STUDIES ON THE USE OF
1, 2-POLYBUTADIENE IN MICROCELLULAR SOLINGS

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REQUIREMENTS FOR THE DEGREE
OF

MASTER OF TECHNOLOGY
IN
RUBBER TECHNOLOGY

BY
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CERTIFICATE

This is to certify that the thesis entitled "Studies on the use of 1,2 Poly-butadiene in Microcellular Solings" is being submitted by Shri Jacob K. Varkey for the award of the degree of Master of Technology in Rubber Technology, to the Indian Institute of Technology, Kharagpur, is a record of bonafide research work carried out by him under the joint supervision and guidance of Dr. N. M. Mathew, Deputy Director, Rubber Research Institute of India, and myself In my opinion, the thesis has fulfilled the requirements according to the regulations and has reached the standard necessary for submission. The result of this thesis has not been submitted for the award of any other degree or diploma.

Prajna P. De 16/12/88
(P. P. De)

Date : December 16, 1988

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3rd December 1988

N.M.MATHEW

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Kottayam,
8-12-1988.

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GLOSSARY

NR - Natural Rubber

SBR - Styrene - Butadiene Rubber

1,2 PB - 1,2 Polybutadiene

EVA - Ethylene Vinyl Acetate

PVC - Poly Vinyl Chloride

NBR - Acrylonitrile - Butadiene Rubber

CR - Chloroprene Rubber

MBTS - Mercapto benzothiazyl disulfide

TMTD - Tetramethyl thiuram disulfide

DNPT - N-N' Dinitrosopentamethylene Tetramine

DEG - Diethylene Glycol

SYNOPSIS

Adaptability of 1,2 Polybutadiene as a substitute for high styrene resin in conventional microcellular applications was studied. Microcellular sheets prepared from six different compounds with varying 1,2 polybutadiene content in NR/1,2 PB blends were evaluated for their technical properties in comparison with those of the conventional high styrene based one. Different combinations of fillers such as clay, silica, aluminium silicate and microcrumb were also evaluated for the technical properties in 1,2 polybutadiene based soles. The effect of different extents of blowing on sole properties were also examined. Cell characteristics of seven selected vulcanizates were studied using scanning electron microscope.

The above studies revealed that 1,2 polybutadiene can contribute to lightness of the product, higher production output, high flex life, less blooming and saving on chemicals such as blowing agent. However some of the desirable properties like split tear strength, hardness, compression set, etc. are slightly inferior compared to those of the conventional product.

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CONTENTS

CHAPTER - 1 :: INTRODUCTION

1. INTRODUCTION

There has been tremendous growth in various types of rubbers and plastics in recent years and its effects are found in footwear industry also. Various types of polymers and its blends are used in footwear to achieve specific combination of properties such as lightness, wearing comfort, durability, stiffness, etc.

Until comparatively recent times leather was the material largely used for footwear soling application. It was about 50 years back that rubber started competing with leather in soling applications.

The most significant milestones in the development of rubber solings in footwear were the introduction of resin rubber just after the world war and the introduction of direct moulded sole in 1955(1).

The important requirements of a modern soling material are:

(1) Economic availability
(2) Adequate durability
(3) Flex resistance
(4) High coefficient of friction
(5) Dimensional stability
(6) Comfort and 'fashion' appeal

Leather and cellular solings are the right materials(2) recommended as footwear soling material. Production and processing of leather solings are expensive compared to synthetic solings. Average leather is still only one third wear resistant compared to synthetic sole.

1.1. Synthetic Cellular Solings

1.1.1. Cellular or Expanded Materials(3)

Cellular materials have been important to man since primitive man began to use wood, a cellular form of the polymer Cellulose. The world **Cellula** of latin origin, means very small cell or room. High strength-to-weight ratio of wood, good insulating properties of cork and balsa have given the background for the development of synthetic cellular polymers. The first commercial cellular polymer was sponge rubber, introduced between 1910 and 1920. Cellular polymers have been commercially accepted in a wide variety of applications since 1940's. These include furniture, bedding, comfort cushioning, automotive seats, electrical insulation, packaging, swimming belts, life buoys, aircraft application, etc.

Cellular polymer is defined as a polymer the apparent density of which is decreased substantially by the presence of numerous cells dispersed throughout its mass. Cellular polymers consist of a two-phase gas-solid system in which the solid is a synthetic plastic or rubber and is continuous. The gas phase in a cellular polymer is usually distributed in voids or pockets called cells. These cells may be inter-connected in a manner such that gas may pass from one to another, in which case the material is termed Open celled. If the cells are discrete and the gas phase of each one is independent of that of the other cells the material is termed **Closed celled**.

Sponge rubber and expanded rubber describe, those cellular rubbers produced by expanding bulk rubber stocks and are open-celled and closed-celled respectively. Latex foam rubber also is an open cellular rubber and is produced by frothing compounded rubber latex and then vulcanising it in the expanded state.

1.1.2. Development of expanded rubbers(4)

(a) By using inorganic blowing agents and solvents

The first experiment on the preparation of expanded rubber was reported in England by the middle of the last century. Natural Rubber and Gutta percha were the only suitable high polymeric substances at that time. These initial processes utilised an expanding agent, the comparatively easily decomposable ammonium carbonate, in the mix along with turpentine and other solvents. In 1856, the first commercial manufacture of expanded rubber material in a very small scale in the shape of a stick which was used for cleansing leather gloves was started in England. In America the manufacture of expanded rubber started in 1902 to 1905. In Germany and America from where France was supplied with expanded rubber in the period before the first world war, a series of low boiling solvents like alcohol, amyl acetate, carbon tetrachloride, etc were used. Mixing of solvents was however found disadvantageous on account of the occurance of large quantity of solvent loss.

Good dispersion of the blowing agent in the mix, the timing of vulcanization process and the rate of decomposition of the blowing agent are decisive factors for a good expanded material. With the introduction of organic accelerators and stearic acid in rubber processing, the inorganic carbonates, ammonium carbonate and ammonium bicarbonate, gained importance. Stearic acid is simultaneously an activator for the blowing agent and is a softening agent for the rubber mixes. By timing the vulcanization with the blowing process and using suitable accelerators, a variation is possible in the density and cell structure of the blown material.

(b) By Gasification with inert gas

For the development of cellular rubber with closed and mostly very fine pure structure which is distinguished by their special mechanical properties (eg: damping of oscillation) as well as their superior thermal and acoustic insulation properties in the form of cellular hard rubber, the investigation of Plfeumer laid the ground work. He discovered that rubber can be charged with an inert gas like Nitrogen, under pressure at very high temperature. That is, these gases are dissolved in rubber under the conditions employed on it. The first basic patent was taken by Pfleumer in 1910 and cellular rubber was produced by this method in England in 1911. Later many development work had taken place in UK, USA and Germany, to improve this process. The prepared mix was gassed in special autoclave preferably with Nitrogen under a pressure of 100-300 atm. and very high temperature. During this process prevulcanization will occur which hinder the formation of large dimension pores. Thus after complete vulcanization a cellular rubber with completely closed pores will be obtained. The degree of expansion is dependent on the applied gas pressure, the duration of gassing, the initial plasticity and the method of mixing. Some modification to the Plfeumer's method was done by Denhon in England in 1930.

Due to the unsatisfactory properties of inorganic salts and other blowing agents, organic blowing agents were developed. Organic blowing agents which liberate nitrogen are preferred.

1.1.3. Theory of Expansion Process(5)

Cellular polymers may be prepared by a variety of methods. The most important process, by far, consists of expanding a fluid polymer phase to a low density cellular state and then preserving this state. This has been termed foaming or expansion process.

The expansion process may be divided into three steps.

(1) Creating small discontinuities or cells in a fluid or plastic phase,
(2) Expansion of the cells formed,
(3) Stabilisation of the cells.

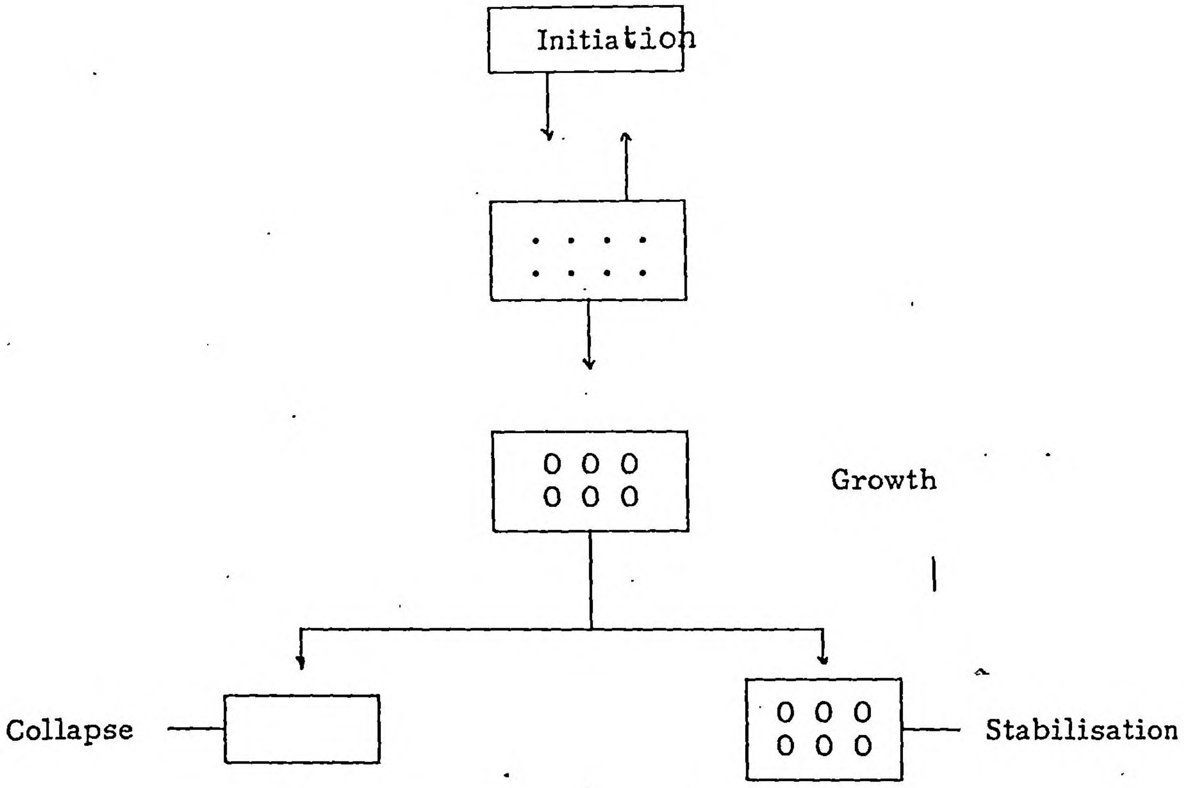
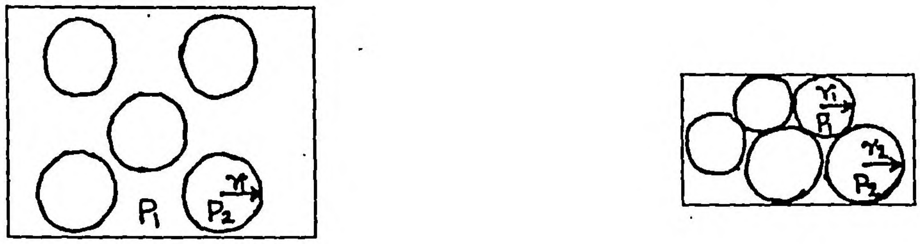


FIG 1*A STEPS IN PREPARATION OF CELLULAR POLYMERS



$$P_2 - P_1 = \Delta P = \frac{2\gamma}{r}$$

GROWTH OF CELLS

$$P_2 - P_1 = \Delta P = 2\gamma\left[\frac{1}{r_2} - \frac{1}{r_1}\right]$$

COALESENCE OF CELLS

FIGURE 1 B

INITIATION AND GROWTH OF CELLS

The initiation or nucleation of cells will be spoken of here as the formation of cells of such size that it can grow under the experimental conditions. The growth of a cell in a fluid medium is controlled by the pressure difference of the cell, the surface tension of the fluid phase γ , and the radius r, of the cell according to the equation

$$P = \frac{2\gamma}{r} \qquad \text{..........} \; (1)$$

The pressure outside the cell is the pressure imposed on the fluid surface by its surroundings. The pressure inside the cell is the pressure generated by the blowing agent which is dispersed or dissolved in the fluid.

During the time of cell growth the following factors are to be accounted for.

(1) The fluid viscosity is changing considerably which tends to influence the cell growth rate and the flow of polymers from cell walls to intersections leading to collapse.

(2) The rate of growth of cell depends on the viscoelastic nature of the polymer phase, the blowing gas pressure, the external pressure on the foam and the permeation rate of the blowing agent through the polymer phase.

(3) As a consequence of equation (1), the pressure in the cell of smaller raidus r_2 is greater than that in the cell of larger

radius, r_1. There will thus be a tendency to equalise these pressures either by breaking the wall separating the cells or by diffusion of the blowing gas from the small to the larger cells. The pressure difference (ΔP) between cells of radius r_1 and r_2 is shown by the equation (2)

$$P = 2\gamma \left[\frac{1}{r_2} - \frac{1}{r_1} \right] \qquad \ldots\ldots\ldots\ldots (2)$$

A schematic representation is given in Fig. 1A & 1B

STABILIZATION OF THE CELLULAR STATE

The increase in surface area corresponding to the formation of many cells in the plastic phase is accompanied by an increase in the free energy of the system and hence the expanded state is inherently unstable. Methods of stabilising this expanded state can be classified as

(a) Chemical:- By this the fluid phase is changing into a three dimensional thermoset polymer

(b) Physical:- In this, thermoplastic polymers are stabilised by cooling the expanded polymer to a temperature below its second order transition temperature or its crystalline melting point to prevent polymer flow.

1.1.4. Manufacturing Process for Cellular Polymers$^{(6)}$

Cellular polymers have been prepared by a wide variety of process involving many methods of cell initiation, cell growth and cell stabilisation. Most convenient classification is based on cell growth and stabilisation.

According to equation (1), the growth of cell depends upon the ΔP between the inside of the cell and the surrounding medium. Such pressure difference may be generated by lowering the external pressure (decompression) or by increasing the internal pressure (pressure generation) or known as expandable type.

Manufacturing methods are given in a chart form in Figure 1C.

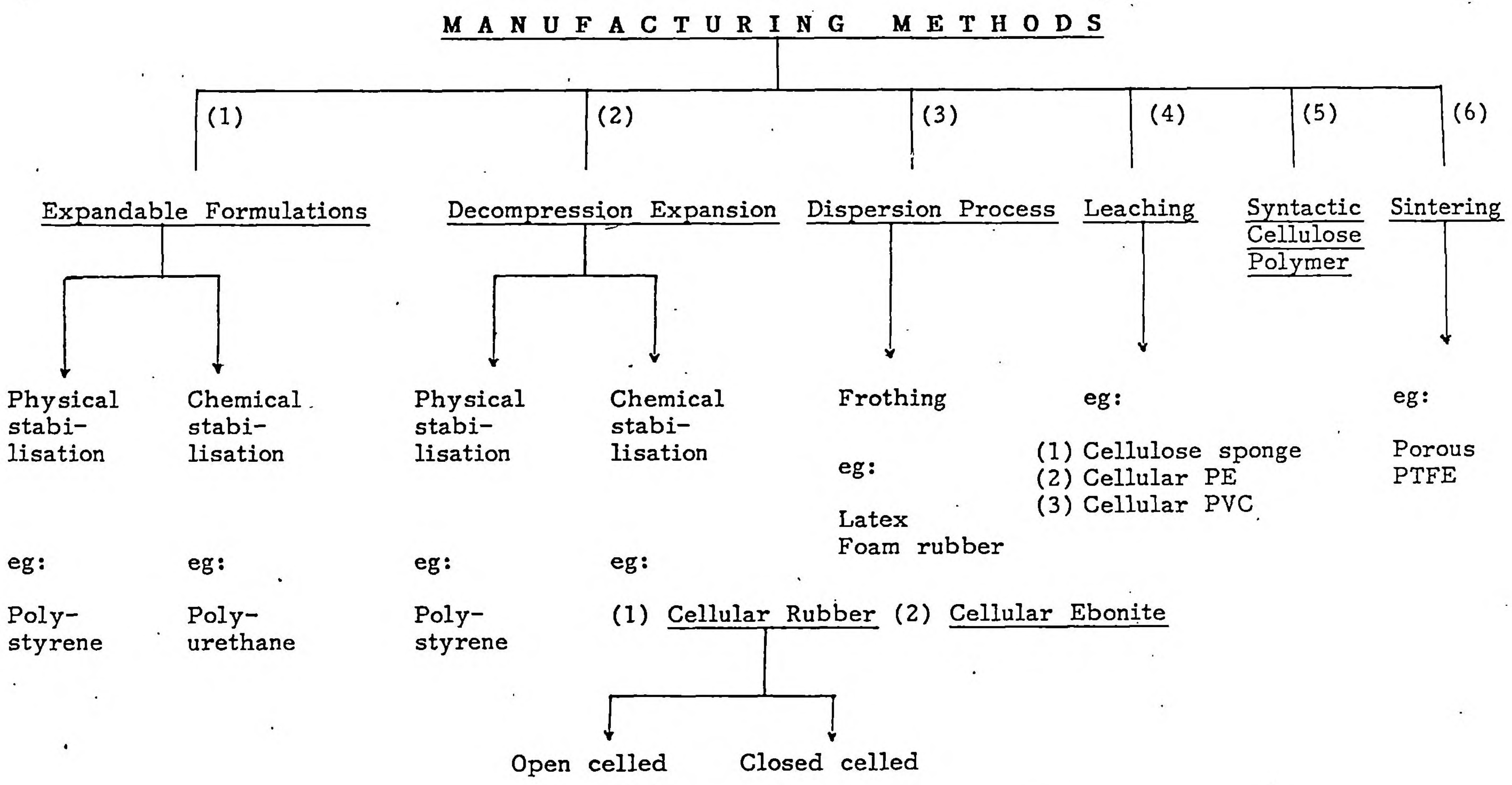

MANUFACTURING METHODS
(1)
(2)
(3)
(4)
(5)
(6)
Expandable Formulations
Decompression Expansion
Dispersion Process
Leaching
Syntactic Cellulose Polymer
Sintering
Physical stabilisation
Chemical stabilisation
Physical stabilisation
Chemical stabilisation
Frothing
eg:
(1) Cellulose sponge
(2) Cellular PE
(3) Cellular PVC
eg:
Porous PTFE
eg:
Latex Foam rubber
eg:
eg:
eg:
eg:
Polystyrene
Polyurethane
Polystyrene
(1) Cellular Rubber (2) Cellular Ebonite
Open celled
Closed celled

FIGURE 1C

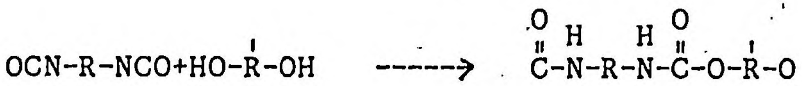
1.4.1. Expandable formulations

(1) Physical Stabilization Process

eg:- Polystyrene:- This is prepared by heating polymer particles in the presence of a blowing agent and stabilizing the cellular structure by cooling the moulded article.

(2) Chemical Stabilization

eg:- Polyurethane foam:- Chemical ingredients of PU foam system are a polyfunctional isocyanate and a hydroxyl containing polymer.



$$\mathrm{OCN{-}R{-}NCO{+}HO{-}R'{-}OH} \;\text{------}\!\!> \; \overset{O}{\overset{\|}{C}}\mathrm{-}\overset{H}{N}\mathrm{-R-}\overset{H}{N}\mathrm{-}\overset{O}{\overset{\|}{C}}\mathrm{-O-R'-O}$$

Originally CO_2 was generated **In-situ** as a blowing agent. Now rigid PU foam is produced by using volatile liquids. Physical properties of the final cellular material can be varied by controlling the degree of cross-linking and also by the structure of R and R'. Average molecular weight between cross-links for different types of PU foams are given below:

400 - 700 - For rigid PU

700 - 2500 - For semi rigid PU

2500 - 20000 - For flexible PU

1.4.2. Decompression Expansion Process

(1) Physical Stabilisation

eg: Cellular Polystyrene:- Extrusion method is used in this process. A solution of blowing agent in molten polymer is formed in an extruder under pressure. This solution is forced out through an orifice onto a moving belt at ambient temperature and pressure. Blowing agent then vapourises and causes the polymer to expand. The polymer is simultaneously expanded and cooled under such conditions that it has developed enough strength to attain dimensional stability. In this case stabilisation is achieved by cooling the polymer phase to a temperature below its Tg.

(2) Chemical Stabilisation Process

Cellular rubber and cellular ebonite are produced by this method.

Cellular Rubber:- The term **Cellular** rubber refers to an expanded elastomer which has been produced by expansion of a rubber stock in contrast to latex foam rubber, which has been produced from latex.

A decomposable blowing agent along with vulcanising systems and other additives is compounded with the uncured elastomer at a temperature below the decomposition temperature of the blowing agent.

When the uncured elastomer is heated in a foaming mold it undergoes a viscosity change as shown in the following figure 1D.

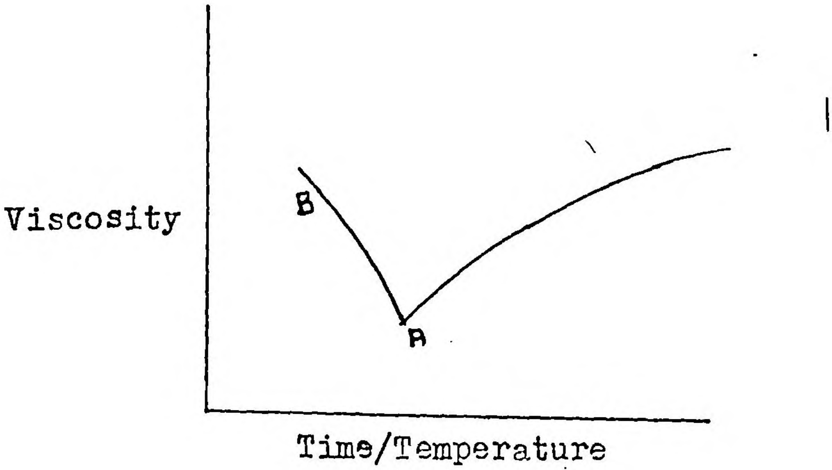


Figure 1D

Fig. Viscosity of cellular rubber stock during production cycle

Blowing agent and vulcanising system are so chosen to obtain cellular rubber of different qualities ie. open celled or closed celled.

(1) Open celled cellular rubber:-

To produce this type of rubber the blowing agent is decomposed just prior to point 'B' in the figure. So that the gas is released at the point of minimum viscosity. As the polymer expands, the cell walls becomes thin and rupture, however the connecting walls have developed enough strength to support the foam. The process is carried out in one step inside a mold under pressure.

(2) Closed cell rubber:-

The timing of blowing agent decomposition is more critical in this case - it must occur soon enough after point 'A', to allow the cell walls to become strong enough not to rupture under the blowing stress.

The expansion of closed cell rubber is carried out in two steps. Initial step is a partial cure and is carried out in a mould that is a reduced scale replica of the final mold. On removal from this, the specimen expands partly to its final form. It is then post-cured in a larger size mold or oven to complete the curing process.

Most of the elastomers can be made into either open celled or closed celled materials. NR, SBR, NBR, CR, CSM, EP terpolymer, IIR and Polyacrylates can be successfully used.

Cellular ebonite: It is the oldest rigid cellular plastic. It was produced in the early 1920's, using a similar method described for cellular rubber.

1.1.4.3. Dispersion Process

In this a gaseous material is mechanically dispersed in a fluid polymer by a technique called **Frothing technique** and is stabilised.

Latex foam is produced by this method. Four steps are involved in this.

(a) A gas is dispersed in a suitable latex.

(b) Rubber latex particles are caused to coalesce and forms a continuous rubber phase.

(c) Aqueous soap film breaks due to deactivation of the surfactant.

(d) Expanded matrix is cured and dried to stabilise it.

Two processes are used for latex foam production.

(a) Dunlop Process:- In this a gelling agent sodium silico-fluroide is used to destabilise the rubber particles and deactivate the soap.

(b) Talalay Process:- In this a freeze coagulation followed by deactivation of the soap with CO_2 is used.

NR, carboxylated styrene - butadiene copolymer, acrylic, nitrile and vinyl polymers can be used for producing foam.

1.1.4.4. Leaching Method

In this solid particles are dispersed in a fluid polymer phase, stabilise the dispersion and then leach out the solid particles to get a cellular material. eg:- Cellular PE, Cellular PVC and Cellulose sponges.

1.1.4.5. Syntactic Cellular Polymer

In this cellular polymer is produced by dispersing rigid, foamed microscopic particles in a fluid polymer and then stabilise the system.

1.1.4.6. Sintering method

This technique is used to produce porous PTFE. In this small particles of resin are heated under pressure sufficient to produce fusion of the polymer interfaces without sealing the gaseous interstices between granules.

1.2. Different Types of Polymers Used in Footwear Industry

Practically all type of rubbers except silicone, butyl and fluorocarbons can be used in soling applications. Different general purpose polymers used in footwear soling application are natural rubber, styrene-butadiene rubber, oil extended SBR, isoprene rubber and butadiene rubber in different combinations. Conventional polymers used are a combination of natural rubber and styrene-butadiene polymer with high styrene content(7). OESBR is used where price is important and general physical properties are less important. Polyisoprene rubbers are used where flow properties are important. eg: cases like injection moulding, direct moulding on and in-sole units. Polybutadiene is used as a blend with NR or SBR to improve abrasion resistance or to reduce the overall cost by increasing the amount of filler(8).

The disadvantage of natural rubber or general purpose synthetic rubber based M.C. product are its high density, vulnerability to weathering, wear and difficulty to make bright coloured products.

Polyurethane, PVC and thermoplastic rubbers[9,10,11] are later additions in footwear industry. A blend of Nitrile-PVC is being used in soling applications where oil and chemical resistance are required.

Another recent development is the use of a combination of rubber and ethylene vinyl acetate co-polymer in microcellular applications(12). This material is of low density. It is reported to have acceptable physical and wear properties and can be obtained in a range of attractive colours(13). Its main weakness compared with normal microcellular rubber is its tendency to shrink drastically at temperatures above 70°C.

The different types of plastics along with their applications(14) are given below:

PLASTIC	APPLICATION
PVC	Soles, Uppers, Upper lining and Insoles.
Polystyrene	Heels, Toe puffs.
Polypropylene	Heels, Fibre component in some poromeric uppers.
LDPE	Toe puffs, Insoles.
EVA	Adhensives, Soles.
Polyurethane	Heels, Poromeric uppers, Adhesives, Soles, Foam lining.
Polyesters	Fibre component in some poromeric uppers, Adhensives.
Polyamides	Adhesives, Toe puffs, Fibre component in some poromeric uppers.

International Synthetic Rubber Company of UK have reported commercialisation of vinyl polybutadiene having properties similar to that of SBR/BR blends(15,16). It is expected that medium vinyl polybutadine with a vinyl content of 50 per cent closely matches standard emulsion SBR.

A recent technological advancement in the polymer field is the development of 1,2 polybutadiene of controlled crystallinity(17,18). Japan Synthetic Rubber Company started commercial production of 1,2 polybutadiene with 90 per cent 1,2 content and a controlled degree of crystallinity between 15 to 25 per cent(19). 1,2 polybutadine is expected to partially replace high styrene resin in footwear applications.

1.2.1 1,2 Polybutadiene

International Synthetic Rubber Company of UK has announced the commercialisation of new medium range, vinyl polybutadiene rubber having properties equivalent to those of SBR/BR blends(20). In the synthesis of this rubber, the pendent bulky phenyl groups in SBR have been replaced by vinyl groups. In view of the smaller size of vinyl groups, more pendant vinyl groups are needed along the chain to produce a matching polymer. Various grades of medium vinyl polybutadiene rubbers with 42, 48 and 63 per cent of vinyl contents have been offered by ISR. It has been considered by many as the tyre rubber of the future.

There is a useful relationship between glass transition temperature (Tg) and physical properties of elastomers(21). It can be concluded that as Tg decreases, abrasion resistance, elasticity, low temperature resistance and diffusion rate increases, whereas skid resistance decreases.

High cis polybutadiene with Tg of -105°C has excellent abrasion resistance but it possess poor skid resistance. A compromise between abrasion and skid resistance in high cis polybutadiene (BR) can be reached by blending 60 parts of SBR with 40 parts of BR to get a Tg of -70°C. This value of Tg is close to that of NR (-72°C). The Tg of random co-polymer of styrene and butadiene prepared by solution technique varies inversely with styrene content and with 1,2 vinyl content of butadiene. In the case of new vinyl polybutadiene rubber, it is seen that Tg increases with 1,2 vinyl content. An illustration is given in Fig. 1.1 to 1.3. For a rubber with 35 per cent vinyl content corresponding Tg is +70°C, and this rubber has processing characteristics similar to general purpose emulsion SBR. Apparent Tg of -50°C to -70°C in an elastomer comprises the acceptable range of properties for various applications and this can be available in the new polybutadiene rubber with 35-55 per cent 1,2 vinyl content.

Kuntz(22) reported that by using lithium based catalyst in hydrocarbon medium gave PB with 8-12 per cent of 1,2 vinyl groups. 1,2 vinyl content can be increased by modifying the lithium based catalyst by introducing electron donors such as ether and amines in the system. Strong anionic catalysts will give higher percentage of 1,2 vinyl groups in polybutadiene rubber.

Nordseik(23) carried out extensive studies on testing and performance of tyres made from vinyl polybutadiene rubber. Mixing of filler, oil, etc. was as trouble free as SBR/BR mix. Test data on passenger tyre treads and vulcanisates of vinyl polybutadiene rubber compare favourably with those on SBR/BR blends. A tripolymer blend of 45 per cent vinyl polybutadiene with SBR and cis polybutadiene (30/35/35) shows 10 per cent improvement in treadwear compared to 65/35 SBR/PB blend. The medium vinyl polybutadiene are also effective as partial or complete replacement of SBR in several non-tyre applications Medium vinyl polybutadiene with a vinyl content of about 50 per cent is expected to match emulsion SBR in important properties.

Homopolymers of butadiene with 1,2 vinyl content between 35-55 per cent represents an alternative to solution SBR and SBR/BR blends(24). Vinyl polybutadiene manufactured by solution polymerisation technique is more expensive than emulsion techniques as it uses solvents like tetrahydrofuran (THF) in place of water, and also alkalimetal catalyst like butyl lithium, which are expensive. Polymerisation using single monomer is comparatively easy to handle. Possibility of obtaining desired properties by simply varying the vinyl content, enhances the scope of its application. Its lower specific gravity and ability to accept greater amount of filler are an added advantage.

JSR 1,2 Polybutadiene Rubber(25)

This new thermoplastic elastomer is having 1,2 content greater than 90 per cent and a controlled degree of crystallinity between 15 to 25 per cent. The crystallinity of this new 1,2 polybutadiene is markedly less than previously reported syndiotactic 1,2 polybutadiene. As the crystallinity is less, crystalline melting point is 80-90°C, which permits fabrication on plastics fabrication equipments.

As reported(21) by JSR scientists the polymer is prepared by a solution polymerisation technique with Ziegler-type catalyst systems

Japan Synthetic Rubber Company have introduced two grades of 1,2 polybutadiene JSR RB 810 and JSR RB 820 which differ in crystallinity.

Physical Properties(26)

Some important physical properties of 1,2 polybutadiene are shown in Table 1.1. Properties of 1,2 polybutadiene is somewhat similar to LDPE except for its greater flexibility. This can be seen in Fig. 1.6 (viscosity Vs shear rate graph). From Fig. 1.4 it is seen that 1,2 polybutadiene has a stress-strain relation that is intermediate to that of the plastics and rubber. The dynamic elastic modulus of 1,2 polybutadiene is shown in Fig. 1.5 and is compared with that of plasticised PVC, low density polyethylene and ethylene vinyl acetate. At temperatures below 20°C, 1,2 pBD is more flexible than EVA or an EVA LDPE. A comparison of physical properties for JSR 1,2 polybutadine, EVA and Styrene-Butadiene thermoplastic elastomer is given in Table 1.2.

Chemical Properties

1,2 PBD can be readily sulfur vulcanised making it suitable suitable for blending with other sulfur vulcanisable systems. It is reported that cured products based on 1,2 PBD exhibit weatherability and ozone resistance similar to that of EPDM.

Processing

Viscosity-shear rate relationship for 1,2 PBD of about 100,000 molecular weight is shown in Fig. 1.6 and is similar to that of LDPE. It is desirable to keep the temperature of fabrication relatively low to avoid cross-linking. Recommended maximum temperature is 150°C.

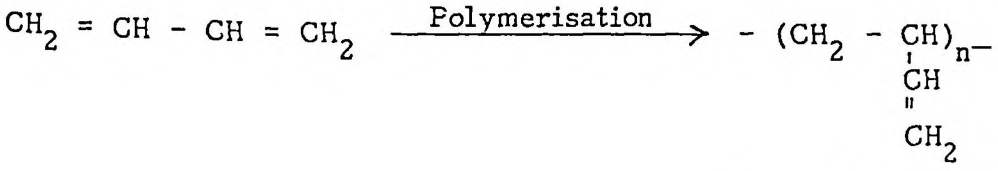
Applications

Areas of application are thermoplastics, thermosetting resins, coatings, rubber, fibres, adhesives, film, injection molded articles, sponge or cellular applications, etc.

In the area of footwear JSR 1,2 polybutadiene is proposed as a suitable material for non-curing low blow molded shoe soles.

In physical properties JSR 1,2 polybutadiene is reported to rank between polyurethane and EVA.

Structure of 1,2 polybutadiene



$$CH_2 = CH - CH = CH_2 \xrightarrow{\text{Polymerisation}} -(CH_2 - \underset{\underset{\displaystyle CH_2}{\|}}{\underset{|}{\underset{\displaystyle CH}{CH}}})_n-$$

1,2 polybutadiene.

1.3. Fillers Used in Microcellular Applications

The selection of fillers for particular application is governed in the first instance by their chemical constitution, availability and price. The limit of their usefulness as filling materials is dependent on their physical characteristics. Many of the treatments applied to fillers in extraction process is merely for obtaining them in a physically useful form.

Thus an ideal filler would have to comply with a wide range of both chemical and physical requirement(27).

Some of the requirements needed are listed below.

(1) Ability to impart improvement in physical properties of the polymer compound.
(2) Low moisture absorption.
(3) Specific gravity appropriate for the application.
(4) Good wetting characteristics.
(5) Free from deleterious chemical impurities.
(6) Low cost and good availability.
(7) Non-inflammability.
(8) Absence of odour.
(9) Good colour retention.
(10) Chemical and heat resistance.
(11) Controlled particle size.
(12) Good dispersion characteristics.
(13) Low solubility in water and environmental solvents.

Physical properties

Some of the important physical properties of fillers used in rubber are indicated.

(1) Particle size, shape and distribution.

(2) Surface area.

(3) Bulk density.

(4) Density.

(5) Refractive index, opacity and colour.

(6) Hygroscopicity and moisture content

(7) Hardness.

As most of the microcellular products are coloured, non-black fillers are used as reinforcing agents. Non-black fillers have certain features in common, compared to carbon black. They have higher specific gravity from 1.95 for precipitated silica to 5.6 for zinc oxide. At the same loading by weight they have lower tensile strength than blacks. Modulus also is lower at the same hardness. Non-black fillers impart less abrasion resistance to rubber.

There is every chance that natural non-black fillers will have more oversize particles (particles not passing through a 325 mesh size) than blacks. Such particles can easily lower the tensile strength or tear strength as they can well be the point of initial rupture(28).

In general, pigments of number average particle size less than 50 M and/or specific area in excess of 50 m^2/gm have been considered reinforcing. Elastomer reinforcement is considered as an application phenomena defined as the "enhancement of one or more properties of an elastomer by the incorporation of some ingredient thus making it more suitable for a given application"(24).

Although carbon blacks (except thermal) are aggregates of particles whereas most non-black fillers are not. They consists of acicular, platey or blocky particles. It is reported that clay, silica and silicates are ideal for microcellular applications(30).

1.3.1. Clay(31)

The most widely used non-black filler for rubber is clay. Its use is based on its low comparative cost, versatility and stiffening properties.

Clay refers to a physical condition and not chemical composition. The type of clay used in rubber is called kaolin clay and has been derived from the weathering of aluminous minerals such as mica and feldspar. The clos est approach to its chemical composition would probably be $Al_2O_3.2\ SiO_2.\ 2\ H_2O$.

Rubber grade clays are white to cream powder with a density of 2.6. Clay is not hygroscopic, with a 1 per cent maximum moisture. Clay is prepared in four different ways and they are air floated, water washed, calcined and chemically modified.

A majority of clay used in rubber industry is either air-floated or water washed.

Calcined clay is used in cable industry for better electrical properties.

Clay is an adsorptive material and can adsorb organic accelerators. This effect can be mitigated by using small amounts of triethanolamine or polyethylene glycol. They will preferentially be adsorbed at the active sites on the silica layer of the clay; thereby preventing adsorption of curatives.

1.3.2. Silica and Silicates

Fine particle silica gives the utmost in reinforcement of rubber among the non-black fillers. The silicates will come next to silica.

Silica can be produced by a pyrogenic or precipitation process. Silicates for rubber compounding are produced mostly by precipitation.

Silica produced by thermal process is called fumed silica. The original process was developed by Degussa Company in 1940's and the product marketed under the trade name "Aerosil".

Fumed silicas are only occasionally used in polymers as they are expensive. Much of this is used in silicone rubber compounding.

Precipitated silicas are made by the action of acids on waterglass. The acid used is sulfuric and waterglass an alkaline solution of sodium silicate. The reaction involved is

$$n.\ SiO_2 .\ 1\ Na_2O + H_2SO_4 \longrightarrow Na_2SO_4 + 10\ SiO_2\ .\ H_2O$$

The hydrated precipitated silica is filtered out and washed to remove the sodium sulfate. It is then dried and ground to obtain the required product. Those used in rubber would have surface area approximately 170 m^2/gm.

The moisture which is driven off at 105°C must be carefully controlled in silica's for rubber use. Compared to carbon black precipitated silica particles are much porous.

An approximate composition and properties of precipitated silica used in rubber industry is given below.

	Feature	Amount
(1)	Drying loss	4 - 7 %
(2)	Ignition loss	8 - 12 %
(3)	SiO_2 (Dry basis).	83 - 90 %
(4)	Surface Area (m^2/gm) (BET method)	45 - 700
(5)	Particle size m (Arithmetic mean dia)	10 - 100
(6)	Refractive Index	1.45
(7)	Density in rubber	2.0

SILICATES

Silicates used in rubber industry are mostly calcium and aluminium silicates. These are prepared in much the same way as precipitated silica but the acid is replaced completely or in part by metal salts like calcium chloride or aluminium sulfate. Process conditions can be varied widely to produce different quality silicates.

Approximate composition and properties of aluminium silicate is given below.

(1)	Moisture (2 hr 105°C) %	6
(2)	Ignition loss (2 hr 1000°C) %	7
(3)	SiO_2, %	82
(4)	CaO, %	-
(5)	Al_2O_3, %	9.5
(6)	Na, %	8
(7)	pH	10.4
(8)	Sieve residue (45 m), %	0.1
(9)	Average particle size (nm)	15
(10)	B.E.T. surface area (m^2/gm)	100

Adding silica to a rubber quickly increases the stiffness of the mix, so that in practice not more than 50 parts are included. The stiffening will increase the Mooney viscosity of the compound making it difficult to process.

Stiffening is supposed to cause by the incompatibility between silica and hydrocarbon rubber.

Compounding with precipitated silica is very different from that with carbon black. There is an affinity between carbon black and hydrocarbon rubbers. Silica is hydrophilic and incompatible. Thus two situations arise.

(1) Silica to silica attraction is high and large aggregates are formed impending flow and the mix becomes very stiff.

(2) Silica filled compounds will have inferior abrasion resistance compared to carbon black filled compounds, as in the former the polymer filler bonding is weak.

MICRO CRUMB

It is a finely ground material produced from the scrap of microcellular sheetings. It will have a density of approximately 0.5.

1.4. Blowing Agents(31)

Blowing agents are used to make soft, light impact resistant sponge rubber. They are either used alone or with some diluting fillers and other activators. These materials will release gases at curing temperatures thereby introducing the cellular structure in the rubber and makes it sponge like. If the cells are inter-connecting the product is refered to as open celled and if not closed celled.

There are also cellular materials which are produced without the use of blowing agents. Latex foam produced by whipping air into latex and urethane foam produced by using CO_2 as blowing gas which is produced <u>in situ</u> in the reaction medium by the reaction between water and isocyanate, are examples for this.

Sodium bicarbonate was the first blowing agent reported. It reacts with stearic acid giving CO_2, as the temperature is increased.

Because of the permeability of CO_2 interconnecting cells are produced. A disadvantage of using sodium bicarbonate is that it will leave residual soap in the sponge.

Closed cell structures like microcellular solings are made by using blowing agents which evolve gas largely Nitrogen, by thermal decomposition.

Choice of blowing gas(32)

Nitrogen is prefered as the blowing gas due to the following reasons.

(1) It is an inert, odourless, non-toxic gas.

(2) Permeability of Nitrogen is the least compared to other blowing gases.

Measured relative permeability of NR to different gases are listed below (taking hydrogen as 100).

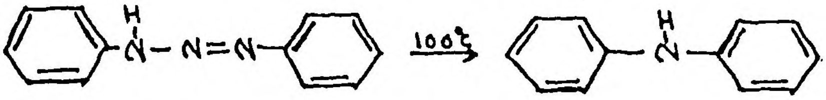
CO_2 = 260
H_2 = 100
O_2 = 46
N_2 = 17

Organic blowing agents

Organic blowing agents vary widely in their properties. Importantly, they vary in the temperature at which they produce gas and in the nature of their decomposition products. Some produce odor, while other may yield coloured or toxic substances on decomposition. Sometimes the blowing agents or their decomposition products may function as activators or retarders. These factors are important in the selection of blowing agent.

Some of the common blowing agents(33) are Diazoaminobenzene, Dinitrosopentamethylene tetramine, Azodicarbonamide, p-tolueue sulfonyl semicarbazide, etc.

(1) Diazoaminobenzene



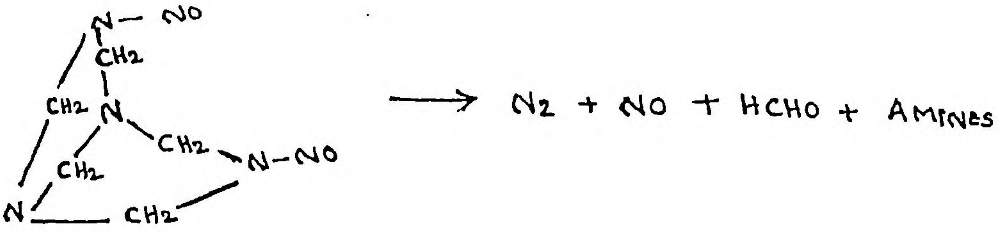
Diazoaminobenzene

This compound is soluble in rubber and is capable of producing fine unicellular structure.

But the disadvantage of using this chemical is that the decomposition product diphenylamine is a staining chemical and Diazoaminobenzene is a suspect carcinogen.

(2) Dinitroso Pentamethylene Tetramine

This compound is prepared by the nitrosation of hexamethylene tetramine.



When heated alone or in presence of inert diluents the chemical decomposes near 195°C, but when used in rubber or plastics in presence of certain activators, produce gas within a temperature range of 130 to 190°C.

The decomposition products include Nitrogen, Nitrous oxide, formaldehyde and certain amines which gives rise to a "fishy odour" in the expanded product. The odor can be suppressed by the addition of urea, melamine, etc.

Some of the factors to be considered in selecting a blowing agent are:

(1) Its chemical composition and whether activators are needed or not.

(2) Gas evolved per gram of blowing agent.
(For DNPT it is 200 cm^3/gm).

(3) The decomposition temperature. This may vary from 100°C to 235°C, depending on the type of blowing agent and the catalyst used.

(4) The decomposition products.

(5) Uniformity of colour and cell structure in successive batches.

(6) Absence of odour.

(7) Influence of vulcanisation and ageing.

(8) Possibility of discoloration.

(9) Cost.

One of the difficulties involved in making sponge is the determination of the right plasticity of the stock for proper blow with the rate of vulcanisation. If it is not, blowing may occur rapidly and the expanded material may collapse before vulcanisation.

1.5. Rubber Footwear Industry in India

Rubber footwear industry ranks third, following the automotive tyre and cycle tyre sectors accounting for about 9.8 per cent of the total rubber consumption. There are over 30 units manufacturing quality footwear of which about half a dozen units account for substantial production. Besides about 660 units(34) are engaged in the manufacture of hawai chappals, soles, heels, straps, etc.

Indian footwear industry manufactures a wide range of footwear including all rubber, canvas/leather upper with rubber soles, sports shoes of various types, gum boots, combat boots, defence boots, ladies and children's wear, etc.

Development of synthetic materials in footwear especially PVC has slightly adversely affected the rubber footwear industry.

The per capita use of footwear was reported to be about 5.03 pairs in USA, 4.45 pairs in UK, 4.16 pairs in France, 3.63 in Europe whereas that in India it is still around 0.5(35). However the per capita consumption is likely to go up steadily in the wake of improved standards of living.

Microcellular solings have become popular for their lightness, durability, soft feel and good looking. Due to all these factors and economic availability, M.C. soling has become the common man's footwear

1.6. Scope of the Work

The supply of general purpose and special purpose styrene-butadiene polymer will be inadequate as the production of styrene monomer is insufficient to meet the demand(36,37). Some attempt have been made to reduce the content of styrene in general purpose SBR. Hence a substantial replacement of SBR co-polymers is necessary in the near future. Supply of styrene monomer is reported diminishing and the cost of it is increasing much faster compared to butadiene(38). Attempts are going on to develop a substitute for SBR in general purpose applications(39).

One of the most promising partial or complete replacement for solution or emulsion SBR in tyre and non-tyre application is polybutadiene of medium to high vinyl content. Heat build-up and blow out resistance were reported better for vinyl polybutadiene (of 45% vinyl) compared to SBR 1712. Abrasion and cut growth resistance are also reported better for vinyl PB compared to SBR 1712(40).

Some of the features of expected advantage(25) of using 1,2 polybutadiene in microcellular application as a substitute for high styrene resin are the following.

(1) Lightness or low density.

(2) Lower shrinkage.

(3) Clear colour.

(4) Excellent snappiness.

(5) Sponge scrap utilisation.

(6) Good abrasion resistance.

The present work is a scientific evaluation of the adaptability of 1,2 polybutadiene as a substitute for high styrene resin in microcellular applications.

TABLE 1.1 Typical physical properties of JSR 1,2 polybutadiene

Properties	Testing methods	Units	Measuremed values	
			JSR RB810	JSR RB820
Density	Density-gradient tube method	g/cm^3	0.901	0.906
Crystallinity	Density-gradient tube method	%	approx. 15	approx. 25
Microstructure 1,2-unit content	Infrared ray spectrum (Moreromethod)	%	90	92
Refractive index n_{25}^{d}	ASTM D542		1.513	1.515
MFI (Melt flow index) 150°C, 2,160 g	ASTM D1238	g/10 min	3	3
Thermal properties				
Vicat softening point	ASTM D1525	°C	39	52
Melting point	(DSC method)	°C	75	80
glass transition point	(DSC method)	°C	-30	-25
Tensile properties	JIS K6301			
300% modulus		kg/cm^2	40	60
Tensile strength		kg/cm^2	65	105
Elongation		%	750	700
Hardness - Shore D	ASTM D1706	Degrees	25	34
JIS A	JIS K6301	Degrees	77	89
Izod impact (notched, at room temperature)	ASTM D256	kg-cm/cm	Not broken	Not broken
Light transmittance	JIS K6714	%	91	91
Haze	JIS K6714	%	1.0	1.0

TABLE 1.2 Physical Properties of JSR RB, EVA and SB-TPE as sole materials for Footwear

	JSR RB	EVA	SB-TPE
Lightness	O	Δ	X
Rubbery feeling	Δ	X	O
Hardness	Δ	O	X
Permanent set	Δ	X	O
Compression set	O	X	X
Tear strength	O	O	X
Flex resilience	O	X	Δ
Weatherability	Δ	O	X
Ozone resistance	O	O	X
Abrasion resistance	O	O	Δ
Oil resistance	O	O	X
Flowability	O	O	X

NOTE : O : Excellent
Δ : Moderate
X : Poor

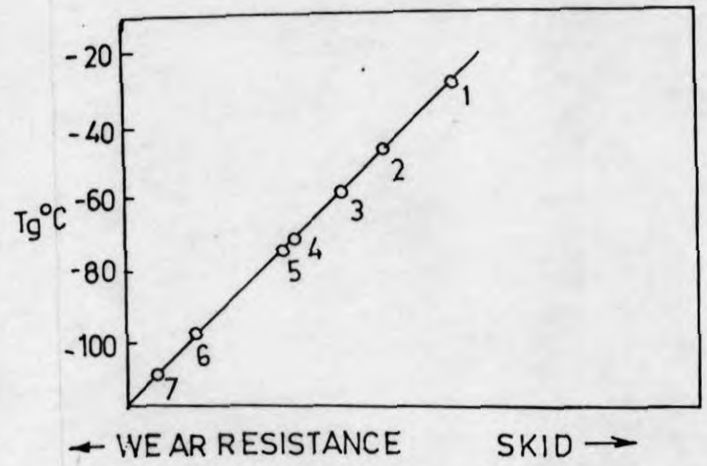


FIG.1·1. RELATIONSHIP BETWEEN ELASTOMERIC PROPERTIES AND Tg

1. NBR 2. Em. SBR 3. Sln. SBR(25% St.) 4. Sln. SBR(10% St.)
5. NR 6. Li based PB 7. Cis-PB

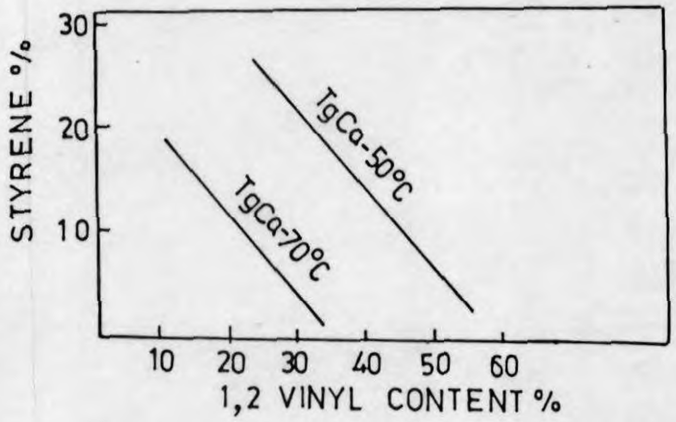


FIG.1·2. THE RELATION SHOWING Tg AS AS A FUNCTION OF STYRENE CONTENT AND OF 1,2-BUTDIENE

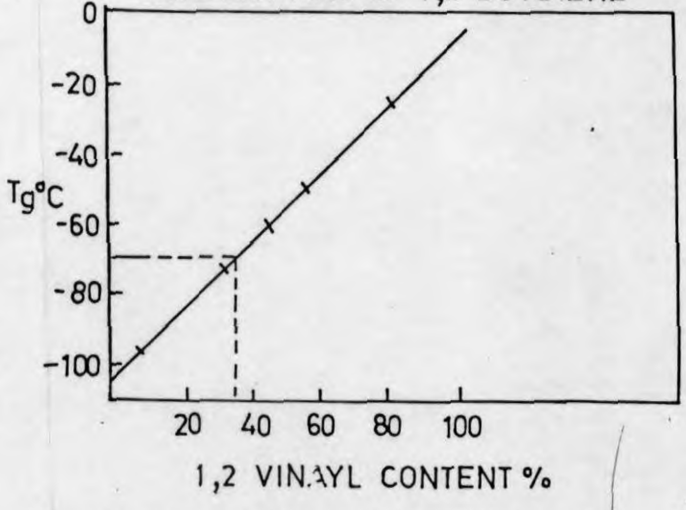


FIG. 1·3. RELATIONSHIP BETWEEN 1,2-VINYL CONTENT AND Tg IN POLYBUTADIENE

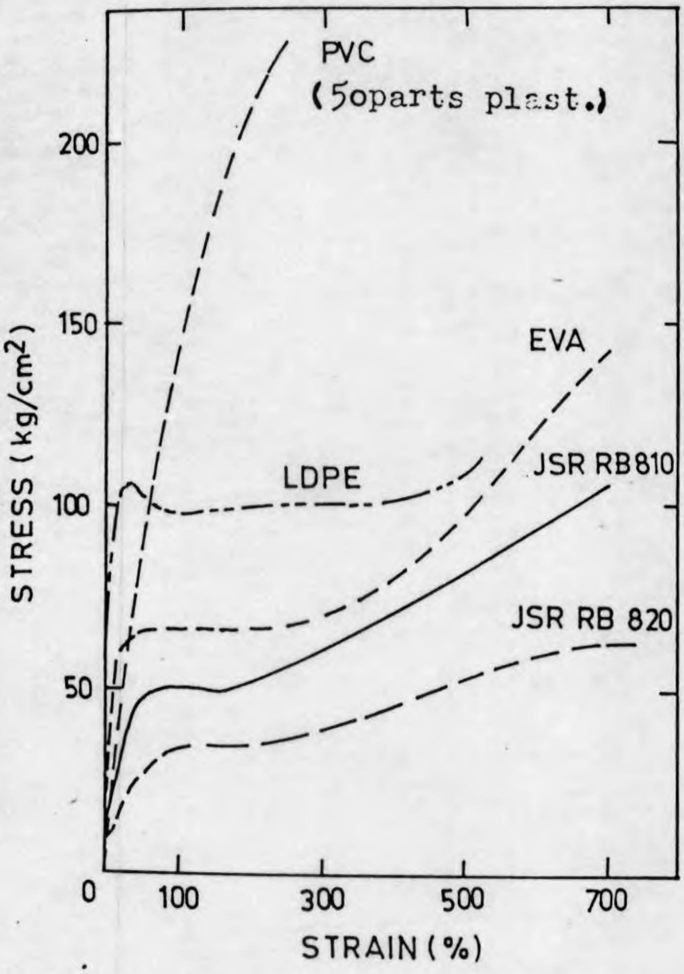


FIG. 1·4. STRESS VS STRAIN CURVE OF 1,2 PBD.

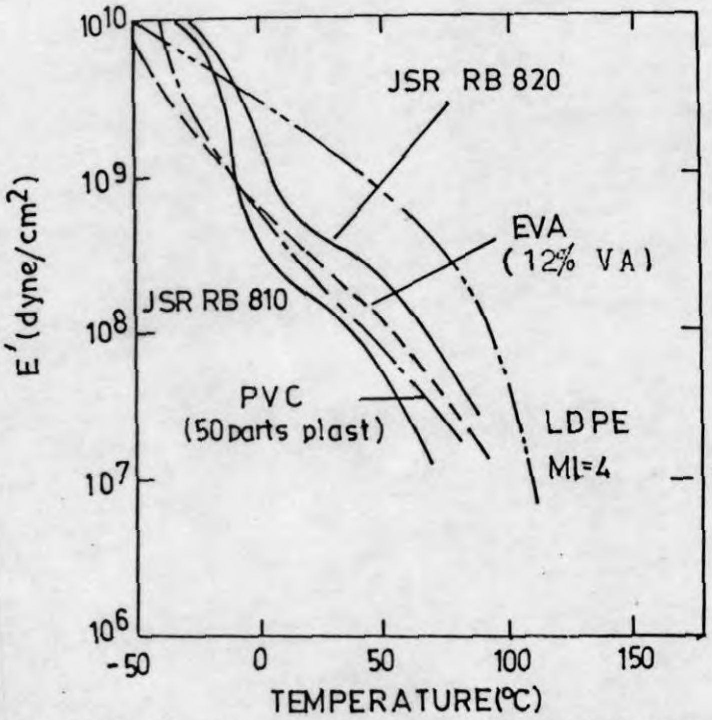


FIG.1·5.TEMP. VS ELASTIC MODULUS CURVE OF JSR RB

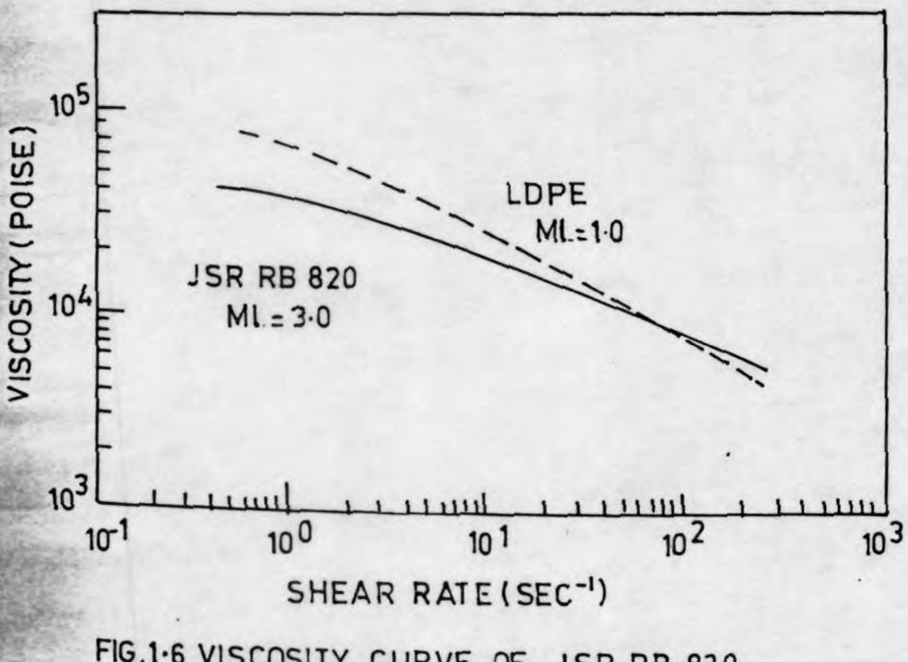


FIG.1·6 VISCOSITY CURVE OF JSR RB 820

CHAPTER - 2 :: EXPERIMENTAL

2. EXPERIMENTAL

2.1. Materials Used

(A) POLYMERS:

(1) Natural Rubber:

Natural rubber used was crumb rubber, ISNR-5 as obtained from the pilot crumb rubber factory, Rubber Board. The Indian standards specifications for ISNR-5 grade is given below.

	Parameters	Limit
1.	Dirt content (%) by mass, Max	0.05
2.	Volatile matter, (%) by mass, Max	0.8
3.	Nitrogen (%) by mass, Max	0.6
4.	Ash (%) by mass, Max	0.6
5.	Initial Plasticity, Po, Min	30
6.	Plasticity Retention Index (PRI), Min	60

Since it is known that the molecular weight, molecular weight distribution and non-rubber constituents of natural rubber are affected by clonal variation, season, use of yield stimulants and method of preparation(41,42), rubber from the same lot has been used in this study.

(2) SBR 1958[(43)] (Synaprene S-1958)

This was supplied by M/s. Synthetics and Chemicals Ltd. It is a self-reinforcing type of styrene butadiene rubber produced from a blend of synaprene S-1502 base latex and a reinforcing type latex. The blend is prepared at latex stage ensuring perfect dispersion of the reinforcing polymer. This rubber is available in the form of bales.

Raw Rubber Properties	Min.	Max.
Volatile matter (%)	-	0.75
Organic acid (%)	4.0	7.0
Soap (%)	-	0.50
Ash (%)	-	0.75
Antioxidant (%)	1.0	1.75

Synaprene S-1958 is light coloured and non-staining type rubber. It is widely used in microcellular applications, leather like products, high hardness products, coloured hard rubber (ebonite), highly abrasion resistant products, etc.

(3) SBR - 1502[(43)] (Synaprene S-1502)

This polymer is supplied by M/s. Synthetics and Chemicals Ltd. Synaprene S-1502 is a co-polymer of styrene and butadiene manufacture by cold emulsion polymerisation system using fatty acid and rosin acid soap as emulsifier. It is a non-staining and a non-discolouring grade of SBR. Specifications of this rubber is given below.

Raw Rubber Properties	Min.	Max.
Mooney visocisty, ML_4 at 100°C	46	58
Volatile matter (%)	-	0.75
Organic acid (%)	4.75	7.0
Soap (%)	-	0.50
Bound styrene (%)	21.5	25.5
Ash (%)	-	1.5
Antioxidant (%)	0.5	1.5

It has balanced properties as regards to loading capacity, good flex resistance and abrasion resistance which makes it useful for shoe soles, heels and bright coloured mechanical goods, microcellular soling, etc.

(4) 1,2 Polybutadine (JSR RB 820)

This polymer was supplied by M/s. Japan Synthetic Rubber Company. Typical properties of the raw polymer are given below.

Properties	JSR RB 820
Microstructure 1,2 unit content (%)	92
Stabilizer	Non-staining
Density gm/cm^3	0.91
Crystallinity (%)	Approx. 25

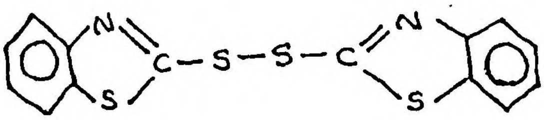
(B) FILLERS

Fillers used are precipitated silica, clay, aluminium silicate and micro crumb. All these are commercial grade materials.

(C) CURATIVES

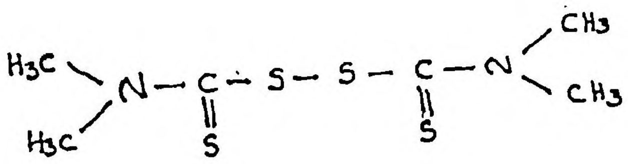
MBTS and TMTD were used as accelerators. These chemicals are supplied by M/s. Bayer India Limited. Chemical Composition of these chemicals are given below.

MBTS:



Mercapto benzothiazyl disulfide

TMTD:



Tetramethyl thiuram disulfide

Sulphur: Rubber grade sulfur was used as the curing agent.

(D) PLASTICISERS

Napthenic oil was used as plasticiser.

(E) BLOWING AGENT

N-N'-Dinitroso pentamethylene tetramine (DNPT) supplied by M/s. Dipak Nitrite was used as the blowing agent.

(F) OTHER INGREDIENTS

TiO_2 supplied by M/s. Travancore Titanium Products was used as the brightening agent. Laboratory reagent grade Diethylene glycol was used for the work.

2.2. Mixing and Process of Production

The compounds were prepared in two stages. Initial mixing of polymers, fillers and other additives excluding curatives and blowing agent was done in a laboratory model intermix (KO Intermix) and the final mixing of curatives and blowing agent was done in a laboratory model (30 cm x 15 cm) mixing mill.

Mixing in Internal Mixer

Intermix was set at a speed of 40 rpm and an initial chamber temperature of 80°C. Total mixing time was 8 minutes. Natural rubber was masticated for 2 minutes followed by the addition of the second polymer 1,2 polybutadiene, SBR 1958 or SBR 1502. Blending was done for another 2 minutes. Fillers and other additives were added at the end of 4 minutes and mixing continued for another 4 minutes. Mix was dumped at the end of 8 minutes.

Internal mixer model	:	KO Intermix MK3
Capacity	:	1 Litre

Mixing in laboratory mixing mill

Final mixing of curatives and blowing agent was done in the two roll mixing mill at a friction ratio 1:1.25. Mixing roll temperature was 80°C. Total mixing time was about 12 minutes. Order of addition was accelerators, followed by sulphur and finally the blowing agent.

After complete mixing, the stock was sheeted out and passed six times endwise through a tight nip (0.3 mm) and finally sheeted out at 8 mm.

Compound Maturation

For proper dispersion of the ingredients, the mix was stored for one day.

Molding of the Sheet

Molding was carried out in a 18" x 18" hydraulic press having steam heated platens. Platens were maintained at 150°C and at a pressure of 45 kg/cm^2 on the mold. Mold was loaded with 3 per cent excess compound than the mold volume.

The mold was of rectangular base with a loose fitting top. The mold, completely filled with rubber compound, placed in the press, mold closed and sufficient hydraulic pressure applied. The top cove of the mold was so close fitting that the gas generated by the blowin agent was retained in the rubber. When the rubber was sufficientl cured (80 per cent of the maximum cure) the press was opened quickl and the sheet expanded out of the mold in all the three directions.

Trimming of sheets

The excess material flown out was trimmed immediately after removal from the mold so as to avoid bending of sheets.

Stabilization at room temperature

Expanded sheets were allowed to stabilize for one day at room temperature.

Post curing

In precure in the mold, only a partial vulcanisation was given so that the rubber got adequate strength to hold the nitrogen gas released after expansion. In our studies 80 per cent of the maximum cure time and an extra time of 2.5 minutes to compensate for the thickness of the sheet was taken as the precure time.

As it is undercured the vulcanised sheet will have still a large permanent set. By postcuring the sheet becomes permanently stabilised in the expanded size. Postcuring will complete the cure of the precured sheets and will help in attaining the maximum physical properties.

In the present experiments the postcuring given was for 3 hou at 80°C in a thermostatically controlled hot air oven.

2.3. Experiments

A preliminary study was conducted to standardise the curati concentration and temperature of precure. Further studies were conduct with the selected cure system and it consists of three important parts

(1) Study of the effect of 1,2 polybutadiene in expanded rubbe soles.

(2) Effect of filler on sole properties.

(3) Effect of blowing agent concentration on sole properties.

SELECTION OF CURE SYSTEM AND TEMPERATURE

Compound with curative combination of MBTS/TMTD/Sulphu in the ratio 1.0/0.2/1.6 was prepared and its cure characteristics were studied. Cure time for this system was found to be around five minutes, thus making the process very difficult. To increase the cure time for the same cure system, the temperature of cure was reduced to 140°C. By this, though the cure time was increased considerably, the resultant sheet was of poor quality with big blow holes in it. This might have occured due to improper curing. This difficulty was overcome by the use of lesser proportion of curatives and the temperature of cure being maintained at 150°C.

Further studies were conducted with a curative combination of MBTS/TMTD/Sulphur in the ratio 0.8/0.1/1.6 which does not cause any processing problem with a convenient cure time of around 7 minutes.

Table 2.1 and 2.2 give the compounds used and their precure time.

I. STUDY ON THE EFFECT OF POLYMER RATIO ON SOLE PROPERTIES

Eight compounds with varying natural rubber/1,2 polybutadiene ratio of 100/0, 90/10, 80/20, 70/30, 60/40, 40/60, 20/80 and 0/100 were prepared. Control compounds were also prepared using NR/SBR-1958 and NR/SBR-1502/SBR-1958 in the ratio 70/30 and 35/35/30 respectively. Microcellular sheets were prepared from these compounds using the method given earlier. These were then postcured and tested for their properties as per the relevant ISI standards.

Rheographs are given in Figure 2a

II. EFFECT OF DIFFERENT FILLERS ON 1,2 PB BASED MICROCELLULAR SOLE

Seven compounds were prepared to study the effect of varying proportions of commonly used fillers like clay, silica, aluminiun silicate and microcrumb in 1,2 polybutadiene based microcellular soles. Compounds were prepared in the intermix. Curatives and blowing agent were added in the two roll mixing mill. Microcellular sheets were prepared from these compounds using the method described earlier. Sheets were then postcured and tested for its properties as per the relevant ISI Standards.

Rheographs are given in Figure 2b.

III. STUDY OF THE EFFECT OF BLOWING AGENT CONCENTRATION

Varying levels of blowing was studied for three sets of compoun In all these compounds Natural Rubber/1,2 polybutadiene ratio was 70/30. In the first set of compounds the filler combination used was clay/silica/aluminium silicate in the ratio 60/30/15. The blowing agent concentrations studied for this compound was four, five, six and seven parts per hundred rubber. In the second set the filler combination used was clay/silica/aluminium silicate in the ratio 40/40/25. The blowing agent concentrations studied were five, six and seven parts per hundred rubber. In the last set the filler combination used was clay/cilica in the ratio 40/40 and the blowing agent concentrations studied for it was five and six parts per hundred rubber.

Compound preparation and sheet moulding were done as described earlier. Sheets were thentested for its technical properties as per the relevant ISI Standards.

Rheographs are given in Figure 2 c

2.4. Testing of Microcellular Sheets

In the present work all tests were carried out as per IS 6664-1972, IS 3400-1974 and IS 10702-1985.

2.4.1. Determination of compression set

The 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.

Testing:-

The test piece having diameter 30 ± 0.2 mm and thickness 9.5 ± 0.2 mm was conditioned at 27 ± 1°C and 65 ± 5 per cent relative humidity for 24 hours. Thickness of each test piece at the centre was measured using the guage. Test pieces were then placed between the parallel plates of the Wallace Constant Stress Compression Set Apparatus and a load of 140 ± 1 kg was applied for 24 hours.

When the test period was over samples were removed and allowed to recover. After the recovery period of one hour the thickness of the samples was noted.

Compression set was calculated using the formula

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

t_0 = Initial thickness in mm.

t_1 = Final thickness in mm.

2.4.2. Determination of Split Tear Strength

It is the maximum load required to split off a sample test piece of specific size, which was expected at a constant speed of 75 mm per minute.

Testing:-

Four rectangular pieces of size 25 x 100 x 7 ± 0.2 mm were cut out along and across the molded sheet. The test piece was prepared by splitting the sample midway between the top and bottom surface for a distance of 30 mm from one end and thus forms two tongues at the end.

The two tongues of the test piece were clamped between the jaws of the Zwick UTM, Model 1474 and allowed to separate at a constant rate of 75 mm per minute. The load was noted with the help of a recorder. Mean of the maximum load of the 4 samples was taken as the split tear strength.

2.4.3. Determination of Heat Shrinkage

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

Testing:-

Sample of size 150 x 25 x 15 mm was cut from the sheet after splitting all sides of the sample.

The test piece was conditioned in an atmosphere of relative humidity 65 ± 5 per cent and at a temperature of 27 ± 2°C for 24 hours prior to testing.

Length of the test piece was measured to the nearest 0.1 mm and placed in a heating chamber maintained at 100 ± 1°C for one hour.

Test piece was then removed from the heating chamber and allowed to cool for 2 hours at 27 ± 2°C. Length of the test piece was again noted. Heat shrinkage was calculated using the equation

$$\text{Heat shrinkage, \%} = \frac{(L_0 - L_1) \times 100}{L_0}$$

L_0 = Length before heating, in mm.

L_1 = Length after heating, in mm.

2.4.4. Determination of Relative Density

A sample of size 50 x 50 mm was cut from vulcanized and post cured sheets/soles.

Test piece was conditioned at an atmosphere of 65 ± 5 per cent relative humidity at a temperature of 27 ± 2°C for 24 hours prior to testing. After conditioning, the mass, length, breadth and thickness of the sample were noted.

Relative density was then calculated as follows:

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

Where M = Mass of the test piece in grams after conditioning.

L = Length of the test piece after conditioning.

B = Breadth of the test piece after conditioning.

T = Thickness of the test piece after conditioning.

2.4.5. Determination of Hardness

Hardness is measured as the resistance offered by the material for the indentation of a pointer of specified dimentions attached to a precalibrated spring and is expressed as a number. Test piece of size 50 x 50 mm was conditioned at 65 ± 5 per cent relative humidity and at a temperature of 27 ± 2°C for 24 hours. Hardness was then measured using Shore - A Durometer.

Result is expressed directly in Shore-A.

2.4.6. Determination of Change in Hardness After Ageing at 100 ± 1°C for 24 hours

It is the change in hardness that may occur to a sole sample that undergoes ageing at a specified temperature and for a definite time. Difference in hardness of the sample before and after ageing at 100 ± 1°C for 24 hours is taken as the change in hardness.

2.4.7. Determination of Room Temperature Shrinkage

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

Testing:-

Test pieces of size 125 x 5 x 15 mm was cut from the sample sheet after splitting off all the sides of the sample. It was then conditioned in an atmosphere of 65 ± 5 per cent relative humidity and at a temperature of 27 ± 2°C for 24 hours prior to testing. Initial length of the test piece was noted to the nearest 0.1 mm. The test piece was placed in a chamber maintained at 27 ± 2°C for two weeks. It was then removed and its length noted.

Room temperature shrinkage is expected as

$$\text{Shrinkage, \%} = \frac{L - L_1 \times 100}{L_0}$$

L_0 = Length of test piece in mm before testing.

L_1 = Length of test piece in mm after testing.

2.4.8. Determination of Water Absorption

It is the increase in weight that may occur to a sample of specified size due to absorption of water by it after keeping it in distilled water for a specified period.

Testing:-

Test piece of size 5 x 5 x 5 mm was cut from the sample after removing the skin from both sides.

After conditioning for 24 hours at 27 ± 2°C the test piece was weighed to the nearest 0.5 mg and then kept immersed in distilled water for a period of 24 hours, at 27 ± 2°C. The test piece was reweighed within two minutes of the removal from water.

Result is expressed as

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

Where M_1 = Mass in grams of sample after immersion.

M_0 = Mass in grams of sample before immersion in water.

2.4.9. Determination of Abrasion Resistance

Abrasion loss is expressed as the volume of test piece getting abraded by its travel through 42 meter standard abrasion surface, as

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

V = Abrasion (volume loss of mm^3 unit).

Δm = Mass loss (mg unit)

ρ = Density (mg/mm^3 unit).

Testing:-

Abrasion test was conducted using DIN abrader. It consists of a drum which provides the abrasive surface for the sample. The drum rotates at an rpm of 40 ± 1 and the total abrasion length of the same is 42 metres. The sample having a diameter 16 ± 0.2 mm and length of 6 to 10 mm, keeps a horizontal feed of 4.2 mm/rotation.

Die cut sample of the dimension specified was fixed on the sample holder and a load of 5 N was applied. Sample holder with the sample was allowed to travel through the specified distance. After giving an initial surface smoothening run the weight of the sample was noted. Then the test run was conducted and the weight was again noted. From difference in weight the abrasion loss can be calculated.

2.4.10. Determination of Flex Life

In this test the number of flexing cycles required for a sample with an initial cut of definite size to grow to a definite length and for complete crack failure are noted.

Ross flexing machine is used to determine the cut growth of rubber samples. The machine allows the pierced flexing area of the test specimen to bend freely over a rod of 10 mm dia by an angle of 90°. The machine runs at 100 ± 5 cycles per minute. One end of the test specimen is clamped firmly to a holder arm and the other end is placed between two rollers which permit a free bending movement of the test specimen during each cycle.

Sample was given a cut of 2.50 ± 0.02 mm in length at the centre of the flexing face at a definite length of 62.0 ± 1.0 mm from the clamping side. Test piece was having a length of 150 mm, width of 25.0 ± 1.0 mm and thickness of 6.30 ± 0.2 mm.

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.

Adjustable top rollers are let down till it touches the specimen and permits the specimen to travel freely between rollers.

Frequent observations were taken for determining the rate of increase in cut length.

Observations were taken for

(1) Number of cycles required for propagation of the initial crack given.

(2) Extent of crack growth for 100,000 cycles.

2.4.11. Determination of Shrinkage

Sheet size of each sample was noted on 2 occasions to study the extent of shrinkage of whole sheet.

(a) After stabilization of the precured sheet at room temperature for 24 hours.

(b) After stabilization of the post cured sheet at room temperature for 24 hours.

2.4.12. Cell Structure Study - by SEM

(a) PRINCIPLE OF SEM[46,47]:-

A simplified block diagram showing the principle of working of SEM is given in the Fig. 2.1. Electrons from an emission source or filament are accelerated by a voltage usually in the range of 1-30 KV and directed down the centre of an electron-optical column consisting of two to three magnetic lenses. These lenses cause a fine electron beam to be focussed in the specimen surface. Scanning coils placed before the final lens cause the electron spot to be scanned across the specimen surface in the form of a square raster, similar to that of a television screen. The currents passing through the scanning coils are made to pass through the corresponding deflection coils of a cathode ray tube, so as to produce a similar but larger raster on the viewing screen in a synchronous manner.

The electron beam incident on the specimen surface causes various phenomena, of which the emission of secondary electrons is used in SEM. The emitted electrons strike the collector and the resulting current is amplified and used to modulate the brightness of the cathode ray tube. The time for the emission and collection of the secondary electrons is negligibly small compared with the time for the scanning of the incident electron beam across the specimen surface. Hence there is a one-to-one correspondance between the number of secondary electrons collected from any particular point of the specimen surface and the brightness of the analogous point on the screen, and thus an image of the surface is progressively built up on the screen.

In SEM, the image magnification is determined solely by the ratio of the sizes of the rasters on the screen and on the specimen surface. In order to increase the magnification, it is only necessary to reduce the currents in the SEM scanning coils. As a consequence of this, it is easy to obtain high magnification in SEM, while for every low magnification of 10X, it would be necessary to scan a specimen, approximately 10 mm across and this presents difficulties because of the large deflection angles required.

(b) TESTING:-

The SEM observations reported in the present investigations were made using a Jeol 35 C model scanning electron microscope. Cell structure was investigated using a thin sample cut from the centre of the microcellular sheeting. The surface to be examined was then sputter coated with gold within two hours after sample preparation. It was then investigated for cell characteristics within five hours after gold coating. Photomicrographs of the special features of each sample were taken.

TABLE - 2.1

MATERIAL	COMPOUND NUMBER		
	1	2	3
Natural Rubber	70	35	60
SBR - 1502	-	35	-
SBR - 1958	30	30	-
1,2 Polybutadiene	-	-	40
Zinc oxide	5	5	5
Stearic acid	2	2	2
Alox SP	1	1	1
TiO_2	5	5	5
Precipitated silica	30	30	30
China clay	60	60	60
Aluminium silicate	15	15	15
Diethylene glycol	2	2	2
Naphthenic oil	10	10	10
MBTS	1.0	1.0	1.0
TMTD	0.2	0.2	0.2
Sulphur	1.6	1.6	1.6
DNPT	7.0	7.0	7.0

TABLE - 2.2

TEMPERATURE OF CURE	PRECURE TIME (t_{80} + 2.5) MINUTES		
	Compound 1	Compound 2	Compound 3
150°C	6.0	7.25	5.6
140°C	7.8	9.7	6.5

t_{80} - 80 per cent of maximum cure.

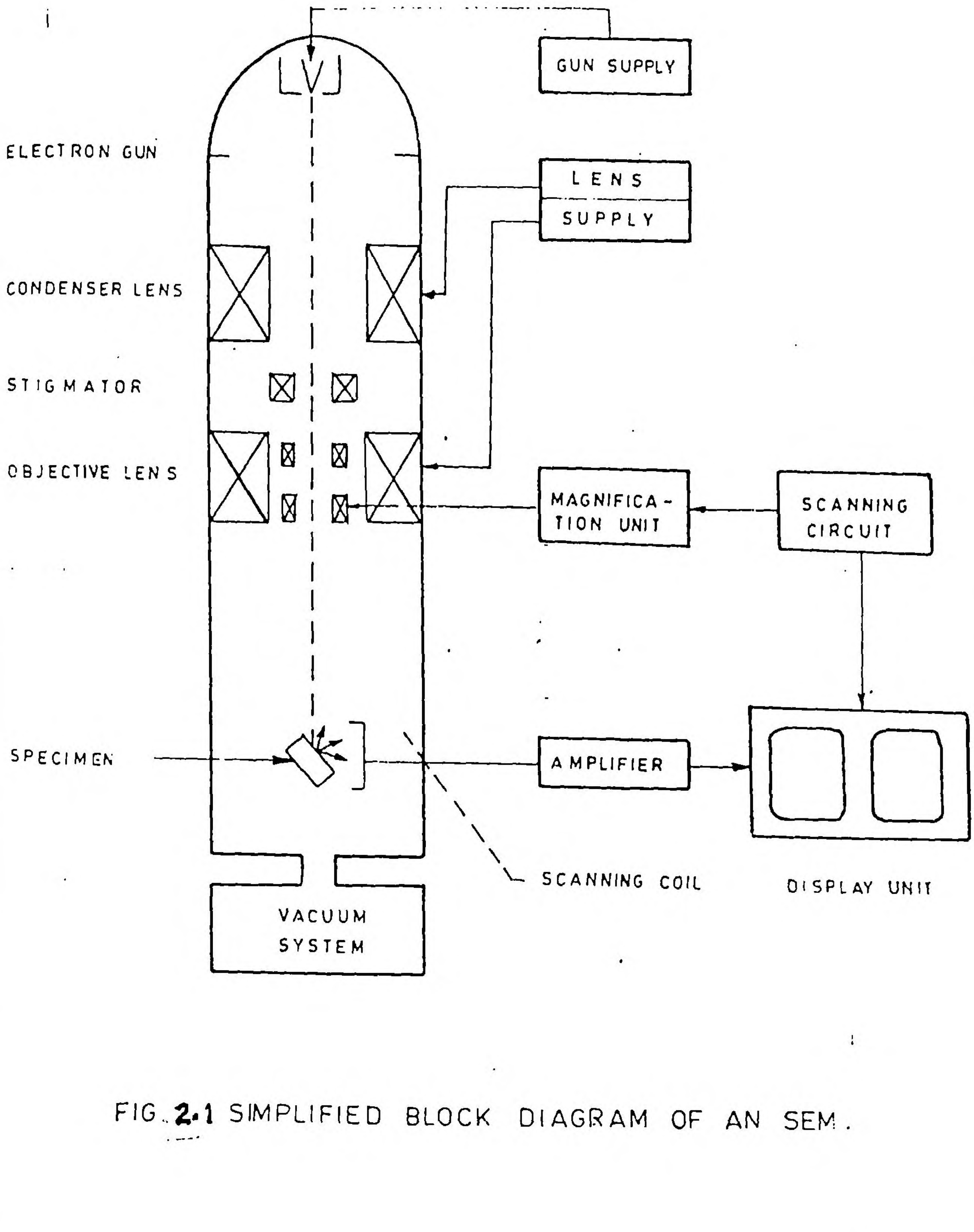


FIG. 2.1 SIMPLIFIED BLOCK DIAGRAM OF AN SEM.

CHAPTER - 3 :: RESULTS AND DISCUSSION

3. RESULTS AND DISCUSSION

In this chapter results of our studies on expanded rubber based on blends of natural rubber/1,2 polybutadiene are discussed in comparison with the conventional type blends based on natural rubber/high styrene rubber. Results are discussed in three different parts.

(1) Effect of 1,2 polybutadiene in NR/1,2 PB based expanded soles.

(2) Effect of fillers in 1,2 PB based expanded soles.

(3) Effect of varying blowing agent concentration on the properties of 1,2 PB based expanded soles.

3.1. Effect of Polybutadiene Ratio in NR/1,2 PB based MC Soles

Eight compounds with varying NR/1,2 PB ratio of 100/0, 90/10, 80/20, 70/30, 60/40, 40/60, 20/80 and 0/100 were prepared. Two control compounds with NR/SBR-1958 and NR/SBR-1502/SBR-1958 were also prepared. MC sheets were prepared from these compounds and evaluated for its technical properties. Sheets prepared from compounds containing more than 60 parts of PB were defective and hence we have limited our studies to a maximum of 60 parts 1,2 PB in the blend. The technical properties are given in Table 3.2 and Fig. 3.1 to 3.9.

Relative density variations with varying PB content are plotted in Fig. 3.1. Relative density was found to decrease from 0.75 to 0.35 as the content of 1,2 polybutadiene in the blend increased from zero to sixty parts. The probable reasons for the lowering of relative density with increasing 1,2 polybutadiene content is the relatively lower density of the polymer and the higher expansion that it causes due to its thermoplastic nature. As a lower density is always desirable for soling materials, the use of 1,2 PB in MC compounds is thus found to be advantageous.

Hardness variations with varying PB content are plotted in Fig. 3.2. Though the hardness of MC sheet increased initially, it decreased with increasing amount of 1,2 polybutadiene. The observed increase in hardness may be due to the inherent polymer character(44,45) Lowering of hardness beyond 30 parts of 1,2 PB is due to the higher expansion of the sheet at this level. .

Compression set variations with varying PB content are plotted in Fig. 3.3. Compression set was found to increase as the 1,2 PB content in the blend increased. This is due to the thermoplastic nature of 1,2 PB and the lesser extent of crosslinking in this polymer.

Observations on heat shrinkage are plotted in Fig. 3.4. Heat shrinkage also increased with increasing PB content. This is because of the fact that, the 1,2 polybutadiene which is getting softened at higher temperature enhances the diffusion of the entrapped gas from the cells causing higher shrinkage$^{(26)}$. Room temperature shrinkage was found to be almost constant irrespective of the polymer variation.

Split tear strength variations with PB content are plotted in Fig. 3.5. It also was found decreasing, with increasing PB content. Higher expansion will result in thinner polymer wall giving lower split tear strength for the product. The SEM observations reported later in this chapter also support this view.

Sheet area is a measure of the production output. Fig. 3.6 gives a plot of sheet area against PB content. It increases as the PB content in the blend increased. Thus even within acceptable property limits, increasing PB content in the blend will increase the production output. Higher expansion of the sheet may be due to the lower compound viscosity and better thermoplasticity at the molten stage associated with the higher PB content. The rheographic data as given in Fig. 3.7 also support this view. Area of the postcured sheet is less than the precured sheet. This has occurred due to the enhanced diffusion of the gases at the postcuring conditions.

Water absorption is a measure of the open cells produced in the expanded sheet. The observations on water absorption are plotted against 1,2 PB content in Fig. 3.8. As the 1,2 PB content increased the water absorption also increased indicating higher number of open cells at higher PB content. Thus the chances of cell wall breakage is more as the PB content is increased.

Abrasion data with varying PB content is plotted in Fig. 3.9. Abrasion loss was found to increase as the PB content increased. As 1,2 PB is a known abrasion resistant polymer, the increase in abrasion loss may be due to the higher expansion of the MC sheet.

Ross flexing data is given in Table 3.2. Flex resistance is high for 1,2 PB based soles. In this respect PB based MC soles are better in performance compared to high styrene based MC sole.

On keeping for 3 weeks natural rubber and high styrene based soles have shown blooming tendency, whereas PB based sole did not show any blooming tendency.

Therefore it is concluded that addition of 1,2 PB to NR in MC sheet production is beneficial in decreasing the relative density, increasing flex life and increased expansion resulting in increased production. However, properties like split tear strnegth, abrasion resistance, hardness, etc. are adversely affected.

It is also observed that the properties of MC sole produced from natural rubber/1,2 polybutadiene blends are generally inferior to natural rubber/SBR-1958 blend.

3.2. Effect of Different Fillers on 1,2 PB Based Microcellular Soles

Seven compounds were prepared to study the effect of varying proportions of commonly used fillers such as clay, silica, aluminium silicate and microcrumb in 1,2 polybutadiene based microcellular soles. MC sheets were molded and tested for its technical properties. Recipe used is given Table 3.3. Technical properties are given in Table 3.4 and Fig.3 10 to 17.

Variation in relative density with different filler loadings are given in Fig. 3.10. Relative density of the product decreased as the silica/silicate content in the product increased. This is due to the lower density of these materials compared to clay and the higher expansion obtained for the sheet. Higher expansion of the product may be due to the lower viscosity of the compound. This view is supported by the rheograph data given in Fig. 3.11. Microcrumb also reduces the relative density of the product. This is due to the lower specific gravity of this material and the higher expansion it favours.

Hardness data with varying filler loading is given in Fig. 3.12. Although silica and silicates are more reinforcing than clay, hardness of MC was found to decrease as the silica and silicate content increased. This may be due to the higher expansion caused by these fillers.

Observations on split tear strength are plotted in Fig. 3.13. Split tear strength decreased as the silica and silicate content increased. Substitution of clay with microcrumb also gave comparatively low split tear value. The higher expansion resulting from this filler alteration caused reduction of cell wall thickness and hence lowered the split tear strength.

Compression set variations with filler variations are plotted in Fig. 3.14. Higher compression set values are observed for sheets made from increased silica/silicate/microcrumb loaded compounds. This also may be due to the higher expansion and the consequent lower wall thickness of the products obtained from these compounds.

Sheets area observations are plotted in Fig. 3.15. Substituting clay with silica, silicates and microcrumb resulted in increased sheet area. Hence for higher expansion and higher output it is preferable to reduce clay and substitute it with silica/silicate/microcrumb. However, some of the desirable properties of the MC sheet will be adversely affected by this change.

Fig. 3.16 gives a plot of water absorption against varying filler loading. It also shows an increasing trend with increased substitution of clay with silica/silicate/microcrumb. Due to the increased expansion, chances for cell interconnection is high and hence it may have caused higher water absorption.

Abrasion data for different filler loadings are given in Fig. 3.17. An increased abrasion loss was observed for increased silica/silicate/microcrumb loading. From the filler reinforcement point of view silica/silicate loaded compounds might have higher abrasion resistance. Observed poor abrasion resistance may be due to the higher expansion and consequent easy wear of the sheet. The flex resistance data given in Table 3.3 showed that microcrumb filled sheets have less flex resistance compared to other fillers.

From the above results, it is concluded that substitution of china clay with silica/silicate/microcrumb causes higher expansion for microcellular sheet. Although this is beneficial in increasing the output, some of the desirable properties of the product are found to be adversely affected.

3.3. Extent of Blowing and Sole Properties

Varying levels of blowing was studied for three sets of compounds. In all these compounds natural rubber/1,2 polybutadiene ratio was 70/30. In the first set of compounds the filler combination used was clay/silica/aluminium silicate in the ratio 60/30/15. The blowing agent concentrations studied for this compound were four, five, six and seven parts per hundred polymer. In the second set, the filler combination used was clay/silica/aluminium silicate in the ratio 40/40/25 and the blowing concentrations studied were five, six and seven parts per hudred polymer. In the third set the filler combination used was clay/silica in the ratio 40/40 and the blowing agent concentrations studied for it were five and six parts per hundred polymer. Compound preparation and molding was done as described earlier. Compound recipe is given in Table 3.4. The technical properties are given in Table 3.5 and in Fig. 3.18 to 3.24. Relative density variation with varying blowing agent is ploted in Fig. 3.18. In all the above three sets, relative density was found to decrease with increase in blowing agent. Higher dosage of blowing agent results in increased extent of blowing and increased number of cells per unit volume, which in turn will result in lower polymer content per unit volume of the sheet.

Observations on hardness data for the three sets of compounds are plotted in Fig. 3.19. For all the three cases hardness was found to decrease with increased blowing agent concentration. This occurs due to the increased expansion.

Compression set data for varying blowing agent concentrations are given in Fig. 3.20. It showed an increasing trend with increased blowing agent concentration. This is due to the increased expansion of the sheet with increased blowing agent.

Split tear strength variations for different extents of expansion are given in Fig. 3.21. For all the three sets of experiments split tear strength was found to decrease with increased blowing agent concentration. As the expansion increased, polymer cell walls may be getting thinner resulting in lower split tear strength. SEM Photomicrograph given later also supports this view.

Sheet area variations of precured and postcured product for varying extent of blowing are given in Fig. 3.22. As the extent of blowing increased, sheet area also increased. Increased blowing agent increases the expansion and the number of cells. SEM photomicrograph gives evidence for this view.

Change in water absorption percentage with change in blowing agent concentrations are plotted in Fig. 3.23. Increased water absorption with increased extent of blowing indicated breakage of cells resulting in interconnection of cells at higher expansion.

Abrasion data for all the three set of experiments are fiven in Fig. 3.24. Abrasion loss was found to increase with increase in blowing agent concentration. This may be due to the fact that as the extent of blowing decreased, the polymer walls may be getting thicker thus preventing the easy wear of the microcellular sheets at lower blowing levels.

The results indicated that increase in blowing agent concentration increased the extent of blowing which in turn adversely affected some of the critical properties. Therefore the optimum level of blowing has to be used for producing microcellular of acceptable quality.

TABLE - 3.1

MATERIALS	COMPOUND NUMBER									
	1	2	3	4	5	6	7	8	9	10
Natural Rubber	70	35	100	90	80	70	60	40	20	0
SBR - 1958	30	30	-	-	-	-	-	-	-	-
SBR 1502	-	35	-	-	-	-	-	-	-	-
1,2 Polybutadiene	-	-	-	10	20	30	40	60	80	100
Stearic acid	2	2	2	2	2	2	2	2	2	2
Zinc oxide	5	5	5	5	5	5	5	5	5	5
Alox SP	1	1	1	1	1	1	1	1	1	1
Titanium dioxide	5	5	5	5	5	5	5	5	5	5
Precipitated silica	30	30	30	30	30	30	30	30	30	30
China clay	60	60	60	60	60	60	60	60	60	60
Aluminium silicate	15	15	15	15	15	15	15	15	15	15
Diethylene glycol	2	2	2	2	2	2	2	2	2	2
Naphthenic oil	10	10	10	10	10	10	10	10	10	10
MBTS	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
TMT	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sulphur	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
DNPT	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Colour	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8

TABLE - 3.2

PROPERTY	COMPOUND NUMBER							
	1	2	3	4	5	6	7	8
PRECURE TIME (t_{80} + 2.5) minutes	6.5	6.6	5.5	5.2	5.4	5.9	6.5	7.6
CHANGE IN HARDNESS AFTER AGEING AT 100±1°C FOR 24 HOURS	1	1	-1	0	0	2	2	0
ROOM TEMPERATURE SHRINKAGE	0.2	0.33	0.34	0.32	0.33	0.33	0.33	0.33
<u>FLEX RESISTANCE</u>:-								
(a) Crack Initiation	3.0×10^5	5.0×10^5	$>8.0 \times 10^5$	$>8.0 \times 10^5$	$>8.0 \times 10^5$	$>8.0 \times 10^5$	$>8.0 \times 10^5$	$>8.0 \times 10^5$
(b) Cut growth at the end of 100,000 cycles	-	-	-	-	-	-	-	-

TABLE - 3.3

MATERIAL	COMPOUND NUMBER						
	1	2	3	4	5	6	7
Natural Rubber	70	70	70	70	70	70	70
1,2 Polybutadiene	30	30	30	30	30	30	30
Stearic acid	2	2	2	2	2	2	2
Zinc oxide	5	5	5	5	5	5	5
Titanium dioxide	5	5	5	5	5	5	5
Alox SP	1	1	1	1	1	1	1
Precipitated silica	30	40	40	40	40	40	40
Clay	60	50	40	30	20	10	0
Aluminium silicate	15	15	25	35	35	35	35
Microcrumb	-	-	-	-	10	20	30
Diethylene glycol	2	2	2	2	2	2	2
Naphthenic oil	10	10	10	10	10	10	10
MBTS	0.8	0.8	0.8	0.8	0.8	0.8	0.8
TMTD	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sulphur	1.6	1.6	1.6	1.6	1.6	1.6	1.6
DNPT —	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Colour	0.8	0.8	0.8	0.8	0.8	0.8	0.8

TABLE - 3.4

PROPERTY	COMPOUND NUMBER						
	1	2	3	4	5	6	7
TIME FOR MAXIMUM CURE (t_{100}) minutes	7.5	8.2	8.2	8.9	7.8	7.8	7.2
TIME OF PRECURE (t_{80} + 2.5) minutes	5.9	6.7	6.5	7.5	6.7	6.1	5.7
RHEOMETER MAXIMUM TORQUE	45.5	42.5	42	39	38	38.5	38.5
RHEOMETER MINIMUM TORQUE	11.0	7.0	6.5	5.5	6.0	6.5	6.5
CHANGE IN HARDNESS AFTER AGEING AT 100±1°C FOR 24 HOURS.	2	4	2	3	3	4	2
ROOM TEMPERATURE SHRINKAGE (%)	0.33	0.35	0.36	0.36	0.36	0.37	0.34
<u>FLEX RESISTANCE</u>:-							
(a) Crack Initiation	$>5.0\text{x}10^5$	$>5.0\text{x}10^5$	$>5.0\text{x}10^5$	$>5.0\text{x}10^5$	$1.7\text{x}10^5$	$2.0\text{x}10^5$	$1.7\text{x}10^5$
(b) Crack growth at the end of 100,000 cycls	-	-	-	-	-	-	-

TABLE - 3.5

MATERIALS	COMPOUND NUMBER								
	1st SET				IInd SET			IIIrd SET	
	1	2	3	4	5	6	7	8	9
Natural Rubber	70	70	70	70	70	70	70	70	70
1,2 Polybutadiene	30	30	30	30	30	30	30	30	30
Stearic acid	2	2	2	2	2	2	2	2	2
Zinc oxide	5	5	5	5	5	5	5	5	5
Titanium dioxide	5	5	5	5	5	5	5	5	5
Alox SP	1	1	1	1	1	1	1	1	1
Precipitated silica	30	30	30	30	40	40	40	40	40
Clay	60	60	60	60	40	40	40	40	40
Aluminium silicate	15	15	15	15	25	25	25	0	0
Diethylene glycol	2	2	2	2	2	2	2	2	2
Naphthenic oil	10	10	10	10	10	10	10	10	10
MBTS	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
TMTD	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sulphur	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
DNPT	7.0	6.0	5.0	4.0	7.0	6.0	5.0	6.0	5.0
Colour	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8

TABLE - 3.6

PROPERTY	COMPOUND NUMBER								
	Ist SET				IInd SET			IIIrd SET	
	1	2	3	4	5	6	7	8	9
TIME FOR MAXIMUM CURE (t_{100}) minutes	6.6	7.2	5.3	7.2	8.2	9.7	10.3	10.0	10.8
PRECURE TIME (t_{80} + 2.5) minutes	6.1	6.1	6.5	6.5	6.5	7.2	7.8	7.8	7.5
RHEOMETER MAXIMUM TORQUE , dN.m	42.0	44.0	46.5	50.0	42.5	40.0	40.0	39.0	39.0
RHEOMETER MINIMUM TORQUE , dN.m	5	5	5	5	7	6	6.5	7	7
CHANGE IN HARDNESS AFTER AGEING AT 100±1°C FOR 24 HOURS	4	4	5	6	2	3	6	4	1
ROOM TEMPERATURE SHRINKAGE AT 27±2°C FOR TWO WEEKS	0.34	0.28	0.22	0.2	0.36	0.3	0.24	0.35	0.32
<u>FLEX RESISTANCE</u>:-									
(a) Crack Initiation , cycles	$>6.0 \times 10^5$	$>6.0 \times 10^5$	$>6.0 \times 10^5$	$>6.0 \times 10^5$	$>6.0 \times 10^5$	$>6.0 \times 10^5$	$>6.0 \times 10^5$	$>6.0 \times 10^5$	$>6.0 \times 10^5$
(b) Crack growth at the end of 100,000 cycles.	-	-	-	-	-	-	-	-	-

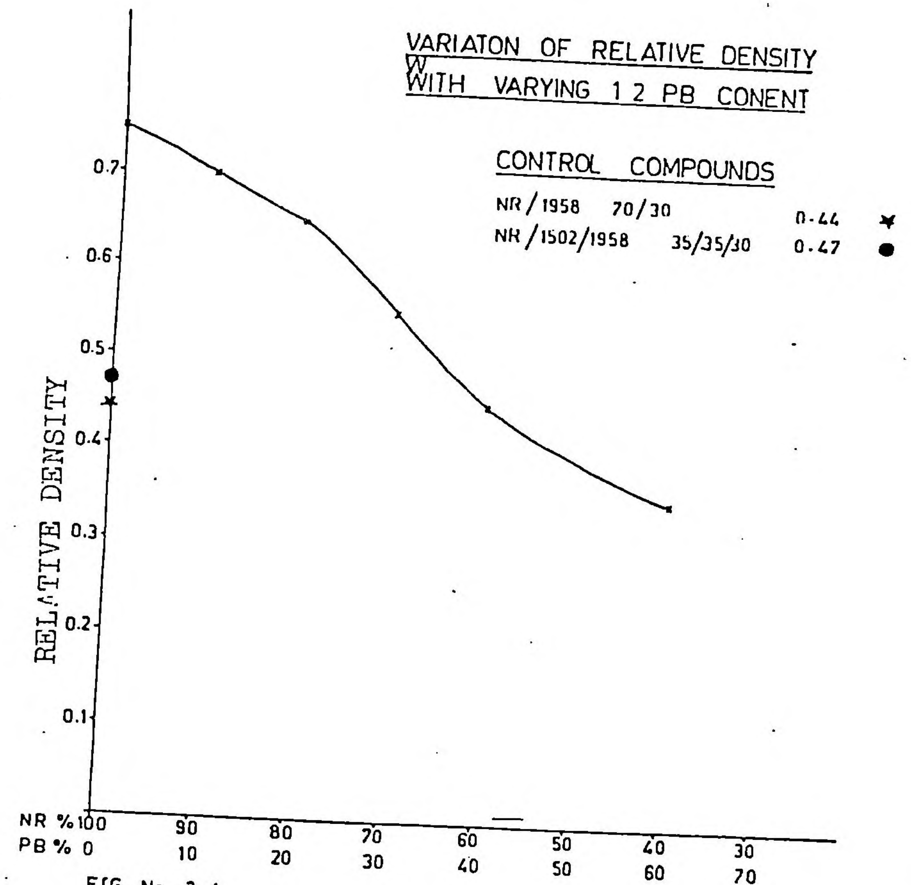


FIG. No. 3.1

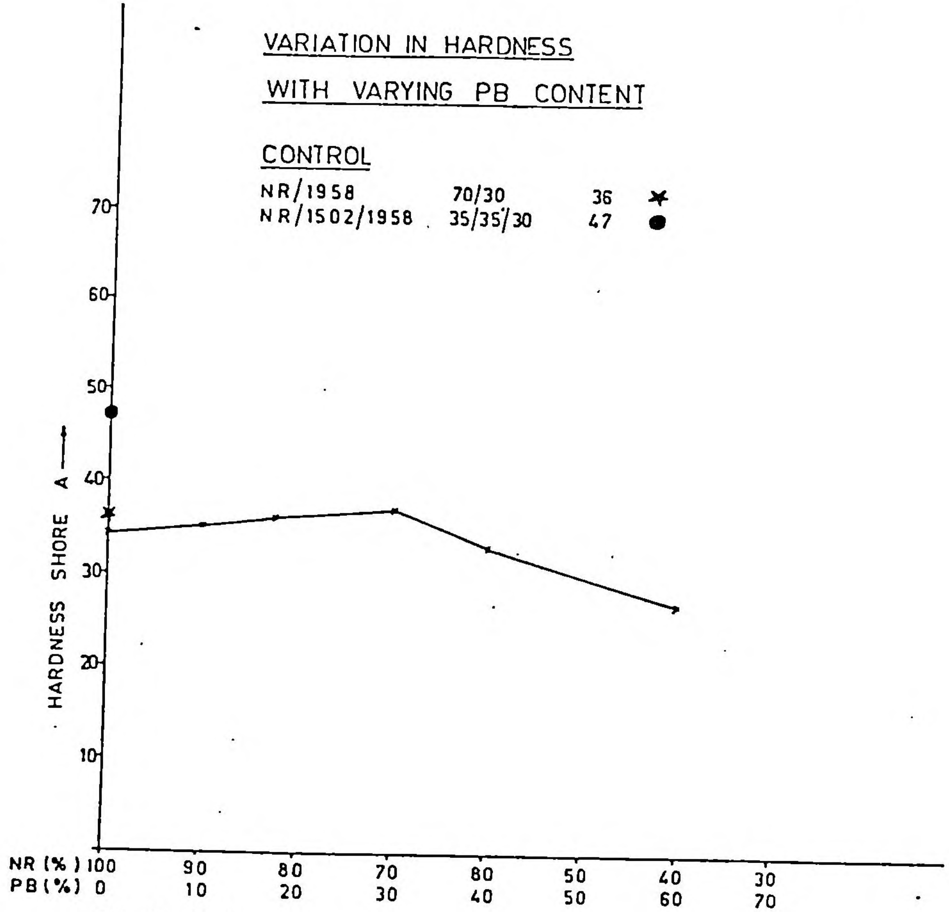
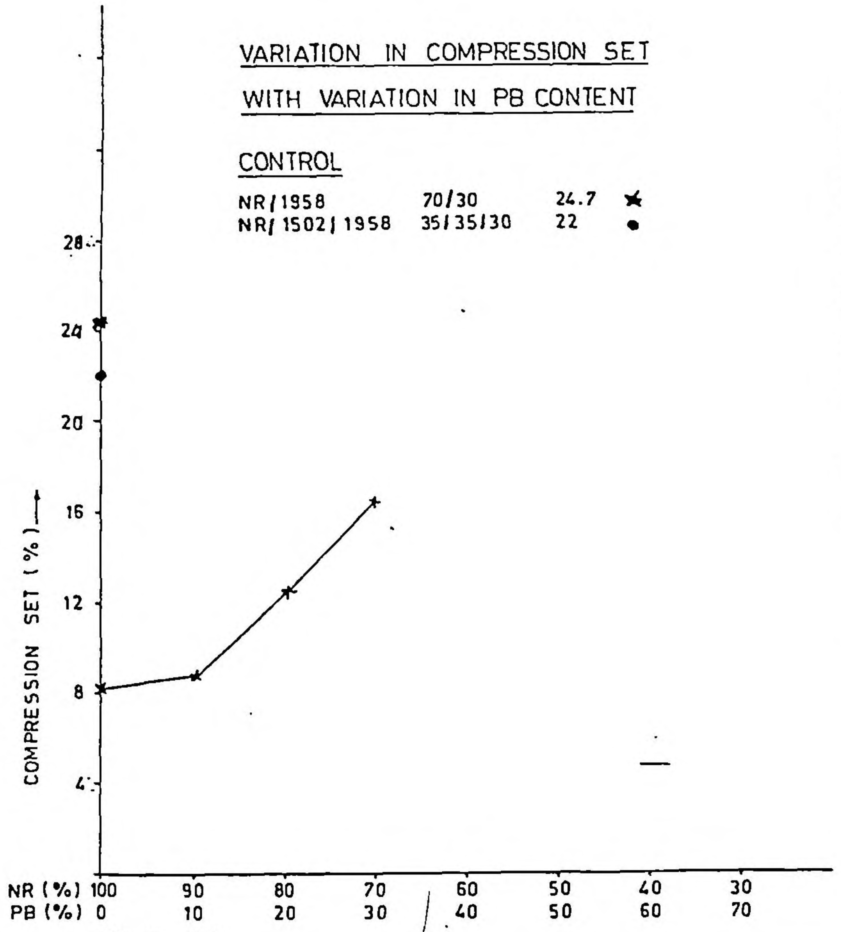
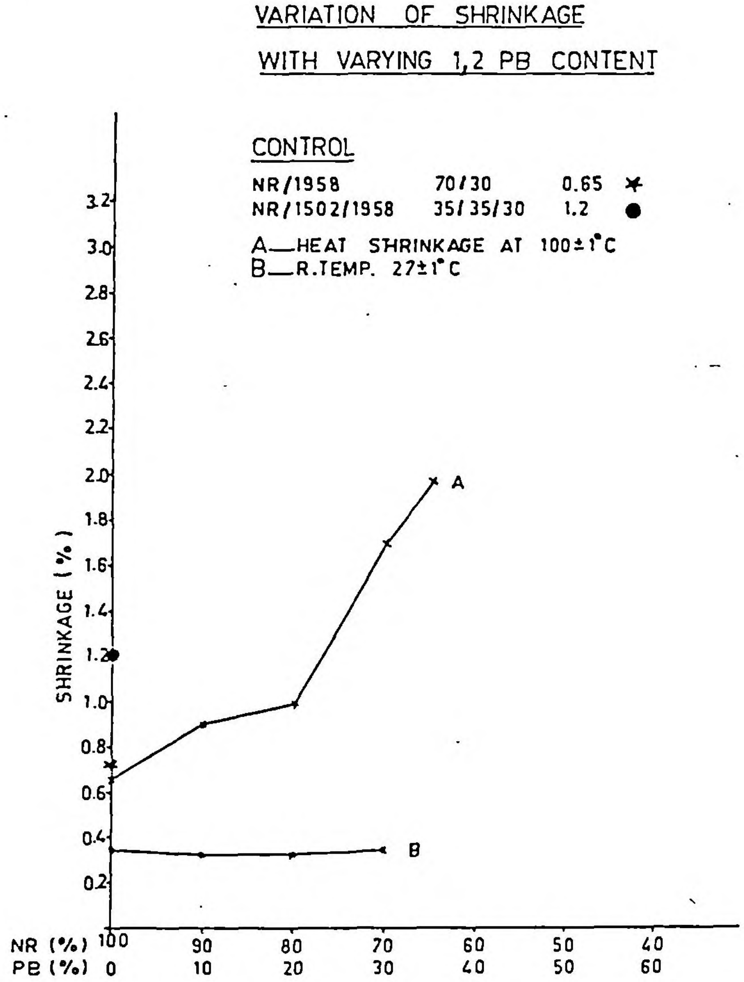


FIG. No. 3.2



VARIATION IN COMPRESSION SET
WITH VARIATION IN PB CONTENT

FIG. No. 3.3



VARIATION OF SHRINKAGE
WITH VARYING 1,2 PB CONTENT

FIG. No. 3.4

VARIATION OF SPLIT TEAR STRENGTH
WITH VARYING 1,2 PB CONTENT

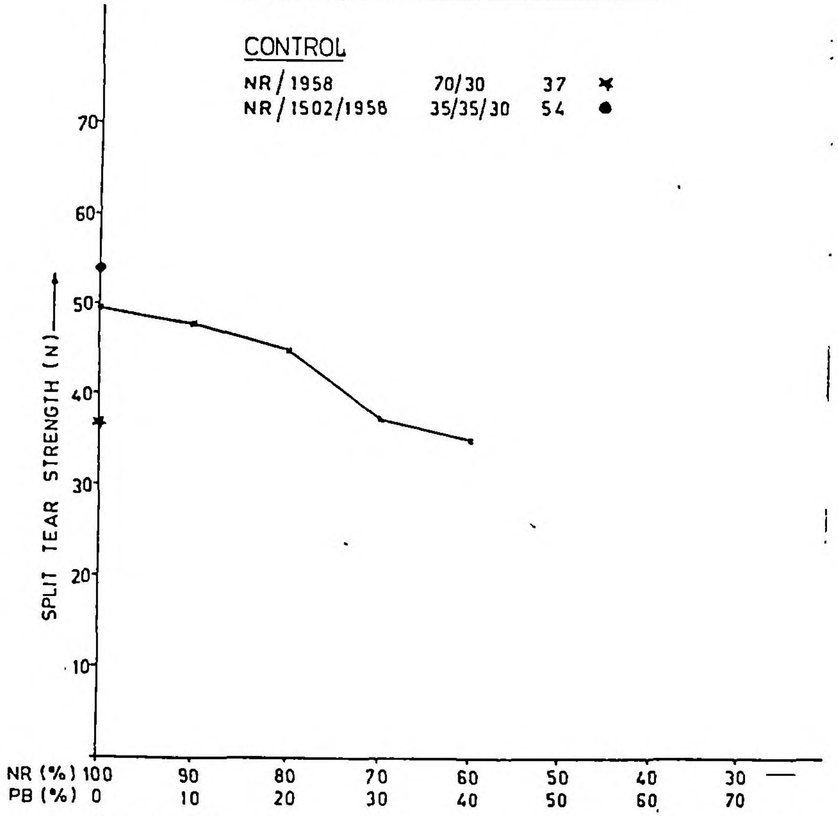


FIG No. 3.5

SHEET AREA VARIATION
WITH VARYING 1,2 PB CONTENT

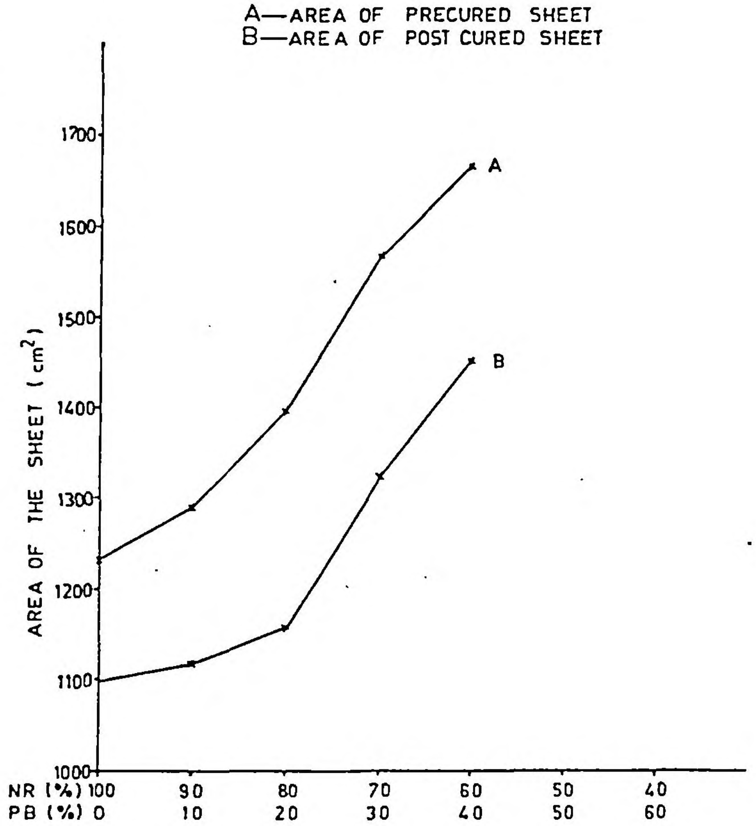


FIG. No. 3.6

RHEOMETER TORQUE VARIATION
WITH VARYING 1,2 PB CONTENT

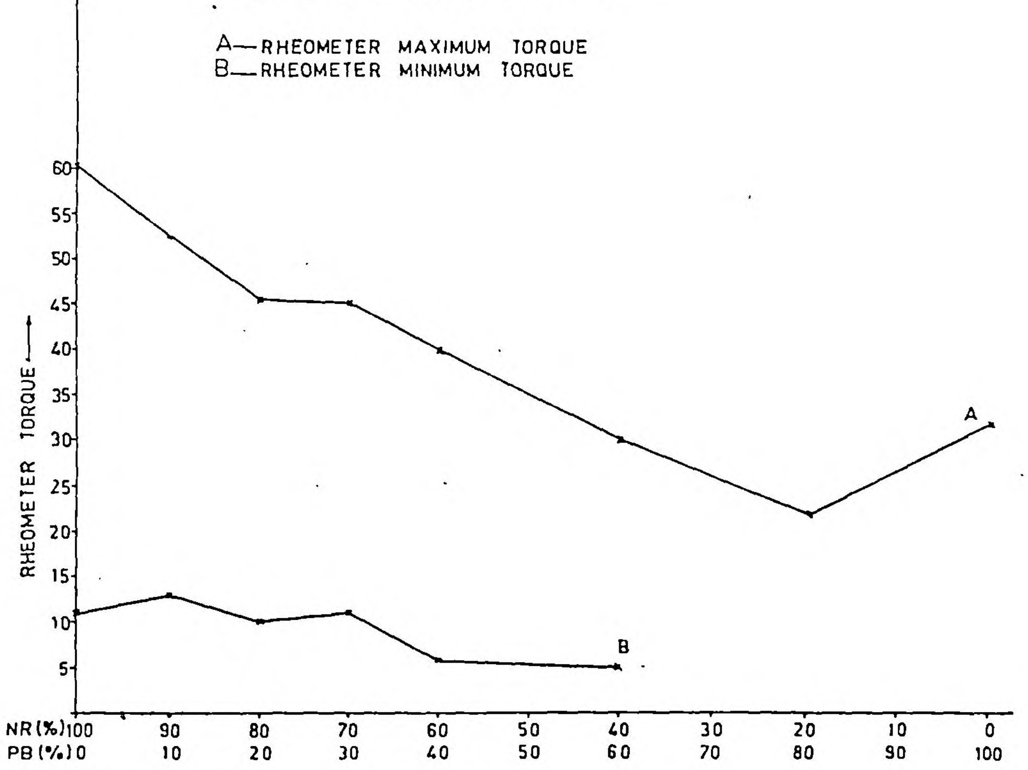


FIG. No. 3.7

VARIATION OF WATER ABSORPTION
WITH VARYING 1,2 PB CONTENT

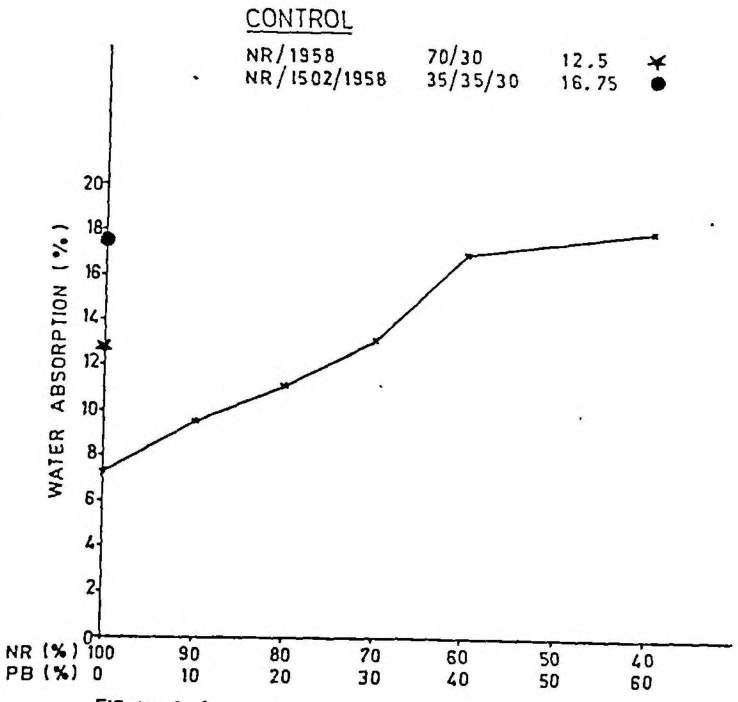


FIG. No. 3.8

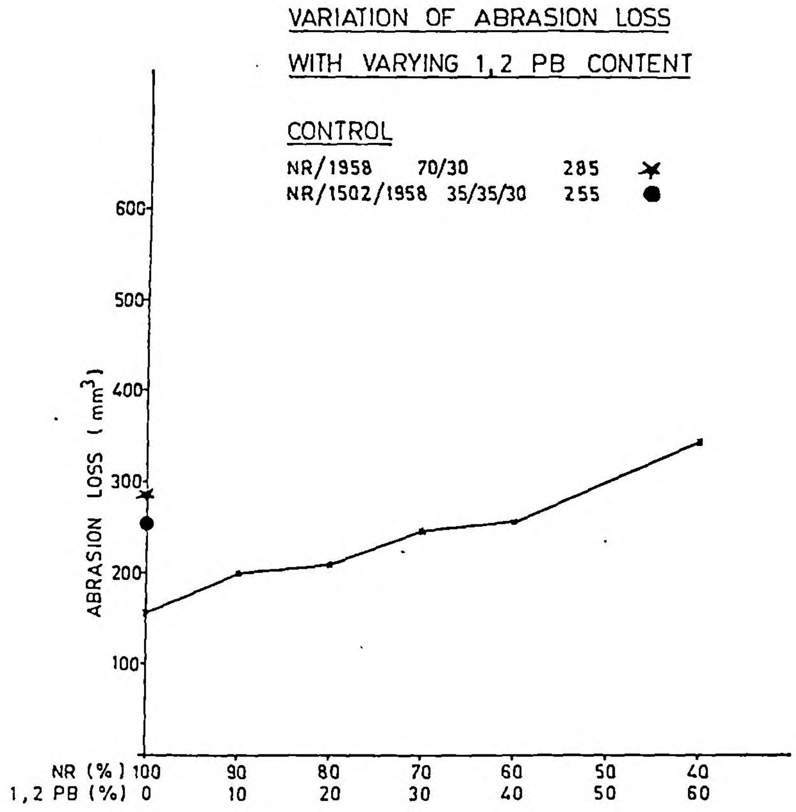


FIG. No. 3 . 9

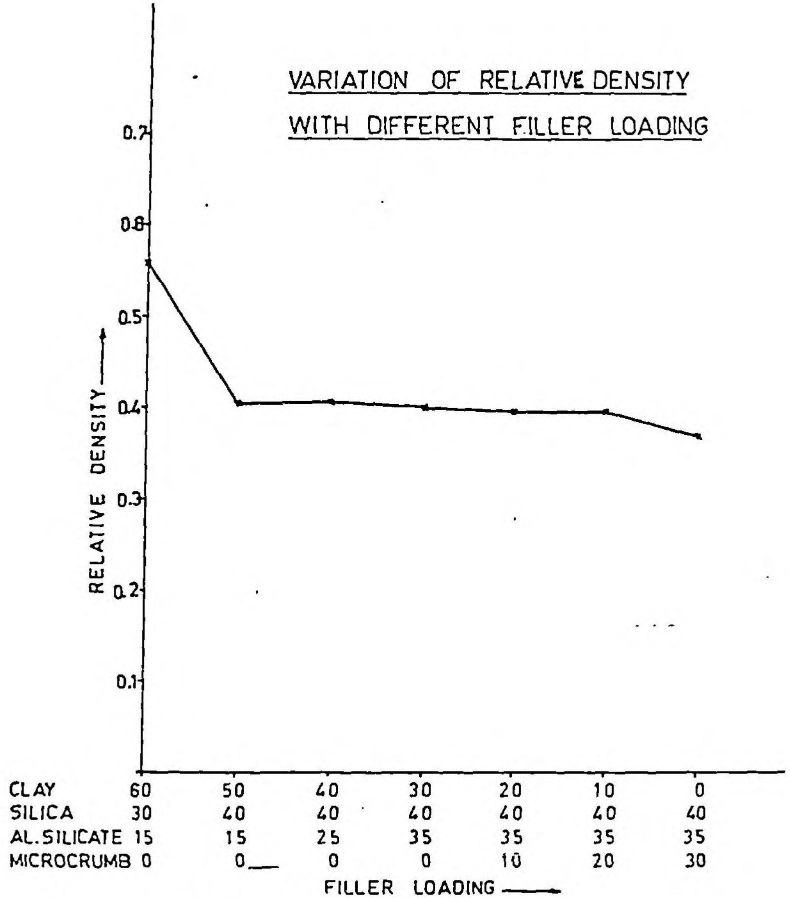


FIG. No. 3 . 10

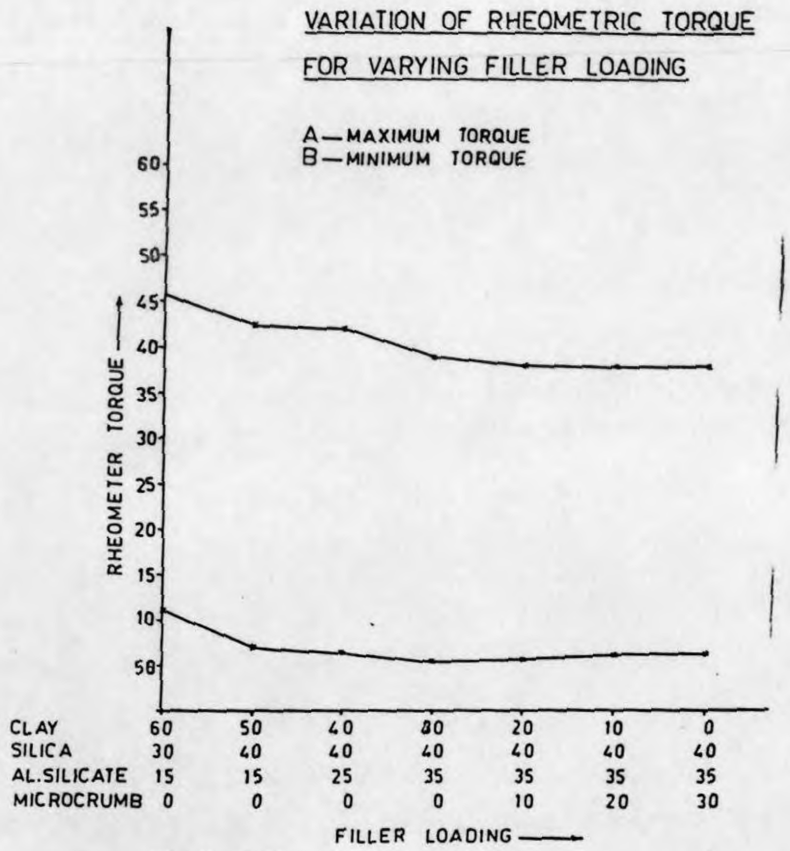


FIG. No. 3.11

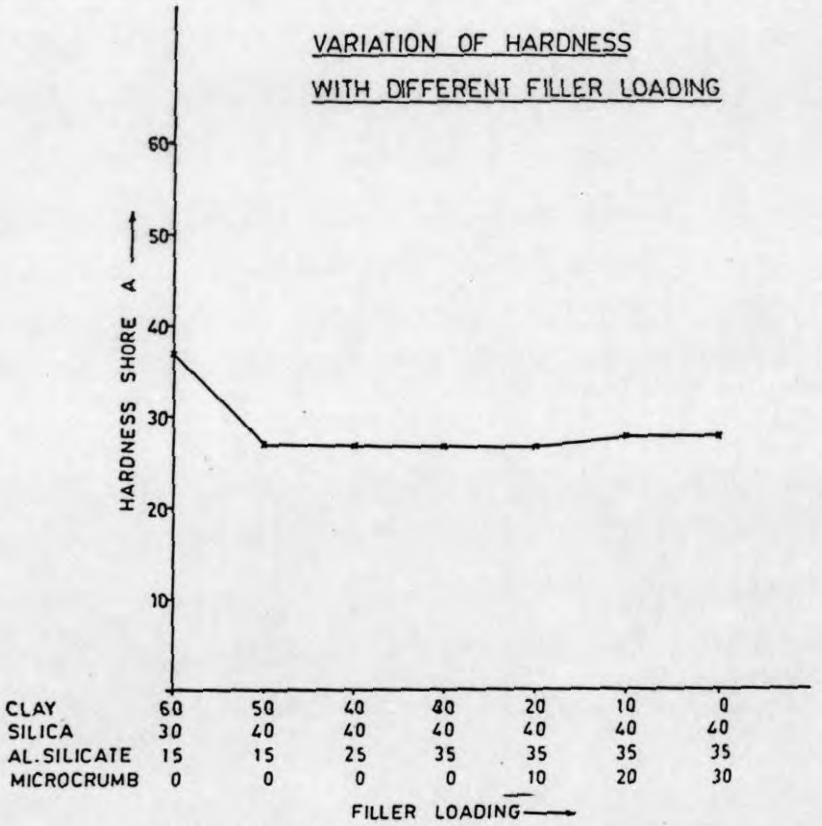


FIG. No. 3.12

VARIATION OF SPLIT TEAR STRENGTH
[illegible]

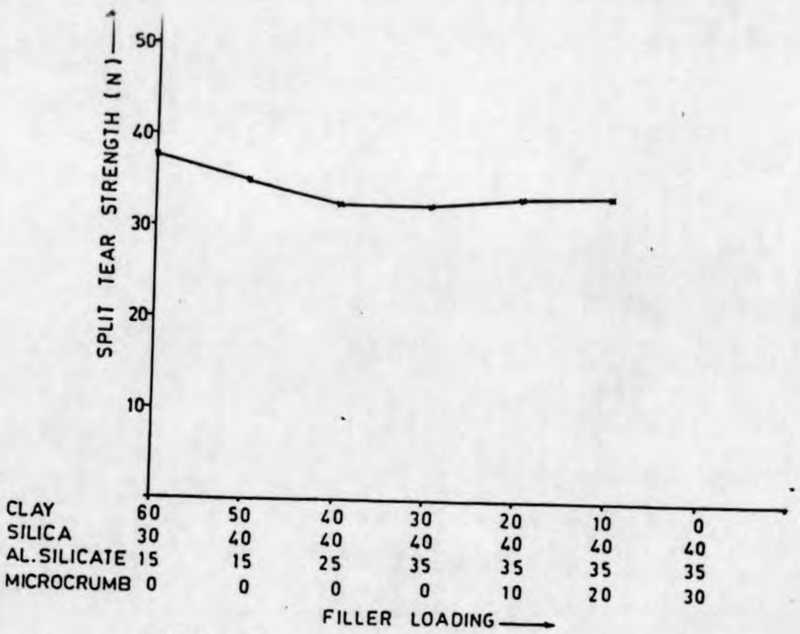


FIG. No. 3.13

[illegible]

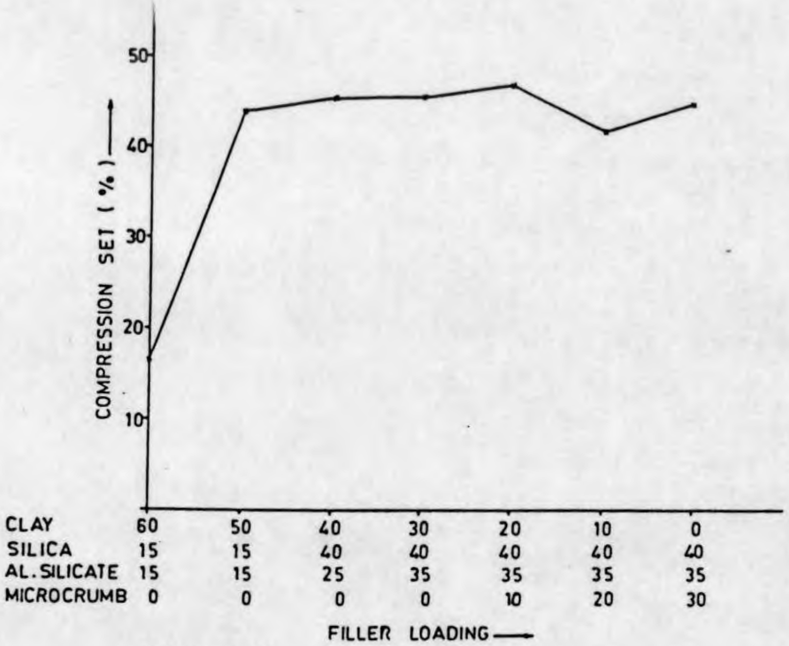


FIG. No. 3.14

SHEET AREA VARIATION
WITH VARYING FILLER LOADING

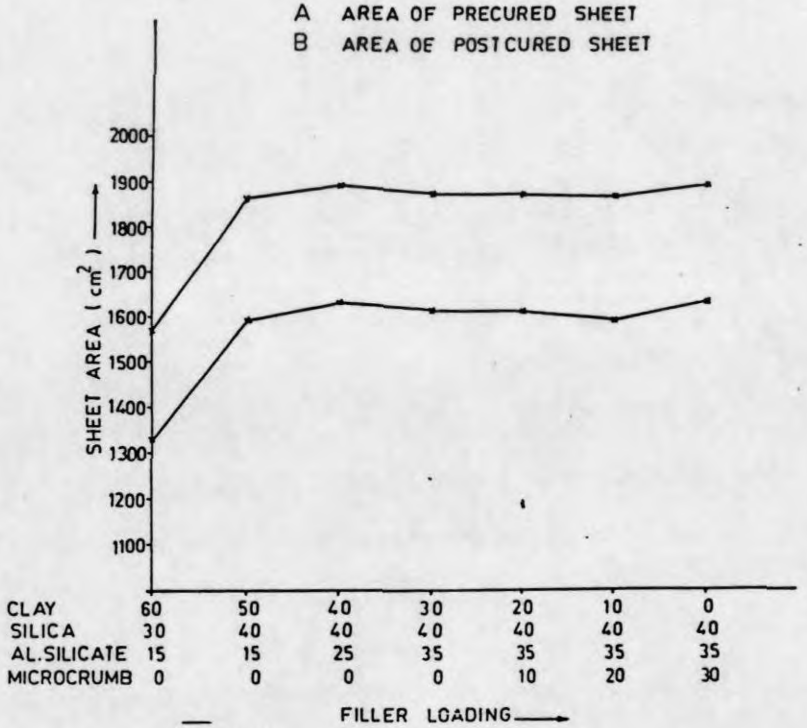


FIG. No. 3.15

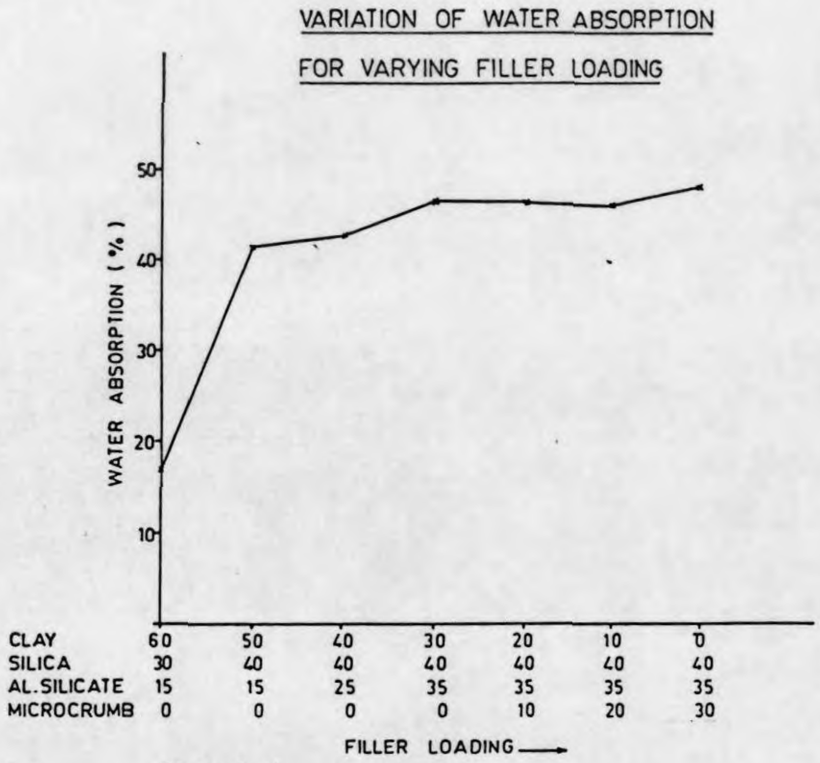

VARIATION OF WATER ABSORPTION
FOR VARYING FILLER LOADING

FIG. No. 3.16

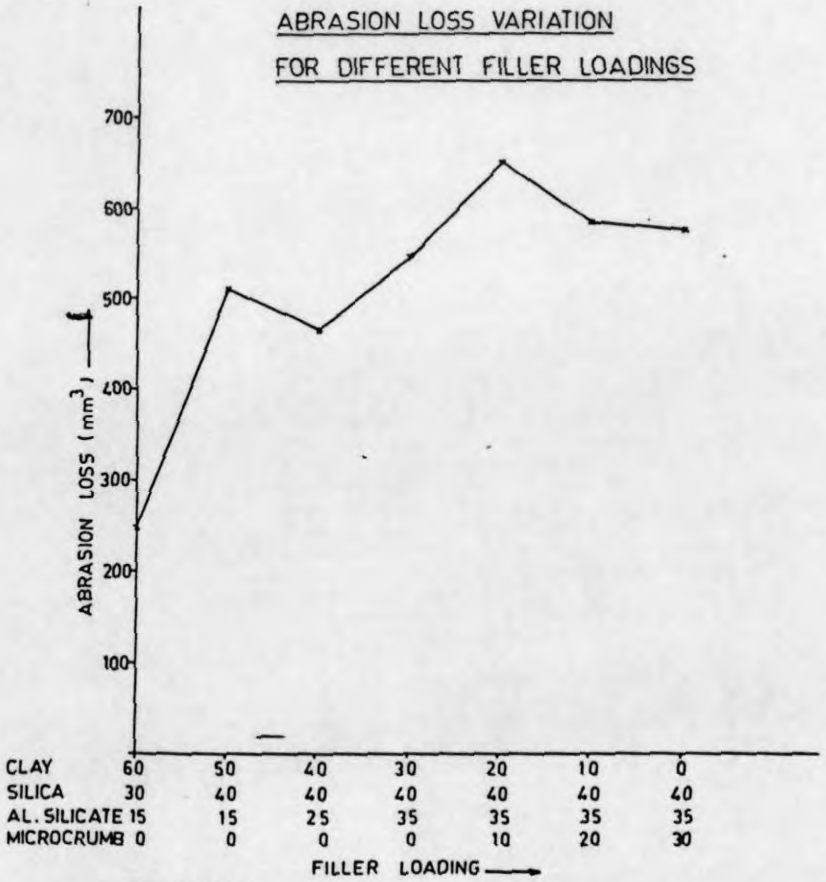


FIG. No. 3.17

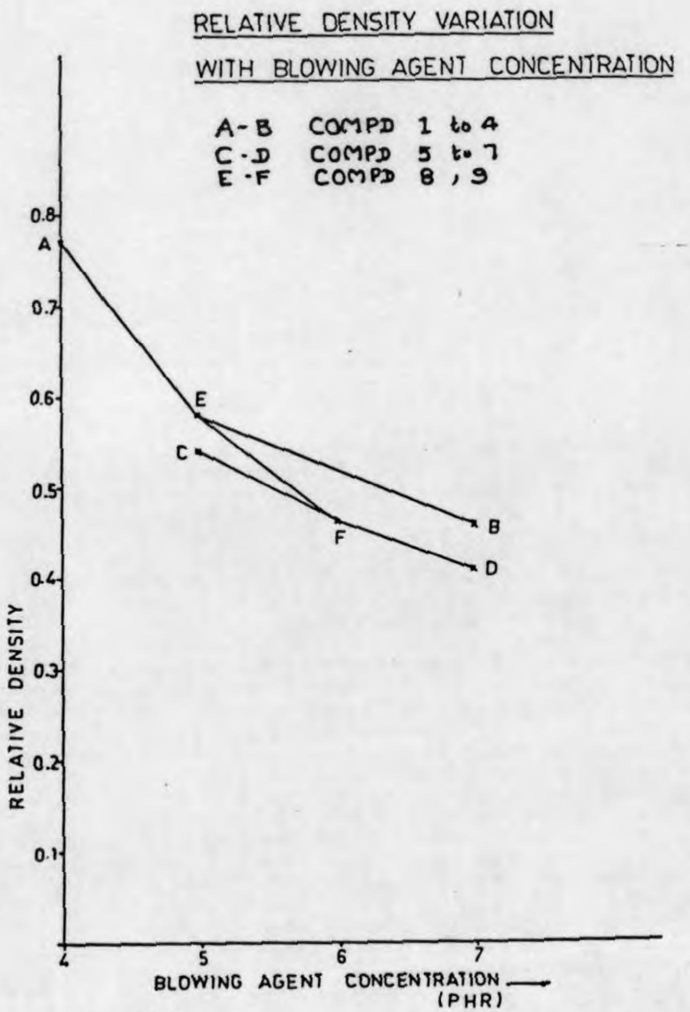


FIG. No. 3.18

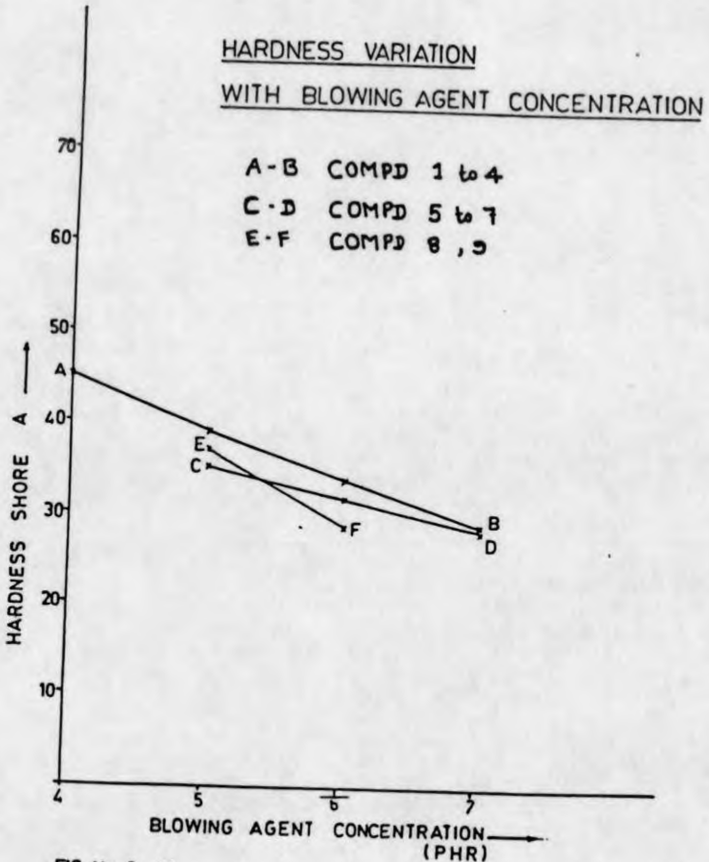


FIG. No. 3 . 19

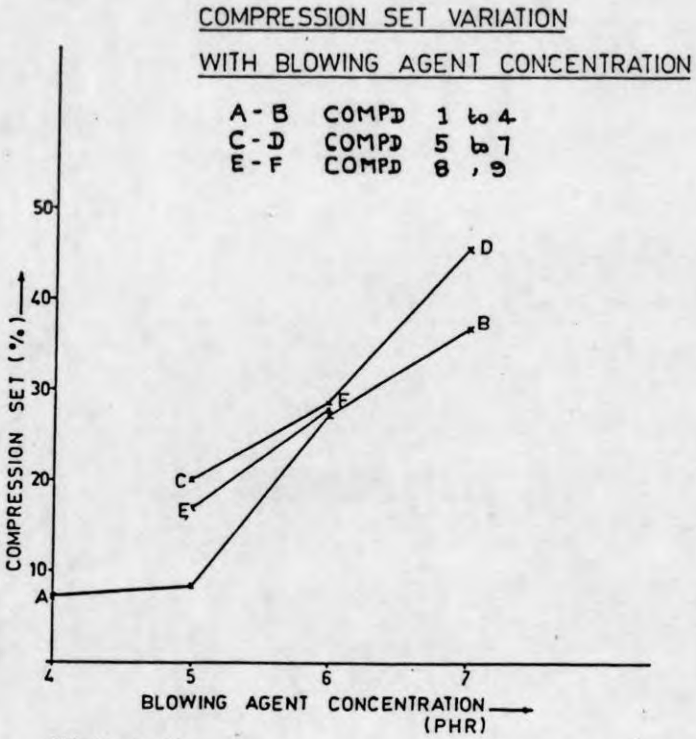
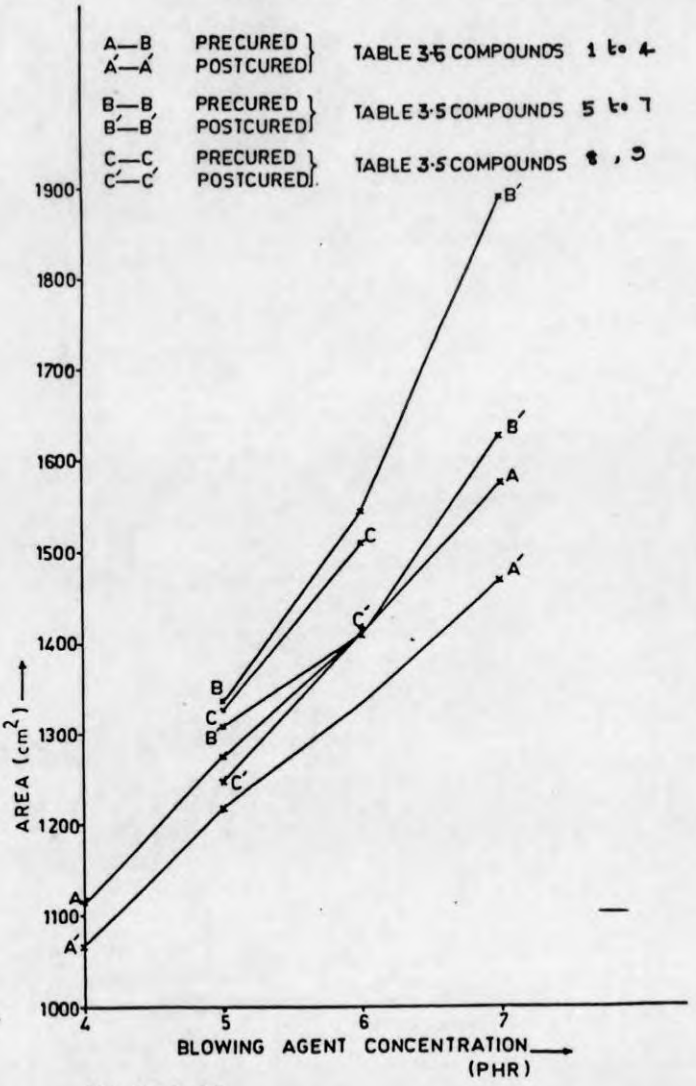
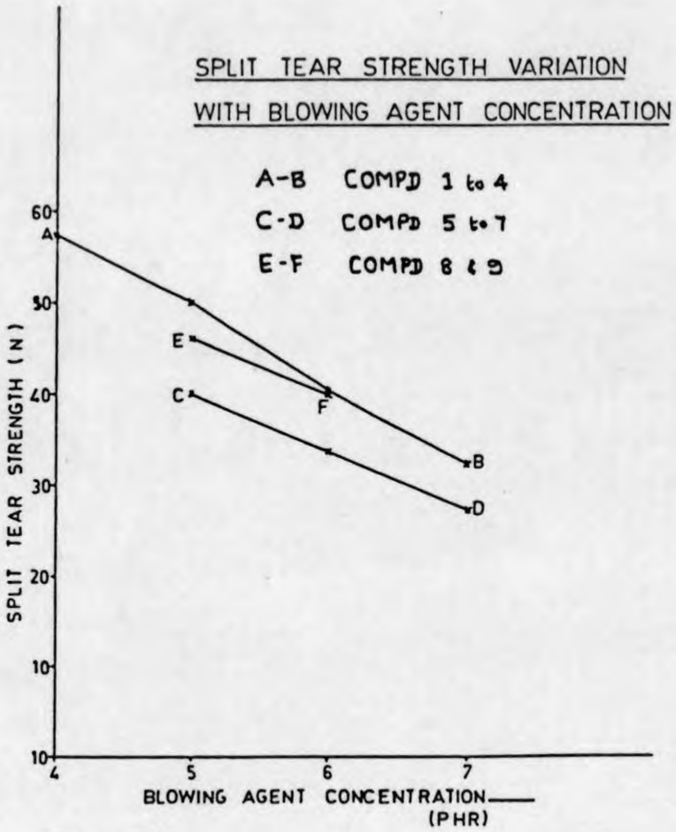


FIG. No. 3 . 20



VARIATION OF SHEET AREA WITH BLOWING AGENT CONCENTRATION

FIG. No. 3. 22



SPLIT TEAR STRENGTH VARIATION WITH BLOWING AGENT CONCENTRATION

FIG. No. 3.21

VARIATION IN WATER ABSORPTION
WITH BLOWING AGENT CONCENTRATION

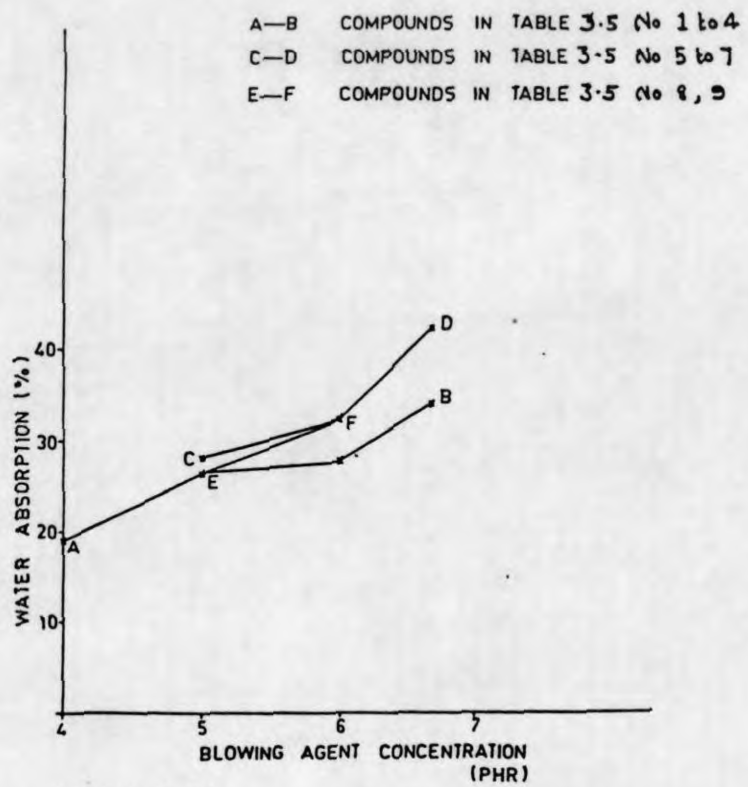


FIG. No. 3 . 23

VARIATION IN ABRASION LOSS
WITH BLOWING AGENT CONCENTRATION

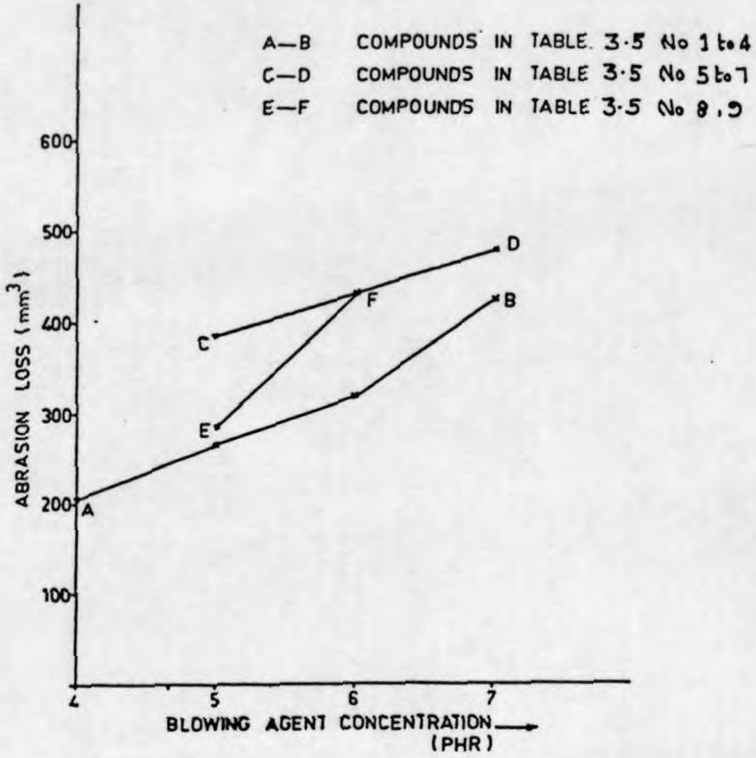
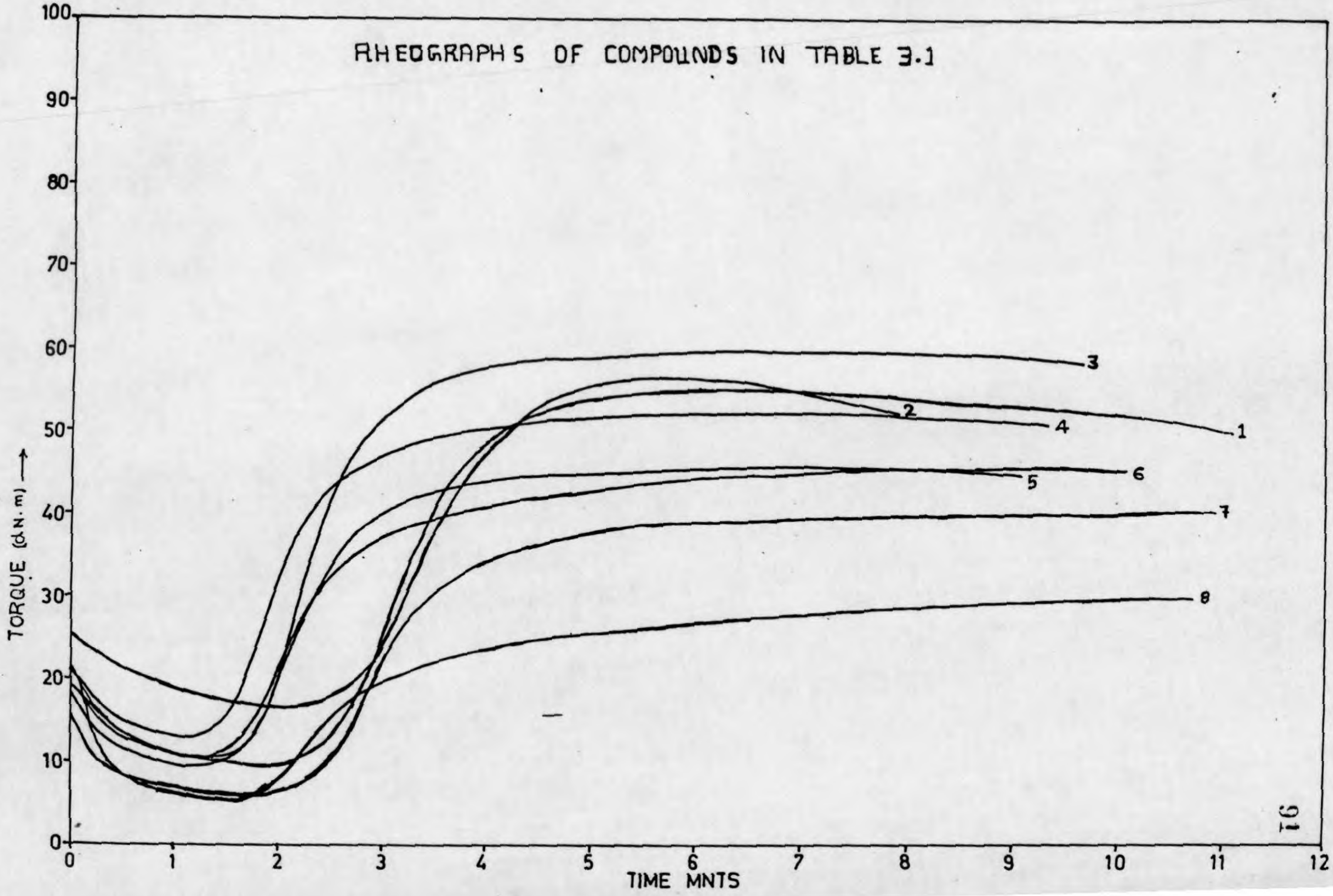
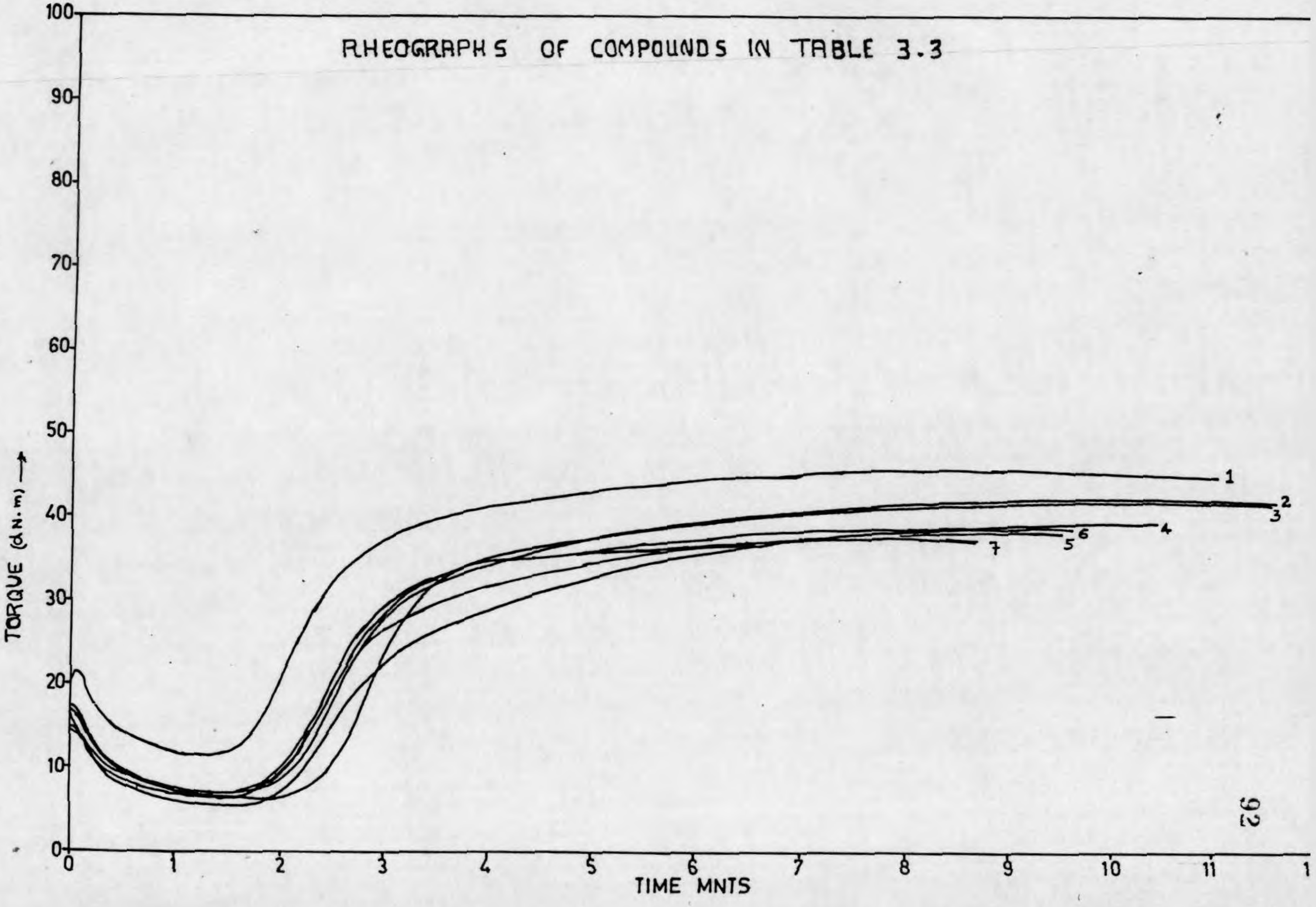


FIG. No. 3 . 24


RHEOGRAPHS OF COMPOUNDS IN TABLE 3.1
TORQUE (d.N.m) →
TIME MNTS
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10
11
12
1
2
3
4
5
6
7
8



RHEOGRAPHS OF COMPOUNDS IN TABLE 3.3

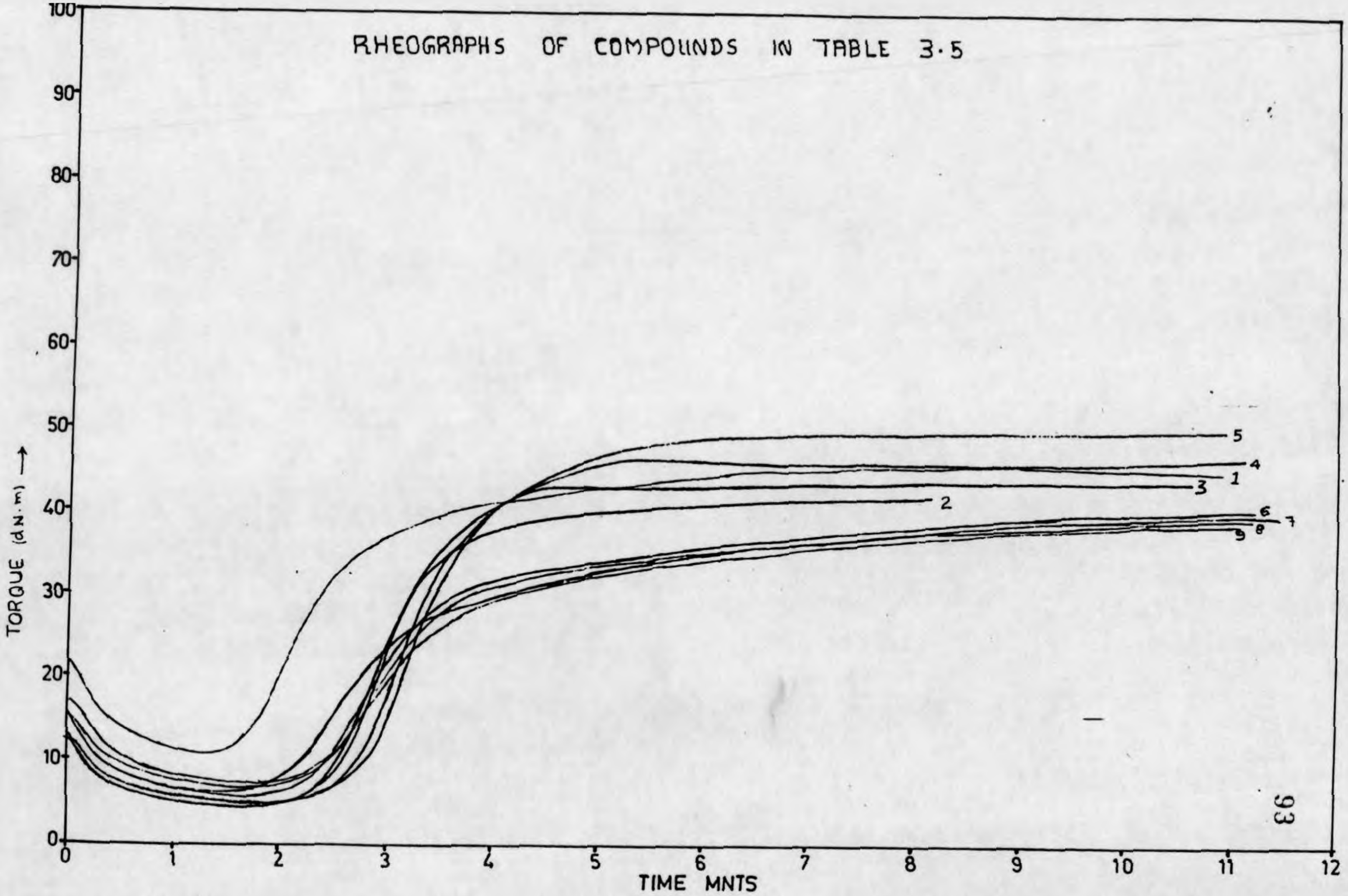

RHEOGRAPHS OF COMPOUNDS IN TABLE 3·5
TORQUE (dN·m) →
100
90
80
70
60
50
40
30
20
10
0
TIME MNTS
0
1
2
3
4
5
6
7
8
9
10
11
12
5
4
1
3
2
6
7
8
9

FIG No 2 (c)

CHAPTER - 4 :: OBSERVATIONS OF SEM STUDIES

4. OBSERVATIONS OF SEM STUDIES

The SEM observations were made only on seven selected vulcanizates. Formulations are given in Table 4.1. The SEM photomicrographs are given in Figs. 4.1 to 4.7.

Fig. 4.1 is the photomicrograph prepared from natural rubber alone. The cells are found to be comparatively small in size, the cell walls are appreciably thick. Cells of different diameters are seen. The larger cells have an approximate diameter of 10 μm. The introduction of SBR-1958 (Compound Number 2) caused a larger expansion to the microcellular sheet. This larger expansion is also clear from the SEM photomicrograph, of the sample as given in Fig. 4.2. The average size of the cell is larger and the number of cells are also higher. The cell walls are not thick and continuous as in the case of pure natural rubber. Here also the maximum diameter of the cell is around 100 μm. However when 1,2 polybutadiene is blended with natural rubber instead of SBR-1958 as in Compound Number 3, the expansion of the sheet is still larger and SEM photographs given in Fig. 4.3 shows evidence for this larger expansion. The cells are larger in size, the maximum diameter exceeding well over 100 μm.

The cell walls were also found to be much thinner compared to those observed in Compound Number 1.

A reduction in blowing agent level reduced expansion, however this does not cause a reduction in the cell size as is evident from Figs. 4.4 to 4.6 which are the SEM photomicrographs of compounds 4 to 6 containing six, five and four phr each of the blowing agent. The cells in these vulcanizates were found to be of more circular shape and the cell walls were found to be becoming more thick as the blowing agent is reduced.

Fig. 4.7 is the SEM photomicrograph of sheet prepared from Compound Number 7 in which microcrumb was added as a filler in place of clay. A comparison of Fig. 4.3 and 4.7 clearly indicated that the higher expansion of the mix containing microcrumb correlated with a larger number of cells. The cell walls in this microcellular sheets are also found to be much thinner.

It was observed that as the 1,2 polybutadiene content is increased, the expansion of microcellular sheet increases. However, most of the desirable properties like split tear strength, compression set, etc. are adversely affected. Water absorption also is found to be more as the expansion increased. Some of the explanations are supported by the SEM photomicrographs. As the expansion of microcellular increased cell walls became thinner and at least some of the cells are getting interconnected. The thinner walls accounts for the lower split tear strength and higher compression set. The partial interconnection of the cells accounts for the higher water absorption.

TABLE - 4.1

MATERIALS	COMPOUND NUMBER						
	1	2	3	4	5	6	7
Natural Rubber	100	70	70	70	70	70	70
SBR - 1958	-	30	-	-	-	-	-
1,2 Polybutadiene	-	-	30	30	30	30	30
Stearic acid	2	2	2	2	2	2	2
Zinc oxide	5	5	5	5	5	5	5
Alox SP	1	1	1	1	1	1	1
Titanium dioxide	5	5	5	5	5	5	5
Precipitated silica	30	30	30	30	30	30	30
China clay	60	60	60	60	60	60	0
Aluminium silicate	15	15	15	15	15	15	15
Microcrumb	-	-	-	-	-	-	30
Diethylene glycol	2	2	2	2	2	2	2
Naphthenic oil	10	10	10	10	10	10	10
MBTS	0.8	0.8	0.8	0.8	0.8	0.8	0.8
TMTD	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sulphur	1.6	1.6	1.6	1.6	1.6	1.6	1.6
DNPT	7.0	7.0	7.0	6.0	5.0	4.0	7.0
Colour	0.8	0.8	0.8	0.8	0.8	0.8	0.8

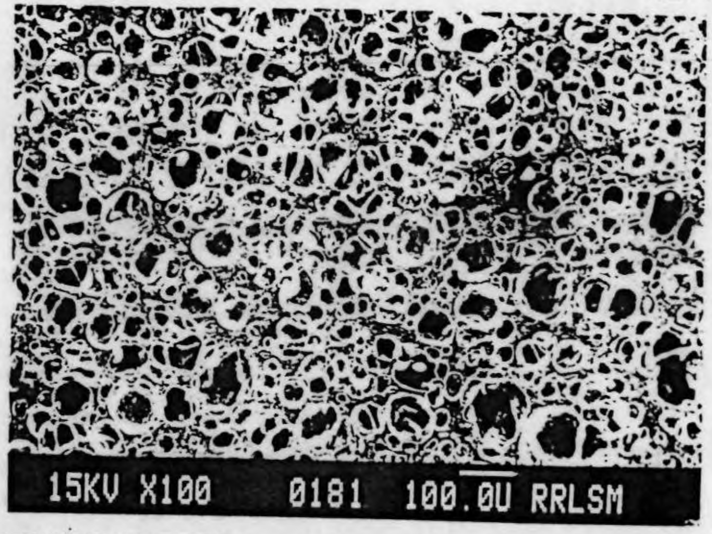


Figure 4.1

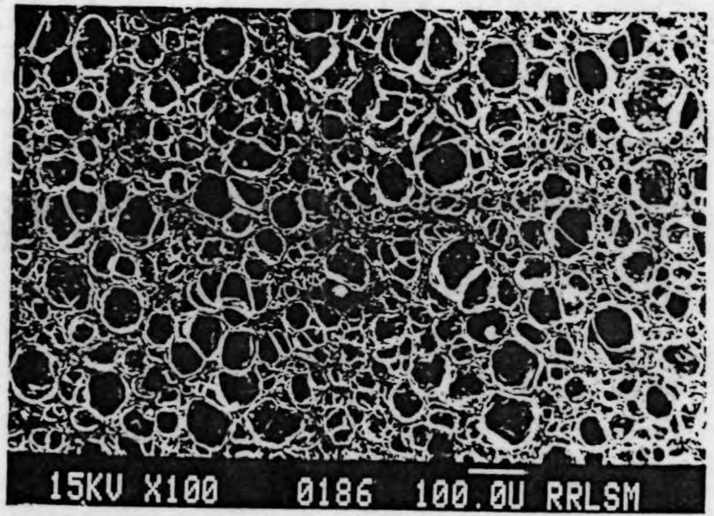


Figure 4.2

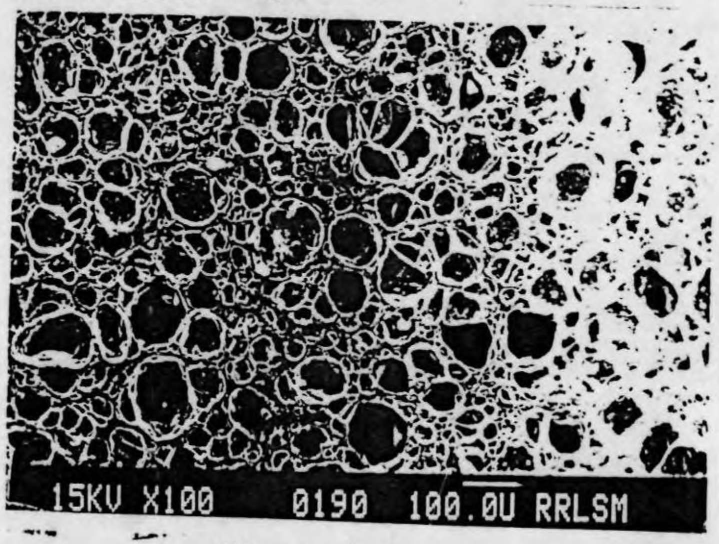


Figure 4.3

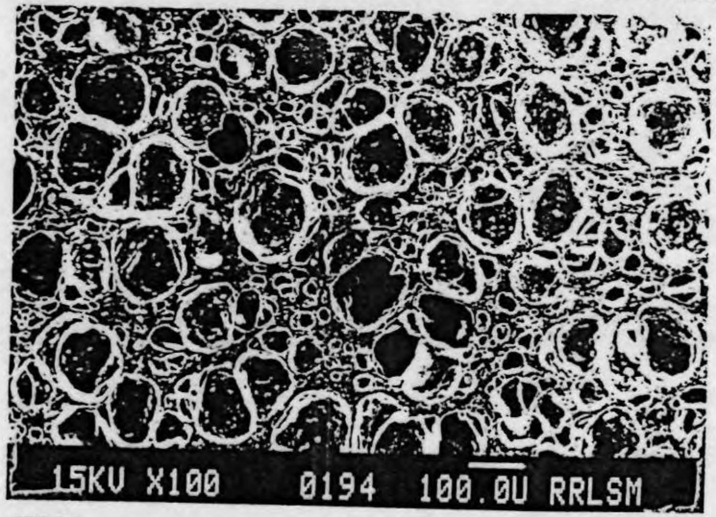


Figure 4.4

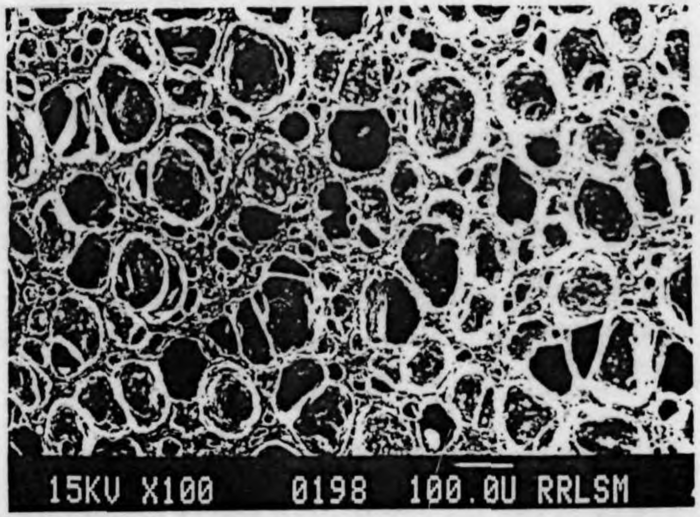


Figure 4.5

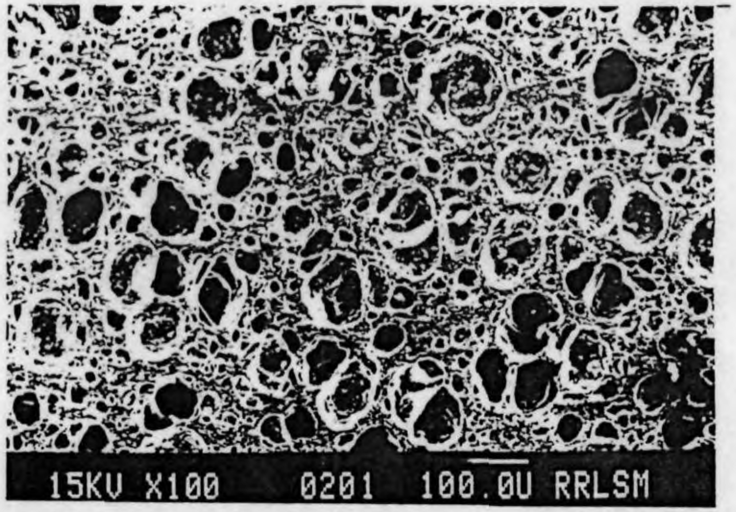


Figure 4.6

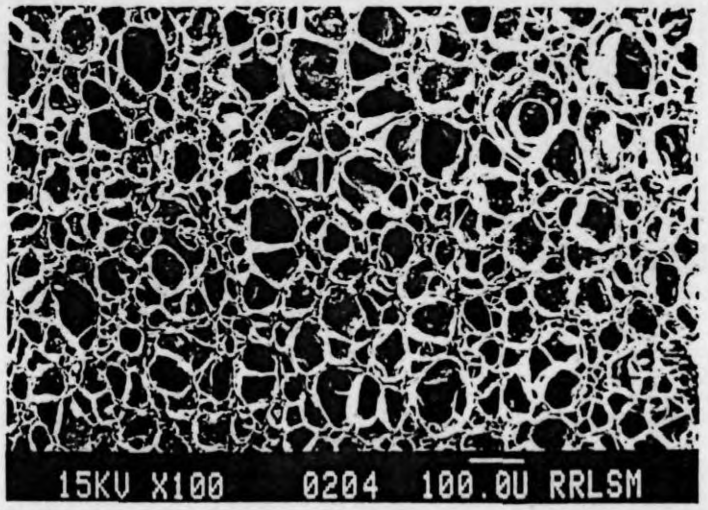


Figure 4.7

CHAPTER - 5 :: SUMMARY AND CONCLUSIONS

5. SUMMARY OF THE WORK

Effect of different proportions of 1,2 polybutadiene in blend with natural rubber was evaluated for their application in microcellular solings, in comparison with the conventional natural rubber-high styrene based blend.

In a selected blend different filler combinations were also evaluated. Finally in three selected systems having different extent of blowing were also studied.

(1) Microcellular sheet prepared from a 70/30 blend of natural rubber/1,2 polybutadiene, though is slightly inferior in technical physical properties compared to the conventional type, has got specific advantage of light weight and higher production output.

(2) A suitable filler combination for 1,2 polybutadiene based microcellular soling was found to be clay/silica/aluminium silicate in the ratio 60/30/15.

(3) Fillers such as silica, aluminium silicate, and microcrumb can favour higher expansion.

(4) Increased 1,2 polybutadiene content causes higher expansion.

(5) As the 1,2 polybutadiene content increases sheet becomes lighter.

(6) For the same level of expansion addition of 1,2 polybutadiene in natural rubber can increase hardness.

(7) For the same level of expansion, abrasion properties are comparable with that of the conventional type.

(8) As compared to the high styrene based sole for the same level of expansion, only lesser amount of blowing agent is needed.

CHAPTER - 6 :: REFERENCES

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