends

Properties	HSR			Cyclized rubber		
	20	30	40	20	30	40
Optimum cure time at 150°C min.	8.9	9.9	11	6	7	9
Initial expansion (%)	78.57	76.78	71.83	66.67	61.10	59.52
Expansion after 5 min. (%)	41.66	40.07	34.92	39.28	38.09	36.9
Expansion after 24 h (%)	38.69	34.51	29.76	38.09	36.9	35.7
Change in hardness after ageing 100°C 24 h	+2	+1	+1	+1	+1	+2
Shrinkage after post curing (%)	2.74	2.7	2.4	3.29	3.08	2.99
Flex resistance						
a) Crack initiation in cycles	129.965	127.185	128.000	95.452	84.000	775.82
b) Crack growth at the end of 100,000 cycles (%)	<600	<600	<600	<600	<600	crack size increases

MC sheets start cracking at a very early state as compared to the microcellular soling with HSR [38]. So the service life of the product with cyclized rubber is less eventhough adequate hardness, strength or load bearing capabilities are shown by cyclized rubber based MC sheets [44]. But the flex resistance value is within IS specifications.

Figs.6.3.7 and 6.3.8 are the cell structure of 70/30 NR/HSR and NR/cyclized rubber blend based MC sheets. The cell structure of NR/HSR blend is more uniform than that of NR/cyclized rubber blends. The number of cells is less in NR/cyclized rubber based MC sheets. The non-uniformity in the cell structure may be the reason for the reduced split tear strength of NR/cyclized rubber based MC sheets.

CONCLUSION

1. NR/cyclized rubber blend can be used as a base material for MC soles.
2. Cyclized rubber increases the hardness of the MC sheets and gives a leathery flexibility desirable in a soling material.
3. Cyclized rubber based MC soles show lower shrinkage and improved abrasion resistance but have a reduced flex resistance compared to HSR based MC soles.

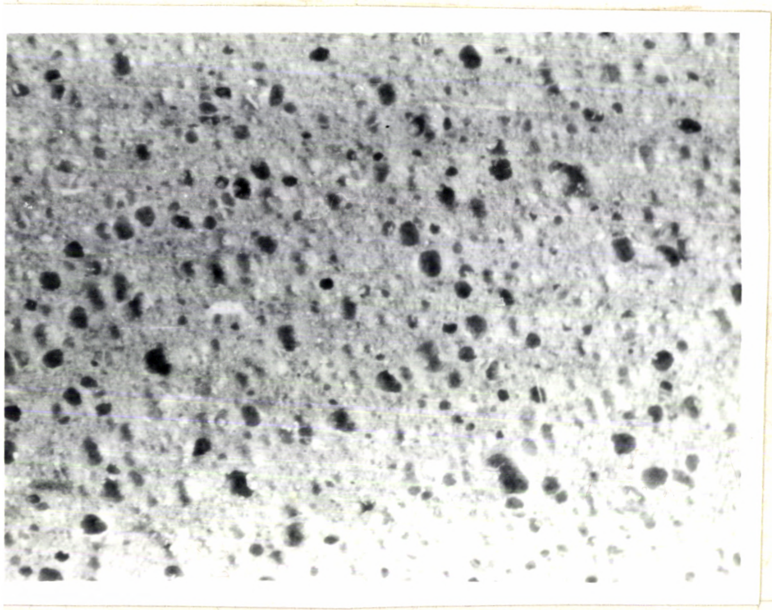


Fig.6.3.7: 70/30 NR/HSR

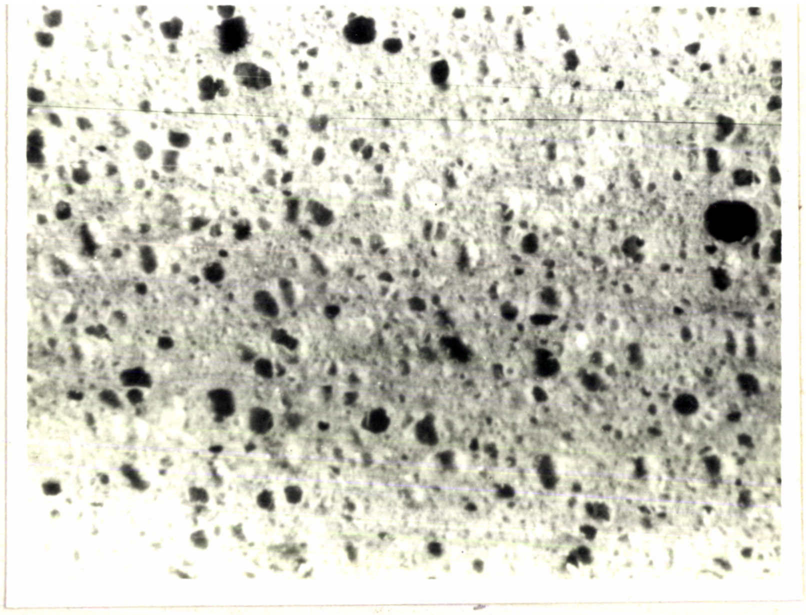


Fig.6.3.8: 70/30 NR/cyclized rubber

Optical microscope photographs of MC sheets

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CHAPTER 7

SUMMARY AND CONCLUSIONS

The main objective of this study has been to identify/develop novel base materials for cost effective and attractive microcellular soles having excellent wearing comfort.

The first part of the study was on NBR/PVC based microcellular soles. Both suspension PVC (S-PVC) and emulsion PVC (E-PVC) were tried for preparing NBR/PVC blends. The effect of PVC type and content, percentage precure, plasticizer content, blowing agent concentration etc. on the properties of MC soles based on NBR/PVC blends were studied. The optimum level of PVC, plasticizer, blowing agent etc. were determined. NBR/E-PVC based MC soles showed higher expansion, lower split tear strength and abrasion resistance compared to NBR/S-PVC based soles. The main drawback of the NBR/PVC based MC sole was found to be low resistance to crack formation and growth during service. In order to improve the crack resistance, a novel polymeric plasticizer - amine terminated liquid natural rubber (ATNR) - was tried in NBR/PVC blends. ATNR was found to be more resistant to migration compared to conventional plasticizers thereby improving the resistance to crack initiation. Further, ATNR was also found to be successful in resisting crack growth.

The effect of addition of common fillers such as clay, silica, precipitated calcium carbonate, aluminium silicate and NBR/PVC sole waste (known as NBR/PVC microcrumb) on properties of MC soles based on NBR/PVC was studied. It was found that addition of most of the fillers improved the properties such as split tear strength, abrasion resistance and hardness up to a certain level except in the case of calcium carbonate in which case no improvement was observed. For property improvement and cost reduction a part of NBR in NBR/PVC blend was replaced by NR, SBR and HSR and the effect of this substitution on the technical properties was studied. The study revealed that NR, SBR and HSR could replace about 15 parts of NBR without much reduction in properties. The technical properties of NBR/PVC based MC soles correlated well with their cell structure. Studies on NBR/PVC based MC soles are outlined in part I of chapter 3.

The suitability of NR/PVC blend as base material for MC soles was investigated as the next study. Since NR and PVC are incompatible, ATNR and ENR were tried as compatibilizers. It was found that ATNR and ENR are potential compatibilizers in NR/PVC blends. Cell structure of the MC sheets was found to be more uniform in the presence of the compatibilizers. This part of the study is described in part II of chapter 3.

The use of styrene-butadiene-styrene (SBS) as a base material for MC soles is described in chapter 4. SBS was blended with different elastomers such as NR and SBR. It was found that MC soles based on SBS/SBR blends possess superior technical properties compared to conventional NR/HSR based MC soles and that they are resistant to fungal growth on storage. These studies are described in part I of chapter 4.

SBS/NR blends were also tried as new base material for MC soles. It was found that compared to SBS/SBR based MC soles, SBS/NR based MC soles possess low split tear strength, higher expansion and higher shrinkage. To improve the properties of SBS/NR based MC soles it was modified by replacing a part of NR by HSR. The addition of HSR improved the hardness, split tear strength, and abrasion resistance of the SBS/NR based MC soles. Also, SBS/NR blend based MC soles were found to be more resistant to fungal growth on storage. As in the case of the NBR/PVC blends the technical properties of the SBS based MC soles correlated with their cell structure. This part of the study is described in part II of chapter 4.

Part I of chapter 5 describes the use of NR/EVA blends for MC soles. Various parameters like EVA content, amount of blowing agent, effect of post curing temperature and time on properties of NR/EVA blends were studied. It was found that MC soles based on 30/70 NR/EVA blend possess excellent properties with extra light weight. EVA was also used to modify conventional NR/HSR based MC soles. Addition of EVA increased the volume of expansion resulting in lower density. It was also found to impart wearing comfort, light weight and white colour to the conventional soles. Compared to NBR/PVC and SBS based MC soles, EVA based MC soles were found to possess a more fine and uniform cell structure which accounts for its better mechanical properties.

The next part of the study was on NR/LDPE and NR/HDPE blends. Both sulphur and DCP cured blends were tried for making MC soles. A part of HSR in a 70/30 or 60/40 NR/HSR blend was replaced by LDPE in order to obtain good technical properties. The study showed that NR/LDPE/HSR blends based MC soles possess improved properties with lightness and low cost. The details of the study are given in part II of chapter 5.

BR/PE and BR/NR/PE blends were tried next for making MC soles especially for low temperature applications. Low temperature flexibility of the MC sheets were measured at -5°C. Study showed that BR/PE and BR/NR/PE blends can be used for making MC soles for low temperature application. This part of the study is described in part III of chapter 5.

The suitability of BR/HSR blend for making MC soles was tried as the next part of the study. It was found that BR/HSR blend based MC soles possess light weight, low shrinkage, good abrasion resistance and flex resistance compared to conventional soles. The cell structure o these blends became more uniform with addition of BR. This part of the study is described in part IV of chapter 5.

In the next part of the study MC sole waste and latex foam wastes were modified as processible materials and were used in MC soles based on NR/HSR blend. NR/HSR sole waste was modified by different methods and was used as a reinforcing filler in NR/HSR based MC soles. Addition of modified and autoclaved crumb, resulted in better mechanical properties compared to unmodified crumb. A further observation was that modified latex foam waste can replace upto 15 parts of natural rubber in NR/HSR based MC soles without much deterioration in properties. The details of this part of the study are given in part I of chapter 6.

Rice hull ash was tried as a low cost filler in NR/HSR based MC soles as the next part of the study. The technical properties of the soles containing silica and white ash were found to be comparable. Coir pith was modified and used as filler in NR/HSR based MC soles. Modified coir pith showed improved properties. Use of these fillers can reduce the cost of the product without much reduction in properties. Modified coir pith was found to give more uniform cell structure to the MC soles compared to the unmodified forms. This study is outlined in part II of chapter 6.

Cyclized rubber was prepared in the laboratory from NR latex in the form of a fine powder. The product was characterized by IR, TGA and melting point. Cyclized rubber was blended with NR and the blend was used as a base material for MC soles. Properties were compared with those of NR/HSR based MC soles. NR/cyclized rubber based MC soles possess high hardness, low water absorption and shrinkage. This part of the study is described in part III of chapter 6.

Of the several base materials investigated NBR/PVC blends were found to be best for MC soles due to their attractive properties such as light weight, low shrinkage on storage, colour stability, adequate abrasion resistance and tear strength. High tear strength, light weight, excellent flex and abrasion resistance were also found for SBS/SBR blend based MC soles. BR/HSR blends based MC soles also possess light weight, low shrinkage, good flex and abrasion resistance compared to conventional NR/HSR blend based MC soles. Further, BR/HSR blends showed the lowest cure time compared to other blends and hence may have the advantage of lower processing cost. NR/EVA blend based MC soles are very light in weight and also possess colour stability, good flexibility and excellent flex resistance.

LIST OF PUBLICATIONS FROM THE WORK

1. Studies on the properties of microcellular soles based on NBR/PVC blends, Polymer-Plastics Technology and Engineering, 35, 97 (1996).

2. Effect of fillers on the properties of NBR/PVC microcellular shoe soles, Kautschuk Gummi Kunststoffe, 51, 44 (1998).

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5. Studies on microcellular soles based on Natural rubber/Polyethylene blends, Journal of Materials Science (Communicated).

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