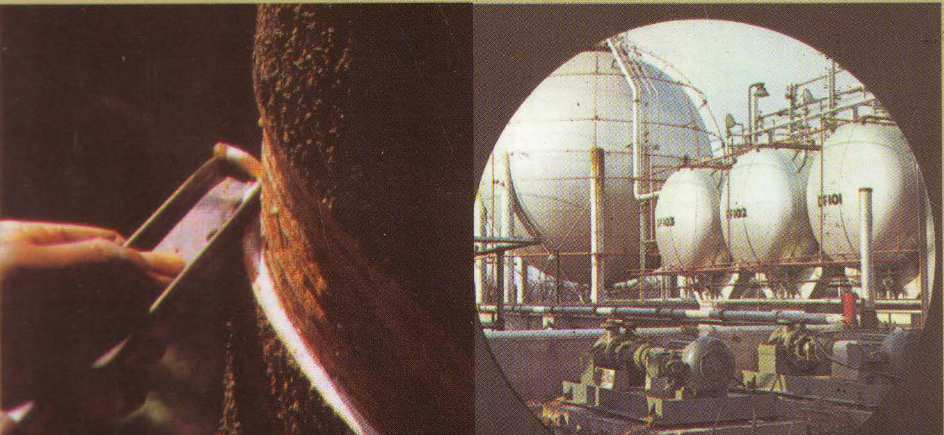
FUNDAMENTALS OF RUBBER TECHNOLOGY



KANTHAPPU SUBRAMANIAM

FUNDAMENTALS OF RUBBER TECHNOLOGY

Kanthappu Subramaniam
B.sc (Cey.), M.Sc (C.N.A.A.U.K), A.N.C.R.T (Lond.) F.P.R.I, F.I.M (U.K)
Head, Division of Polymer, Chemical and Textile Engineering Technology
Institute of Technology,
University of Moratuwa.

2002

Title of book :

Fundamentals of
Rubber Technology

Author :

Kanthappu Subramaniam ©

ISBN 955 - 97957 - 0 - 8

First Edition :

August, 2002

Published by :

Author

e-mail address :

Subramanium@cheng.mrt.ac.lk

Printed by :

Kumaran Press (Pvt) Ltd.,
201, Dam Street,
Colombo - 12.

Dedicated to late

M. Nadarajah,

the Sri Lankan rubber Scientist.

Forward

Synthetic and natural rubber materials have an important role to play in the design of both domestic and industrial items. Within Sri Lanka their production represents one of the oldest and still major sectors of manufacturing industry. This book by Kanthappu Subramaniam is a very welcome addition to the literature available. It is based on his experience of over thirty years, as an industrialist and teacher, in rubber technology.

Starting from the basic science of latex he develops his subject through the various processing stages, to testing, compound design and product manufacture. He deals with each of these subjects in a most practical way, even introducing aspects of quality assurance, and health and safety where appropriate. Particularly welcome are the product case histories, which are again drawn from personal experience. For students studying Plastics and Rubber Technology, Process, Materials, or Mechanical Engineering, this book provides a through grounding in the theory and practice of the subject. I congratulate Mr. Subramaniam on a job well done and recommend this text to students and teachers in Sri Lanka.

J. F. Harper
Director, and Head of Department,
Institute of Polymer Technology and Materials Engineering,
Loughborough University,
Loughborough,
Leicestershire,
U.K.

Preface

The book on rubber technology has been written for the students of diploma and degree courses in polymer technology and all those engaged in various branches of rubber industry. I have tried to cover all areas on the subject as comprehensive as possible and I hope that the students may find complete requirement in this book alone.

Many standard books have been freely consulted for preparing the manuscript of the book and I am greatly indebted to the authors and publishers of these books.

I am grateful to Mr. S.H. Waidyasekera, University of Moratuwa, for helpful suggestions in regard to the front cover design and other diagrams.

My special thanks are due to Mr. John Harper, the Director, Institute of Polymer Technology and Materials Engineering, Loughborough University, United Kingdom, for kindly consenting to write a forward to this book.

Last but not least, I wish to record my gratitude to the printers, Kumaran Press (Pvt) Ltd. for bringing out this book in an attractive form, within a short time.

Suggestions and comments for improvement from students and staff are welcome.

Kanthappu Subramaniam

Kuppilan,
J/Earlali,
Sri Lanka.
August, 2002.

Contents

Chapter 1 Basic Polymer Science

Chapter 2 Natural Rubber - Production and grades

Chapter 3 Natural Rubber - Properties and Derivatives

Chapter 4 Synthetic Rubbers

Chapter 5 Rubber Compounding Ingredients and Reinforcing Textiles

Chapter 6 Processing of Rubbers

Chapter 7 Designing of Rubber Compounds

Chapter 8 Rubber Products - Manufacturing Methods

Chapter 9 Physical Testing of Rubber

Chapter 10 Latex Technology

Chapter 1

Basic Polymer Science

Rubbers, Plastics and fibres are polymeric materials, the molecules of which consist of many number of same simple chemical units. Apart from the polymeric materials of natural origin, the other polymeric materials are produced by chemical reaction, called polymerisation.

1.1 Monomers

The reacting substances at the start of a polymerisation are simple molecular substances which are generally referred to as monomers. The monomers are usually liquids or gases and they differ from the polymers completely in their properties.

Most monomers are obtained from crude petroleum which contains mainly of a complex mixture of hydrocarbons. The hydrocarbon content of petroleum covers the range from low molecular weight gases such as methane upto heavy oils, containing 70 or more carbon atoms per molecule. There are two processes mainly carried out to obtain the low molecular weight monomers from these long hydrocarbons. First process is a distillation process where various fractions of different boiling points are separated from the crude oil. The second process is called cracking process. In this process, the high molecular fractions are broken down into smaller molecules by purely thermal or catalytic cracking.

Functionality of monomers

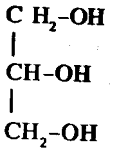
The number of functional groups in a monomer is said to be the functionality of the monomer. The functionality of a monomer is an important factor in determining the physical and chemical nature of the reaction product, polymer. Generally the reaction of monomers of functionality two, will lead to linear, thermally softning polymers, while the reaction of monomers of which atleast one in trifunctional or more gives infusible cross - linked products.

Examples :

a) Bifunctional monomers - Diamine $H_2N-R-NH_2$

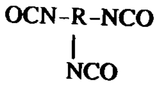
Glycoi $HO-R-OH$

b) Trifunctional monomers - Glycerol



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

Triisocyanate



$$\begin{array}{l} OCN-R-NCO \\ \quad\quad\ | \\ \quad\quad NCO \end{array}$$

Note : A monomer containing a double bond can also be considered as a bifunctional monomer.

1.2 Polymerisation

Polymerisation reactions are divided into chain growth and stepwise reactions. The latter group of reactions are of two types, viz. polycondensation and polyaddition.

In chain growth reactions, a combination of a large number of monomer molecules with one another occurs resulting into polymer molecules. There are no low molecular by-products formed in these reactions and the polymer molecule has the same empirical formula as that of the monomer.

The monomers are either unsaturated or ring structured simple molecules which are converted into active species during the reaction by free-radical or ionic initiator chemicals. The active species of monomers are capable of joining in sequence to form a long chain of monomer units. The process continues until the polymer chain is terminated. For instance, the generalised free-radical reaction mechanism is as follows:

i. Initiation

Initiator $R-R \rightarrow R^* + R^*$ where R^* is initiator active radical

$R^* + M \rightarrow RM^*$ (active monomer radical)

ii. Propagation

$RM^* + M \rightarrow RMM^*$

$RMM^* + M \rightarrow RMMM^*$ (growing Units)

iii. Termination

$$RMMM^* + RMMM^* \xrightarrow{\text{coupling}} RMMMMMMR$$

Polymer

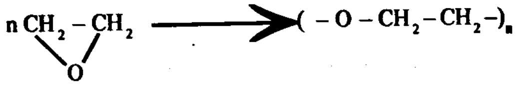
Disproportionation

→ Polymer Molecule I
+ Polymer Molecule II
(with relatively low molecular weights)

Typical examples of addition polymerisdation

$$n\,CH_2=CH_2 \longrightarrow (-CH_2CH_2-)_n$$

Ethylene Polyethylene



$$n\,CH_2-CH_2\ (\text{ring via } O) \longrightarrow (-O-CH_2-CH_2-)_n$$

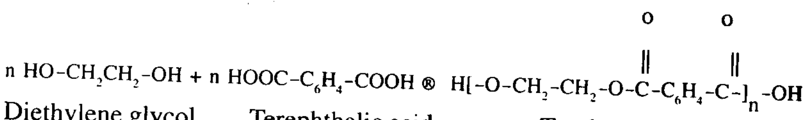
Ethylene oxide
(ring structure)

Polyethylene oxide

In stepwise polymerisation (both types - condensation and polyaddition) reactions, a large number of monomer molecules combine with one another by interaction of their functional groups with the formation of polymer molecules. In the case of condensation polymerisation, every stepof reaction of these functional groups is accompanied by elimination of simple molecular substance (often water); but in the case of stepwise polyaddition the functional group atoms are rebuilt into polymer molecules without the elimination of such simple molecules.

Examples :

Polycondensation

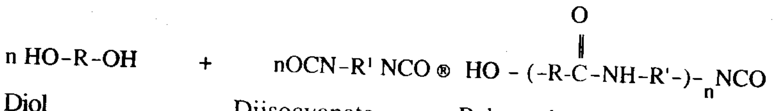


$$n\ HO\text{-}CH_2CH_2\text{-}OH + n\ HOOC\text{-}C_6H_4\text{-}COOH \text{ ® } H[\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}]_n\text{-}OH$$

Diethylene glycol   Terephthalic acid   Terylene polyester

$(2n - 1)\ H_2O$

Polyaddition



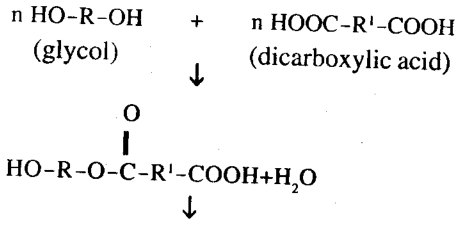
$$n\ HO\text{-}R\text{-}OH \quad + \quad nOCN\text{-}R^1\ NCO \text{ ® } HO - (\text{-}R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}R'\text{-})\text{-}_n NCO$$

Diol   Diisocyanate   Polyurethane

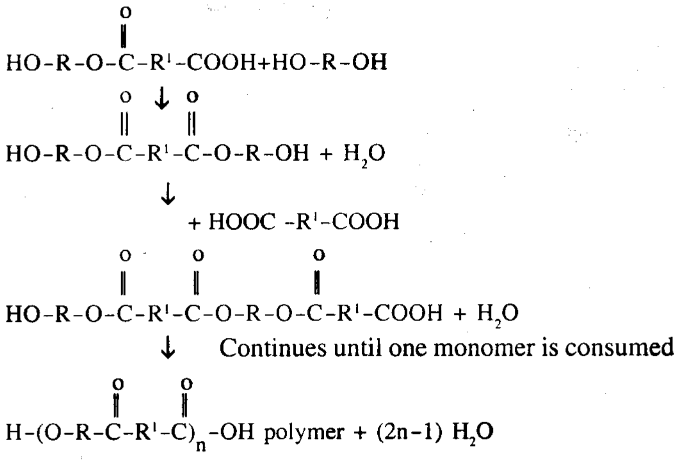
Steps involved in condensation polymerisation

The condensation polymerisation of monomers -- glycol and dicarboxylic acid is given below as a typical example.

The steps involved in the polymerisation reaction are as follows:



$$\begin{array}{l} n\ HO\text{-}R\text{-}OH \quad + \quad n\ HOOC\text{-}R^1\text{-}COOH \\ \text{(glycol)} \qquad \downarrow \qquad \text{(dicarboxylic acid)} \\ HO\text{-}R\text{-}O\text{-}\overset{O}{\overset{|}{C}}\text{-}R^1\text{-}COOH + H_2O \\ \downarrow \end{array}$$



$$\begin{array}{l} HO\text{-}R\text{-}O\text{-}\overset{O}{\overset{|}{C}}\text{-}R^1\text{-}COOH + HO\text{-}R\text{-}OH \\ \downarrow \\ HO\text{-}R\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R\text{-}OH + H_2O \\ \downarrow \\ \quad + HOOC\ \text{-}R^1\text{-}COOH \\ HO\text{-}R\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R\text{-}O\text{-}\overset{O}{\overset{|}{C}}\text{-}R^1\text{-}COOH + H_2O \\ \downarrow \quad \text{Continues until one monomer is consumed} \\ H\text{-}(O\text{-}R\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^1\text{-}\overset{O}{\overset{\|}{C}})_n\text{-}OH \text{ polymer} + (2n-1)\ H_2O \end{array}$$

1.3 Polymer form and structure

Polymers may exist in one of the following forms :

i. Linear

ii. Branched

iii. Cross - Linked

The physical and mechanical properties of linear polymers differ greatly from those of polymers consisting of branched molecules. The chemical bonds in the cross-linked polymers make their properties differ still more from the other two forms of polymers.

If a polymer consists of same monomeric units in its molecular structures, the polymer is called homopolymer.

If two different monomeric units are repeated in the molecules of a polymer, the polymer is said to be a copolymer. Copolymers have four different types of molecular structures as given below:

i. Linear random copolymer AAABAABBBABBA where A and B are the two different monomeric units

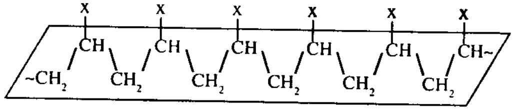
ii. Linear alternating copolymer ABABABABABABABA

iii. Linear block copolymer AAAAAABBBBBBBAAAAA

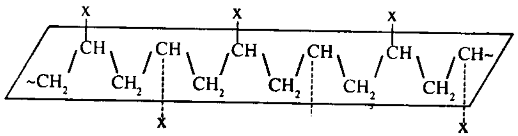
iv. Branched, graft copolymer

Stereoisomers in polymers

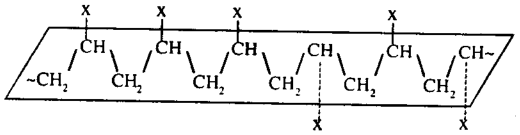
Polymers having asymmetric carbon atoms in their molecules exist in the following structural forms:



a. Isotactic polymer



b. Syndiotactic polymer



c. Atatic polymer

Of these isotactic and syndiotactic polymers have regular pattern of subtituents in their molecules and such polymers are generally said to be stereoisomers.

In the isotactic polymer molecule, the substituents at the asymmetric carbon atoms are arranged at one side of the plane of the main chain, where as in the syndiotactic polymer molecule, the substituents at the asymmetric carbon atoms are arranged alternatively at different sides of the plane.

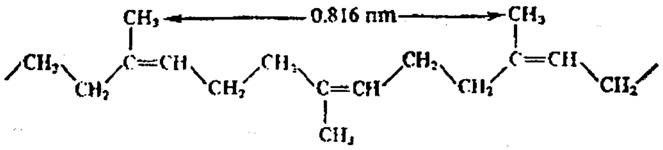
Different stereoisomers have different mechanical properties, which differ vastly from those of atatic polymers.

Cis-trans isomers

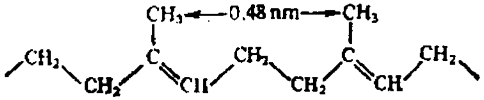
Polymer molecules having unsaturated (double - bonded) structures may exist in cis-trans isomeric forms. The isomers are distinguished by the arrangement of the substituents relative to double bonds in the molecular chains.

cis - - isomer trans -isomer

Since these two different kinds of configurations (the spatial arrangement of the atoms or groups) are stable in time and do not change in the process of thermal motion, the two isomers are stable in the polymer molecules. Although, these isomers possess same chemical properties, they differ greatly in their physical and mechanical properties. To exemplify this difference, the natural polymers - Natural rubber and Gutta percha or Balata can be considered. The molecular structures of these polymers are cis and trans polyisoprenes.



Natural rubber *(cis- polyisoprene)*



Gutta-percha *(trans- polyisoprene)*

At ambient temperatures natural rubber is an elastomer whereas gutta percha or balata is a crystalline thermoplastic, with softening temperature about 50°-70°C.

1.4 Different processes of polymerisation

Polymerisation reactions can be carried out generally in four different processes namely -

- i. Bulk polymerisation process
- ii. Solution polymerisation process
- iii. Suspension polymerisation process
- iv. Emulsion polymerisation process

The summary of each process is given below:

Bulk polymerisation

In this polymerisation, a monomer is converted into a polymer by reacting with an initiator in the absence of any other substances. The reaction temparature is generally high to keep the system in liquid state. There will be an increase in viscosity as the reaction proceeds. The polymer formed in the process is pure and is not contaminated with chemicals other than the monomer and initiator fragments. However heat dissipation from the system is difficult due to rise in viscosity and there be localised over heating causing degradation and discolouration in the polymer.

Solution polymerisation

In solution polymerisation, the reaction between the monomer and initiator occurs in a solvent medium. Heat removal in this system is easy. However the polymer formed is contaminated with solvent and is not as pure as polymer from bulk oplymerisation.

Suspension polymerisation

In suspension polymerisation, monomer is dispersed in water in the form of droplets. The polymerisation reaction is initiated in these droplets by adding an initiator which is soluble in the monomer phase. Generally, a water soluble protective substance for the droplets is also incorporated to enhance the stability of the suspension system. The polymer produced in the process is in the form of granules (beads) which can be easily dried after collection. Since the protective coating substance of the polymer granules and other impurities are washed off readily, the polymer produced is also pure in quality.

Emulsion polymerisation

An emulsion polymerisation system contains monomer, water (as the dispersing mediun) initiators, emulsifiers (soaps) and various additives such as buffer, molecular size modifiers, etc. The emulsification of monomers in water, in the presence of emulsifiers causes a heterogeneous colloidal system. When the temperature is sufficiently high to allow the production of initiators, the polymerisation begins in the system. It is considered that the polymerisation proceeds in the micelles of soap molecules, into which the monomer and initiator are supplied from the surrounding medium.

The polymer which results from the reaction, exists in the form of dispersion (latex) and can be separated out, by the addition of an acid or a salt. There are a number of advantages in the emulsion process, some of which are given below:

- i. Rate of conversion of monomer to polymer is fast.
- ii. Molecular weight of polymer formed is high.

iii. Viscosity of polymerising system is low.

iv. Unreactive monomer can be removed without destablising the emulsion.

v. Synthetic latex can be directly produced.

The disadvantage of the process is that the removal of soap molecules completely from the polymer is difficult. This may affect electrical insulation property and optical clarity of the polymer.

Ziegler Natta solution polymerisation

From the researches of Ziegler and Natta in the 1950s a completely new class of polymerization catalysts is emerged. The chief characteristic of Ziegler Natta catalysts is their ability to produce stereoregular linear polymers. By the use of these catalysts both the stereo-isomerism of asymmetric carbon atoms (isotactic and syndiotactic) and the geometrical isomerism about the carbon-carbon double bond (cis-trans) are controlled. The Ziegler Natta catalysts are usually heterogeneous systems consisting of solid phase and liquid phase. The catalyst is made of complexes of transitional metal halides with alkyl derivatives of aluminium or other metals.

Examples : $TiCl_3/AlEt_3$

$VCl_3/AlEt_3$

A large number of stereospecific polymers both plastics and rubbers are prepared by using Ziegler Natta catalysts.

1.5 Molecular weight distribution in polymers

Unlike the molecules of simple substances, the molecules of a polymer are found to be different in their lengths and sizes. Some molecules of polymer are relatively small and others relatively large, with a predominance of molecules somewhere between them. This spread of different molecular fractions in a polymer is referred to as the molecular weight distribution (MWD) of the polymer (see Fig, 1.1)

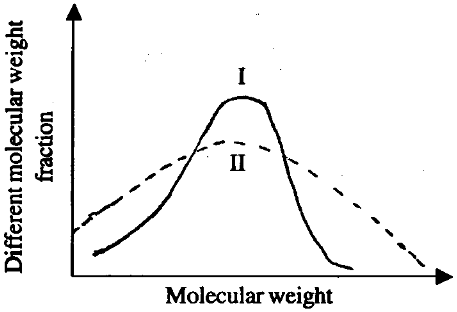


Fig. 1.1 Molecular weight distribution in polymers.(I - Narrow molecular weight distribution ,II - Broad Molecular weight distribution)

Since the flow property, strength and softening point of a polymer material are dependent in its MWD, the manufacturers of polymers control the MWD during the polymerization stage of the materials.

For evaluation of MWD, there are two methods, employed. The first method which gives the actual MWD involves a laborious process of fractionation from a solution of the polymer and the second method is a quicker evaluation method. In this method the MWD of a polymer can be inferred from the ratio of its weight average molecular weight (M_w) to number average molecular weight (M_n). This ratio is generally called heterogenity or polydispersity index. The relationship between heterogenity index and MWD for a polymer is given in table 1.1.

Table 1.1. Inference of MWD from heterogenity index

Heterogenity index (M_w/M_n)	MWD
Approches 1	Polymer molecules are alomost of the same size. But this monodispersity, very rarely occurs in polymers
Lies between 1 and 5	Narrow
Lies between 5 and 20	Medium
Greater than 20	Broad

Expressions for M_w and M_n

i. M_w is defined as $\Sigma w_i M_i$ where w_i is the weight fraction of molcules of size i and $w_i = \frac{M_iN_i}{\Sigma M_iN_i}$

where
Mi - the molecular weight of polymer molecule of size i

Ni - the number of polymer molecules of size i

$$\text{i.e } M_w = \sum \frac{M_iN_iM_i}{M_iN_i}$$

$$= \frac{\Sigma N_iM_i^2}{\Sigma N_iM_i}$$

ii. M_n is defined as Σx_iM_i where x_i is the mole fraction of the molecules of size i and $x_i = \frac{N_i}{\Sigma N_i}$

$$\text{i.e. } M_n = \frac{\Sigma M_iN_i}{\Sigma N_i}$$

The M_w of a polymer can be determined from the results of measurement of light scattering in its solution.

To evaluate M_n of the polymer, generally one of the following colligative properties of its solution is considered:

Depression of freezing point

Elevation of boiling point

Osmotic pressure

For certain polymers having detectable end groups, a different method called end group analysis method is also employed to determine their M_n values.

Effect of MWD on processability of polymers

A polymer having broad MWD is easier to process than a narrow MWD polymer, because the large number of small chain molecules present in the former will have a plasticizing effect on the long chain molecules of the polymer and improve its flow behaviour in the processing machinery (see Fig. 1.2)

Many commercial rubbers have molecular weight in the range 10^4 to 10^5 with heterogencity index approximately equals 3 to 4. This range of values is chosen to give a balance of desirable rubber processing and physical properties.

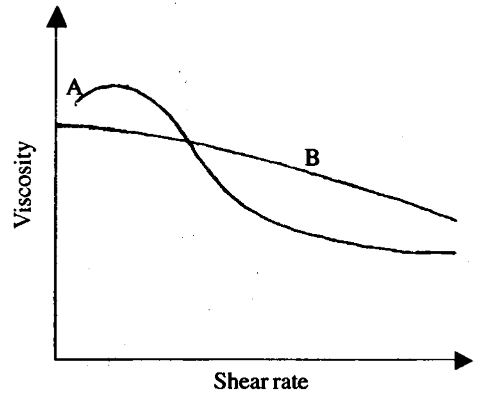


Fig. 1.2 Effect of shear rate on melt viscosity of polymers (A - broad MWD, B - narrow MWD)

Chapter 2

Natural Rubber - Production and Grades

2.1 Natural rubber plant

Natural rubber has been known to mankind for many centuries. It is obtained form latex which is found in over thousand species of plants and trees. Of all these species, the plant Heavea Brasiliensis is practically the sole source of commercial rubber today, due to its high productivity and economics.

Hevea Braziliensis plant is indigenous to Brazil, South America and requires same geographical climate for its healthy growth.

The following conditions are considered necessary for the plantation :

i. Altitude of land ---- about 300 m
ii. Annual rain fall ---- not less than 200 cm
iii. Climate temperature ---- 25 to 35^{0}C
iv. pH of soil ---- 4.5 to 6

Plantation in South East Asia

In 1876, Sir Henry Wickham, an english man collected many thousands of seeds of rubber trees in South America and shipped them to Kew gardens, London. Many of the seeds grew into young plants which were then sent to south eastern Countries, first to Sri Lanka in 1876 and then to Malaysia in the following year. Since then the estates and small holdings in these countries and neighbouring eastern countries have been the major sources of natural rubber and a world total production of about six million tons of natural rubber is now produced. The major natural rubber producing countries are given in table 2.1

TABLE 2. 1 Natural Rubber production (2000)

Countries	Production (10^3MT)
Thailand	2270
Indonesia	1590
Malaysia	770
India	620
China	460
Vietnam	100
Sri Lanka	100
Philippines	65

Commercially Hevea Braziliensis is propagated by the method of budding or by using specially selected seeds. The young plants are raised in a nursery for the first year and then transplanted to the permanent field; about 200 - 300 trees/hectare is typical. The trees will not normally be ready to yield rubber until about six years after planting out. Soil fertility is maintained by the use of fertilizer and by growing cover crops. These are grown between the trees to hold and shade the soil for the improvement of water supply and fertility.

2.2 Method of tapping latex

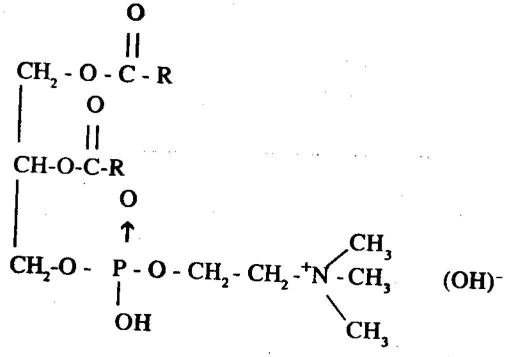
In the tapping process, a sliver of bark about 1 mm thick is cut off with a special knife to a depth of 6 mm. This is made at a slope of about 30^0 to the horizontal falling from left to right. In general a tree is tapped halfway round its circumference every other day (half spiral, alternate daily-s/2,d/2). A good tree yields 60 g of latex on each tapping.

Collection of field latex

The latex which flows out from a tree on tapping is channelled into a container such as a coconut shell or plastic cup, which is mounted to its trunk. When latex ceases to flow, it is transferred in to buckets first and then to tanks at the latex collecting stations.

2.3 Natural rubber field latex

Latex is a milky fluid with relative density between 0.97 - 0.99. It is a colloidal system of rubber particles, each particle of which is surrounded by a protective layer of phospholipids and proteins. The particles, as a result, carry negative charges and bring about colloidal stability by mutual repulsive forces. The main phospholipid presents in the field latex has been, identified as alpha - lecithin having the following structure :-



Where R is $C_{17}H_{35}$ or $C_{17}H_{33}$

The protein has been identified as chiefly alpha - globulin and the latex particles have been found to be predominantly spherical particles with size from 0.05 to 5 micrometer in diameter.

The composition of field latex, in general, varies for the factors such as clone, age of tree, chemical nature of the soil and tapping frequency. The typical composition of field latex is presented in table 2.2.

Table 2. 2 General composition of field latex

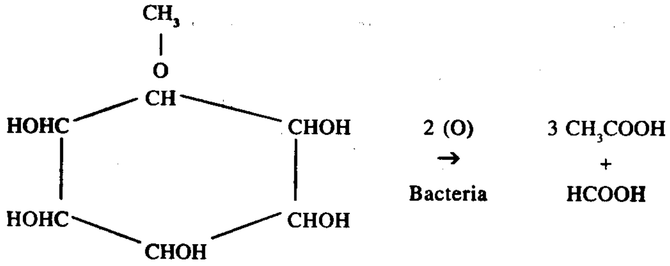
Components	% variation
Rubber	30.0 - 35.0
Protein	1.0 - 1.5
Resins	1.0 - 2.5
Ash	0.7 - 1.0
Water	60.0 - 65.0

Spontaneous coagulation of field latex

As latex is a fluid of biological origin, it is an ideal medium for the growth of bacteria. The growth of bacteria decays the carbohydrates, particularly sugars, leading to the production of simple organic acids, which in turn cause colloidal instability in latex (i.e. coagulation of latex). This normally occurs in fresh latex within 8 to 24 hours if preservatives (anticoagulants) are not incorporated in time.

Decomposition of sugar

eg. quebrachitol by aerobic bacteria is as follows :



Preservation of field latex

The anticoagulants used for preserving the field latex are generally basic substances which also function as bacteriacides in the latex. Commonly used anticoagulants are :-

i. ammonia

ii. sodium sulphite (anhydrous powder)

iii. formalin (38% solution)

iv. washing soda (powder)

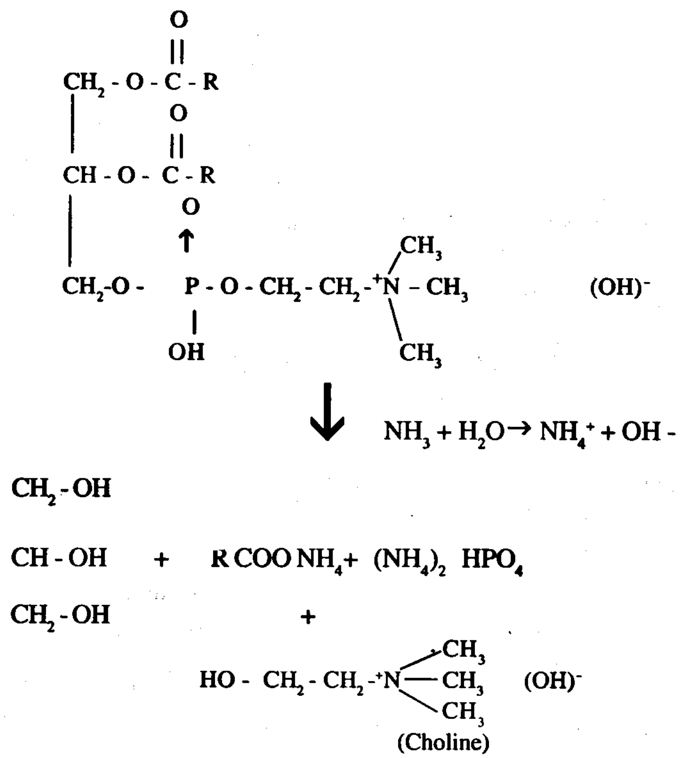
The choice of chemical for preservation of latex largely depends on how the latex is to be processed in the next stage.

The anticoagulants that are chosen for the preservation of latex for various processes are given below:

Choice of anticoagulant	Process in the next stage
0.01% Ammonia on weight of latex	RSS production
0.05% Sodium sulphite on weight of latex	crepe production
0.75% Ammonia on weight of latex	centrifuging of latex
1.25% Ammonia on weight of latex	creaming of latex
0.05% Sodium Sulphite and 0.02% Formalin on weight of latex	RSS production from latex that is likely to putrefy

Action of ammonia on field latex

Ammonia hydrolyses proteins and phospholipids layers of latex particles to polypeptides, ammonium salts of fatty acids and choline. The ammonium salts of fatty acids, in consequence, become the protective layers of latex particles in the ammonia preserved latex.



2.4 Production of natural rubber

Raw natural rubber is produced mainly in the form of thick sheets and block as illustrated in Fig. 2.1. The grades available in the form of sheets are :

i. Ribbed smoked sheet (RSS)

ii. Scrap crepe sheet

iii. Pale crepe sheet

iv. Sole crepe sheet

The production of rubber in the form of block was introduced about four decades ago. As this block rubber is specified with technical properties it is generally termed technically specified rubber (TSR). Irrespective of the grade of rubber, the production methods involved with the following primary step :

Field latex is first preserved with suitable anticoagulant chemicals to prevent its spontaneous coagulation. The latex is then transported to raw rubber production centers, where it is strained through sieve fitted with steel wire mesh in order to remove coarse dirt such as bark shavings, lumps of rubber. etc. The latex is then stored in bulking tanks, normally constructed of stone bricks or concrete lined with porcelain tiles.

The procedure of coagulation of latex is then carried out in suitable tanks fitted with metal separation plates. In the procedure, organic acid such as acetic acid or formic acid is added into the latex, until its pH is brought down to 4.8. A simple and quick determinant of pH can be carried out by means of bromocresol green (BCG) indicator paper which indicates colour as pH of latex changes.

For instance :

Blue to Bluish green → pH = 5

Green → pH = 4.5 (Reasonably suitable for RSS production)

Greenish yellow → pH = 4 (Results in hard coagulum)

Yellow → pH < 4

At pH - 4.8. latex loses its colloidal nature and slowly turns into lump of rubber. This is then removed as a continuous thick sheet (slab) by lifting out the metal plates.

Finally the thick sheet of coagulum is washed from its non rubber contaminants and further processed by different methods to obtain various grades of rubber. Formic acid is preferred to acetic acid for coagulation of latex for the following reasons :

i. It coagulates the latex in short time

ii. It has antiseptic property and hence prevents mould growth or discolouration

iii. The volume required for coagulation in the case of formic acid is one half of the volume of acetic acid.

Production of ribbed smoked sheet

The slabs of coagulum are then sheeted out to a reduced thickness through a set of rollers consisting of grooved cuts. The ribbed pattern which is embossed on the sheets facilitates the removal of one sheet from the other. Smoking rubber sheet is done in smoke houses where the sheets are suspended on reapers and exposed to smoke from burning firewood or coconut shells in limited supply of air. The duration of smoking is about 5 to 6 days at temperatures around 60^{0}C. This treatment dries the rubber to less than 0.8% moisture and develops the resistance of the rubber to mould - growth.

Production of crepe rubber

Crepe rubber is produced by passing the coagulum of rubber through a series of rollers to produce crinkled laces. These are then air - dried and baled.

There are two grades of crepe rubber produced especially in Sri Lanka namely i. unfractionated and bleached crepe (U.F.B.) and ii. fractionated and bleached crepe. (F.B.) The latter grade is more whitish than the other grade, because of the removal of yellowish matter (carotene mainly) by fractionation process. The process is done prior to coagulation of latex with acids. Figure 2.2 illustrates the process flow - line for the production of these crepe rubbers.

Production of scrap rubber

The production of scrap rubber is same as that of crepe rubber but in this case, cleaned tree- laces and cup - lumps are used instead of latex coagulum.

Production of technically specified rubber

Production of block rubber is carried out in two processes, namely (i) Hevea crumb process and (ii) Comminutation process. In the first process, up to 0.75 by weight castor oil is added into the rubber to assist crumbling of the coagulum during milling. The comminutation process employs size reduction machinery such as hammer mills, extruder machines, or shredders to produce the crumbs. The crumbs by either process is then dried for 4 -8 hours at about 100 - 110°C in tunnel driers. The dried crumbs are then pressed into bales by means of hydraulic presses. The bales are subsequently tested, graded, wrapped in polythene sheet and marketed to standard specifications.

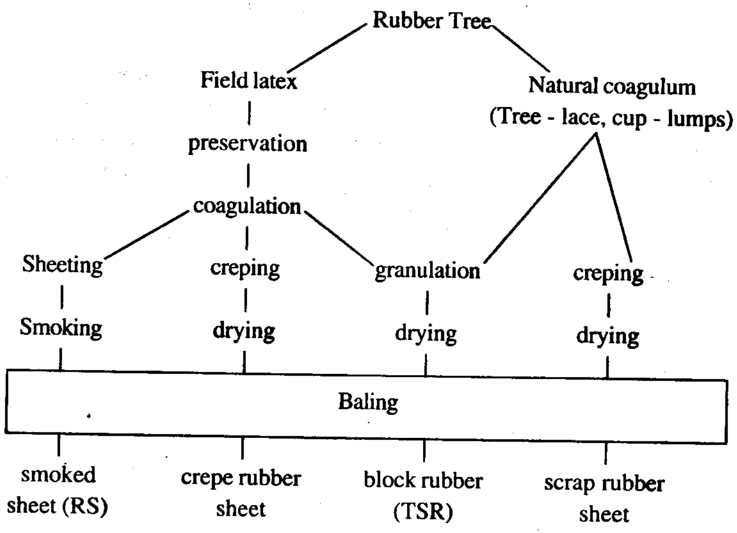


Fig. 2. 1 Flow line diagram for the production of different grades of natural rubber

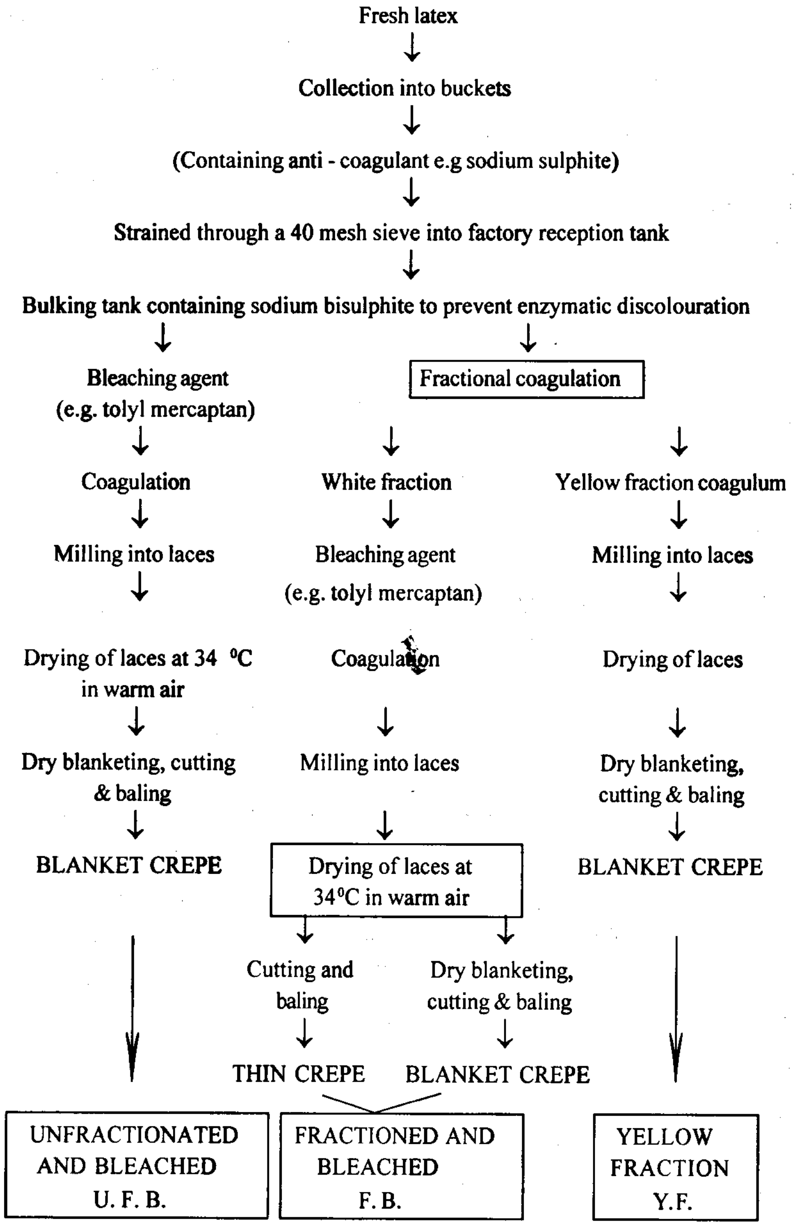


Fig. 2. 2 Process flow line diagram for production of crepe rubbers.

2.5. Grading of natural rubber

Visual inspection

Natural rubber sheets, especially RSS and crepe rubbers are graded by visual inspection and assessment. A book named green book titled International standards of quality and packing for NR - grades" is referred to for this assessment. The book describes the types and grades of various natural rubber sheets according to odour, dirt, blemishes, blister, rust etc. However the visual grade and normal packing of rubber sheets present many problems to the consumers; as indicated below :

i. Handling problem (bales are big and each weighs about 70 - 115 kg.)
ii. Non uniformity in quality within a particular grade
iii. Non availability of technical information relevant to end use of rubber.
iv. Needs precleaning, thawing, reduction in size by bale cutting, premastication etc.

The visual grading system

Type	Source	Grades
i. Ribbed smoked sheet	Coagulated field latex	IX,1,2,3,4,5,6
ii. Pale crepe rubber	Coagulated field latex	IX,1,2,3(thick and thin)
iii. Estate brown crepe	High grade natural coagulum from estates excluding earth scrap smoked scrap, wet slab	IX,2X,3X (thick and thin)
iv. Thin brown crepe	Natural coagulum excluding earth scrap & smoked scrap	1,2,3,4
v. Thick blanket crepe	Natural coagulum excluding earth scrap	2,3,4
vi. Flat bark crepe pure	Natural coagulum of all kinds	Standard & hard
vii. Pure smoked blanket crepe	Remilled ribbed smoked sheets or cuttings	

Technical specification

To eliminate the drawbacks in the visual grading assessment and to simplify the system of grading to confirm more closely to the end-use of rubber, a different grading system called the technical specification scheme was launched in 1965, by R.R.I Malaysia. The scheme was later modified by the institute in 1991. The summary of each specification test used in the scheme with its technical importance is given below :

i. Determination of dirt content

A sample of rubber is dissolved in a hydrocarbon solvent and its dirt retained on 44 mµ aperture metal wire mesh is determined and expressed as a percentage weight in the sample of rubber. Dirt content is mainly due to bark shavings and sand, which can cause damages to rubber products and shorten their service life.

ii. Determination of ash content

A sample of rubber wrapped in ashless filter paper is reduced to ash by burning in a muffle furnace at temperature 550 ± 20^0C. The ash content thus obtained is expressed as a percentage weight in the rubber. The oxides, carbonates, phosphates of inorganic metals such as K, Mg, Ca, Na, and other trace metals are the main constituents present in the ash content. These substances can have an influence on the cure rate of rubber and ageing.

iii. Determination of nitrogen content

Nitrogen occurs in rubber chiefly as proteins. It is determined by the kjeldhal method, where the nitrogen present in the rubber is converted into ammonium ion with conc, sulphuric acid and some specific catalysts. After neutralization the ammonia is distilled off and estimated by titration after absorption. The nitrogenous matter in rubber assists moisture absorption and can have detrimental effects on the strength of rubber especially when used in engineering applications. It induces high creep and stress relaxation in rubbers. (see Chapter 9)

iv. Determination of volatile matter

In this determination, rubber sample is kept in an oven at 100°C for about 4 hours. The loss in weight in the rubber due to this treatment is expressed as percentage volatile matter in the rubber. Volatile matter generally causes surface defects in rubber sheets, extrudates, calendered sheets etc. by forming blisters and porosity.

v. Determination of plasticity retention index (PRI)

The PRI is a measure of the resistance of raw rubber to oxidative breakdown during processing at temperatures above 100°C and to ageing.

For the determination of plasticity retention index plasticity measurements on rubber samples are measured before and after ageing at 140°C, for 30 mins on a standard plastimeter (Wallace rapid plastimeter). The PRI value is then calculated from the following expression :

$$\text{PRI Value} = \frac{\text{W.R.P.N. of aged Sample}}{\text{W.R.P.N. of original sample}} \times 100$$

where W.R.P.N. is the wallace rapid plastimeter number (see chapter 9).

The limits of the above parameters as quoted in SLR (Sri Lanka) specification scheme are presented in table 2.3

Table 2.3 The Sri Lanka (SLR) specification scheme for technically specified raw natural rubber (TSR)

Type	SLR grade max.	Dirt (%wt) max.	Ash (%wt) max.	Nitrogen (%wt) max.	Volatile matter (%wt) max.	Initial Wallace plasticity min.	Retention (PRI) min.
	*5 L	0.05	0.50	0.55	0.70	30	60
Latex crepe	5 WF(LC)	0.05	0.50	0.55	0.70	30	60
Latex	L	0.03	0.50	0.55	0.70	30	70
	5 L	0.05	0.50	0.55	0.70	30	70
	5 WF	0.05	0.50	0.55	0.70	30	70
Sheet material by :							
a. comminuted process	5	0.05	0.60	0.55	0.70	30	70
b. pressed process	5 (RSS)	0.05	0.60	0.55	0.70	30	70
Field material	10	0.10	0.60	0.55	0.50	30	70
	20	0.20	1.00	0.55	0.50	30	50
	30	0.50	1.50	0.55	0.50	30	40

* Made from unbleached fraction removed latex.

From : Hand book of rubber culture and processing RRI, Sri Lanka.

2.6 Composition of natural rubber sheet

Raw natural rubber produced in sheet form has the following components generally.

Table 2. 4 General composition of raw natural rubber (sheet)

Components	Percentage (%)
Rubber hydrocarbon	93 - 96
Dirt [a]	0.001 - 0.3
Inorganic ash	0.2 - 1.5
Water	0.1 - 0.5
Protein	1 - 3
Organic material [b]	2 - 3

a. Organic origin e. g. bark and inorganic origin e.g. sand - contaminants

b. Of low molecular weight and extractable by acetone.

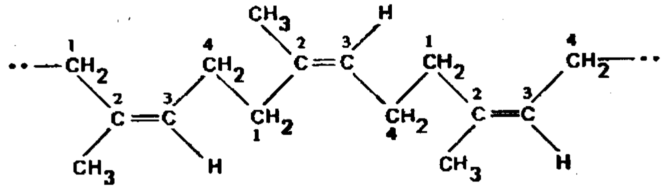
Chapter 3

Natural Rubber - Properties and Derivatives

3.1 Natural rubber - chemical properties

Chemical structure of natural rubber molecule

The empirical formula of natural rubber molecule as C_5H_8 was found by Faraday in his early work in 1826. Later Grivelle William and other subsequent workers have shown that the rubber molecule has the following microstructure :



The molecule consists of thousands of isoprene units joined end to end (i.e., carbon atom 4 of each is connected to carbon atom 1 of the next) and in the chain, all the double bonds have cis-stereo chemistry (the carbon chain at each end, i.e., at carbon atom 2 and carbon atom 3, is connected to the same side of the double bond).

The number average molecular weight (M_n) and the weight average molecular weight (M_w) of the rubber have been found to be in the following ranges:

$Mn = 2.5$ to 27×10^5 and $Mw = 3.4$ to 10×10^6

This indicates that the rubber has fairly wide MWD.

Chemical reactivity

Natural rubber is non-polar and has molecules with weak intermolecular attractive forces. It mixes easily with non-polar substances and is soluble in hydrocarbon solvents.

The presence of CH_3 group adjacent to double bonds of the molecule makes the rubber more reactive and the rubber can readily undergo reactions with a) halogens, b) hydrochloric acid, c) sulphur, d) protonic acid, e) oxygen, f) ozone.

3.2 Natural rubber - physical properties

Elastic property of natural rubber

Natural rubber possesses good elastic property. Because its entropy, the degree of disorder of rubber molecules resulting from their thermal movements is reasonably high, in the normal undeformed state.

Glass transition temperature

It has been shown that the stiffness of natural rubber increases as the temperature is lowered below - 20°C and when the temperature reaches below - 70° C, the rubber becomes a glass-like and brittle material. The temperature at which this change occurs is generally referred to as the glass transition temperature of the rubber (T_g). It is said that at this temperature, the rubber molecular movements cease and the molecules attain a frozen state.

The glass transition temperatures of common synthetic rubbers (except butadiene rubber) are relatively lower than the glass transition temperature of natural rubber, because the molecules of the natural rubber have more freedom for their movements in the rubber mass.

The factors attributed to the ease of molecular movements in natural rubber mass are that the atoms and groups attached to the main chains of molecules are small and light (CH_3, H) and the intermolecular attractive forces among the molecules are rather weak and caused due to Vanderwaal's forces only.

Comparision of natural rubber vulcanisates and metals

As the natural rubber molecules and its vulcanisates (i.e the rubber after cross - linking with chemicals - refer Chapter 5) are covalently bonded, unlike the metallic structure, the molecules are non-polar and have no free electrons. In consequence, the physical properties of natural rubber vulcanisates vastly differ from those of metals (see table 3.1)

For examples :

i. **Thermal conductivity**

When a metal is heated, thermal energy is transmitted from one atom to atom, owing to the free electrons it has in its structure. The temperature comparatively rapidly levels out through out the entire mass. In the case of rubber, when it is heated, the transport of thermal energy is extremely slow and occurs mainly due to waves which are produced by the thermal motion of atoms and vibrations of molecules.

ii. **Stress - Strain behaviour**

Deformation (strain) of a metal involves with changes in the interatomic distances and generally, very large forces are needed to change these distances. The forces involved are indeed so great that before the deformation has reached more than perhaps a few percent, other actions come into play, involving slippage between adjacent crystals.

In other words, the metal shows a yeild point above which the deformation increases much rapidly than the stress so that the stress-strain curve turns away from stress axis. Moreover, the deformation above this point is irreversible or plastic.

With rubber, the deformation does not involve any straining of the inter - atomic bonds and hence the forces required are very much less than a metal. The stress - strain curve turns upwards toward stress axis and there is no yeild point. The rubber recovers almost though not quite to its original form from any point on the stress - strain curve (See Fig. 3.1)

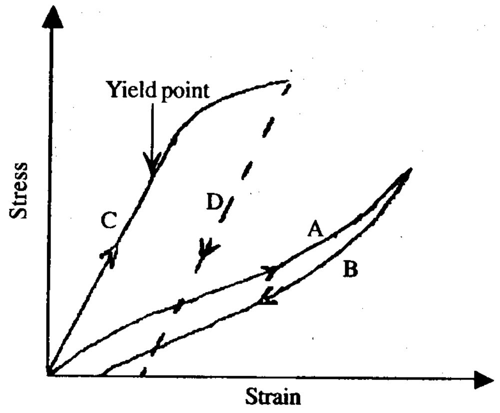


Fig. 3.1., Comparison of stress - strain curves, for loading and unloading of rubber (A →B) and metal (C →D)

The increase in stiffness at high strains in rubber could be attributed to two main features:

i. The sections of the molecules between adjacent cross - links approach their limiting extension and;

ii. the occurence of strain - induced crystallisation (i.e the rubber molecules orient in the direction of straining, forming crystal like structures among their chains).

Besides these, it has also been noted that the deformation of rubber is not accompanied by any substantial change of volume. This shows that rubber is incompressible under stresses that are normally encountered in engineering applications.

Effect of temperature on modulus

In a metal, the force holding two atoms together varies with distance and also with temperature. As the temperature rises, the force required to increase the distance between the atoms decreases, so that the Young's modulus has a negative temperature coefficient. This does not occur in the case of rubber, because as the temperature rises, the vibration of the atoms in rubber becomes of greater amplitude, and brings about a much greater

effect on the motion of the long chain molecule than it has on the force between neighbouring atoms in the chain. In consequence, the molecules tend to from a disordered state and enhance their coiling effect (retraction) at high temperature. This means that the force required to stretch a rubber to any extent (modulus) increases with temperature. It has been found that if the temperature is in absolute units, the equilibrium force which set up in the rubber increases in proportion to the temperature. It also follows that when a rubber is stretched, heat is evolved and vice versa. These effects are generally termed Gough - Joule effects.

Table 3.1 Comparision of physical properties of a soft gum natural rubber, a carbon black filled natural rubber and mild steel

Physical properties	Natural rubber (gum)	Carbon black filled natural rubber (45 phr)	Mild steel
Tensile strength (MN/m^2)	28	24	420
Elongation at break (%)	700	430	40
Young's modulus (MN/m^2)	2.0	6.0	21 x 10^4
Shear modulus (MN/m^2)	0.5	1.5	81 x 10^3
Bulk modulus (MN/m^2)	1000	1200	176 x 10^3
Poisson's ratio	0.5	0.5	0.3
Resilience (%)	80	60	100
Velocity of sound transmission (m/s)	37	37	5000
Specific heat	0.45	0.41	0.12
Thermal conductivity relative to water	0.25	0.31	73
Coefficient of cubical expansion/degree C	67 x 10^{-5}	56 x 10^{-5}	3.5 x 10^{-5}
Electrical resistivity (ohms/cm^3)	1.7 x 10^{16}	3 x 10^{10}	
Power factor	0.002	0.1	
Specific gravity	0.96	1.16	7.7

3.3 Natural rubber derivatives and blends

The work carried out so far on natural rubber to widen the areas of its applications have resulted in the production of derivatives of natural rubber as well as blends comprised of natural rubber and other polymers. The methods of preparations of such materials as well as the applications of them are summarised below:

Viscosity stablised rubber

Natural rubber has tendency to harden during the time that elapses between preparation and use. This stroage hardening is a problem because the manufacturer has to breakdown the hardened rubber by premastication before it is able to be mixed with compounding ingredients. It has been found that storage hardening is the consequence of a chemical reaction between naturally occuring aldehyde groups in the natural rubber molecules and these groups could be blocked by treatment with small proportions of hydroxylamine hydrogen chloride about 0.15% by weight of rubber content. This treated rubber is generally termed as CV rubber. Its normal viscosity is 60±5 mooney units. There is another grade of viscosity stabilized called LV rubber in which the viscosity is further reduced normally to 50±5 mooney units, by adding a small proportion of oil (e. g. Naphthenic oil).

Superior processing rubber (SP Rubber)

SP rubber is produced from the coagulum of a mixture of unvulcanised latex and vulcanized latex. Vulcanised latex is obtained by treating latex with low sulphur levels (about 2 phr). The outstanding feature of this rubber is its reduced tendency to recover deformation, i.e. to reduce 'nervy' character of rubber. Thus it finds applications in rubber mixes to improve their processing character. Examples : mixes for extrusion and calendering. It is also used in rubber adhesives.

Oil extended natural rubber (OENR)

Mineral oils are commonly used in rubber compounding to improve processability of rubber and to facilitate easy incorporation of fillers. especially the carbon black. When oil is used at 20% or more it acts as extender as well. Natural rubber containing more than 20% oil is referred to as oil extended natural rubber.

Oil extension of natural rubber could be carried out both in the latex and dry rubber grades. Both naphthenic & aromatic types are used.

In the latex method, oil is added as an aqueous emulsion at pH 8 to 8.5 and in dry rubber method, mixing of oil with rubber is done by soaking followed by extrusion method.

One of the outstanding properties of oil extended rubber is excellent skid resistance on wet icy roads which leads to its outlet as tread component in winter tyres.

Thermoplastic natural rubber (TPNR)

Thermoplastic natural rubber shows combined functional properties of vulcanized rubber and processing characteristics of thermoplastic material. TPNR is prepared by blending natural rubber with polyolefines such as polypropylene, the percentage proportion of which varies from 40% to 60% in the blend. At high rubber content, the material behaves as thermoplastic elastomer in which the rubber phase normally contains some cross links. The blend in which the rubber content is low, is a semi-regid material. The rubber phase in the blend dispersed in the continuous matrix of polypropylene phase. This leads to improved toughness, ductility and high elongation at break. Potential applications of the soft grade of TPNR are in products such as foot wear, sports goods, seals and hoses. Hard grades of TPNR generally find applications in automobile sector as bumpers, body protective strips e.t.c.

Deproteinised natural rubber (DPNR)

DPNR is a purified form of natural rubber with very low nitrogen and ash content. It is normally prepared by treating NR - latex with a proteinase, such as enzyme present in papain or pine apple juice, which hydrolyses the protein in the latex to polypeptides. These can then be washed away during processing. The removal of most of the proteins together with the ash component make DPNR, a much purer rubber. Consequently it has an even lower water absorption compared to that of normal natural rubber. When it is cured with low level of sulphur, DPNR shows very low creep and stress - relaxation, low compression set, good damping properties and much more consistent modulus. Based on these special features the potential areas of applications for DPNR can be summarised as follows:

Features	Potential Applications
1. Low creep and stress relaxation	Seals, Joint rings, Building mounts, Engine mounts, e.t.c.
ii. Low water absorption	Marine applications, Electrical insulation
iii. Damping	Antivibration mountings Shock absorbers
iv. Low protein	Health care and food applications

Methyl methacrylate grafted natural rubber (Heveaplus MG)

Heveaplus MG rubbers are graft copolymers of natural rubber and polymethyl methacrylate. The grafted Polymethyl methacrylate are relatively long side chains in the natural rubber molecules. The material can be compounded and cured like natural rubber. The graft copolymerisation is carried out in latex phase until the copolymer has its composition generally 30% to 50% polymethlymethacrylate. In the polymerization the monomer methyl methacrylate is incorporated into the latex in the form of emulsion and the initiator used is generally a peroxide (Eg - Cumene hydroperoxide).

Applications of heveaplus MG

It is used in conjunction with natural rubber to obtain leather like products. It also finds application in adhesives especially in pressure sensitive adhesives.

Liquid natural rubber (LNR)

LNR is prepared by means of depolymerising natural rubber. In the process, the normal natural rubber molecules are reduced in size from 10^6 to 10^4. In a method, LNR is produced in latex phase in which natural rubber is treated with phenyl hydrazine and atmospheric oxygen. The oxidation of phenyl hydrazine gives a phenyl radical which by addition or transfer reaction with natural rubber molecules initiate the formation of hydro or cycloperoxides. These peroxides are unstable in atmosphere and broken into low molecular weight molecules.

The latex thus containing low molecular weight rubber molecules is subsequently coagulated with formic acid for the production of LNR. The depolymerised latex can also be concentrated by the normal centrifuging process up to 80% total solids content.

Applications of liquid natural rubber

i. LNR can be used to make adhesives, binders and sealants.

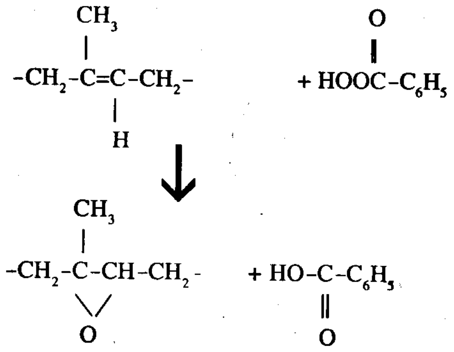
ii. It can also be employed as a vulcanisable processing aid for rubbers.

iii. LNR in latex concentrate form can be directly used to prepare aqueous based adhesives.

Epoxidised natural rubber

When natural rubber reacts with peracids (eg. Perbenzoic acid), its epoxidation occurs. The extent of epoxidation is generally varied in the reaction according to the end use of the reaction product, commonly up to 10% to 50%.

Reaction scheme



As the introduction of epoxide rings brings about polarity to the natural rubber the expoxidised NR is a chemically reactive substance and finds many applications which include:

i. It can be employed alone or as a blend with other rubbers to improve:
  a. Oil resistance
  b. Impermeability to air (eg. in inner tubes)
  c. Wet grip and skid resistance of tyre tread

ii. Modification with aromatic amines yields graft antioxidants.

Isomerised natural rubber

Isomerisation of natural rubber involves a change in the configuration of the backbone of the molecular structure. For instance, when natural rubber is heated with SO_2 or butadiene sulphone or thio benzoic acid at about 120°C to 140° C, transition of cis - structures to trans - ones occurs in the molecules of rubber. The extent of transition has been increasing with heating time until an equilibrium ratio of the cis and trans is attained.

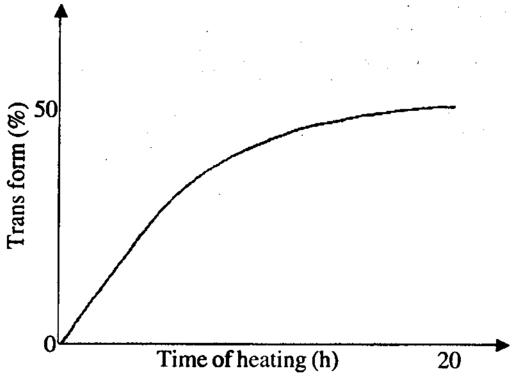


Fig. 3.2 Isomerisation of natural rubber with butadiene sulphone (3phr) at 140°C for 20 hours

As the change in the molecular configuration affects the strain induced crystallisation of NR, the strength of NR is reduced with increasing trans structures.

Applications of isomerised natural rubber

Isomerised NR can be blended with natural rubber to reduce the power consumption during processing and to inhibit the stiffening effect of the vulcanisates at sub - zero level temperatures.

Cylised natural rubber

When natural rubber is treated with acidic catalysts such as paratoluene sulphonic acid, conc. Sulphuric acid, and lewis acids, the material becomes hard and brittle. The treatment of acid can be performed in latex or in rubber solution or in masticated rubber. This is usually followed by heating up to 100° C to proceed the cyclisation reaction.

Cyclisation of natural rubber

Generalized reaction scheme :

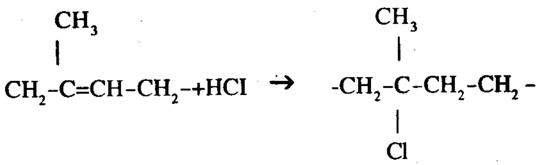
$$\begin{tikzcd} \text{Natural rubber} \arrow[d, "\text{Stage I}"', "H^{+}\text{ (from acids)}"] \\ \text{Monocyclic structures} \arrow[d, "\text{Stage II}"'] \\ \text{Polycyclic structures} \end{tikzcd}$$

The monocyclic structures do not affect the mobility of the adjacent macramolecular segments. The rubbery character is retained, at the initial stage of the reaction.

With the increase in degree of cyclisation, the monocyclic structures trnsform into polycylic ones which restrict the movements of molecular segments. As a result the product shows rigid plastic character. As degradation of rubber molecules also proceeds along with cyclisation, the molecular weight of cyclised rubber drops drastically to 3000 to 4000. The products with such molecular weight range are used in the production of chemically resistant coatings and quick drying printing inks.

Natural rubber hydrogen chloride

When Hydrogen chloride is passed into a solution of natural rubber, an addition reaction takes place. The reaction obeys Markownikov's rule in the absence of free-radical initiators, and follows ionic mechanism as shown below:



$$CH_2\text{-}\overset{\overset{CH_3}{|}}{C}{=}CH\text{-}CH_2\text{-}{+}HCl \rightarrow \text{-}CH_2\text{-}\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_2\text{-}CH_2\text{-}$$

The properties of the product (rubber hydrogen chloride) depend upon the degree of hydrochlorination. It has been found that the products containing above 30% of added chlorine are crystalline in nature,

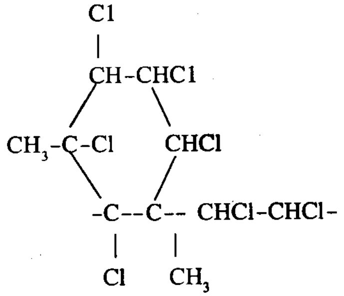
Applications :

i. It is used as a protective film to resist grease and vegetable oils.

ii. It also finds use for laminating papers and aluminium.

Chlorinated natural rubber

When gaseous chloride is passed into a solution of natural rubber in carbon tetra chloride, a series of cyclising seactions proceeds at room temperature or at a temperature not exceeding 80° C. The product is found to be thermoplastic and has the following structure:



Chlorinated natural rubber is a linear polymer with cyclised structural units. It softens at about 70° C and shows good tack property. It finds application in surface coating and adhesive compounds.

Powdered natural rubber

Powdered natural rubber can be prepared by one of the following methods:

i. By granulation of dusting powder loaded natural rubber. Here dusting powder acts as an antiagglomerating agent.

ii. By spray drying of dusting powder added natural rubber latex.

iii. By encapsulation of natural rubber particles with other polymeric materials. The typical polymeric materials which find applications are : a) starch xanthate, b) carboxy cellulose, c) alginates of polyvalent metals.

In comparision to conventional forms of rubbers, the powdered natural rubber has many advantages which include:

a. Elimination of rubber bale cutting or thawing operation before mixing process.

b. Lower power consumption and shorter mixing time.

c. Direct feeding of extruder and injection moulding machines.

d. Direct mixing of rubber with bitumen, especially for road surfacing applications.

Chapter 4

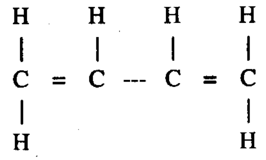
Synthetic Rubbers

4.1 Synthetic rubbers - structures

Commercially used synthetic rubbers are mainly carbon chain polymers which are produced either from diene monomers or from combinations of diene and olefin monomers. The names and molecular formulae/structures of the dienes and olefins as well as the rubbers derived from them are given below and in the table 4.1

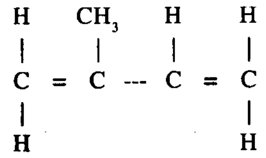
Dienes :

i. Butadiene



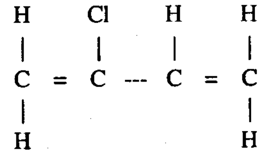
$H_2C = CH - CH = CH_2$

ii. Isoprene



$H_2C = C(CH_3) - CH = CH_2$

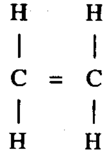
iii. Chloroprene



$H_2C = C(Cl) - CH = CH_2$

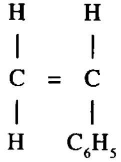
Olefins :

i. Ethylene



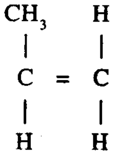
$\underset{H}{\overset{H}{C}} = \underset{H}{\overset{H}{C}}$

ii. Styrene



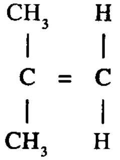
$\underset{H}{\overset{H}{C}} = \underset{C_6H_5}{\overset{H}{C}}$

iii. Propylene



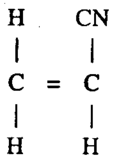
$\underset{H}{\overset{CH_3}{C}} = \underset{H}{\overset{H}{C}}$

v. Isobutylene



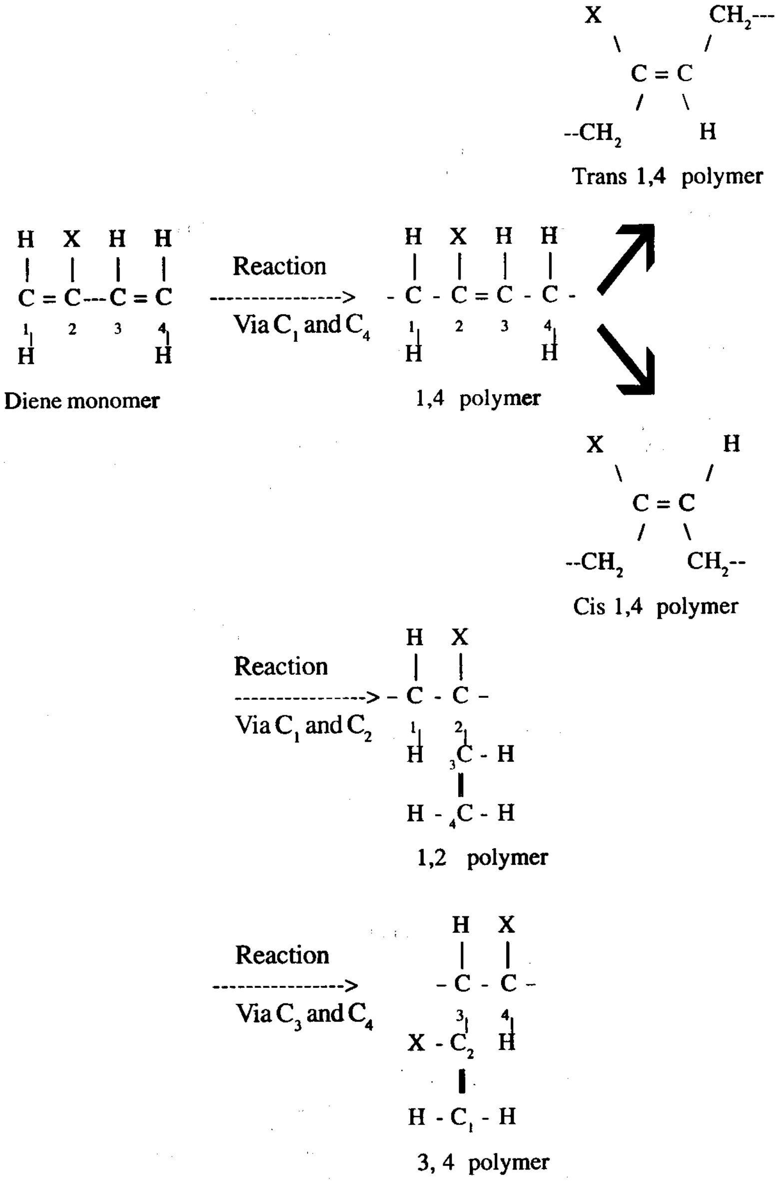
$\underset{CH_3}{\overset{CH_3}{C}} = \underset{H}{\overset{H}{C}}$

v. Acrylonitrile

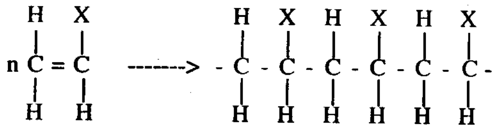


$\underset{H}{\overset{H}{C}} = \underset{H}{\overset{CN}{C}}$

During polymerisation, the diene monomers generally undergo reactions in three possible ways forming polymer molecules with unsaturated double bonds at different positions in the molecular structures.



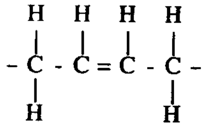
In the case of polymerisation of an olefin monomer, due to the presence of double bond in the monomer, the above types of unsaturated polymer molecules are not formed and only saturated polymer molecules are produced as illustrated below :



$$n\,\overset{H}{\underset{H}{C}}=\overset{X}{\underset{H}{C}} \dashrightarrow -\overset{H}{\underset{H}{C}}-\overset{X}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{X}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{X}{\underset{H}{C}}-$$

Table 4.1 Commercially used synthetic rubbers and their molecular structures

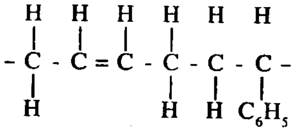
1. Butadiene rubber (BR)



$$-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-$$

	Low cis - BR	High cis - BR
Cis 1, 4 (%)	45	96.5
Trans 1,4 (%)	46	1.9
1,2 Structure (%)	9	1.6

2. Styrene butadiene rubber (SBR)

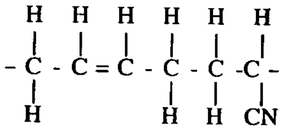


$$-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{C_6H_5}{C}}-$$

	Cold SBR	Hot SBR
Cis 1, 4 (%)	10	14
Trans 1,4 (%)	69	63
1,2 Structure (%)	21	23

Butadiene $\simeq$ 77%
Styrene $\simeq$ 23%

3. Acrylonitrile butadiene (NBR)

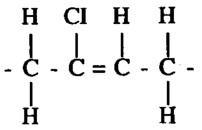


$$-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CN}{C}}-$$

	Low nitrile	High nitrile
Butadiene (%)	85	50
Nitrile (%)	15	50

microstructures of butadiene as given in SBR

4. Chloroprene rubber (CR)

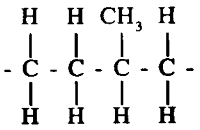


$$-\overset{H}{\underset{H}{C}}-\overset{Cl}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-$$

Cis 1, 4 (%)	13--0
Trans 1,4 (%)	85--98
1,2 Structure (%)	1.5
3,4 Structure (%)	1.0

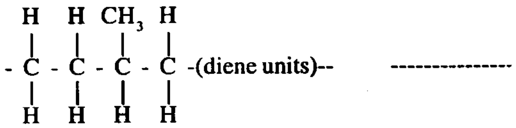
5. Ethylene propylene rubber (EPR, EPM)

Ethylene $\simeq$ 50%
Propylene $\simeq$ 50%



$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$$

6. Ethylene propylene diene monomer rubber (EPDM, EPT)

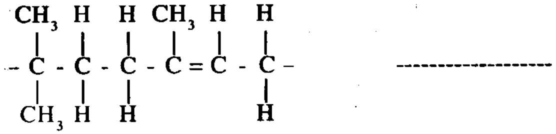


$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}\text{-(diene units)--}\quad\text{--------------}$$

Ethylene + Propylene = 98%

Diene units = 2%

7. Butyl rubber (II R)

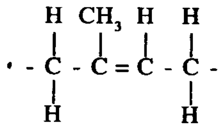


$$-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-\quad\text{------------------}$$

Isobutylene $\simeq$ 97 to 99%

Isoprene $\simeq$ 1 to 3%

8. Isoprene rubber (IR)



$$- \overset{H}{\underset{H}{C}} - \overset{CH_3}{C} = \overset{H}{C} - \overset{H}{\underset{H}{C}} -$$

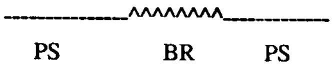
High Cis - BR

	Prepared with Ziegler - Natta catalysts	Prepared with lithium catalysts
Cis 1, 4 (%)	96	92
Trans 1,4 (%) + 3,4 Structure (%)	4	8

9. Styrene - Butadiene - Styrene block rubber (thermoplastic rubber)

Butadiene units ~ 75%

Styrene block units ~ 25%



4.2 Synthetic rubbers - production, properties and applications

Styrene butadiene rubber (SBR)

Generally two types of styrene butadiene rubber are produced for common applications. Cold SBR, the first type is made by emulsion polymerisation at low temperature (ca. 5°C) and the other type called hot SBR is also polymerised by the same method, but at hot temperature, around 50°C. A typical recipe for each type of polymerisation is given below (see table 4.2 and table 4.3). The flow line diagrams illustrating the stages of SBR production are given in Figs. 4.1 and 4.2.

These rubbers contain about 23% styrene units which are randomly dispersed with about 77% butadiene units. The butadiene generally comprises about 65% trans, 15% cis & 20% vinyl contents. Hot SBR has wide molecular weight distribution where as cold SBR has narrow MWD. Cold SBR, as a result, has better strength properties than hot SBR and can be extended easily with petroleum oils. The cold rubber has also been found to be more suitable for the preparation of carbon black master batches and tyre tread compounds. Hot SBR on the other hand can be processed more easily than cold SBR (see table 4.4)

General properties of SBR

SBR can be regarded as a general purpose replacement for NR in many applications, Unlike NR, it has poor physical properties in gum stocks, where no reinforcing fillers are used. It does not crystallize on stretching. This means that the molecules do not tend to align themselves in the direction of the extension and the rubber tensile strength is low. SBR is less resilient than NR. It requires longer cure time due to its lower level of unsaturation, unless it contains a higher level of accelerator. However it offers a number of advantages in mixing and processing. If suitably compounded SBR has superior ageing and tread wear properties. Hence it is extensively used in passenger car tyres. For heavy duty tyres it is not suitable because of its inferior dynamic properties.

Table 4.2 A typical receipe for cold emulsion SBR polymerisation at 5°C

	Parts by weight	Function
butadiene	72	monomer
styrene	28	monomer
di-isopropyl benzene hydroperoxide	0.08	initiator
ferrous sulphate	0.14	activator of initiator
n-dodecylmercaptan	0.2	modifier (to limit mol.wt)
potassium pyrophosphate	0.18	buffer
rosin acid soap	4.0	emulsifier
water	180	

Table 4. 3 A typical receipe for hot emulsion SBR polymerisation at 50°C

	Parts by weight	Function
butadiene	75	monomer
styrene	25	monomer
potassium peroxydisulphate	0.3	initiator
n-dodecylmercaptan	0.5	modifier
rosin acid soap	5	emulsifier
water	180	–

All solutions cooled prior to entering reactor

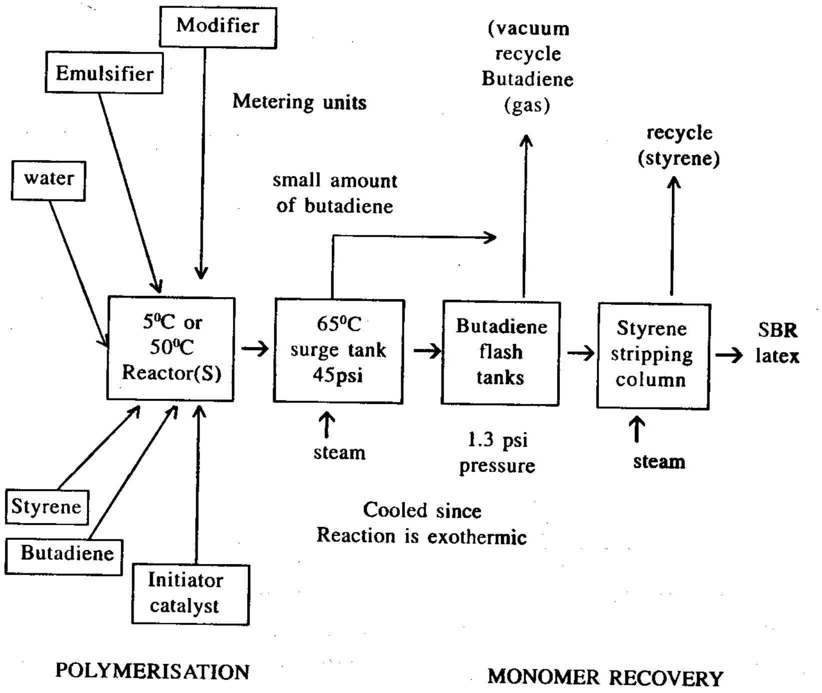


Fig. 4. 1 Production of SBR latex (stage I)

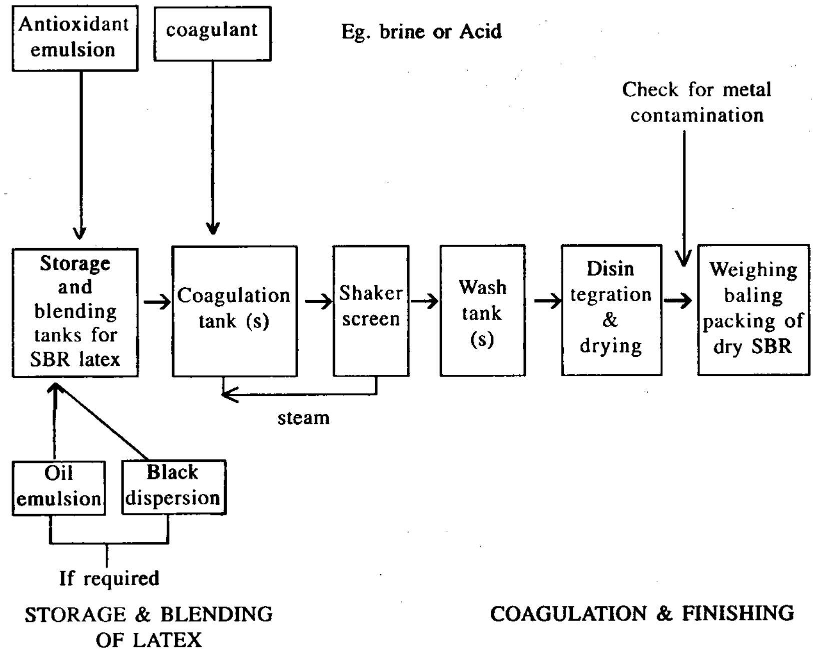


Fig. 4. 2 Production of dry SBR from SBR latex (stage II)

Table 4.4 Differences in molecular features of cold, hot and oil - extended styrene butadiene rubbers

Emulsion	Microstructure of butadiene					
polymerisation temperature	trans 1,4	Cis 1,4	Vinyl 1,2	Mol.wt	M.W.D.	Oil %
50°C (Hot SBR)	62	14	24	3×10^5	10.15	
5°C (cold SBR)	72	7	21	4×10^5	2.55	
5°C (cold oil extended SBR)	72	12	16	7.5×10^5	7.5	27

Solution polymerised styrene butadiene rubbers

The rubbers produced by solution polymerisation have their butadiene units with lower trans, higher cis and slightly lower vinyl, contents than their emulsion counter parts. Both random and block copolymers are made in the process. The random type has narrower MWD, than the block type polymer.

i. **Structure of Random Type Solution Polymerised SBR**

- SBBBSSSSBBBSSSBBS - where S is styrene unit
and B is butadiene unit

ii. **Structure of Block Type SBR**

- SSSSSSSSBBBBBBBBBBSSSSSSS - where S is styrene unit
and B is butadiene unit
(see Fig. 4.3)

Properties of solution polymerised styrene butadiene rubber

The random type solution SBR has higher cis content and narrower MWD than emulsion polymerised SBR and shows better resilience character. It also has higher degree of polymer purity and less water absorption properties. It is processed like emulsion SBR and cured with sulphur vulcanizing systems.

In the block type SBR, the styrene units are said to be like domains in the matrices of butadiene chains. The structural features of the molecules appear as a cross-linked molecular structure and the rubber does not need curing systems to make its products. It is a thermoplastic rubber and shows less nerve and improved extrusion and calendering characteristics. The rubber finds applications in adhesive compounds, foot wear - shoe soles, floor tiles, e. t. c.

Butadiene rubber (BR)

BR is a homopolymer of butadiene prepared by emulsion and solution polymerisation methods. Rubbers with high cis contents are prepared by solution method using Ziegler Natta catalysts and these rubbers show high resilience and low hysteresis, improved tread wear and reduced groove

cracking. As the wet - traction property is inferior, it is not used as the sole rubber, but finds application in blends with NR and SBR for automotive tyre treads.

Isoprene rubber (IR)

IR is polymerized by using Zeigler Natta catalysts. Both high - cis content rubber and high trans content rubbers are produced. The high cis rubber is comparable to NR whereas the high-trans content is similar to gutta percha, balata. The more popular grades have cis - contents in excess of 95%. An antioxidant is incorporated in IR to assist its storage as with other synthetic rubbers.

The IR with high cis content can crystallize like NR and yield high tensile strength and exhibits self reinforcement at high elongation in combination with low hysteresis. Heat build up of which is even lower than that of NR. This is an advantageous property for truck tyres.

In non - tyre applications the light colour, excellent flow characteristics and low ash content of IR are distinct advantages. Such applications include hot - water bottles, bathing caps and moulding even in the injection machine used for thermoplastics.

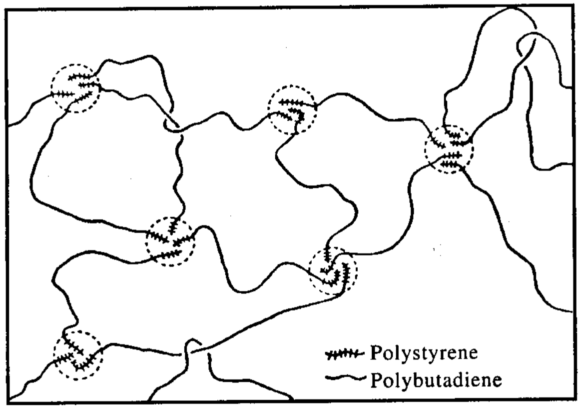


Fig. 4. 3 Structural features of block SBR (Solution polymerised)

Butyl rubber (IIR)

Butyl rubber is produced by copolymerising isobutylene with small amount of isoprene about 1.5 to 4.5%, to add the unsaturation necessary for vulcanization. The polymerization reaction of IIR takes place at extremely low temperatures (ca-100^{0}C) and as the reaction is exothermic, continuous cooling must be applied. The reaction is catalysed with anhydrous aluminium chloride and carried out in an inert diluent methyl chloride.

The two factors which govern most of the commercial grades are viscosity related to the molecular weight and the degree of unsaturation controlled by the amount of isoprene. Due to the low degree of unsaturation IIR is very slow curing but has excellent resistance to a wide range of chemicals including ozone. Other important features are low gas and moisture permeability, heat resistance, electrical insulation properties and high shock absorption. Uses of IIR include shock absorbers, dock - fenders, chemical resistant hose and plant linings, electrical insulation, membranes of all types, inner tubes.

Ethylene propylene rubber (EPR)

Ethylene propylene rubber is a saturated copolymer of ethylene and propylene units. It is polymerised in solution with Ziegler - Natta type catalysts such as vanadium oxychloride and alkyl aluminium.

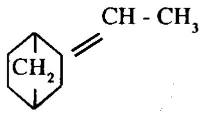
To obtain good elastomeric properties, the monomers ethylene and propylene are made to arrange randomly in the ratios from 50:50 to 65 : 35. The rubbers thus obtained are amorphous and stereo regular. They are cross - linked with organic peroxides and the pure gum products show low tensile strength. Unlike butyl rubber, EPR, is highly resilient like NR. The rubber possesses excellent resistance to O_2, O_3 and ionization effects.

Ethylene propylene diene terpolymer (EPDM)

EPDM rubber contains ethylene, propylene and a non - conjugated diene. The diene monomer concentration is about 3% of the rubber and the use of conjugated diene type allows the rubber to be cross - linked with sulphur curing systems, at the side - chains of the carbon - carbon backbone of the rubber molecules. As there are no unsaturation in the main

chain rubber molecules the physical properties and applications of EPDM rubbers are almost same as that of saturated EPM rubbers.

An example of conjugated diene monomer is norbornene.



Acrylonitrile butadiene rubber (NBR)

Rubbers produced from copolymerising butadiene and acrylonitrile are commonly referred to as nitrile rubbers. The rubbers contain between 15 - 40 percent of acrylonitrile. Nitrile rubbers may be prepared by either hot or cold emulsion polymerisation like the method used for SBR.

The most significant property of these rubbers is their excellent oil resistance and aromatic solvent resistance which is governed to a large extent by the polar acrylonitrile content. The higher this value, the better the oil resistance. The rubbers also exhibit excellent abrasion resistance and compression - set characteristics. However the elastic property and low temperature flexibility are reduced with increase in content of acrylonitrile.

The use of nitrile rubbers as oil seals is extensive while other applications include flexible fuel tanks, oil - resistant hoses and printing rollers. Because of the polar nature of these rubbers, they are also blended with plastic materials e.g. PVC and Phenolic resins in some applications.

The main advantages which can be obtained by the PVC/NBR blends are resistance to ozone and weathering, better gloss of extrudates and mouldings, bright colours, higher abrasion and oil resistance and flame resistance if suitable plasticizers are used.

Carboxyl modification greatly increases the abrasion resistance and hardness and the rubber resembles almost like polyurethane rubbers in its toughness.

Chloroprene rubber (CR)

Chloroprene rubber is an emulsion polymer, polymerized at 40^0 - 50^0C using persulphate as initiator. The chloroprene monomer units mostly polymerise in the 1:4 position but there is occasional 1 : 2 addition. The typical chloroprene rubber grade have a molecular structure comprising 88 - 92% trans - 1, 4 contents, 7 - 12% cis - 1, 4 content, 1.5% 1, 2 addition and 1% 3, 4 addition. The degree of crystallization of CR is largely dependent on the amount of the trans - configuration in the molecules.

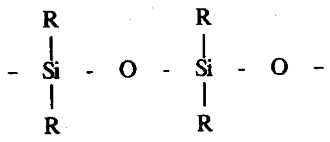
Chloroprene rubber possesses many of the excellent physical characteristics of natural rubber such as strength and resilience. In addition to these, the rubber is resistant to oils, greases and paraffinic solvents owing to the presence of polar electro negative chlorine atom in its molecular structure. It is also stable towards sunlight and the oxidizing effect of ozone and heat ageing. Chloroprene rubber also possesses outstanding abrasion resistance and other advantageous properties which include flame and chemical resistance. Chloroprene rubber is widely used as a gasketing material in the aircraft and automobile industries. Whether used in tension, compression or shear, the rubber displays less deformation under load and is therefore ideally suitable for use as packing, engine or building mounts. The rubber also finds applications as covers for conveyer belts and petroleum delivery hoses. In the field of synthetic adhesives and rubber cements, it is mainly used as a base material.

Chlorosulphonated polyethylene rubber (CSM. Hypalon)

The chlorosulphonated polyethylene rubber is produced by treating the solution of polyethylene with chlorine and sulphur - di - oxide. The chlorine content of the molecular structure varies in different grades of the rubber from 26 to 43%. As the rubber molecule is saturated, sulphur vulcanising system is not used. But a combination of metal oxides e. g. Mgo/Pbo is chosen to cure the rubber. The rubber has excellent chemical resistance, ozone resistance, colour stability and good heat and abrasion resistance. Applications of the rubber include - electrical insulation sheathing, hose for hot or cold corrosive chemicals, coatings of fabrics.

Silicone rubber (SR)

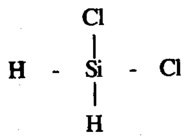
Silicone rubbers differ from the organic rubbers because they do not have a carbon backbone. The rubbers are chemically polysiloxanes of the general formula.



$$-\mathop{Si}\limits_{R}^{R}-O-\mathop{Si}\limits_{R}^{R}-O-$$

Where R is methyl, phenyl, vinyl or trifluoropropyl.

They are manufactured by the following steps :



$$H-\mathop{Si}\limits_{H}^{Cl}-Cl$$

i. Hydrolysis of the appropriate dichlorosilanes to form cyclic tetrasiloxanes. and

ii. Conversion of cyclotetrasiloxanes to long chains siloxanes, in the presence of suitable catalysts.

Silicone rubbers available in the form of solids are processed by the conventional methods of the rubber industry. The rubbers are also obtainable as liquid materials. and are room temperature vulcanizing. These can be used for sealants, encapsulants, adhesives etc.

The rubbers are serviceable from 100^0C to 300^0C and have outstanding resistance to heat, oxidation, oils and chemicals. They have only modest physical properties at room temperature but maintain strength and resilience at the temperature extremes where other rubbers fail. Applications taking advantage of the properties of silicone rubber are in many fields, such as in (i) air space (ii) electrical (iii) medical e.t.c. In the medical field, the rubbers find applications especially in surgical uses because they are physiologically inert, odourless tasteless and non - toxic.

Polyacrylic rubbers (ACM)

Polyacrylic rubbers are generally based on butylacrylate or ethyl acrylate or on both acrylates. A minor proportion of second monomer like 2 - chlorovinyl ether is also incorporated in the polymerizing system.

$CH_2 = CH\text{-}COOC_2H_5$	$CH_2 = CH - COOC_3H_7$	$CH_2 = CH - O - CH_2 - CH_2 - Cl$
Ethyl acrylate	Butylacrylate	2 - chloroethylvinylether

The properties of rubbers vary with the type of acrylate and the type of comonomer, but the overall properties of them include excellent heat and oil resistance. The oil resistance is similar to that of a medium acrylonitrile rubber but the heat resistance is similar to that of a medium acrylonitrile rubber but the heat resistance in both air and oil is extended up to 180°C. Unlike NBR, the ozone resistance is good, because of the saturated backbone of the molecules. The combination of heat and oil resistance of the acrylic polymers has been put to good use in a number of automotive seals.

Polyurethane rubbers (PU)

Polyurethane rubbers may be divided into two broad classes of liquid casting types and millable types. Thus, rubber products with different degrees of hardness can be easily produced. The rubbers are obtained from the reactions of liquid polyols and diisocyanates. Their molecular units are, therefore composed of polyethers and polyesters with terminal hydroxyl groups linked by diisocyanates. In some applications, the liquid components are cast and then polymerized. In others a prepolymer is used. There is also a number of more conventional types which are processed in the same way as other normal rubbers.

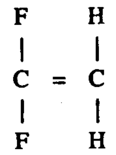
The main features of the polyurethane rubbers are excellent abrasion resistance at moderate temperatures, high tensile and tear strength and excellent oil and solvent resistance.

The usage of polyurethanes rubbers range from soft printing rollers to hard industrial wheels. They also find applications as soles and heels, in elastic thread and in foam. In these products they compete very strongly with conventional rubbers.

Fluorocarbon rubbers (FKM, CFM)

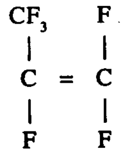
The monomers chosen for the preparation of fluorocarbon rubbers are :

i. Vinylidene fluoride



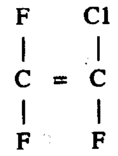
$$F_2C = CH_2$$

ii. Hexa fluoropropylene



$$(CF_3)FC = CF_2$$

iii. Chlorotrifluoroethylene



$$F_2C = CFCl$$

The copolymers of vinylidene fluoride and hexafluoropropylene are designated as FKM rubbers and copolymers of vinylidene fluoride and chlorotrifluroethylene as CFM rubbers.

The rubbers are of particular interest due to their stability to most lubricant and hydraulic fluids used in the air - craft industry. They also exhibit a high degree of resistance to ozone which to the aircraft industry is extremely important. It is serviceable even at high temperatures around 200°C.

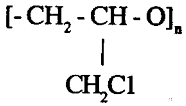
Polysulphide rubbers (Thiokol)

These rubbers are produced by condensing a dichlorocompound with sodium polysulphide.

Thiokol has outstanding resistance to ketones, ethers and most aliphatic and aromatic solvents except the more active chlorinated solvents such as ethylenedi - chloride. It is thus considered as a better elastomer than NBR for solvent resistance. The rubber is serviceable from - 45° to 120°C. As the rubber has excellent weather resistance, it finds extensive use in putties that will not harden, shrink or crack on prolonged exposure. Other applications include gaskets, solvent hose, cements, printing rolls.

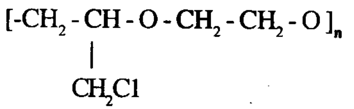
Epichlorohyrin rubbers

There are two types of epichlorohydrin rubbers currently produced. The first type is a homopolymer and the other is a copolymer of epichlorohydrin and ethylene oxide.



$[-CH_2-\underset{\underset{CH_2Cl}{|}}{CH}-O]_n$

homopolymer



$[-CH_2-\underset{\underset{CH_2Cl}{|}}{CH}-O-CH_2-CH_2-O]_n$

copolymer

Homo polymer possesses outstanding resistance to ozone and good resistance to swelling by oils. It has also good heat resistance, excellent weather resistance. Its low permeability to gases is also good but somewhat less than that of butyl rubber.

Chapter 5

Rubber Compounding Ingredients and Reinforcing Textiles

5.1 Principles of compounding

Raw natural rubber alone, is not used for the production of useful articles for the following reasons.

i. It is tough and cannot be shaped easily in the form of article
ii. Its strength is weak
iii. It softens at low temperature (ca. 70°C)
iv. It undergoes molecular degradation in air, easily.

Thus, to make useful articles, raw natural rubber as well as similar synthetic rubbers are generally incorporated with other substances, called compounding ingredients. These ingredients can be classified on the basis of their functions in rubbers, as given below :

Compounding ingredients	Functions in rubbers
i. Chemical plasticizers	To increase the level of plasticity of rubber in short time during mastication process.
ii. Vulcanising (Curing) systems	To form cross - links among rubber molecules and thereby to increase the strength and elastic properties of rubber.

iii. Fillers	To improve the resistance of rubber to any type of deformation.
iv. Softeners	To aid filler incorporation into rubber and to facilitate processing of rubber.
v. Antidegradants	To prolong the service life of rubber.

Besides the above groups, some auxillary ingredients are also added into rubbers for special reasons. For examples :

i. Blowing agents - To produce cellular rubber products.
ii. Deodourants - To obtain pleasant odour in rubber products.
iii. Pigments / Dyes - To produce coloured products
iv. Flame retardants - To prevent spreading of flame when rubber catches fire.
v. Antistatic agents - To dissipate static charges accumulated on rubber surface due to any friction.

5.2 Chemical plasticizer

An alternative name of chemical plasticizer is peptizer. The chemical is incorporated especially in natural rubber to reduce the time of breakdown of its long molecules and thereby to impart required level of plasticity for processing. It is not required in synthetic rubbers, because the desired levels of plasticity in the rubbers are obtained during their manufacture.

During milling or mastication of natural rubber, the plasticizer added either accepts the free-radical chains formed in the process or catalyzes the oxidation reactions of free - radical chains or does both actions, as illustrated below:

i. Mastication of natural rubber in air

$$\text{NR molecules} \xrightarrow{\text{milling}} \text{free - radical chains} \xrightarrow[(O_2)]{\text{air}} \text{stablised broken units (slow reaction)}$$

ii. Mastication of natural rubber with peptizer in air

$$\text{NR molecules} \xrightarrow{\text{Milling}} \text{free - radical Chains} \xrightarrow{\text{air}(O_2)} \underset{\substack{(PX)\\ \downarrow \\ (P. + .X)}}{\text{Peptizer}} \xrightarrow{} \text{stablised broken units (fast reaction)}$$

Note : The action of peptizer is inhibited if sulphur is added.

Typical Examples of peptizers

Xylyl mercaptain
Thio- β-Naphthol
Pentachlorothiophenol
Di-o-benzamido diphenyl disulphide

5.3 Vulcanising systems

Vulcanising systems which are also known as chemical cross - linking systems or curing systems are very important in rubbers. They cross - link the rubber molecules and thereby enhance the mechanical strength and elastic property of rubbers. They also reduce the sensitivity of the rubber to changes of temperature. The vulcanising systems can be classified in to:

i. Sulphur vulcanising system
ii. Sulphur donor vulcanising system
iii. Non-sulphur vulcanising system

Monitoring the vulcanisation process

The following parameters are of technical importance, in the course of vulcanisation.

i. the time elapsed before the onset of vulcanization (delayed time)
ii. the rate at which the vulcanisation occurs (cure rate)
iii. the extent of vulcanisation (cross - linking)

These parameters can be determined from the changes of one of the following physical properties of rubber during vulcanisation (see Fig. 5.1)

i. Plasticity
ii. Shear modulus
iii. Tensile modulus
iv. Elongation at break

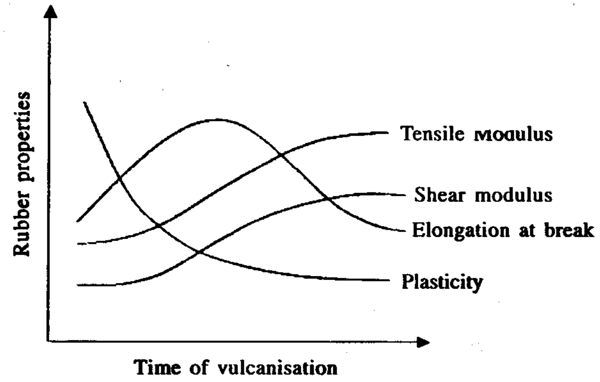


Fig. 5. 1 Changes of rubber properties with time of vulcanisation

Of all these properties the shear modulus of rubber is commonly considered to monitor the vulcanisation process because the property can be continuously measured in a testing equipment much more easily than other properties. The Fig. 5.2 illustrates a typical cure curve obtained by measuring shear modulus at various times of curing.

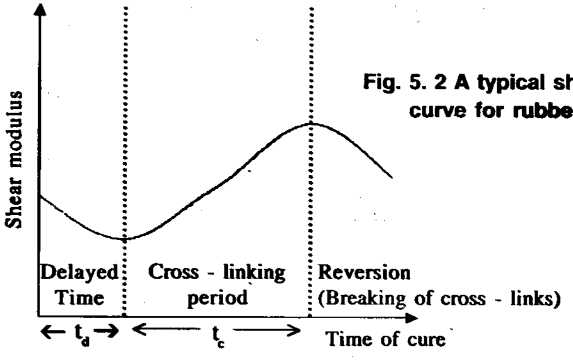


Fig. 5. 2 A typical shear modulus - time curve for rubber vulcanisation

Sulphur vulcanising system

The vulcanisation of natural rubber with elemental sulphur was discovered by Charles Good Year (U.S.A.) and Thomas Hancock (U. K.) in mid eighteenth century. In their work, vulcanisation was carried out by heating natural rubber with sulphur alone.

NR (100 parts by weight) + S (8 parts by weight) $\xrightarrow[8\ hrs]{140^0\ C}$ vulcanised rubber

Many shortcomings were experienced in the process, such as :

i. Long reaction time (8 hrs)
ii. Sulphur blooming on the vulcanised rubber
iii. Large amount of heat generation

To overcome these problems, chemical substances named activators (metal oxides and fatty acids) and accelerators (mainly aniline and amine derivatives) are being used with sulphur today. The addition of these substances with sulphur gives many advantages to the vulcanisation process, which include :

i. Reduced time of vulcanisation (the time of reaction is reduced to minutes rather than hours)
ii. Vulcanization reaction can be easily controlled to suit the moulding process.
iii. Less amount of sulphur is needed.
iv. Products have good surface finish, without showing any sulphur bloom.

Sulphur

Sulphur is a yellow solid and it exists as S_8 ring molecules. Ordinary sulphur is available as flowers of sulphur or cylindrical sticks (roll sulphur). At ordinary temperature it is in octahedral crystalline form and is called rhombic sulphur. The particle size of the sulphur powder ranges from 50 to 500 μm. Its solubility in rubbers is rather low at ordinary temperature but increases with rise in temperature (see table 5.1)

Table 5. 1 Solubility of rhombic sulphur in NR

Temperature	IN NR
25°C	0.7
50°C	3.2
75°C	4.8

Sulphur is not readily soluble because its particles tend to form aggregates in rubbers. Petroleum oil can help to improve its dispersion.

Instead of rhombic sulphur. There are also other types of sulphur which find use in rubber compounds for some additional benefits.

Coated sulphur

This is a modified form of sulphur. The particles of which are coated with about 2.5% magnesium carbonate. The coating reduces the tendency of agglomeration of the particles and helps to produce good dispersion in rubber. For fine dispersion of sulphur in nitrile and butyl rubbers, this type of sulphur is needed.

Insoluble sulphur

This grade of sulphur is an allotropic form of rhombic sulphur. It is prepared by chilling molten sulphur in water. As the name implies, the sulphur insoluble in rubber and solvent carbon - di sulphide, at ambient temperature. It remains in the rubber mix and does not migrate to the surface of rubber. The sulphur is useful in rubber mixes, which have to be stored for considerable time in the uncured state.

Examples of such rubber mixes are :

Tyre tread rubber mix (camel back compound)
Tube - repair gum mix
Tank lining mix sheet etc.

However the insoluble sulphur changes into ordinary rhombic sulphur when temperature is raised to about 105°C.

Colloidal sulphur

This kind of sulphur is obtained by grinding ordinary sulphur in a colloid mill or precipitating from colloidal sulphur solution. It is generally needed in latex compounds.

Activators and accelerators

In order to produce the full effect in sulphur vulcanisation, activators and accelerators are very essential. The activators such as zinc oxide and stearic acid are mostly used. They first combine at the onset of vulcanisation reaction to form an active chemical complex with accelerator and then react with sulphur leading to rubber reactive sulphurating agent. The Fig. 5.3 illustrates the generalised mechanism of sulphur vulcanisation.

Functions of accelerators

i. Increase the rate of sulphur combination with rubber
ii. Increase the efficiency of sulphur utilization in the cross - links.
iii. Control - the vulcanisation process to suit different conditions.
iv. Enhance the physical properties and resistance of rubber to aging.

Most of the accelerators used today are amine or aniline derivatives, which are modified to eliminate the toxicity problem to improve factory handling and to widen the range of cure characteristics.

Accelerators and their effects in natural rubber compounds

Guanidines	- medium - vulcanisates have excellent flex - properties - poor heat age resistance - stain coloured rubber articles - very useful boosters for the thiazole type accelerators
Thiazoles	- medium fast cure rates , - good resistance to scorch - flat cure

- very good age resistance
- good colour
- low modulus rubber
- can be boosted with thiuram, guanidines or dithiocarbamates

Zinc mercaptobenzothiazole

- medium fast cure rate
- used in latex compounds, in combination with ZDC to impart high modulus and low set.

Sulphenamides

- long delayed action
- outstanding resistance to scorch
- medium fast cure rate
- flat cure
- good age resistance
- reasonably good colour

Thiurams

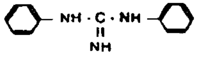
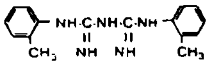
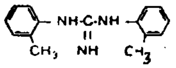
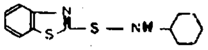
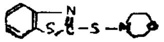
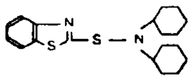
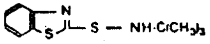
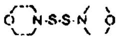
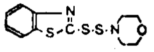
- fast cure rate
- rather peaky cure
- scorchy
- excellent colour
- good age resistance
- some of them can cure rubber without sulphur (eg. TMTD)

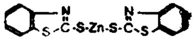
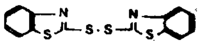
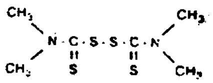
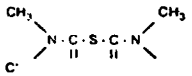
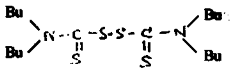
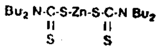
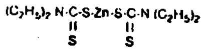
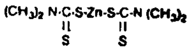
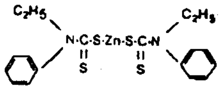
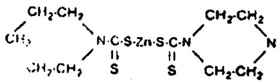
Carbamates

- very fast cure rate
- very scorchy
- peaky cure
- excellent colour
- excellent age resistance
- widely used in latex

The structures of common accelerators used in sulphur vulcanisation are given in table 5.2

Table 5.1 Chemical structure of common acclerators

Chemical name	Structure	Abbreviation
Guanidine Derivatives		
Diphenylguanidine		DPG
o - Tolyl biguanidine		OTBG
Di-o-tolylguanidine		DOTG
Sulphenamides		
N-Cyclohexyl -2- benzothiazole sulphenamide		CBS
4. morpholinothio - 2 -benzothiazole		MBS
N. Dicyclohexyl 2 - benzothiazolesulphenamide		DCBS
N-tert-butyl - 2- benzothiazole sulphenamide		TBBS
Sulphur Donors		
4.4. Dithiodimorpholine		DTDM
4 - Morpholiny 2 - benzothiazole disulphide		MBDS

Chemical name	Structure	Abbreviation
Thiazoles		
2 -Mercaptobenzothiazole		MBT
Zinc 2 - mercaptobenzothiazole		ZMBT
Dibenzothiazyl disulphide		MBTS
Thiurams		
Tetramethylthiuram disulphide		TMTD
Tetramethylthiuram monosulphide		TMTM
Tetrabutylthiuram disulphide		TBTD
Dithiocarbamates		
Zinc dibutyldithiocarbamate	 $Bu_2N\text{-}\underset{\underset{S}{\|}}{C}\text{-}S\text{-}Zn\text{-}S\text{-}\underset{\underset{S}{\|}}{C}\text{-}NBu_2$	ZDBC
Zinc diethyldithiocarbamate	 $(C_2H_5)_2N\text{-}\underset{\underset{S}{\|}}{C}\text{-}S\text{-}Zn\text{-}S\text{-}\underset{\underset{S}{\|}}{C}\text{-}N(C_2H_5)_2$	ZDEC
Zinc dimethyldithiocarbamate	 $(CH_3)_2N\text{-}\underset{\underset{S}{\|}}{C}\text{-}S\text{-}Zn\text{-}S\text{-}\underset{\underset{S}{\|}}{C}\text{-}N(CH_3)_2$	ZDMC
Zinc ethylphenyldithiocarbamate		ZEPC
Zinc pentamethylene dithiocarbamate		ZPMC

Structure of accelerated sulphur vulcanisate

The sulphur atoms forming the cross - links among the molecules of a rubber vulcanisate, generally exist as a. monosulphide b. disulphide and c. polysulphide. Chemical structures of these sulphides are represented by the following :

a. Monosulphide ----C---- rubber molecule I
|
S
|
----C---- rubber molecule II

The cross - link of this type is formed only with C-S bonds, the bond energy of which is about 270 kJ.

b. Disulphide ----C---- rubber molecule I
|
S
|
S
|
----C---- rubber molecule II

The bonds which are present in this type of cross - link are C-S and S-S. The latter bond is weaker and has bond energy about 200 kJ.

c. Polysulphide ----C---- rubber molecule I
|
Sx where $2 \leq x \leq 7$
|
----C---- rubber molecule II

The cross - linking bonds in this case are same as that of disulphide type.

It has been found that the proportion of each type of cross - link, can be altered by varying the ratio of sulphur to accelerator in vulcanizing system as illustrated in the table 5.2

Table 5. 3 Effect of sulphur to accelerator ratio on nature of cross - links

Vulcanizing system	Amount - ratio of sulphur to Accelerator	Nature of Cross - links
Conventional vulcanizing system	Greater than 1 (sulphur = 2 to 4 phr accelerator = 1 to 0.5 phr)	Predominantly Polysulphidic type
Efficient vulcanizing system (EV - system)	Less than 1 (sulphur = 0.4 to 0.8 phr accelerator = 3 to 0.5 phr)	Predominantly monosulphidic type
Semi - efficient vulcanizing system (semi EV system)	Approches 1 (sulphur = 1 to 1.5 phr accelerator = 1.5 to 1.0 phr)	More or less equal proportion of monosulphidic and Polysulphidic type

It is claimed that polysulphidic cross - links in excess, improve the tensile strength, flexibility and low temperature crystallization resistance. However the cross - links are found to be less stable to heat.

Properties dependent only on degree of cross - linking

Properties	Increase in number of cross - links
Stiffness (Modulus)	Increases
Hardness	Increases
Resilience	Increases
Elongation at break	Decreases
Creep and stress realization	Decreases
Set	Decreases
Low temperature crystallisation	Decreases in rate
Tensile strength/Tear resistance	Increases to maximum and then decreases
Solvent swelling	Decreases
Abrasion resistance	Decreases

Soluble EV system

For applications requiring the lowest possible creep rate coupled with good heat resistance and high precision of stiffness, soluble EV systems are recommended to NR. The principle of soluble EV systems is that the accelerators, activators and sulphur are completely dissolved in the rubber giving a truly homogeneous compound. In practice to achieve this, fairly highly soluble accelerators and activators at room temperature are selected. Zinc oxide is added in the usual amount of about 3.5 to 5 phr and sulphur up to 0.8 phr. Sulphur will remain dissolved with no tendency to bloom.

Examples of
a. Soluble accelerators - DPG, TBTD and
b. Soluble activators - Zinc salts of 2 - ethyl hexanoic acid and naphthenic acid

The advantages of soluble EV - system over other vulcanising systems are as follows :

i. Very low creep, especially with deproteinised natural rubber (see chapter 9)
ii. Good dynamic properties
iii. High precision of modulus
iv. Better fatigue resistance

Sulphur donor vulcanising system

The system does not contain elemental sulphur, but is composed of sulphurdonor accelerator and activators - ZnO and stearic acid. The accelerators TMTD and MBDS are usually employed as sulphur donors. The vulcanisates produced have mostly monosulphidic cross - links and show good resistance to heat and ageing.

Cold temperature curing with sulphur monochloride

Sulphur monochloride solution prepared with carbondisulphide solvent is also used as a sulphur donor system for curing thin sheets of rubber at low temperature. The rubber sheets can be dipped into the solution or exposed to the vapor of the solution. The HCl which is generally formed as a by - product in the reaction has to be neutralized by treating the rubber vulcanisates with ammonia solution.

Retarders

Retarders are added to encounter scorch problems. They give long processing safety to avoid premature cure in factory process. The chemicals are added in amount about 0.5 to 2.5 phr. Examples of retarder :

Phthalic anhydride

Nitroso diphenyl amine

Salicylic acid

Disadvantages of retarders

They can have side effects such as slow rate of curing and can modify the modulus property of rubber.

Prevulcanisation inhibitor (PVI)

To overcome the problems associated with the existing retarders this chemical is developed. e.g. N-cyclohexyl thiophthalimide (CTP). The chemical increases processing safety by an amount directly proportional to the quantity added with minimal effects on curing properties and performance characteristics. Normally, in the range of 0.1 to 0.5 phr, it is used.

Advantages of using prevulcanisation inhibitor

i. Improved mixing efficiency

ii. Improved storage stability of mixed compound

iii. Reduction of cure times

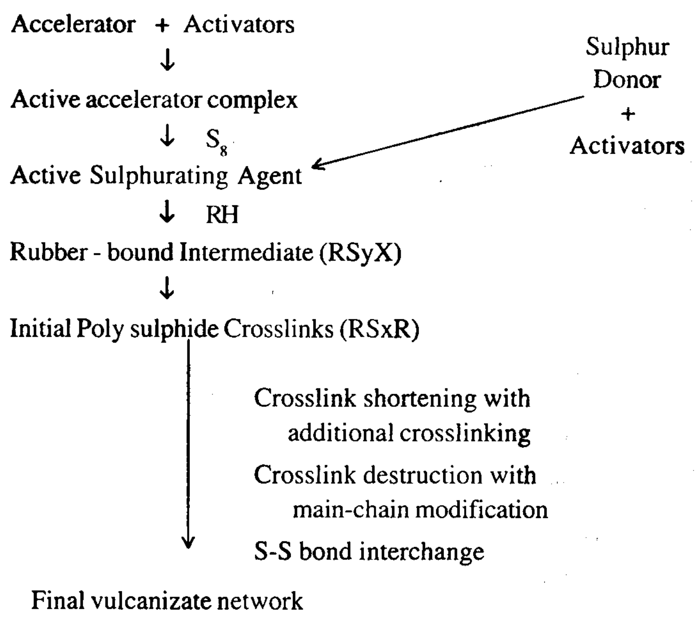


Fig. 5.3 Generalised mechanism of sulphur vulcanisation
R = rubber chain, H = allylic proton and, X = accelerator residue

Binary accelerator system

A binary accelerator system refers to the use of two (or more) accelerators in a given formulation. Many amines such as DPG are used in combination with other accelerators such as MBT or sulphenamides to activate the vulcanisation reaction. However present day binary accelerator systems usually consists of benzothiazoles and thiocarbamate derivatives. Additionally MBT and sulphenamides are often added to thiuram systems to increase the scorch delay of these systems.

Curing of rubbers with non-sulphur systems

I. Peroxide curing of rubbers

Organic peroxide can also be used as an alternating cross - linking agent for rubbers. Both unsaturated and saturated rubbers having labile hydrogen atoms are cross - linked with peroxides. Rubbers that can be cured with peroxides are :

Natural rubber

Styrene butadiene rubber

Butadiene rubber

Isoprene rubber

Ethylene Propylene rubbers*

Silicone rubbers *

Some Polyurethane rubbers

* Only peroxides can cure these rubbers

Classification of peroxides

Peroxides that may used for curing polymers are of two types :

i. Diacyl peroxides ROC.O.COR
eg. Benzoyl peroxide

ii. Dialkyl or diaryalkyl peroxides R - OO - R
eg. Ditertiary butyl peroxide
Dicumyl peroxide

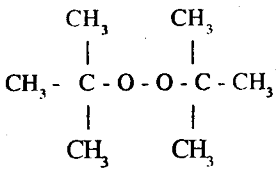
Typical dosage of each type used in rubber mix formulation = 3 to 5 phr.

Structures of some peroxides

Benzoyl peroxide

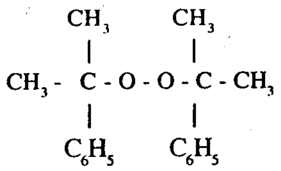
$C_6H_5CO.OO.COC_6H_5$

Di tertiary butyl peroxide :



$$\begin{array}{ccccccc} & & CH_3 & & & CH_3 & \\ & & | & & & | & \\ CH_3 - & & C & - O - & O - & C & - CH_3 \\ & & | & & & | & \\ & & CH_3 & & & CH_3 & \end{array}$$

Di cumyl peroxide :



$$\begin{array}{ccccccc} & & CH_3 & & & CH_3 & \\ & & | & & & | & \\ CH_3 - & & C & - O - & O - & C & - CH_3 \\ & & | & & & | & \\ & & C_6H_5 & & & C_6H_5 & \end{array}$$

Chemistry of peroxide cure

i. Decomposition of Peroxide

R - R → 2R. (Radical)

ii. Abstraction of hydrogen from a polymer chain PH

R. + PH → RH + P. (Polymer radical)

iii. Cross - link formation

P. + P. → P - P

In addition to the above reactions, chain scission, radical destruction, intrachain cyclisation reactions may also occur in some rubbers, due to their structural nature.

For efficient cross - linking, chain scissions are generally suppressed by chemicals called coagents.

Examples of coagents used : Triallyl cyanurate

Triallyl phosphate

Triallyl isocyanurate

Ethylene glycol dimethyl acrylate

Scorchiness can be reduced by the use of radical scavengers such as N-nitrosodiphenylamine.

Effects of compounding ingredients on peroxide cure

i. Fillers

Fillers with acidic surfaces tend to cause the heterolytic fission of peroxides. Neutral and basic fillers appear to have no effect on peroxides. The fission reactions leads to peroxide fragements which cannot initiate cure and consequently a reduction in the efficiency of the peroxide as a cross - linking agent.

This detrimental influence on the cross - linking process due to acidic fillers can be corrected by the addition of alkaline activators like DPG.

ii. Oils and plasticizers

All oils and plasticizers reduce the efficiency of peroxides because some of the radicals generated are transferred to them and do not lead to cross - linking.

The extent to which these materials reduce cure efficiency is dependent on the level of addition and the type of oil or plasticizer used. Aromatic oils have the great detrimental effect while paraffinic oils have the least effect. Naphthenic oils are intermediate.

iii. Antidegradants

All antidegradants reduce the efficiency of peroxides during vulcanisation. The amine type antioxidants are preferred since they have the least effect on cure, while phenolic type antioxidants inhibit cure to great extent. Antiozonants are avoided in peroxide curing compounds because they greatly reduce the cure efficiency.

Advantages of peroxide cure

i. Non - reversion during curing

ii. Products have better age and heat resistance compared to S - cured products, because of the highest bond energy of carbon - carbon cross - links. (-C-C bond energy = 343 kJ)

iii. Products show better creep resistance at elevated temperature than S - cured products.

iv. ZnO and fatty acids are not needed.

v. Vulcanisates molecules are free of main chain modifications.

vi. Vulcanisates of high transparency or purity can be produced (eg. for medical field)

Disadvantages of peroxide cure

i. Peroxides need high temperature (ca. 160°C) and long time for curing.

ii. They lack the means of accelerating or retarding the cure rate.

iii. Peroxide cured vulcanisates have lower fatique resistance and strength properties than sulphur cured vulcanisates.

iv. Benzoyl peroxide cured vulcanisates show surface blooming caused by benzoic acid, the reaction by - product.

v. Dicumyl peroxide cured vulcanisates give out unpleasant smell due to the formation of by - product acetophenone.

II. Curing with phenol formaldehyde resins

Phenol - formaldehyde resins with para alkyl substitutes can be used to vulcanize both high and low unsaturated rubbers. Catalysts to speed up the reaction such as $FeCl_3$, $ZnCl_2$, $SnCl_2$ etc. or polymers which liberate hydrogen halide (HX) increase the reaction rate and state of cure. Halogenated resins are autocatalytic. The resin cures are adversely affected by amine antioxidants and conventional accelerators. The physical properties of the vulcanisates are similar to those of peroxide cure. They show little reversion and age resistance. The cure is used for the production of tyre curing bags and diaphragms.

Typical formulation phr

Phenol formaldehyde resin = 6

Stannous chloride = 2

Zinc oxide = 5

III. Curing with quinone dioxime

Quinone di oxime in the presence of an oxidizing agent (lead oxide) can be used to cure diene rubber.

The vulcanisates produced with this curing system give high resilience and heat resistance. However, due to toxicity of lead compounds and the explosive nature of quinone di oxime, generally resin cure is preferred to this type of curing.

Typical formulation phr

Benzoquinone dioxime = 4

Litharge or Red lead = 10

IV. Curing of diene rubbers with urethane system (Novor System)

The curing system was developed by Malaysian Rubber Products Research Association (MRPRA). The urethane reagents which are used for the curing, are the products of an addition reaction between a nitrosophenol and a di-isocyanate. They are stable compounds and contain no free nitroso or isocyanate groups.

When the reagents are heated in rubber to vulcanising temperatures, the addition reaction is reversed and the nitrosophenol is free to react with the rubber molecule to form pendent aminophenol groups. The liberated di-isocyanate then reacts with the aminophenol groups to form cross - links. The principal advantages of the urethane system are as follows:

i. The system can withstand vulcanisation temperature up to 200°C with a marked increase in reversion resistance.

ii. It is useful for curing thick sections of rubber articles and is most suitable for application in high temperature continuous vulcanising and in injection moulding rubber compounds.

iii. The vulcanisates show very good fatique resistance on aging at moderate and high temperatures.

It has been found that mixed urethane and sulphur in the ratio 80 : 20 increases synergistically the cure rate and relaxation modulus of the rubber.

V. Radiation cure

High energy radiation of the order of magnitude of 9 - 10 ev, can break chemical bonds in rubbers, because the bonds have low energy of the order of 2.5 to 4 ev. Irradiation causes a rubber molecule to become ionised and excited. The exited molecule can then break up into two radical chains.

The radical chains thus formed stabilise by combination, leading to cross - linked molecular structures.

Rubbers that can be successfully cross - linked by radiation cure NR, SBR, BR and NBR.

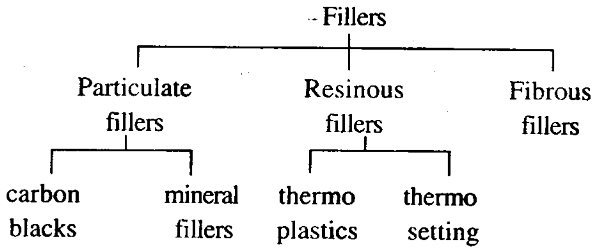
For curing of NR (especially latex articles) gamma radiation from the radiactive source Co - 60 is chosen. The cured articles show high clarity and purity with good surface finish.

VI. Curing of chloroprene rubber with metal oxides

As the presence of chlorine atoms in the chloroprene rubber molecules reduces the unsaturation character of the double bonds, neither sulphur curing system nor peroxide is applicable for cross - linking, the rubber. Hence, a different curing system consisting of the combination of metal oxides such as zinc oxide and magnesium oxide is employed to cure the rubber. The proposed mechanism of the curing reaction suggests that of all the structural components of the rubber only 1, 2 polychloroprene structural units (about 1.5%) take part in the cross - linking reaction.

5.4 Fillers

A rubber containing vulcanising system alone is highly extensible and deformable. To reduce these characteristics fillers are incorporated. Fillers can be grouped as follows :



Some of these fillers are called reinforcing fillers of rubbers because the fillers have remarkable enhancing effect on tensile strength, modulus, and resistance to abrasion, tearing and flexing. The other type of fillers called diluent fillers have no effect on strength properties of rubbers but are added mainly to aid processing and to reduce cost of end - rubber products.

Both reinforcing and diluent fillers improve the rubber hardness and density.

I. Carbon blacks

Carbon blacks are produced from liquid or gaseous hydrocarbons.

They are classified into the following groups :

- Channel blacks
- Furnace blacks
- Thermal blacks
- Lamp black
- Acelylene black

i. Channel Blacks

These blacks are produced by the channel process. In the process. small smoky flames by burning natural gas in a limited supply of air are impinged on the underside of reciprocating iron channels. The carbon black deposited in then removed by scraping.

ii. Furnace Blacks

In the furnace process either natural gas or oil enriched gas is mixed with air in required ratios and burnt in large furnaces. After cooling with water sprays, the blacks are separated out. Compared to channel process, the furnace process is more economical and advantageous, because various grades of carbon black with different particle size can be produced by varying the ratio of raw material (oil / gas) to air and speed of spraying in the process.

iii. Thermal Blacks

To produce thermal blacks, natural gas or atomized oil is decomposed by heat in a large furnace. The black is cooled by water spray and separated from the gaseous products.

iv. Lamp Black

It is produced by burning oils in open pans, the product being collected in a cooling chamber.

v. Acetylene Black

This is classified as a thermal black and is produced by exothermic decomposition of acetylene.

The characteristics of the above types of carbon black are given in table 5.4

Carbon blacks - properties

Carbon blacks are essentially elemental carbon. They are differentiated from coke and charcoal by the fact that carbon blacks are composed of particles having quasi - graphitic structure.

Commercial carbon blacks vary in size in the range of 10 to 400 nm in diameter. The distinction between various types is based on the features such as (i) particle size (surface area) (ii) structure (iii) physico - chemical nature of particle surface and (iv) porosity.

Features of carbon black

(i) Particle size

It has been found that the smaller the particle size of carbon black, the greater its reinforcing effect of rubbers. However, as the particle size becomes finer, the incorporation time, the heat generation and the viscosity of the rubber mix increase, leading to poor dispersability of carbon black and scorch problem in the mix. Thus to avoid these (mixing problems) carbon black together with oil is generally mixed (in high proportion) into the rubber in the absence of other ingredients especially vulcanising ingredients, in a location away from the main factory floor. The mix (rubber + carbon black + oil) so prepared is generally termed master batch, which is found to be a more convenient form to process further in the factory.

(ii) Structure

The chain like aggregate of carbon particles in the carbon black powder is said to be the structure of carbon black. The carbon black which contains a high proportion of these structures is called high structure carbon black. The effect of structure is more noticeable on processing properties than on properties of vulcanisates. In general, the higher the structure, the stiffer and less nervy (elastic) the unvulcanised compound and harder the vulcanisates. The high structure black also allows high oil extension in rubber.

(iii) Physico - chemical nature of particle surface

The surface of carbon black particle has been found to be physically energy active and capable of adhering rubber radical chains. This adherence of radical chains generally occurs in mixing process and results in good strength properties in rubber mixes and in vulcanisates.

Chemically the surface of carbon particle has been detected to contain chemical contaminants with phenolic, carboxylic, ketonic and lactonic groups, in addition to a trace of sulphur. These contaminants are found to have much more effect on the electrical conductance of rubber than on other properties. An increase in content of these contaminants generally decreases the conductivity of the carbon filled rubbers.

(iv) Porosity

Particles with pores cause retardation in cure rate, because of the adherence of curative chemicals. Due to increase in surface area of porous particles, per unit weight, the porous carbon black filled vulcanisates show reduced resilence and increase in electrical conductance.

Naming of carbon blacks based on ASTM numbering system

The ASTM numbering system consists of a letter N or S followed by three numbers. Oil furnace blacks are considered as blacks with normal cure rate (N) and some oxidised or channel blacks as slow curing (S) blacks.

First number refers to particle size (surface area), second number relates to the structure and third number is arbitrarily chosen and has no significance. If second number is repeated as the first number, it indicates the black contains standard level of structure.

Table 5.4Commonly used carbon blacks and their applications

	Type	ASTM naming	Particle size (nm)	Properties	Applications
1.	Super abrasion furnace (SAF)	N 110	22	Highly reinforcing, gives maximum tensile strength and abrasion resistance. High heat generation during processing	Camel black, truck tread. industrial belting and other heavy duty items.
2.	Intermediate super abrasion furnace (ISAF)	N 220	22	Highly reinforcing, imparts high tensile strength and abrasion resistance, better processing than SAF	Treads, camel backs conveyor belts, covers.
3.	High abrasion furnace (HAF)	N330	32	Rein forcing black with good abrasion resistance and better processing properties.	Treads, camel blacks, inner tubes, mechanical goods.
4.	Fast extrusion furnace (FEF)	N550	47	Moderately reinforcing, provides fast and smooth calendering and extrusion.	In tyre carcass stocks, side walls, wire & cable covering.
5.	General purpose furnace (GPF)	N660	70	Moderately reinforcing, high loadings are possible, easy processing.	In carcass, side walls under tread, inner liner compounds, motor mounts.
6.	Semi - reinforcing furnace (SRF)	N770	83	Semi - Reinforcing, High loads are possible, give good processing and dynamic properties	In bead, cusion compounds bicycle tyres, wire cables and other extruded items.
7.	Fine thermal (FT)	N880	190	Low reinforcing, can be used at high loading.	In "v" belts and mechanical goods.
8.	Medium thermal (MT)	N990	300	Low reinforcing, Highly resilience, High loadings are possible.	In "v" belts and mechanical goods.
9.	Lamp pack	--	65 - 100	Have coarse particles, but have high structure used in high hard compounds which are required to be resilient and have low heat build up. when used dynamically.	Engine mount Tank Treads.
10.	Acetylene black	--	42	Produce high hardness compounds which will process easily and be fairly resilient.	For high electrical conductive rubbers
11.	Channel blacks (expensive, and of use is on the decline)	S 330	20 - 30	Have retarding effect on cure, which is advantageous for bonding process and for compounds which require high resilience	cable covers

II. Mineral fillers

Application of mineral fillers in rubber has been small compared to carbon blacks. They are not much effective reinforcing fillers as carbon blacks However they are needed for producing non-black rubber articles and for cost reduction. Some of them impart better heat, water and electrical resistance to rubbers.

The main fillers are : Silica
Whiting
Clays
Silicates of Calcium / Magnisium / Aluminium
Oxides of zinc / Calcium / Magnisium / Aluminium
Carbonates of Magnisium / zinc
Barytes and Lithopone e. t. c.

Silica (Silicon dioxide)

Silica prepared by chemical method only finds application as a filler in rubbers. In the method of preparation, sodium silicate is treated with HCl acid.

$$Na_2SiO_3 + HCl \rightarrow NaCl + SiO_2 \downarrow + H_2O$$

Silica obtained as the precipitate is filtered, washed and dried. The water content in the filler (about 3 - 5%) has been found to be chemically bound. Silica is acidic in nature (pH<7) and has its particle size in the range 10 to 40 nm.

Characteristics of silica

(i) In consequence, of the above properties, the filler dispersion in rubbers is not uniform and a longer mixing time generally needed. This generates excessive heat in the rubber mix.

(ii) Silica particles generally have greater porosity on their surfaces than carbon blacks and hence they require, more softeners or plasticizers to obtain the suitable level of viscosity for processing.

(iii) The bound water molecules on the surface of silica particles also, tend to form H - bonds with conventional nitrogen containing accelerators. This results in retardation of cure rate and needs an increase in cure time. However, to facilitate the mixing and curing processes, one of the following types of chemicals is added.

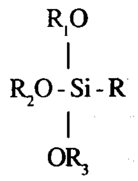
(a) Deactivating agent : This chemical is incorporated into the rubber at an early stage with silica, before the addition of accelerator. The molecules of the chemical first take part in H - bond formation with water layers surrounding the silica particles and thereby allow the accelerator to perform its normal functions in the curing system.

Examples : Diethylene glycol
Polypropylene glycol

(b) Coupling agent : A silane derivative is usually employed as a coupling agent. It has both hydrophilic and hydrophobic groups in its molecular structure. The chemical is added to silica before it is incorporated into the rubber. During mixing the hydrophilic part and hydrophobic part of the chemical, couple the silica particle and rubber molecule respectively. This gives rise to uniform dispersion of the filler in rubber mix.

Example :

A silane derivative



$$\begin{array}{c} R_1O \\ | \\ R_2O-Si-R \\ | \\ OR_3 \end{array}$$

R - hydrophobic part (hydrocarbon)

$OR_1/OR_2/OR_3$ - hydrophilic part.

Instead of above coupling agents, wetting agents eg. Polyols can also be employed to improve the dispersion of silica, but the effect is less when compared to the coupling agents.

Fume silica or pyrogenic silica which contains less than 2% bound water is also prepared by gas phase oxidation of silicon tetra chloride at 1000°C. The particles of this type are about 10 nm. in diameter with an effective surface area of 150 - 500 m^2/g. This is a highly reinforcing filler giving high tensile and tear strength in rubber compounds.

Silica is used in tyres especially in tread compounds (in combination with carbon black) to improve the tear strength and the resistance to chipping and chunking, of the tread in service.

It is also used in textile and steel cord coating compounds with resorcinol formaldehyde system to improve the adhesion level between the rubber compound and the fibres / cords.

Silica also finds applications in non - black mechanical goods and in coloured and transparent shoe solings.

China clays

China clays are chemically hydrated aluminium silicate formed from the weathering of feldspars. They are low cost fillers and give semi - reinforcement in rubbers. Different grades of clays are produced for use in rubbers.

(i) Soft clays- The clays have their particle size greater than 2mm and are used mainly in mechanical goods. A marginal reinforcing effect is given in the products.

(ii) Hard clays - These are of finer particle size, less than 2 mm and give semi - reinforcing effect in rubbers.

(iii) Calcined clays - The clays are calcined to remove their water content and can be used where good colour and electrical insulation are particularly needed. They also impart good tensile strength and hardness.

(iv) Treated clays - The particles of these clays are treated with chemicals like amines or glycols or coupling agents to aid their imcorporation in rubbers and to give better reinforcement in vulcanisates.

Calcium carbonate fillers

There are three types of calcium carbonate fillers used in rubbers.

(i) Naturally occuring calcium carbonate :

Ground lime stone or chalk of particle size in the range 0.5 to 3×10^3nm can be incorporated into rubbers to obtain low cost light coloured articles. The filler increases hardness and gives only little reinforcement in rubbers.

(ii) Precipitated calcium carbonate
This is produced from the following reaction as a precipitate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$$

The filler has fine particle size as low as 0.1 mm and confers rubber with improved strength properties.

(iii) Activated calcium carbonate :

This is produced by treating precipitated calcium carbonate with up to 3% stearic acid or a stearate. The filler shows better dispersion and can be used in higher grade coloured products.

Magnesium carbonate

Chemically precipitated magnesium carbonate imparts semi reinforcement to rubber and improves the green strength of uncured extruded products. It stiffens the rubber and reduces collapse in open - steam cures. It may be useful to make translucent filled natural rubber products, as it has similar refractive index to natural rubber.

Zinc carbonate

This is a fine white powder and cheaper than titanium - di oxide to obtain white rubber products. It also functions as a neutral acid acceptor in place of zinc oxide in chlorine containing rubbers.

Talc (French Chalk)

The filler consists chemically of magnesium and aluminium silicates and largely used to prevent uncured rubber compounds from sticking to each other. As the lamellar forms of its structure helps to reduce gas permeability, in rubbers the filler can be used in heat resistant curing bags and tubes.

Barium sulphate (Barytes / Blanc fixe)

Barium sulphate is an inert filler of relative denisty 4.4. The filler is useful for high density rubber products. eg. for flooring. As they are chemically unreactive, it also finds applications in chemical resistant tank lining and in pharmaceutical rubber goods.

Hydrated aluminium silicate :

It is a fine white powder and used a reinforcing filler in shoe - soling and mechanical goods. The filler can also be added in large amounts in rubber compounds requiring high electrical conductivity. e.g. cable covers.

Magnesium oxide

There are two grades of magnisium oxide namely light grade and heavy grade, available.

Light grade is of fine particle size and used mainly as an acid acceptor in halogen containing rubbers whereas heavy grade is less active than light grade and finds applications mainly in heat resistant rubber products. e. g. Seals & gaskets.

Zinc oxide

It is a fine white powder and mainly used as accelerator activator, when added in small quantity (4 to 5 phr). In large quantity (above 30 phr), the filler gives vulcanisates with high tensile strength and resilience, but only with moderate hardness.

It can be used at high loadings to produce easily moulded compounds, however the compounds are found to be too tacky to handle on processing machinery.

Antimony trioxide

It is a white semi - reinforcing filler, which is in conjunction with chlorinated paraffin wax can be used as a flame retradant in rubber compounds.

Zinc stearate

Zinc stearate is more easily ionisable than zinc oxide and hence it functions as an effective activator of accelerators in sulphur vulcanising system. It also finds use as a lubricant to uncured rubber mixes like talc powder. But unlike the latter, it takes part in curing reactions and gives good surface finish in rubber mouldings.

Titanium dioxide

It is comparable to zinc oxide in its rubber reinforcing character. But it is mainly used as the white pigment. It also enhances heat and weather resistance of rubber products.

Lithopone

This is a mixture of zinc sulphide and barium sulphate in the ratio 30 : 70. It is used as a cheap white pigment in place of expensive titanium oxide.

III. Resinous fillers

Resinous fillers are organic fillers and which either thermoplastic or thermosetting types. They generally aid processing and improve green strength of compounds. The products have high modulus and hardness and have good surface finish. The fillers find use mostly in foot - wear, shoe soles and heels and in leather like rubber articles.

Examples :

(i) Thermoplastic types :

- i. High styrene resin
- ii. Cyclised natural rubber
- iii. Methyl methacrylate grafted NR
- iv. Fish / animal glue

(ii) Thermosetting types :

- i. Phenol formaldehyde resins of low molecular weight
- ii. Urea formaldehyde resin of low molecular weight
- iii. Melamine formaldehyde resin of low molecular weight

IV. Fibrous fillers

The typical fibrous fillers added into rubbers are cotton flock, wool flour, and asbestos.

Cotton flock

This consists of short staple cotton fibre which is of little use for spinning owing to its short fibre length. It provides products with improved impact strength and diemensional stability. It finds applications in shoe - soles and similar products.

Wood flour

This is one of the cheapest fillers. It is normally ground to a particle size of 100, mesh with moisture content of around 6 - 8 percent. The filler imparts products with reasonable strength and good insulation properties.

Asbestos

It is a naturally occuring silicious filler. Both short fibres and ground material find applications in rubber to improve flame resistance and heat resistance. Examples - gaskets, brake shoes. The use of this filler is restricted because of its health hazards.

5.5. Softeners (Processing aids / Extenders)

Softeners plasticize the rubber by physical action. They penetrate into the rubber molecular mass, and separate the individual molecules by lubricating action. This action aids the dispersion of fillers uniformly in the rubber. Further, the softener also prevents the rubber mass from adhering to the hot machinery surfaces, during processing. In the vulcanisates, it modifies their physical properties such as elasticity, flexibility and low temperature performance. In excess of the normal quantity, the softener acts as an exlender to rubbers and permits economic productions of the finished articles. There are three main sources from which softeners are obtained; viz.:

- i. Petroleum
- ii. Vegetable
- iii. Synthetic products

The requirements of an ideal softener for a rubber are that the softener should not vapourise at the processing temperatures and be compatible with the rubber

I. Petroleum products

(i) Petroleum oils

Commercially used oils are high - boiling petroleum fractions. They consist of mainly three structural units in their molecules namely (i) aromatic ring structure (ii) Napthenic (saturated hydrocarbon ring) structure and (iii) Paraffinic (linear saturated hydrocarbon) structure.

Thus the petroleum oils are generally grouped into (i) Highly aromatic oils (ii) Aromatic oils (iii) Naphthenic oils and (iv) paraffinic oils.

Of all these types, oils with high aromatic content are most compatible with unsaturated hydrocarbon rubbers and impart their effects on the carbon black loaded rubbers as given below :

a. **During processing**

Reduce the power consumption during processing

Reduce the overall viscosity of the mixes

Keep heat generation down

Ease the dispersion of ingredients

Increase the extrusion and calendering rate

Give smooth extrudates and calendered sheets

Regulate die - swell and calender shrinkage

Give good mould flow and faster cures.

b. **After vulcanisation :**

Improve tensile strength, tear resistance and crack growth resistance. Decrease resilience and resistance to low temperature flexibility. High heat build - up during flexing.

(ii) **Paraffin wax**

Ordinary paraffin wax (m. pt = 56°C) can be used as a processing aid upto 1 to 2 phr. However in excess quantity, it blooms to the rubber surface. Blooming is considered as an advantage for ozone sensitive rubbers for it protects the surface from being attacked by ozone. The blooming is useful, especially for stationary rubber articles.

(iii) **Bitumen (tar)**

The ordinary road surfacing bitumen (softening point = 40 - 50°C) is not suitable for mixing with rubber due to its sticky nature. However, the tar of air blown grade (blown tar / asphalt) with softening point 110 - 115°C is used in rubber mixes, where good green strength, and tack properties are required. Typical compounds are - Tread and Retreading compounds.

(iv) **Coumarone Indene resin**

This resin is a by - product of coal - industry. It is produced by the polymerisation chemical substances coumarone and indene. There are two grades available. First grade is soft and employed as a tackifier in adhesive rubber compounds. The second grade is hard resinous solid with melting point in the range from 65 to 110°C. This grade is used as a processing aid in rubber mixes for smooth extrusion and calendering. It also imparts shiny smooth surface to the moulded rubber articles.

II. Vegetable by - products

(i) **Pine tar**

This is produced as a viscous liquid by the destructive distillation of pine wood. It aids high filler loading in rubber and tack property.

(ii) **Fatty acids and salts**

These are used to aid filler dispersion and to minimise the adherence of the rubber mixes to the hot machinery surface.

Examples : Stearic acid, Lauric acid, Zinc stearate

(iii) **Vulcanised vegetables oils**

a. **Brown factice**

It is obtained by vulcanising vegetables oils with sulphur. The vegetable oils which are suitable for the reaction, have their unsaturation iodine number above 80. The vulcanisation reaction is exothermic and the reaction temperature is maintained around 160°C. The product is brown and is named brown factice.

Brown factice finds application as a processing aid in rubbers. It aids filler incorporation in rubbers and reduces power consumption during mixing process. It also helps to produce smooth extrudates and calendered sheets, with dimensional control.

b. White factice

This is produced by vulcanising the vegetable oils with sulphur monochloride at low temperatures. The reaction is also exothermic and the product is pale in colour. It is used mainly in eraser compounds and in coating compounds to get shiny rubber layer on substrates.

III. Synthetic products

(i) Ester Plasticizers

These are obtained by esterification of adipic, phthaleic, sebacic and phosphoric acids with high molecular weight alcohols. The esters are polar in nature and mix well with polar rubbers (NBR and CR). They aid incorporation of fillers and impart good low temperature flexibility property to rubbers.

Examples : Dibutyl phathalate
Dixylyl phosphate
Di - iso octyl phthalate

(ii) Partially cross - linked polymers

As the name implies, these are polymer materials with few cross - links. The polymers impart good green strength to the uncured rubber mixes and also act as processing aids.

Examples :

i. PA 80 - This is a special form of natural rubber obtained from 20% prevulcanised latex and 80% ordinary latex.

ii. SBR 1009 - It is lightly cross - linked form of styrene butadiene rubber. Divinyl benzene is used as the cross - linking agent.

(iii) Liquid polymers

These are low molecular weight polymer substances produced in the form of high viscous liquids. They function as plasticizers and take part in crosslinking reactions in rubber compounds.

Examples : Liquid natural rubber, Liquid nitrile rubber etc.

(iv) Plastic materials

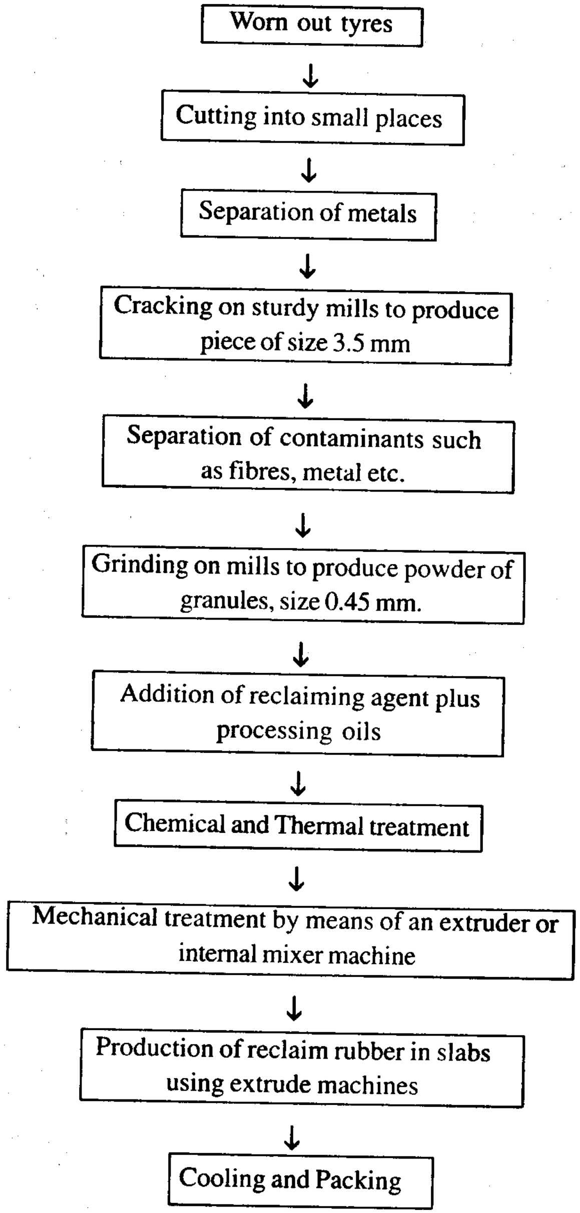
Both thermo plastic and thermosetting types of plastics can be blended with rubbers. During processing, the materials act as plasticizers and improve the compound mould flow character. They also impart high strength and hardness in the vulcanisates.

Examples : High styrene resins (thermoplastics)
Phenol formaldehyde resins (thermosetting type)

(v) Reclaim rubber

This is a regenerated rubber produced from used or worn - out tyres. It can be compounded and revulcanised like raw rubbers. Many methods to reclaim rubber from worn - out tyres have been described in literature. Of these methods, only a few are employed in commercial scale. The main stages involved in the methods are illustrated in the following flow chart :

Flow chart for production of reclaim rubber



Advantages of Incorporating Reclaim rubber into rubbers

- Mixing times and power consumption are reduced
- Faster extrusion and calendering process
- Extrudates hold their shape without sagging during extrusion and open steam curing.
- Extruder die-swell and calender shrinkage are minimised.
- During curing, the compounds have less tendency to revert and give plateau cure.

However, the strength properties such as tensile strength, tear resistance and abrasion resistance of the vulcanisates decrease in proportion to the amount of reclaim rubber in the compound.

5.6 Antidegradants

I. Antioxidants

Rubber undergoes degradative oxidation reaction during its service life. In consequence it loses its strength and elastic properties. This phenomenon is called ageing of rubber which can be delayed by incorporation of antioxidant chemicals into the rubber.

Ageing of rubber in atmosphere

Rubbers containing easily abstractable H - atoms are most vulnerable for the atmospheric oxidation reactions. The H - atoms may be from tertiary carbon atom or alpha methylene group.

Suppose RH represents the rubber molecule with abstractable hydrogen (H) the possible reaction steps involved in the oxidation can be illustrated as follows :

Chain initiation and free radical formation

$$RH + O_2 \rightarrow R. + .OOH$$

$$2RH + O_2 \rightarrow 2R. + H_2O_2$$

Propagation of the reaction chain

$R. + O_2 \rightarrow ROO.$

$ROO. + RH \rightarrow ROOH + R.$

Degenerative branching of the reaction chain

$ROOH \rightarrow RO. + .OH$

$ROOH + RH \rightarrow RO. + R. + H_2O$

$2\,ROOH \rightarrow ROO. + RO. + H_2O$

Termination

$2R. \rightarrow R{-}{-}R$

$2ROO. \rightarrow ROOR + O_2$

$R. + ROO. \rightarrow ROOR$

Since the above reactions are involved with free radicals, both scission and crosslinking reactions occur among the rubber chains. Thus the physical nature of the end product depends upon the kind of reactions which are predominant in the rubber.

Generally, the filler loaded rubber vulcanisates turn into harder products, on ageing, due to the predominant cross - linking reactions.

The studies of the mechanism of rubber oxidation reactions have revealed that the oxidation can be inhibited by two groups of antioxidants.

Antioxidants of first group

The antioxidant of the first group (InH) contains a labile atom (usually H - atom) in its molecule. The atom detaches and participates in the radical reactions more easily than the active hydrogen atoms of rubber molecules.

The free radical of the inhibitor (In.) has a low activity and cannot cause chain propagation in radical chains. Thus, the chain process of development of radical reactions is terminated until the antioxidant is fully consumed.

Examples of this group of antioxidants are amines and phenols and their derivatives. Amine types are better antioxidants than phenolic types but they stain the rubber products and cannot be used in coloured articles.

Amines and their derivatives :

Examples :

Diaryl - p - phenylene diamine

Alkyl / Aryl - p - phenylene diamine

Phenyl β Naphthylamine

Dihydroquinolines

Diphenylamine condensates.

Phenols and their derivatives

These are non-staining but less powerful than amine types. Typical phenolic antioxidants used are either simple hindered phenols or bridged hindered phenols.

A mixture of amine type and phenolic type has been found to impart a synergistic effect or mutual amplification of their effects in the protection of rubbers.

ii. Antioxidants of second group

An antioxidant of this group prevents or excludes the development of reactions that would form radicals which initiate or propagate a chain oxidation process.

The antioxidant mainly prevents the decomposition of hydroperoxides (ROOH) by a radical mechanism. It decomposes hydroperoxides into products that are inactive for the development of an oxidising chain.

Examples :

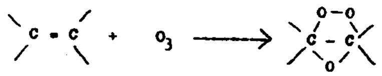
i. Organic sulphides

ii. Thiophosphates

iii. Salts of dialkyl di thio carbamates.

II. Antiozonants

Ozone even in small concentration (about 5 ppm in air) can initiate rubber molecular degradation reactions. Only rubbers having reactive stronger unsaturation character are prone to these reactions. The reaction product is a white film or deposit which forms on the surface of the rubber exposed to ozone gas. The film is fragile in nature and cracks easily under any strain. The direction of the cracks appears generally perpendicular to the direction of straining, as illustrated in Fig. 5.4



Ozonide film (fragile)

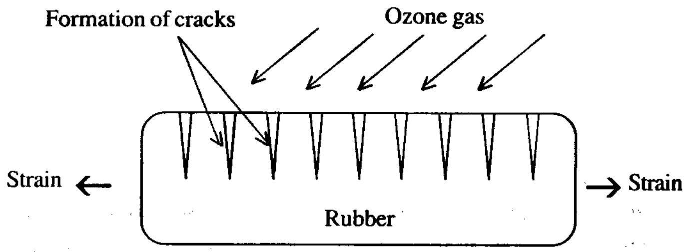


Fig. 5. 4 Effect of ozone attack on rubber surface

To inhibit ozone attack, chemicals called **antiozonants** are incorporated into rubbers. The chemical either increases the surface strength of the rubber or slow down the rate of crack - growth, or does both actions.

Examples :

Quinolines eg. 6 - ethoxy 2,2,4 tri methyl 1,2 dihydroquinoline (EDTQ)

Paraffin wax (useful in stationary rubber articles)

Unsaturated ethers

5.7 Auxillary ingredients

These ingredients are required to impart specific properties in rubbers. For examples :

i. Blowing agents

The chemicals are essential for the production of microcellular, sponge and other blown rubber articles. Earlier inorganic chemicals like sodium bicarbonate, ammonium carbonate which liberate carbon - di - oxide were used. These chemicals are now superseded with nitrogen liberating organic chemicals. The organic chemicals are more readily dispersable in rubbers and produce uniform cellular structure in the articles.

Typical examples :

Dinitroso penta methylene tetramine (DNPT)

Azoisobutyro nitrile (AZDN)

Benzene sulphonyl hydrazide (BSH)

ii. Flame retardants

Hydrocarbon rubbers are easily burnable and can spread flames when they catch fire. To prevent this, flame retardant chemicals are incorporated.

Typical examples :

A mixture of antimony trioxide and chlorinated paraffin wax

Zinc borate

Aluminium tetrahydrate

iii. Antistatic agents

Antistatic agents are needed in rubbers to prevent the build - up of static electricity on their product surfaces. These are essential such as conveyor belting, textile rollers and trolley wheels for use in hospitals. The chemicals are ionisable additives which migrate to the surface of rubber and form conductive path through the absorption of atmospheric moisture.

Examples :

Quarternery ammonium salts
Alkyl aryl sulphonates
Polyethylene glycol derivatives
Conductive blacks

iv. Colouring materials

Both inorganic and organic colouring materials (pigments/dyes) are used. Inorganic substances are more stable to curing conditions and have complete freedom from staining or bleeding. However they give rather dull colours and high specific gravity rubber products as compared to organic pigments and dyes.

Examples :

Antimony sulphide
Cadmium sulphide
Chromium oxide
Iron oxide
Mercury sulphide
Nickel titanate
Ultramarine blue

Organic colouring materials give bright colour, and more covering power. They are available in wide range of colours in the form, of paste or as master batches in rubber which greatly assists its dispersion in rubbers. Some are soluble and produce colour shades in translucent products. But their stability to cure conditions and light is rather poor. Some of them bleed in rubber articles due to incompatibility.

Examples :

Anthraquinone pigments
Azoic dyes
Phthalocyanines and derivatives.

5.8 Rubber reinforcing textiles

Rubber reinforcing textiles are needed for the production of some composite rubber articles. They impart the load - carrying capacity to the rubber and serve as a medium for stress transmission.

Besides these, the textiles also provide dimensional stability and enhance the durability of the composite products.

The textiles which find applications as rubber reinforcements are :

Cotton

Rayon

Nylon

Polyester

Aramid (kevlar)

Fibre glass

Steel strand

Characteristics of textiles

Cotton	● Has small fibre like branches (fibrils) in the main filament and hence can bond well with rubbers without the need of surface treatment. ● Relatively low strength and elongation ● Susceptible to mildew attack ● High resistance to heat and organic solvents
Rayon	● Has same resistance as cotton to chemical and mildew attack ● Relatively high modulus and strength ● Strength reduces with increase in moisture content ● Needs surface treatment

Nylon	● Excellent heat and fatigue resistance as well as strength ● Affected little by moisture and mildew ● Heat resistance of nylon 6.6 > that of nylon 6 ● Needs surface treatment
Polyester	● Imparts modulus and dimentional stability better than nylon ● Good strength but not quite as high as nylon ● needs surface treatment ● Not affected seriously by moisture
Aramid fibre	● extremely high strength, modulus and dimensional stability ● Excellent resistance to heat and humidity ● Less resistance to shear fatique ● Needs surface treatment
Glass fibre	● Excellent strength to weight ratio ● Extremely high modulus ● Excellent heat resistance ● Poor resistance to flexing ● Needs surface treatment
Steel strand	● High modulus ● Excellent strength ● Needs brass / tin / copper coating ● Low cost

Surface treatment

An adhesive used for surface treatment of textiles performs an important function. It transfers the load applied between the relatively low modulus rubber and the high modulus textile material. The chemical components of the adhesive are chosen according the textile material being treated and the rubber matrix employed, Generally, adhesives which consist of high reactive chemicals such as resorcinol formaldehyde resin dispersion in a rubber latex medium or isocyanates which react with rubber during vulcanisation are employed.

Typical applications

Cotton - Sealing rings, washers
Rayon - Bicycle tyre carcass, hoses
Nylon - tyre carcass
Polyester - conveyor belts
Aramid - breakers (belts) in tyres
Glass fibre - breakers (belts) in tyres
Steel strand - conveyor belts, air craft tyres

5.9 Handling of chemicals in rubber industry

Most of the rubber chemicals are generally harmful to human being, if they are not handled carefully. In conditions of industrial exposure, inhalation and skin absorption are the major potential routes for entry, with ingestion is somewhat less importance.

General procedures for personnel protection

i. Industrial and protective clothing should be worn to avoid contact with skin and eyes.

ii. Inhalation of dust and vapour should be avoided.

iii. Hands should be washed before eating, smoking, drinking or using the toilet.

iv. No food or drink should be taken into consumed in working area.

v. Smoking should not be allowed in a handling area to avoid possible accidental ingestion or ignition of flammable materials.

vi. Everyone should be familiar with eye wash facilities and how to use them

vii. Personnel should wash under a shower at the end of the shift or day especially if working in atmospheres containing dusts and vapour.

Special procedures

i. For products which are skin irritants or sensitizers, vinyl coated or nitrile rubber gloves should be worn and should extend over the cuffs.

ii. For products which are eye irritants, goggles should be worn.

iii. If entry into or working in a dusty atmosphere is required a suitable dust mask should be worn.

iv. If liquid products are being handled regularly, it is advisable to wear an impermeable apron to protect clothing from contaminants.

Storage of rubbers and ingredients

i. Store room should have areas allocated for materials and they should be clearly identified.

ii. Incompatible materials should not be stored together, For example : Textiles should be stored away from carbon black and solvents away from rubbers.

iii. Every material should be clearly labelled, identifying the name, date of arrival, any hazards, stores code etc.

iv. Protection from heat, light and moisture where they can do damage.

v. Convenience of cleaning in case of spillage.

vi. Chemical which is brought in first must be first taken out for use.

vii. Good ventilation and lighting.

viii. Special safe areas must be allocated for storing flammable liquids (eg. Petroleum solents, alcohols), flammable solids (eg. Rubber. sulphur, wax explosive materials (eg. peroxides) and blowing agents.

Health hazards associated with rubber and ingredients

Raw rubbers

Raw rubbers do not themselves give rise to any health problems. However, in the case of synthetic raw rubbers, possible trace impurities remaining from the production processed such as unreacted monomers, catalysts, stablisers may need consideration for possible toxic hazard. The levels of concentration of these substances in the rubbers are kept below threshold limit values (TLV) i.e. maximum allowable concentrations in working environments.

TLV of the monomer contents in some synthetic rubbers are as follows :

Rubbers	**Monomer content**	**TLV**
Nitrile rubber	Acrylonitrile	2 mgm^{-3}
Neoprene	Chloroprene	10 mgm^{-3}
Butadiance rubbers	Butadiene	1000 mgm

Ingredients

I. Fillers

i. Carbon black

The main health hazards associated with the exposure to carbon blacks are as follows :

a. Changes in the functions of lungs - This occurs due to the penetration of very small particles of carbon into the lower lung spaces.

b. Cancer hazard - carbon blacks containing polycyclic aromatic hydrocarbons may be carcinogenic after prolonged contact. So the TLV for the hydrocarbon content is kept below 3.5 mgm^{-3}

ii. Mineral fillers

Although this category of substances relatively free from health problems the materials can yet be regarded as nuisance dusts with minimal potential health hazards. Some of the members of this class, have shown to produce physiological effects and require more careful handling.

Substances which cause nuisance dusts are :

Aluminium hydroxide
Aluminium sulphate
Calcium carbonate
Clays
Lithopone
Magnesium oxide
Zinc oxide
Titanium oxide
Zinc stearate

Tale powder may contain asbestos like fibres. Excessive inhalation can cause respiratory disease. This may take in the form of a persistent cough and breathlessness.

Silica - Fine size particles of silica causes Silicosis, a progressive form of lung fibrosis.

II. Curing chemicals

i. Sulphur

Sulphur is also a material, relatively free from health hazards, however the sulphur dust is slightly irritating to skin and eyes.

ii. Organic peroxides

These chemicals are also mildly irritating to eyes and skin.

iii. Accelerators and retarders

Most of them are irritant to eyes and skin. N - nitrosodiphenyl amine may form secondary amines during processing, which are carcinogenic, PVI (prevulcanisation inhibitor) may cause allergic skin reaction.

III. Softeners

Petroleum oils : The aromatic type is the most hazardous because of its high content of polycyclic aromatic hydrocarbons (carcinogenic)

C. I. resins : They may also contain poly cyclic aromatic hydrocarbons, but are less likely to be hazardous than the aromatic petroleum oils.

Easter Plasticizers have lower toxicity than other softener.

Chlorinated paraffin wax mildly irritant to eyes.

IV. Antioxidants

PAN - Irritant to eyes

PBN - Irritant to skin, may cause bladder cancer. Its use is prohibited.

Hindered phenols - can cause eye irritation and respiratory problems.

Quinolines - Slightly irritant to skin and eyes

Diamines - mild irritant to eyes and skin.

Solvents

Inhalation of solvent vapours produce adverse effects such as fatique, headache, drowsiness and nausea to the personnel. Skin contact with solvent may also cause irritation and defatting of skin. Hence the TLV of solvents are kept at minimum levels, as indicated below :

i. **Aromatic solvents**	**TLV mgm^{-3}**
Benzene	10
Toluene	100
Xylene	100

ii. **Aliphatic solvents**

n - Pentane	600
n - Hexane	50
	TLV mgm^{-3}
N - Heptane	400
Octane	300
Nonane	200]
SBP 1,2,3	125, 175, 275
Petroleum rubber solvent	200
White spirit	100

iii. **Alcohols**

Ethyl alcohol	1000
Methyl alcohol	200
Isopropanol	400

These can cause damage to retina and optic nerves which may result in blindness

iv. **Ketones**	TLV mgm
Acetone	750
Methyl Ethyl ketone	350

Ketones can cause eye, nose, throat irritation and dermatitis.

v. **Chlorinated solvents**

Chlorinated solvents such as carbon tetrachloride, methylene chloride, trichloro ethylene and 1,1,1 trichloro ethane can cause chronic damage to the liver and kidneys and are probably carcinogenic in human beings. These solvents must be handled with extra precautions.

Chapter 6

Processing of Rubber

The processes involved in the conversion of raw rubbers to finished products are as follows:

i. Mastication process

ii. Mixing process

iii. Shaping/Forming process

iv. Moulding and curing processes

6.1 Mastication process

As raw natural rubber is extremely tough and elastic, it must be rendered into a soft and pliable condition, before adding with compounding ingredients and shaping into useful articles. To achieve this breakdown the rubber is subjected to severe mechanical treatment on a two roll mill. This treatment resulting in gradual plasticization is termed mastication.

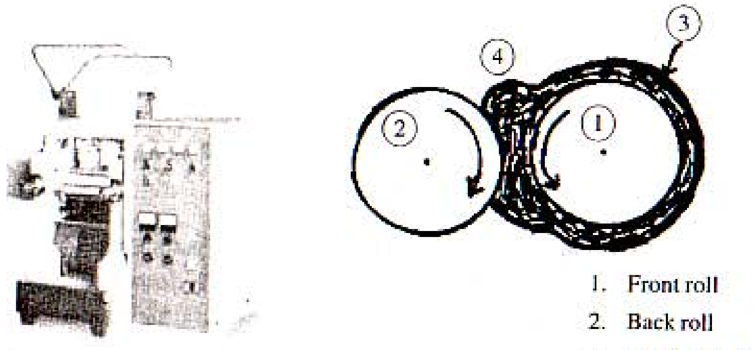
Mastication of rubber on a two roll mill

A two roll mill consists essentially of two horizontal parallel rolls, which are rotating at different speeds, in opposite directions (see fig. 6.1). The rolls which are made of very hard cast iron or special steel are mounted in bearings on a cast iron or moulded steel support. In general the bearings of the rear roll are stationary and those of the front roll movable, so that the clearence between the rolls (nip) can be varied. The rolls are driven by an electric motor and gear boxes. The front roll is rotated at a speed of about 15 to 25 rpm. The speed of the rear roll is higher, the ratio of speeds termed friction ratio being 1:1.2 to 1:1.5.

Passing the raw rubber repeatedly between the rolls of the mill will change its physical properties. The hard and compact raw rubber gradually becomes soft. It loses its elasticity and becomes plastic. After a given period (say 10 to 20 minutes), the raw rubber pieces form a soft and plastic strip (band) which rotates together with the front roll. The rubber is then considered to be plasticized and is suitable for taking up fillers and other ingredients.

The plasticization of rubber is accompanied by considerable heat development, since by friction, tear, compression, shear, e.t.c., a substantial portion of mechanical energy is transformed into heat. The heat thus developed facilitates the plasticization of rubber, but the temperature must be controlled to avoid over heating the rolls and rubber. Mechanical work and heat are not only the factors that affect the softening of rubber. Atmospheric oxygen also plays a very important part. If plasticization is carried out in the absence of air, for example, in a nitrogen atmosphere, the plastic state is obtained much more slowly.

The skill of operator is another important factor. He must carefully maintain the uniformity of operation. He must make sure that all rubber pieces pass between the rolls. To assure homogenity, he cuts off large pieces of rubber and puts them back into the nip of the mill rolls.



1. Front roll
2. Back roll
3. Rubber band
4. Bank

Fig. 6.1 A two roll mill

Effect of temperature on the breakdown of natural rubber in air

As the temperature reached in a mass of a rubber during mastcation is increased, the rubber becomes progressively softer and the rate of mechanical repture is correspondingly reduced. Hence the breakdown efficiency in air falls with increasing temperature. However a second type of breakdown due to oxygen reactions become apparent above 80° C and this increases rapidly with temperature (see fig. 6.2)

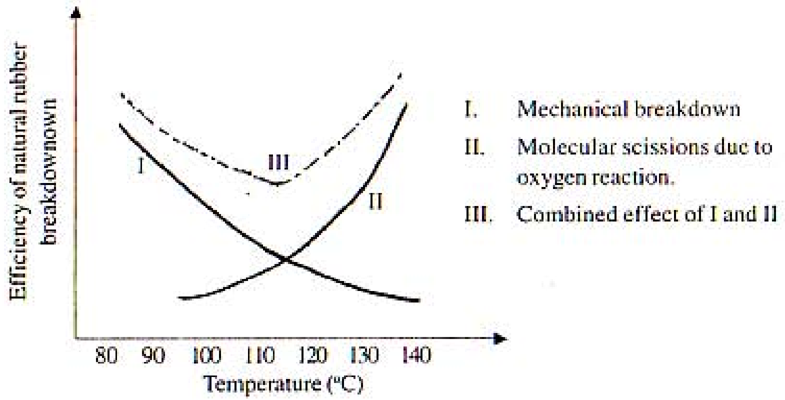


Fig. 6.2 Efficiency of natural rubber breakdown on increasing temperature.

The curves show that the natural rubber breakdown efficiency is at minimum level in the temperature range from 110 to 115°C.

6.2 Mixing process

Mixing on a two roll mill

When the rubber becomes soft with sufficient plasticity, the compounding ingredients are added into the softened rubber on the front roll (band) near the nip. In the nip, the collected rubber mass with the ingredients (bank) is pulled down by the rotation of the rolls. The size of the bank can be controlled by the adjusting the nip opening. Cold or hot water, steam or hot oil may be circulated through the rolls to change the temperature of the mix during the operation.

It is obvious that just as in plasticizing, and even more so, the operator plays a very important part. With his special knife, he cuts off, puts back and transfer pieces of rubber from the band to the bank in order to obtain a very uniform compound.

Shortcomings in mill mixing

Mill mixing is a slow operation which requires constant physical effort from a mill operator. It is not only time-consuming but difficult to control, because it so heavily depends on the skill of the operator. Environmental requirements make the handling of powdered ingredients on an open mill even less likely in the future, unless used in a costly master batchform.

Uses of two - roll mills

Two roll mills in rubber industry can be used for the following:

i. Masticating and mixing of rubbers

ii. Preparation of slab of rubber mix after mixing in internal mixes.

iii. Breaking up cold rubber compounds after storage.

iv. Grinding of vulcanised scrap rubber parts into coarse and fine rubber granules.

v. Refining of reclaimed rubber.

Specifications of two - roll mills

Sizes of Rolls		Approximate batch Weight
Working length (inches)	Diameter (inches)	lbs
12	6	2-4
18	9	5-9
24 28	12	15-20
40 42	16 18	35-40
50	20	55-80
60	20 22	90-120
72	24	130-200

Safety device in two rolls mills

Mills are usually fitted with various safety devices, some to protect the operator, others to protect the mill.

i. Lunn safety bar: This protects the operator. It is a breast high bar which will stop the mill if pressure is applied. The Lunn bar is fitted in such a position that an operator cannot get near the mill nip, but if, by mischange he should be caught and dragged towards the nip, then pressure on the Lunn bar will stop the mill.

ii. Breaker plate : The breaker plate is made of cast iron and is placed between the roll nip adjusting screws and the roll end bearing house. When the mill is over loaded, it breaks cutting out automatically the motor drive.

Auxillary attachments

a. Mill tray : This is placed under the rolls to collect droppings from the mill.

b. Guides : These are plates fitted to the ends of rolls to prevent rubber from being contaminated with grease, e.t.c.

c. Mill apron : This replace the mill tray and consists of a belt running under the nip to the top of the back roll. The belt returns to the mill any powders which fall from the nip.

d. Stock blender : This is a device for blending the rubber mechanically instead of depending upon the operator.

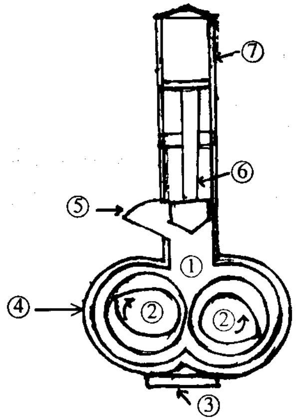
e. Cutting Knives : These are mounted against the roll to produce strips for feeding other equipment for removing the compound from the mill.

f. Scrap plates : These are fitted to remove soft tacky stocks.

Mixing in internal mixers

Internal mixers are a partial substitute for the mixing mills. They are also known as Banbury mixers. The banbury mixers also has two rotors, but their surface are provided with deep grooves of such design as to circulate the compound not only circumferentially but also horizontally, parellel to the axis of the rotors. These rotors are enclosed in a chamber and rubber is worked between the two rotors as well as between the rotors and the walls of the chamber.

The raw rubber and various compounding ingredients are introduced into the mixer through a gravity-fed hopper and are forced into the mixing zone by an air operated plunger (ram). Internal mixers are made of special steels or very good casting for better wear resistance. Cooling by circulating water through the walls and rotors is widely used. Their output is very large and they make automatic production possible, as feeding, mixing and discharge can be controlled by elctric relays and auxillary motors according to a predetermined timing cycle. The disadvantages of internal mixers are high cost as well as complex construction and thus difficult maintenance. The main features of an internal mixer are shown in figs. 6.3 a and b.



1. Mixing chamber
2. Rotors
3. Discharge door
4. Chamber wall
5. Feed hopper
6. Ram
7. Air cylinder

Fig. 6.3. a. Schematic representation of an internal mixer

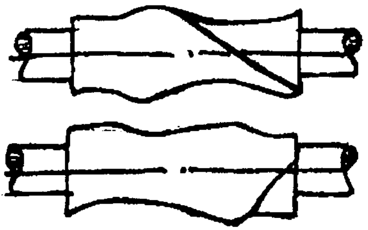


Fig. 6.3.b. A rotor design in banbury mixer

Continuous mixing process

The mixing process carried out on a two roll mill or in an internal mixer is a batch process. To make it as a continuous process the use of one of the following machines is essential.

i. Double R mixer :

This is a type of three roll mill, but after mixing, the compound is forced laterally through a die situated at one end of the machine.

ii. Farrel continuous mixer :

The mixer is similar to a twin-screw extruder. It has a warming zone near the feed throat and this leads to a mixing section within twin rotors; the final stage is an extrusion through a die.

iii. Transfer mix :

The machine consists of a single screw working in a barrel but it differs from normal extruders in that the depth of the teeth on the screw and the barrel is variable, whilst maintaining a constant volume along the length. As a result the compound is transferred from screw to barrel and back again several times along the length of the machine and this process gives the mixing and grinding action required (see fig. 6.4)

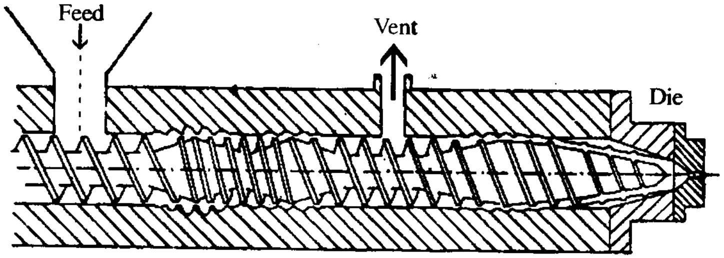


Fig. 6.4 Transfermix machine

Problems encountered in mixing process

Problems	Causes
Poor dispersion of ingredients	Incorrect batch size, Insufficient mixing time, Incorrect order of filler addition moisture in fillers. Insufficient ram pressure in the mixer.
Scorchiness	Loading temperature is high Insufficient cooling during mixing Fast curing system. Insufficient softeners
Difficulty in producing smooth mix sheet	Ineffective control of mill temperature and friction ratio. Viscosity of the mix is either high or very low. High loading of tackifiers.
Batch to batch variation	Variation in initial loading temperature, Variation in ram pressure, Different level of dispersion of ingredients. Variation in dump time and temperature.

6.3 Shaping/Forming Process

Extrusion :

Extrusion techniques are extensively used in the rubber industry. This operation is used when rubber is to be shaped in continuous length of constant cross section. The cross section may be solid, hollow, symmetrical or complex. An extruder consists mainly of a barrel (cylinder) in which a screw is rotating (see fig. 6.5). A rubber strip introduced into the extruder is seized by the screw whose spiral flight take it along and push it toward the end of the cylinder, which has an orifice or die of the desired shape.

Extruder screws are made of steel. They are hollow to permit cooling and their pitch is usually variable. They are driven by a variable speed gear in order to be able to carry out more types of treatment than at constant speed. They are operated by a separate motor with a reducing gear. Temperature control is very important especially for the head and die, which should have automatic control.

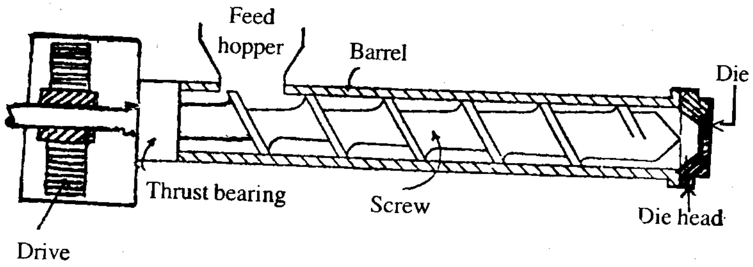


Fig. 6.5 Schematic diagram of a rubber extruder

Various types of extruder machines are in use today. Among these, the most commonly employed machines are as follows:

i. Hot rubber extruder

In general, an extruder which is fed with rubber compound at a temperature above ambient may be considered to be a hot rubber. The length to diameter ratio of the screw is in the range. 5:1 to 8:1. A hot feed extruder is designed so as to minimise the temperature of the compound through the extruder. The flight depth of the screw must be fairly high to hold down the energy imparted to the compound and to keep its temperature low (see fig. 6.6.)

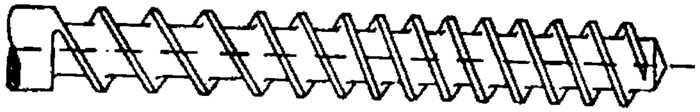


Fig. 6.6 A typical screw geometry for rubber extrusion (hot) - constant depth and variable decreasing pitch (VDP).

ii. Cold feed extruder

As the name implies, a cold feed extruder is fed with rubber compound at room temperature. The feed can be in the form of strip or pellets. Screws used in cold feed extruder requires special considerations in design. To accomplish, the extra mastication necessary, the flight depth must be small and the screw length must be long. A large drive motor and gear box are required to supply and transmit the mechanical energy to the screw. Reduction in the flight depth, high compression ratios, an increase in the number of starts, are the variables used to achieve high shear and high output. The length to diameter ratio of screw is in the range 15:1 to 20:1.

iii. Vented cold feed extruder

The vented or vacuum cold feed extruder was developed to expel unwanted gases from the rubber compound in order to cure extrudates at atmospheric pressure. The screw in a vented extruder has two distinct zones. The first zone has three sections - feed, transition and metering. The second zone has two sections - transtion and metering. A dam separate the two sections (fig. 6.7)

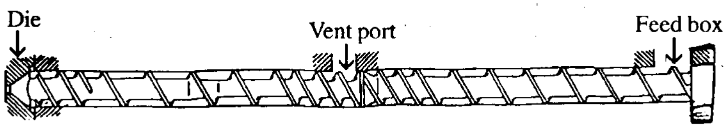


Fig. 6.7 Screw for vented cold feed extruder

iv. Pin extruder

The pin extruder represents the latest innovation in extrusion machinery. Pins mounted in the barrel provide an effective way to interrupt or split the laminar flow of the rubber mix and improve homogenization without using high shear rates. Slipping on the barrel wall is also prevented by the pins. Generally eight to twelve pins are arranged radially in 6 to 10 rows. (fig. 6.8)

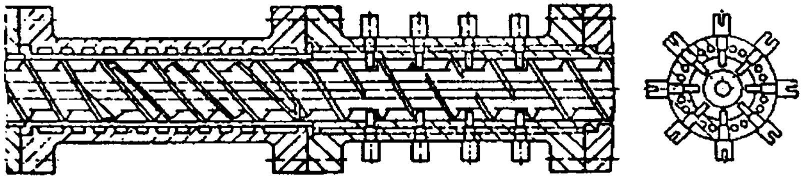


Fig. 6.8 A pin extruder - pins and mixing zone

Extrusion variables

The following extrusion variables are worthy to note for successful operation of the process:

i. Output rate

At low screw speeds, output rate is nearly directly proportional to screw speed (rpm) for most rubber compounds but as the screw increases toward the high end, the output rate decreases.

ii. Extrudate temperature

It rises as screw speed increases. The actual temperature rise is affected by screw design, head pressure, and the properties of the compound being processed.

iii. Money viscosity

Mooney viscosity of the extrudate generally drops due to the additional mastication at the extruder. However the change in mooney viscosity is very little as screw speed increases from 20 to 70rpm.

iv. Scorch time

The scorch time is reduced only slightly at these speeds 20 to 70 rpm. However it is affected by the type of screw, head pressure, and compound formulation. Modifying the compound to reduce viscosity by adding prevulcanisation inhibitants and changing the curing system are other alternatives, the compounder can persue.

v. Die swell

The increase in dimensions of an extrudate relative to the dimensions of die is called die swell. This takes place mainly due to elastic recovery of the rubber molecules in the extrudate, usually in the direction perpendicular to the direction of its flow.

vi. Rough surface of extrudate

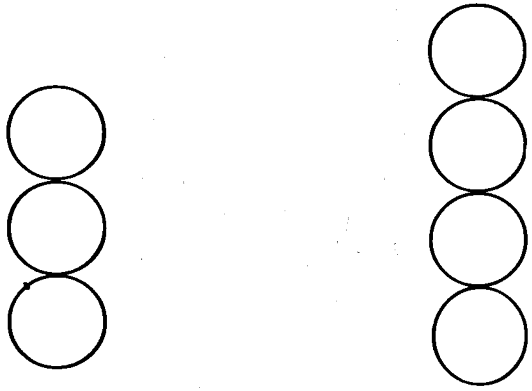
Surface roughess of the extrudate if not caused by scorchy compound is either due to air entrapment or insufficient mastication. Both causes are related to screw design and screw speed. Adjusting the temperature profile to increase mastication, changing screw design for mastication and additional breakdown of the compound in the mixer are solutions to this problem.

Calendering

A calender is a machine with three or more heavy, internally heated or cooled rolls (bowls). The rolls are usually made of best quality cast iron with good surface finish and high gloss. The machine is used mainly for the following purposes:

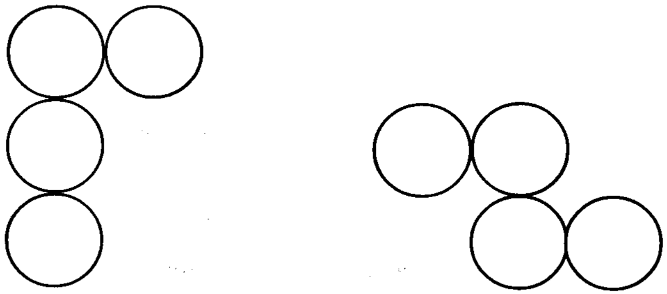
i. For continuous production of rubber sheet.
ii. For plying up rubber components.
iii. For frictioning or coating of fabric with rubber.

Calenders are generally described by the number of rolls and their configurations (arrangements), as shown in fig. 6.9.



a) Three roll calender

b) Four roll calender



Four roll inverted calender

Four roll 'Z' calender

Fig. 6.9 Configurations of calender rolls

Calendering of rubber sheet

Of all the calender machines, the most widely used calender for sheet rubber production has three rolls. The middle roll bearing is stationary, the other two are movable along the machine stand and nips of rolls with respect to the central roll can be adjusted. During calendering, the rubber mix sheet leaving the first pair of rolls (top and intermediate) immediately seized by the second pair (intermediate and bottom), the nip of which is smaller than that of the first pair (see fig. 6.10)

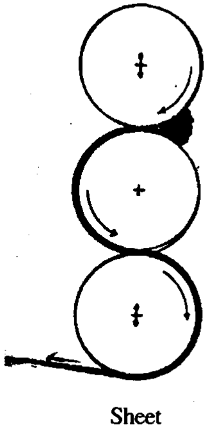


Fig. 6.10 Calendering sheet using three roll calender

Calendering of rubber sheet with uniform thickness

Calendering should yeild rubber sheets of very uniform thickness both in the width and the length. Therefore it is essential to control the parallel position of the rolls. In modern calenders the parallel position of the rolls is assured by set acrews of the bearings operated by auxillary motors. In the case of long roll calender machine, deflection of rolls is unavoidable because of the pressure exerted by the compound fed between the rolls.

To compensate for deflection, the following techniques are adopted:

i. The roll contours are made to counteract the deflections. Technically it is called cambering the rolls. This means deflecting the surface of the rolls to a few thousands of an inch as illustrated in Figs. 6.11 a and b.

ii. Here, the axis of two rolls. instead of being parallel, is kept at controllable angle (Swiveling arrangement). The principle involved is an axial movement of the rolls. so that axis of one roll crosses the axis of the other, thus providing a nip opening which is greater at the end than in the centre of the rolls.

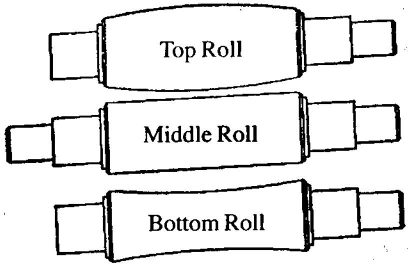


Fig. 6.11.a. Cambering calender rolls

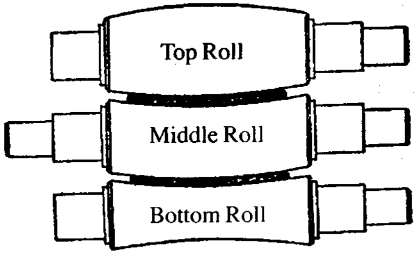


Fig. 6.11.b. Roll contours during calendering

Other factors which have to be considered for the production of rubber sheet of uniform thickness are as follows:

i. The temperature of the calender rolls must be controlled.

ii. The rubber compound should be homogeneous and have high rubber content.

iii. The plastictity of the compound should be carefully controlled.

iv. A constant feed of compound is important.

Advantages of four roll 'Z' calender machine

It has been found that four roll 'Z' calender performs better than other calenders for the production of rubber sheet with uniform quality (fig. 6.12). The better performance of the calender is attributed to the following factors:

i. The arrangement of two rolls in any one plane in 'Z' configuration eliminates three roll pressure and can be swivelled easily.

ii. The rubber mass on the calender is not exposed as much as in normal three roll calender and this simplifies the temperature control.

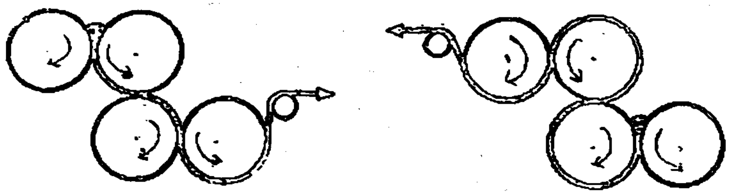
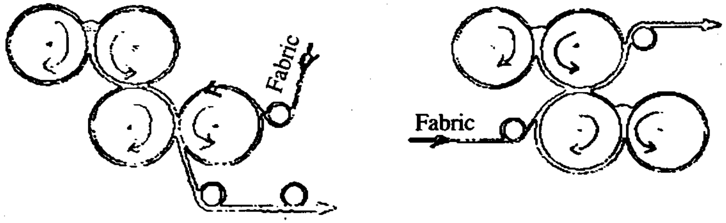


Fig. 6.12 Production of sheet using four roll 'Z' calender

Fabric coating with rubber

Rubber coated fabrics find applications as reinforcing components in some composite rubber products. Typical examples of such products are tyres, conveyor belts, hoses, e.t.c.

Both three roll and four roll calenders are used. The rubber coating operations by means of these machines are illustrated in fig. 6.13.



Single Coating Double Coating

Fig. 6.13 Coating of fabric using four roll 'Z' calender

Unlike, a three roll calender which is suitable for coating only one surface of the fabric, a four roll calender is used to coat both surface of the fabric in the same operation. Operating temperatures for calender rolls vary according to the type of compound. It is however normal practice to operate with low temperature with those rolls around which the rubber films circulate.

Topping

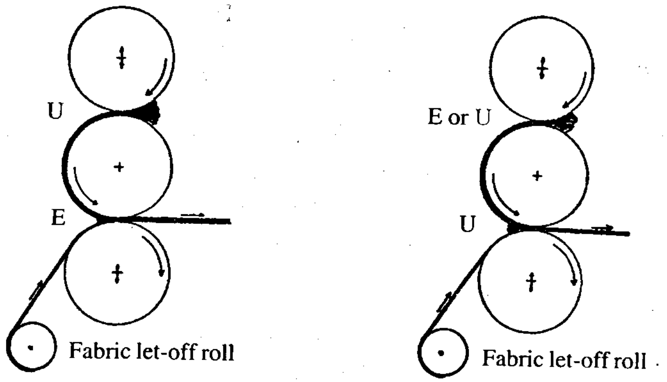
The purpose of this operation is to give the fabric surface a thick rubber coating/film. In setting up three or four roll calenders for topping, even surface speeds are used for the pair of rolls forming the fabric nip and a friction ratio 3:2 between those forming the rubber film nip.

Frictioning

The object of frictioning is to impregnate a length of fabric with soft rubber. The rubber in this operation, penetrates the texture of the fabric and reinforces it.

Frictioning is confined to three roll. Surface operating with a middle roll surface speed of 3:2 for the outer pair of rolls. In contrast to the topping process, it is necessary that the compound adheres well to the middle roll and does not break away under the shearing action, which takes place in the fabric nip. It is essential for the purpose to have a compound with lower black loading and a higher rubber content than is considered desirable for topping.

Roll temperature used will depend upon the processing characteristics of the compound, but the middle-roll which is completely enclosed by a rubber film throughout the run is kept as cool as possible and is generally 20 to 30°C lower than the two outer rolls. A film of approximately 1.2 mm gauge circulates round the middle roll during frictioning. The two operations are illustrated in fig. 6.14.



Topping

Frictioning

Fig. 6.14 Schematic diagrams for topping and frictioning

U - Uneven roll speeds
E - Even roll speeds

Calendering of smooth rubber sheet

The two important problems that have to be encountered in the production of smooth rubber sheets are :

i. Formation of 'crows feet' (V-shaped marks)

This occurs due to insufficient mastication of rubber and low temperature calendering.

ii. Formation of air bubbles or blisters

Over mastication and high temperature calendering are the main causes for occurrence of this defect.

Hence, to produce smooth surface in rubber sheet, appropriate remedial steps should be taken, to overcome the problems.

Chemical plant lining

Calendered sheet for chemical plant lining is usually required 3/16 inch thick, but to obtain a satisfactory surface, the sheet has to be built up in plies at the calender and then doubled on a doubling frame. The plying up on the calender is usually done by means of a rubber covered breasting roller, working against the bottom calender roll. (see fig. 6.15)

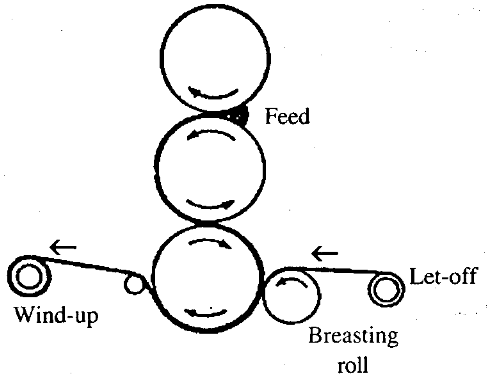


Fig. 6.15 Plying up on a calender

Profile calenders

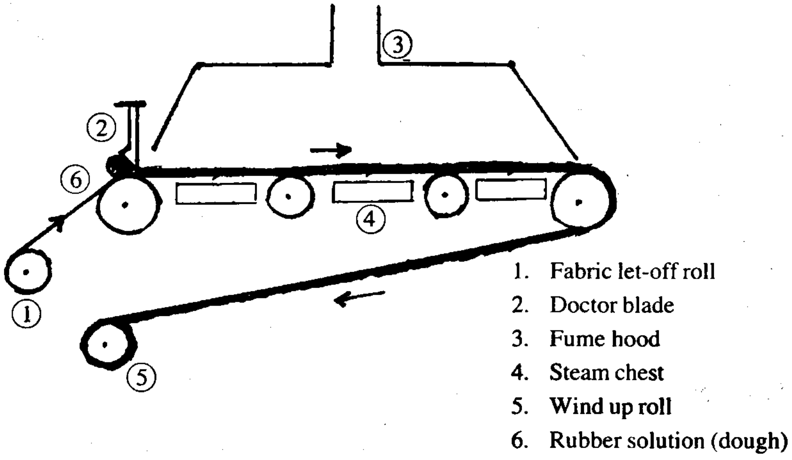
The most widely used calenders for profiling rubber compounds are four roll machines arranged with three rolls in a overhead stack and the fourth profile roll generally mounted level with and in front of bottom roll.

The profile roll is made from a high grade cast iron or mild steel without any chill. This enables the profile contour to be cut as required.

In most factories, the complex production programme will require changes of pattern. This is effected by changing the complete roll with another of the required profile. The profile calenders are used for the manufacture of products like bicycle tyre tread, rubber matting soles, e.t.c.

Coating of fabrics with rubber by means of a spreading machine

The spreading machine consists essentially of a table, over which the fabric to be coated with rubber is passed. At the inlet end of the table, the fabric travels under a distributor which consists of a container filled rubber solution (dough). This container can be opened at the bottom to the desired degree to allow a given of solution to flow on the fabric and spread over it. A doctor or spreader blade that can be accurately adjusted in height is used for controlling the thickness of the rubber coating (see fig. 1.16). The table is heated with steam to evapourate the solvent into a chamber in the upper part of the machine which discharges it into active carbon solvent-recovery units. At the discharge end of the machine, the rubber-coated fabric is wound on reels or rolls.



1. Fabric let-off roll
2. Doctor blade
3. Fume hood
4. Steam chest
5. Wind up roll
6. Rubber solution (dough)

Fig. 6.16 Schematic diagram illustrating the spreading process

The advantage of spreading method is that a heavy weight rubbered fabric can be produced without any surface defects.

6.4 Moulding and Curing processes

In moulding process the rubber is shaped in the form of articles with desired physical and mechanical properties. There are various methods of moulding used and the choice of method is dependent on the following factors:

i. Viscosity of rubber mix
ii. Size of moulding
iii. Time of moulding

A useful and general overview of relationship of the above is provided in the figure 6.17.

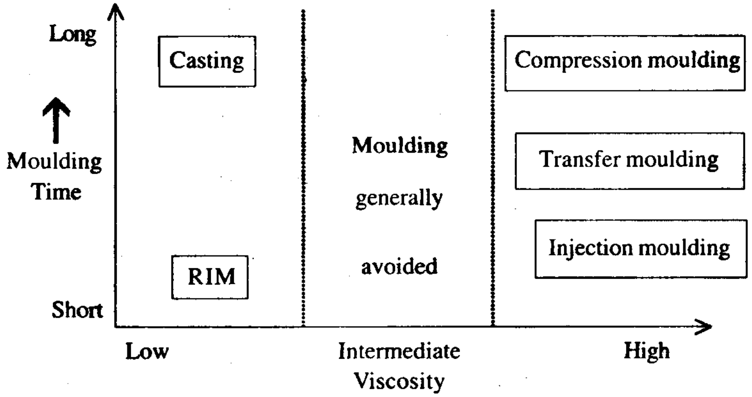


Fig 6.17 Moulding methods and their governing factors

Methods of moulding high viscosity rubber mixes :

Compression moulding

This type of moulding can be carried out by the following techniques:

i. Flash or straight compression

This is the most commonly used moulding method. In the method, the mould cavity is filled with preform (a piece of rubber mix in the shape of mould cavity). During mould closure, the preform is squeezed between the top plate and the land and the excess into the flash groove (fig. 6.18). Typical volume of flash (excess rubber) is 10 to 20% of the mould cavity volume. The mould design is simple and the moulds are inexpensive.

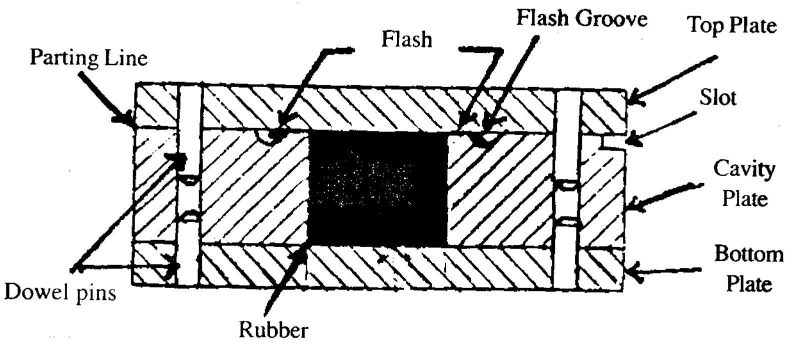


Fig 6.18 Compression moulding of rubber

ii. Positive of plunger compression

The preform exactly fits in the mould cavity, in the method. It is pressed directly by a plunger and there is no provision for flash, as the clearence between plunger and cavity is very close. The mould is single and easy to manufacture. Some of the reasons to discard this type of mould are necessity of preparing an exact preform and difficulty of ejecting the product after curing.

iii. Semi-Positive compression

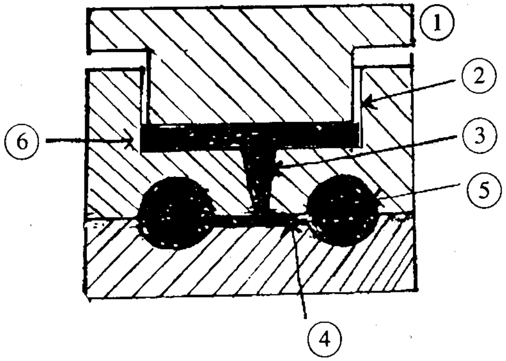
The mould design is a compromise between the above two. The plunger fits loosely and very deeply into the cavity. Flashing is permitted and the preform rubber mix need not be accurate. The rubber gets more pressure, when compared to straight compression and there is less amount of flash. However this type of mould is expensive to manufacture and maintain.

Transfer moulding

Transfer moulding is a variation of compression moulding. In transfer moulding, a plunger compresses a rubber preform in a pot as shown in fig. 6.19. The rubber is heated by contact with the plunger face and pot. When sifficient force is applied to a mould by a press, rubber flows through the sprue and into the mould cavity. Clearence between the transfer pot and plunger is important. This clearence should be small enough to minimize flow of rubber between plunger and the wall of the pot. A clearence of about 0.12 mm is preferred.

An important feature of a transfer mould is the depth of engagement of the plunger and pot. The plunger should engage the pot deeply enough to minimize tilting of plunger in the pot.

The sprue is round in cross-section and becomes narrower as it approaches the mould cavity. Because the sprue is narrowest just above the moulded part; the sprue breaks there when the flash pad is removed from the transfer pot. Transfer moulding has an advantage over compression techniques in that the moulding material is fluid when it enters the mould cavity, which enables slender core pins to be used and intricate sections to be moulded. Faster cycles are also possible by using transfer moulding, due mainly to the local heating produced from the frictional heat during the moulding cycle.



1. Plunger
2. Transfer pot
3. Sprue
4. Runner
5. Moulded rubber good.
6. Flash pad

Fig 6.19 Transfer moulding of rubber

Moulding operations

Both compression and transfer moulding operations are carried out by means of hydraulic presses. The moulds are placed between the platens of the press (see fig. 6.20). The platens are made of steel and are constructed so as to permit circulation of a heating fluid. The platen temperature of a good press does not vary more than 1 or 2^0 C over its entire area. The heating medium is usually high pressure steam. Hot water is also used for this purpose. These heating methods have both advantages and drawbacks. The temperature is controlled by electric or pneumatic valves. The heating medium is introduced through flexible tubes or through elbow pipes.

Electric heating, which is indispensable for the treatment of plastics, because of the high temperature required, is not suitable for rubber processing. The temperature of the platens is seldom as uniform at all points as with steam or hot water heating. The cost of electric power is also high.

The dimensions of platens may vary within wide limits, There are presses of 12" x 12" and smaller and also those up to 10' x10'. Small moulds can be manually handled by an operater but large moulds which are heavy for an operator can be attached to the press platens, so that they are opened and closed by the press.

In operation, the hydraulic fluid under high pressure is supplied to the cylinder. A packing gland prevents leakage of fluid between cylinder and ram. The fluid pushes the ram upward against the ram bolster and provides pressure to the mould.

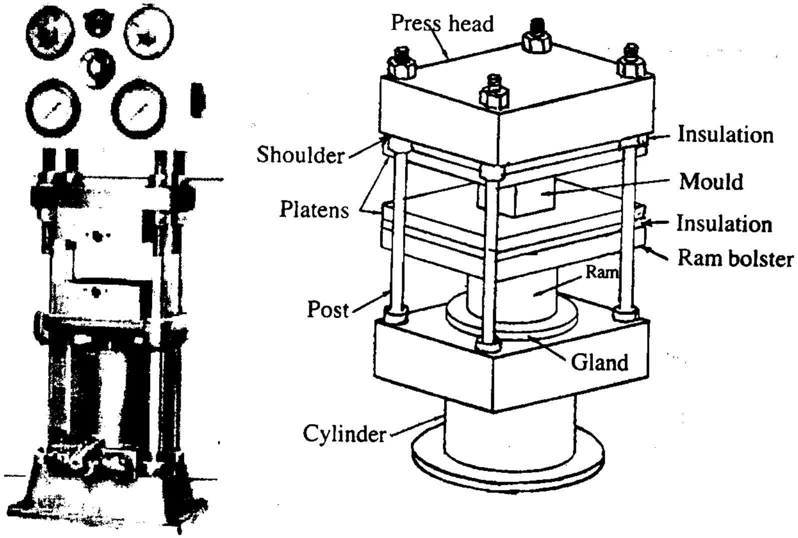


Fig 6.20 A hydraulic press

Injection moulding

The main feature in which injection moulding differs from compression moulding is in the presentation of rubber to the mould at or near moulding temperature. As a result of this, the moulding time is much reduced in the opeartion.

There are two types of injection moulding machines used, namely, ram and reciprocating screw injection moulding machines. They differ basically in the methods of heating and preplasticization of the rubber mix.

Ram injection moulding machine

The main features of the ram injection moulding machine is shown in fig. 6.21. Rubber is fed into the throat/hopper with the ram in the retracted position. During injection, ram forces the rubber forward through the nozzle and mould sprue, where it enters the mould cavity. Before rubber enters the mould cavity, it has been heated by contact with the inner barrel wall. The rubber becomes hot as it passes through the nozzle and sprue at very high shear rate.

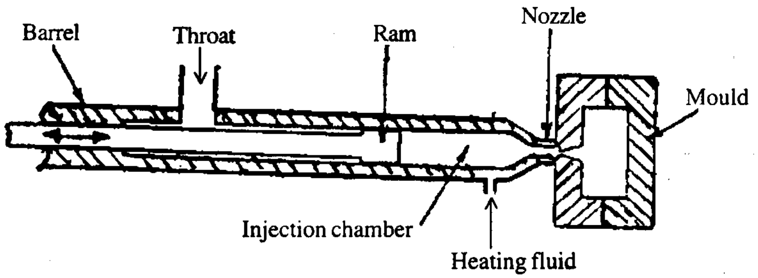


Fig. 6.21 Ram type injection moulding machine

Screw injection moulding machine

The screw injection moulding machine is illustrated in fig. 6.22. Its main features throat, injection chamber, nozzle, heating fluid and mould are nearly identical to that of a ram machine. However the main difference is that the screw machine is fitted with a screw which rotates inside the barrel like an extruder machine. This screw not only rotates, but also moves backward and forward on its axis like the ram in ram injection moulding machine.

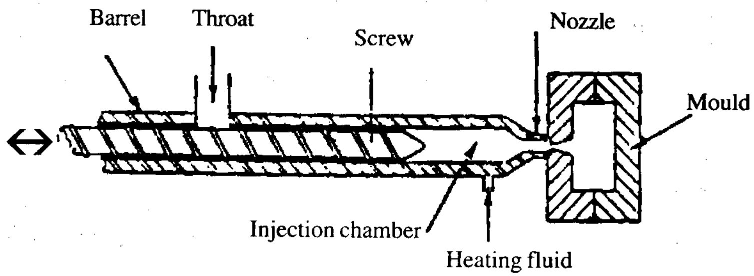
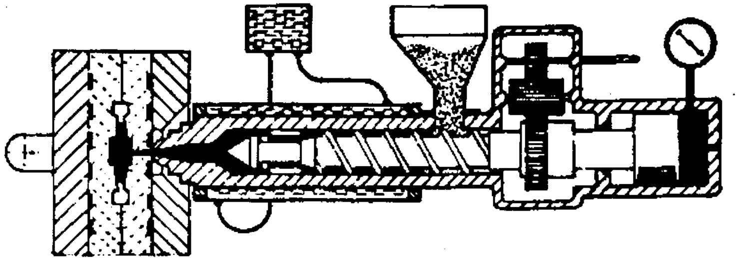
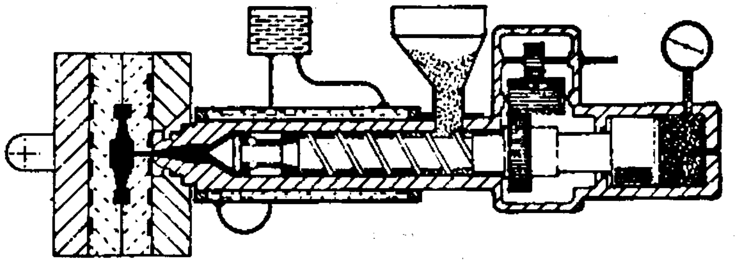


Fig. 6.22 Reciprocating screw injection moulding machine

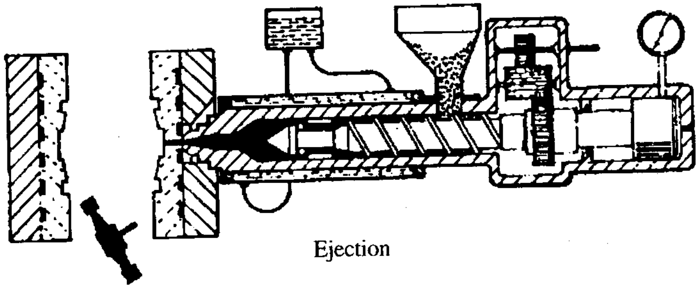
The rubber which is fed into it in strip form contacts the rotating screw. The screw plasticizes the rubber and transports or pumps it to the front of the injection chamber. Rubber accumulates there because the screw retracts backward to provide the needed volume in the injection chamber. When sufficient volume of rubber accumulates, the screw no longer rotating, slides forward to act as a piston and fills the mould with rubber. After the cure time, the screw retracts and the cycle of process is repeated (see fig. 6.23)



Injection



Vulcanization



Ejection

Fig. 6.23 Screw injection moulding cycle

Relative merits of ram and screw injection moulding machines

Screw injection moulding machine

When rubber mix is passed into the screw injection moulding machine, the mix is highly plasticized by the local heating developed due to the shearing action on it. This enhances the flow rate of the mix.

Ram injection moulding machine

In this machine, higher injection pressure and more accurate shots are possible because of the too small clearence between the ram and the barrel wall. (ca. 0.05 mm).

Injection moulds

These moulds must be capable of withstanding extremely high pressures without mould distortion. Since the injection presures up to about 200 MPa (29,000 psi) are used, a high quality steel is recommended for injection moulds. The mould plates should be thick enough to resist bending at the high pressures encountered during injection moulding. For multicavity moulds, the distributing system for the molten rubber mix should be carefully designed to facilitate smooth flow of the mix into the mould cavities. The cross section of the runners should be preferably trapezoidal or half-round.

Mould release agents

The mould release agents are water based solutions. When applied on hot mould surface, water evapourates from the solution, leaving a deposit on the mould surface. The deposit prevents the adherence of rubber to the metal surface while moulding and thereby it facilitates the stripping of the rubber product from the mould.

Typical mould release agents are :

Silicone emulsions, Surfactant solutions. Aqueous dispersions of magnesium, aluminium or calcium silicates.

Mould Cleaning

In mould cleaning, the rust or deposit on the mould surface is removed. If the mould is not cleaned, there is a tendency for the rubber to stick to the mould surface, which makes it difficult for production of good mouldings. The methods widely used are as follows:

i. Manual cleaning (using steel wires, fine abrasive papers, and detergents)

ii. Soft grit blasting (using sand, or metal grits of size 10-30 mesh)

iii. Vapour blasting (a water based solution of detergent is sprayed at a high velocity through a nozzle)

iv. Electrolysis (here the mould is used as an electrode in a detergent bath or caustic soda, through which a low voltage current is passed. The gas generation on the steel surface of the mould assists the detergent action of the electrolyte bath in removal of the deposit or rust)

v. Chemical method (moulds can also be cleaned with dilute acids e.g. Dilute HCI (5%) and then with steam)

Comparison of moulding methods

i.	Feeding		A strip of rubber mix or granulated rubber mix is automatically supplied in injection moulding machine whereas in transfer or compression moulding of rubber mix, a preform or plug is used.
ii.	Temperature, Pressure and other variables	:	Several controls to adjust these variables are provided in injection moulding machine.
iii.	Mould closing and opening	:	In injection moulding a clamp which forms the intergrated part of injection moulding machine provides the force to close and open the mould.
iv.	Shear rate	:	Shear rate varies according to the method of moulding. i. Injection moulding $10^3-10^4 Sec^{-1}$ ii. Transfer moulding $10-10^2 Sec^{-1}$ iii. Compression moulding $1-10 Sec^{-1}$
v.	Moulding pressure	:	pressure applied in injection moulding is about ten times greater than that used in the other two methods.
vi.	Production time	:	Injection Moulding <Transfer Moulding < Compression Moulding

Other curing methods

An autoclave or steam pan curing

An autoclave is a cylindrical pressure vessel, normally used in the horizontal position. The pressure and temperature required for cure are achieved by the use of steam. The vessel is used for the vulcanisation of extrusions, sheetings and components which are of an unsuitable size for conventional mould curing. As direct open-steam is applied in the vessel, the products are usually covered. It is common to support the extrusions and small components by embedding them in talc on trays. Products formed on mandrels and sheeting are generally cloth wrapped to prevent distortion.

Autoclave should be installed so as to avoid condensed water accumulation in the vessel. A slight slope can be useful in avoiding the water accumulation. It can be discharged at the back of the autoclave through a valve or preferably a steam trap.

The autoclave should also be provided with railings for easy loading and unloading operation. It is essential that the autoclave be provided with proper lagging (see fig. 6.24).

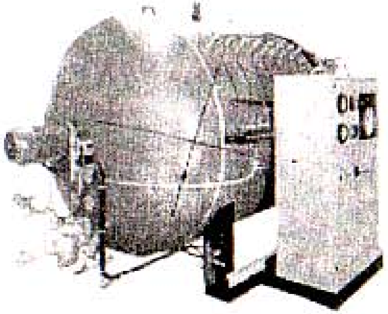


Fig. 6.24 An autoclave (steam - pan)

Curing in hot-air using indirect steam

Rubber articles containing fabric decolourize and loose shine in opensteam. Thus, products such as canvas, rubber proofings e.t.c. are cured in hot air. The process can be carried out in an autoclave provided that it is modified or equipped to supply heat inside the vessel in the absence of steam.

There are two ways to obtain heat inside the vessel ; first way by passing steam under pressure in bundle of steel tubes located inside the autoclave and the other way to provide the autoclave with a jacket in which steam is under high pressure. The normal steam pressure used are 70-100 psi. This heats up the air inside the autoclave. The air is also maintained under pressure to prevent porosity in the rubber product.

Boiling water cure

This method is used for curing a) ebonites and b) tank-linings. Since ebonite compounds involve highly in exothermic reactions, water cures control the heat and yeild very good ebonite products. For example to prepare ebonite combs, the ebonite compound is put in lead foil and embossed with the length design. This is put into water baths and cured for 24 hours.

Rubber lined vessels of small size are preferably cured in a large autoclave for open-steam heating. However for bigger lined vessels which are not possible to cure by putting in autoclaves, water cures are suitable. For this, the lining rubber based on ebonite compound which is curable at 90-100°C is used. The rubber lined vessel is first filled with water at room temperature. The water is then heated by passing steam through it. The heating up time for water should not exceed few hours. If the tank is large, steam should be introduced at various points to heat up water as quickly as possible; usually salt is added into water to raise the temperature.

Festoon hot-air curing

Coated fabrics are generally festooned in heaters and cured at atmospheric pressure (see fig. 6.25)

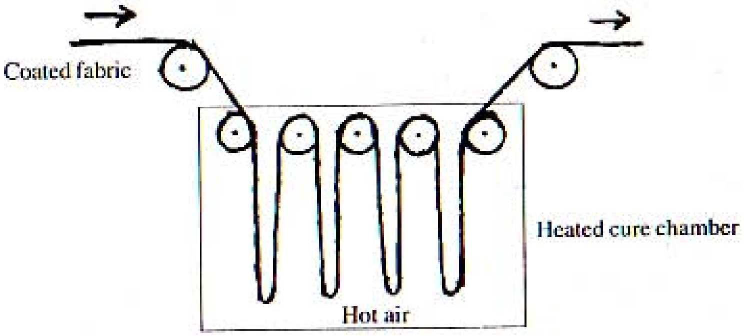


Fig. 6.25 A festoon cure chamber

Continuous curing methods

As curing in presses or autoclaves is a batch process, methods are now devised to cure continuously the products of considerable length. Typical products which are cured by continuous curing methods are : Conveyor belts, Electric cables, Automobile window channels, etc..

i. Long tunnel method

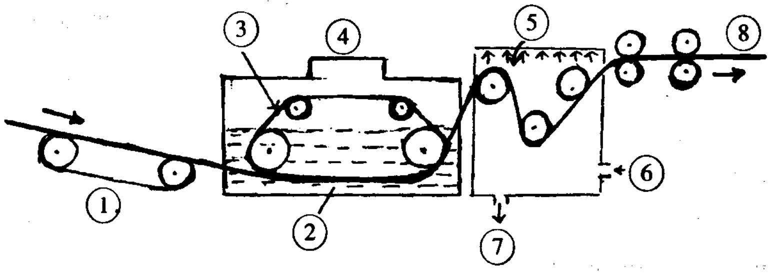
In the method the unvulcanised product enters into a long tunnel pressurised with steam or hot air and leaves the tunnel after fully cured.

The points of entry and exit are especially designed to prevent any leakages. During the traverse in tunnel, which are usually 200 ft long, supports are given at various points along the length. The rate of traverse inside the tunnel depends on the shape of product and type of compound. Rubber cables have been successfully vulcanised by this method.

Steam curing at high pressure (≈ 200 psi) is preferable to hot air curing to eliminate any porosity on the surface of the product.

ii. Fluid bed or liquid curing method (LCM)

Here, the extruded profile especially having solid rubber section is fed into a liquid curing bath made of stainless steel. The length of the bath is generally 5 to 15m. High cure rate, low volatile matter content and good retention of shape are especially required in the pre-shaped rubber to be cured in this LCM method. The curing medium is an eutectic mixture of three inorganic salts potassium nitrate, sodium nitrite, and sodium nitrate in the ratio 53:40:7. The melting point of the mixture is 142° C and its boiling point 500° C. A temperature of 240 °C is used for curing and the dwell time is approximately one minute for the section of the extrudate. Heating of bath is carried out by electrical means. To prevent, floating up of low relative density extrudate in the liquid medium, an endless steel belt conveyor is used as shown in fig. 6.26. The cured extrudate should be passed through wash tank to remove any salt deposits on its surface.



1. Inlet conveyor
2. Salt bath
3. Submerging conveyor
4. Fume extract
5. Water spray
6. Water in
7. Water out
8. Cured rubber product

Fig. 6.26 Schematic diagram for liquid curing method (LCM)

Fluidised bed curing method

The fluidised bed system as shown in fig. 6.27 is used. It consists of a tank of granular solid particles such as sand or glass beds of 0.10-0.20 mm size called 'ballotini', through which a stream of hot air is passed from bottom to top. The particles are held in suspension due to this effect and behave as if they were fluid of high specific gravity and viscosity. The rubber which is to be cured continuously is transported through the bed of ballotinis.

Fluidised bed has a heat transfer coefficient rate which is 50 times the hot air system. Vulcanisation can be done in relatively short time. The maximum temperature achievable is 250° C. Since hot fluidised bed system applies less pressure than the liquid curing system, it is more suited to sponge rubber. The chief problems with this method are : i) glass bead adherence and ii) energy costs. Steam rather than air is used as gas for rubbers which are easily oxidised. The advantages of ballotini are that it is completely chemically inert and non-wetting and that no guides, rollers or coneyor system are required in the bed.

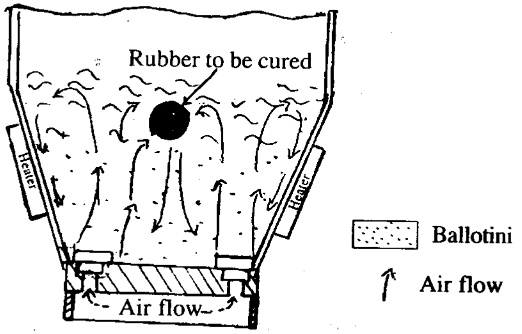


Fig. 6.27 Ballotoni flow pattern in fluidised bed curing method

Rotocure method

The continuous vulcanisation of flat sheets including belting is possible by means of this method, where the rubber is heated and vulcanised while passing between a steel band and a metal drum. The speed of rotation of the drum is variable and is adjusted to achieve the full vulcanisation of the rubber during its passage. (see fig. 6.28)

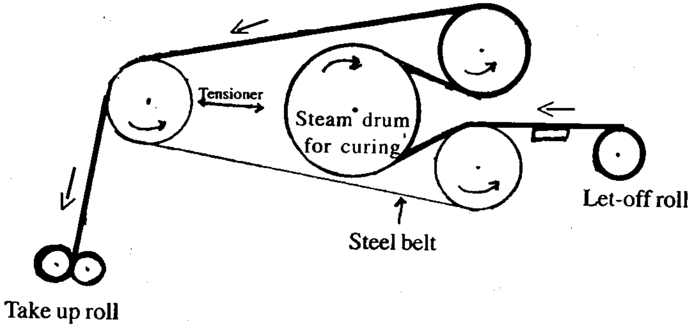


Fig. 6.28 Illustrating the operation of the 'Rotocure' machine.

High frequency radiation cure

In all the above three continuous curing methods, heat transfer takes place from outside towards the interior of the rubber volume. Owing to the low thermal conductivity of rubber, a considerable time is required to cure the innermost part adequately especially in thick rubber articles. In such cases, high frequency radiation cure is most preferable.

The passage of high frequency radiation into the unvulcanised rubber causes rubber molecular vibrations and thereby generates required heat for curing reactions. Large products can be uniformly cured by this method in short time. Typical source of high frequency radiation is gamma rays which can be obtained from cobalt 60. This source of radiation is safe and imparts good mechanical properties to rubber vulcanisates.

Moulding of low viscosity mixes

Reaction injection moulding (RIM)

Reaction injection moulding is developed for mixing and moulding low viscosity liquid materials. A major difference between casting and RIM is the extremely rapid reaction rate for the reactants used to make RIM products.

In the method, streams of starting liquid materials under high pressure, are mixed in the chamber of the machine, where they strike one another at very high velocities causing turbulance. The mixture then flows into the runner at low pressure. From the runner, the mixture flows through the gate into mould cavity to form the product (see fig. 6.29) Some of the polyurethare rubber products are now moulded using by this method.

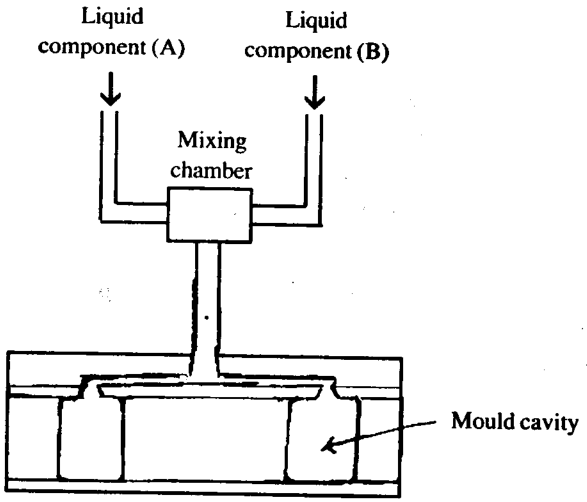


Fig. 6.29 Schematic diagram for reaction injection moulding (RIM)

6.5 Some safety rules for operators

i. Safety devices fitted to mills, calenders, e.t.c. must be checked for correct operation before work is started.

ii. Knives and other cutting tools be kept sharp and be used when necessary .

iii. Machinery in motion must be treated with extreme caution especially in running nips of mills and calenders , feed screws of extruders e.t.c. Although the speed of hydraulic press platens is not high, keep clear of them, whether the press is closing or opening. Loose coats, dangling shirt sleeves and ties should be avoided.

iv. Gloves should be always be worn in handling hot moulds, mandrels, e.t.c. but not for handling rubber stock on mill or calender.

v. Note the position and method of operation of the fire extinguishers, provided and study carefully the action to be taken in case of fire.

Chapter 7

Designing of Rubber Compounds

The important factors considered in designing rubber compounds are ----(i) service requirements (ii) processabilty and (iii) cost. A compounder is therefore concerned with securing an acceptable balance between the demands arising from these three factors. Since the cost of raw materials and production processes fluctuate from time to time, with the innovation of new materials and methods, the cost factor is rather complicated to be considered here and hence only the first two factors will be discussed in this chapter.

7.1 Designing of rubber compounds for service requirements

In designing compounds for service, the physical properties of the vulcanisates and the environment where the vulcanisates are to be used, are primarily taken into account. In this aspect, the data of general properties of more commonly used rubbers as given in table 7.1 are of great significance.

Compounding techniques of producing vulcanisates with desirable physical properties

Hardness :

Hardess values of raw rubbers and gum rubbers are very low, and lie normally in the range of 35 to 42 IRHD. To increase the hardness of these materials, fillers are incorporated into them. Of all types of fillers, reinforcing powdery and resinous types are found to be more effective (see table 7.2).

Table 7.1 Physical properties of common rubbers

	Natural rubber	Styrene butadiene rubber	Butadiene rubber	Butyl rubber	Chloroprene rubber	Nitrile rubber	EPR /EPDM
Specific gravity	0.92	0.94	0.93	0.92	1.23	1.01	0.86
Glass transition temperaturd (T_g °C)	- 70	- 60	- 75	- 65	- 40	- 50	- 40, - 50
Service temperature°C	- 50/100	- 50/100	- 50/100	- 50/110	- 30/150	- 30/110	- 50/150
Solubility parameter (Cal. cm^{-3})$^{1/2}$	8.1	8.4	8.4	7.9	9.5	9.2	7.9
Tensile properties	Excellent	Good	Fair	Fair	Good	Fair	Fair
Heat resistance	Fair	Good	Good	Very good	Very good	good	Very good
Weather resistance	Poor	Poor	Poor	Good	Excellent	Fair	Excellent
Insulation resistance	Excellent	Excellent	Excellent	Excellent	Poor	Poor	Excellent
Flame resistance	Poor	Poor	Poor	Poor	Good	Poor	Poor
Compression set	Good	Good	Good	Fair	Good	Good	Good
Permeability to gases	Fair	Fair	Fair	Very low	Low	Fair	Fair
Resistance to :							
Aliphatic hydrocarbons	Poor	Poor	Poor	Poor	Good	Excellent	Poor
Aromatic hydrocarbons	Poor	Poor	Poor	Poor	Fair	Good	Poor
Ketones	Good	Good	Good	Good	Poor	Fair	Good
Dilute acids	Good	Good	Good	Excellent	Excellent	Good	Very good
Conc. acids	Fair	Fair	Fair	Excellent	Fair	Fair	Very good

Softeners and plasticizers reduce hardness and mineral process oils which are widely used in common hydrocarbon rubbers as extenders produce a hardness drop of approximately I IRHD for every 2 phr added.

Table 7.2 Effect of various of fillers on hardness of natural rubber

	Types of fillers	Particle size (nm)	Parts of filler per 1° IRHD increasein hardness in natural rubber
a. Carbon blacks	ISAF	24	1.7
	HAF	32	1.9
	GPF	70	2.5
	MT	300	4.2
b. Mineral fillers	Silica (hydrated)	20	2.0
	Hard Clay	2 x 10^3	5.0
	Soft Clay	10 x 10^3	7.7
	Whiting	12 x 10^3	6.4
	Calcium silicate	25	3.0
c. Resinous fillers	High styrene resin		2.0
	Phenol formaldehyde resin		2.0

Elasticity

Rubber products, which show high elastic properties, generally have high resilience and show low set, creep and stress relaxation. To improve the elastic property, the molecules of the rubber must be tightly cross - linked with strong chemical bonds. Thus the use of an appropriate curing system, with antioxidant protection will give enhanced elastic property.

Gum rubber products based on NR, IR, CR and BR are most suitable for high elastic properties. Since filler loading and softeners decrease the elastic properties, these ingredients should be added at minium level.

Strength

Rubbers which crystallize on stretching such as NR, IR, CR generally exhibit high levels of tensile strength in their gum rubber products. Other non-crystallising rubbers such as SBR, NBR and BR of low gum strength require fine size reinforcing fillers to develop maximum strength. Fine size carbon blacks (SAF, ISAF, HAF) and silica are the most effective reinforcing fillers for this development. Crystallising rubbers are also found to be at their high level of strengths with these fillers provided that the fillers are dispersed uniformly. Resinous fillers such as high styrene resins and phenolic resins can also produce strength increase in non - crystallising rubbers.

Abrasion resistance

In general fine size particle C - black (ISAF, HAF) filler loading at about 50 phr levels show optimum abrasion resistance in NR and SBR. These rubbers also exhibit better abrasion resistance when they are blended with high abrasion resistant BR. A good level of amine type antioxidant eg. p - phenylenediamine has also been found to enhance the abrasion resistance of NR.

Creep and Stress relaxation

Creep and stress relaxation behaviour of rubber vulcanisates are explained in Chapter 9. Natural rubber vulcanisates generally show lower creep than the vulcanisates of synthetic rubbers though some rubbers like chloroprene rubber can be compounded and vulcanised to give figures comparable with those of natural rubber. To improve further the creep property of natural rubber, the rubber should be lightly loaded with fillers and tightly crosslinked.

The relaxation rate of all natural rubber vulcanisates is generally lower than that of the commonly used synthetic rubbers. The conventional accelerated sulphur vulcanisates of natural rubber, show approximately the relaxation rate variation from 1.5% (in gum rubber) to 6% (in lightly filled rubber). Natural rubber vulcanisates formulated with vulcanising agent dicumyl peroxide or fully soluble EV - system have also been found to be most suitable for applications where lower relaxation rates are required.

Tear resistance

Unlike abrasion resistance, reinforcement with carbon blacks of decreasing particle size does not always produce a noticeable effect on tear resistance. With NR and IIR improvement is evident. But with other rubbers such as CR or SBR, the effects are less marked. Gum rubber products of crystallizing rubbers NR or CR also show higher tear strength levels when compared with that of non - crystallising SBR or NBR. Resinous fillers generally improve tear resistance of all rubbers.

Heat resistance

Heat resistance of a rubber mainly depends on the chemical structure of its molecules. Generally the hydrocarbon showing high unsaturation character possess low heat resistance. However their heat resistant property can be enhanced by giving attention to cross - linking systems and other compounding ingredients.

Thermally stable carbon - carbon cross - links or monosulphidic cross - links as opposed to the normal polysulphidie cross - links increase the heat resistance of unsaturated rubbers. Fillers like mineral fillers, zinc oxide and antioxidants of diphenylamine types also improve the rubber stability in high temperature use. Softener, processing aids and plasticizers with low volatility and high thermal stability are most suitable.

Low temperature resistance

Crystallising rubbers NR and CR generally exhibit stiffening effect with decrease in clastic properties, when exposed to sub - zero level temperatures. To reduce this effect, the rubbers can be blended with non - crystallising rubbers such as low cis - BR, SBR and isomerised NR. Ester plasticizers of the sebacate and adipate types are also found to be useful to hinder the effect.

Electrical properties

Rubber vulcanisates can be grouped into (a) Insulators (b) Anti - static rubbers and (c) Conductive rubbers, in accordance with their electrical resistivity values, as given in table 7.3

Table 7.3 Classification of rubber vulcanisates based on their electrical resistivity values

Rubber vulcanisates	Electrical resistivity (S) ohm - cm
Insulators	$S > 10^8$
Anti - static rubbers	$10^4 < S < 10^8$
Conductive rubbers	$S < 10^4$

Generally compounds of NR, SBR with low water content and IIR exhibit high resistivity values (above 10^{12} ohm - cm) and are most suitable to be used as insulators. Rubbers CR, CSM, and NBR - PVC blend can be employed only for low - voltage use, especially as outer covers of insulators because of their good weather resistance.

Carbon blacks generally reduce the electrical resistivity however, their effect is less noticeable in lightly loaded compounds. Mineral fillers such as clays, whitings, calcined clays and precipitated silica with low water soluble contents give appreciable higher value of electrical resistance and di - electric properties than carbon blacks. In the case of petroleum oils, paraffinic type of oils give highest electrical resistance.

In formulating compounds of antistatic rubbers, special ingredients like conductive furnace blacks or quaternary ammonium salts with ester plasticizers are generally required.

7.2 Designing compounds for processability

It is essential that the compounds designed must process well. This means that they must mix, extrude and or calender, flow into moulds etc. without undue difficulty. Processing problems may arise with rubber mixes due to many factors such as :

(i) Too high or low viscosity

(ii) Adhesion to machinery surfaces

(iii) Premature vulcanization (scorch)

(iv) Poor tack property (especially for bonding rubber components)

Control of viscosity

Raw rubbers must be chosen with correct viscosity level to ensure acceptable mixing and processing characteristics. As viscosity levels for rubbers are commonly expressed in terms of Mooney viscosity readings taken at 100°C. these results have to be considered for right grade of rubber whether the rubber is natural rubber or synthetic rubber.

Since synthetic rubbers are manufactured with appropriate levels of viscosity for mixing process (about 50 Mooney units), the rubbers do not need breakdown of their molecules in the mixing machines. However all grades of natural rubber, except the block rubber (TSR) should require mastication process to bring down their Mooney viscosity values from high to low (ca 50) for efficient mixing process. Further reduction in viscosity values of the order of 30, can be made with NR, (especially for higher filler loading and sponge rubber production), by masticating the rubber in the presence of suitable softeners.

Nervy character in rubber mixes

Since some rubber mixes possess substantial elastic property even after milling their extrudates or calendered sheets show crinkled rough surfaces with poor dimensional stability (nervy character). To overcome this problem, the following remedial actions are suggested :

(a) Masticating the raw rubber to increase the level of plasticity.

(b) Increasing loading of filler in the compounds.

(c) Incorporating processing aids. eg. Mineral rubber, factice, or partially cross - linked rubbers, etc.

(d) Using high structure blacks (If compounds are black loaded)

Adhesion to machinery surfaces

Certain soft tacky compounds or compounds containing lower loading of mineral fillers are most likely to present this problem. To control this, fatty acids, microcrystalline waxes or low molecular weight polyethylenes should be incorporated in rubber compounds, in amount little more than the usual quantities.

Premature vulcanization (scorch)

A rubber mix containing fast curing ingredients may lose its plasticity and change into a dry and stiff mass, once the curing reaction starts due to absorption of heat, even during mixing or any other fabrication processes.

This undesirable premature vulcanization in rubber (scorch) is an economic loss and can be avoided by adopting the following techniques :

(i) Lowering the processing temperatures of the machinery by means of efficient water cooling system.

(ii) Incorporating retarder chemical or prevulcanisation inhibitor into the rubber mix.

(iii) Changing the fast vulcanizing system with slow vulcanizing system.

(iv) Replacing very fine size particle fillers with bigger particle size fillers.

(v) Adding more softeners.

Tack

In some fabricated rubber articles, two or more layers of rubber compounds are built together. These layers must therefore adhere rapidly and strongly between them when their surfaces are brought into contact. This means that the layers must have good tack property (autohesion). To achieve such good autohesion, the following techniques are of great importance.

(i) Compounds must be based on crystallizing rubbers like NR or CR.

(ii) Coumarone - indene resins, phenolic resins, rosin derivatives should be added as tackifier resins in the rubber compounds.

(iii) Waxy compounds like paraffin wax, stearic acid, etc. should be kept at minimum level in the rubber compounds.

(iv) If the rubber mix layers have been stored for a considerable time, the surfaces of the layers ,must be freshened with a solvent wipe, before building operation.

Chapter 8

Rubber Products - Manufacturing Methods

Rubber products are of great importance because of their distinct characteristics such as (i) absorption of shock and vibrational energy (ii) large reversible deformation (iii) impermeability to liquids and gases and (iv) chemical resistance.

Among these products, tyre is unique and most ingeniously made for the service of mankind.

8.1 Pneumatic tyre

A pneumatic tyre is made of rubber which is reinforced with a network of parallel textile cords. The tyre is designed so as to impart the following properties :

i. High sliding friction in wet and dry conditions
ii. Low rolling resistance
iii. High longitudinal and lateral stiffness to enable fast cornering
iv. Low vertical stiffness to cushion the ride
v. Resistance to cutting, puncturing and abrasion

Tyre components :

A tyre consists of a number of components as shown in Fig. 8.1 Each component serves a specific and unique function.

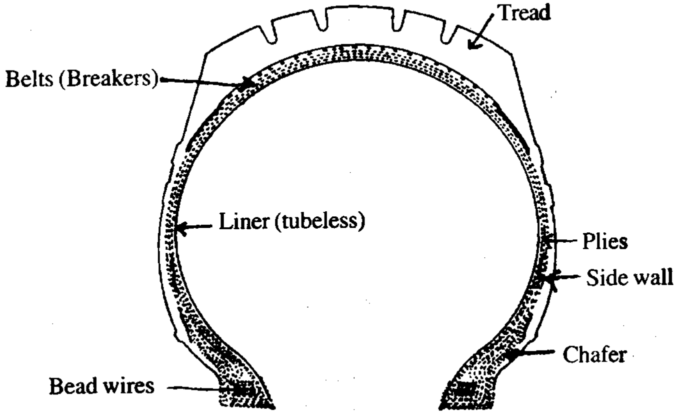


Fig. 8. 1 The main components of a tyre

Tread

The tread is a thick layer of specially compounded rubber with the tread pattern. It has to be strong and tough to withstand wear and tear and has to have good adherence on wet road surfaces too. The tread pattern is designed to provide good grip between tyre and road.

Two compounds may be used for the tread, one for the cap and the other for the base. Tread cap is formulated to achieve maximum traction and minimum abrasive wear, cut growth and rolling resistance. Tread base which connects the cap to the rest of the body of the tyre is compounded for maximum thermal and oxidative resistance and minimum heat build up. Rubbers NR, SBR and / or BR compounded with fine size carbon black and conventional vulcanising system are generally chosen for the tread caps while rubbers NR, SBR and / or IR having semi - EV system with a little coarser furnace blacks are preferred for tread bases. The features of general purpose rubbers which are used for tyre tread are illustrated in table 8.1

Table 8. 1 Features of General Purpose rubbers for use in Tyre tread

Properties	NR	IR	SBR	BR
Wear resistance	Good	Good	Very good	Excellent
Low heat build up	Very good	Excellent	Poor	Excellent
Tear resistance	Excellent	Very good	Poor	Poor
Age resistance	Poor	Poor	Good	Good

plies : These are rubber coated textile cords, which give strength to tyre. The choice of textile cord is based on the need for high stiffness, good resistance to repeated flexing, high strength to weight ratio, good adhesion to rubber. Textile materials such as nylon, rayon and polyester are commonly employed.

sidewall : This is a layer of rubber, covering the plies and allows deflection under load. It also serves to protect the carcass structure from weathering and chafing damage. Rubber compound based on NR, SBR, BR, EPDM or chlorobutyl rubber is commonly used.

bead : Bead is formed with steel wire hoops of high tensile strength. It functions as anchor for plies and holds the tyre body on the rim of the wheel. It is therefore designed to fit well into the contour of the rim flange.

breakers (belts) : These are thin layers of rubber coated textile cords, placed directly underneath the tread. They give additional reinforcement to the tread. Textiles of high tenacity are therefore chosen. Examples : Aramid, Glass fibre, Steel wire.

chafer · This consists of narrow strips of rubberised fabrics. It covers the bead from wear and cutting by the rim. It also helps to prevent moisture and dirt from getting into the tyre.

liner : It is needed in tubeless tyre construction. The important property required of the liner is therefore high resistance to air permeation. The typical liner compound is based on chlorobutyl rubber.

Method of manufacture of tyre

The method of manufacture of tyre involves with the following sequence of processes :

mixing process : Rubber mixes containing suitable ingredients for different rubber components of tyre are prepared by means of internal mixers and two roll mills.

extrusion process : Tread and side wall components are produced in required shapes in extruder machines.

bead production : Brass coated steel wires are covered with rubber and wrapped together (with rubberised fabric). In the form of rings.

production of rubber - coated fabrics : Reinforcing fabrics are frictioned / topped by means of calender machines for production of plies, breakers / belts, etc. (cut at bias angle or straight)

building process : All the components of tyre such as tread, side wall, beads, plies, breakers, etc., are assembled together on a tyre building machine and produced in the form of hollow bulgy cylinder. 'green tyre' (see Fig. 8.2 a. and b.)

curing process : Green tyres are moulded in suitable moulding machines to produce the end - product tyre.

Curing of tyre

Two types of moulding machines namely watch case type and bag - o- matic type are employed to cure the tyres. Both machines have in common, an inflatable inner component and a metal in which the inner side is engraved with tread design. The inflatable component in watch case type machine is a rubber tube called curing bag which is inserted and striped off in every moulding cycle.

In the second type, bag -o- matic machine, a bladder which is attached to the piston of the machine functions as the inflatable inner component. (see Fig. 8.3) The metal mould component in the watch case type machine, consists of two parts where as in the bag - o - matic machine, it constitutes segments of metal parts as shown in Figs. 8.4 a and b).

The mould is generally made of steel or aluminium, engraved inside with tread pattern. It is jacketed for steam supply and heated to temperature about 160°C during curing operation.

At the beginning of the curing process, the green tyre with the inflatable component is placed in the metal mould cavity and then steam or hot water is introduced into the component. Thus, the necessary heat for curing the green tyre is given inside from the inflatable component and outside from the metal component.

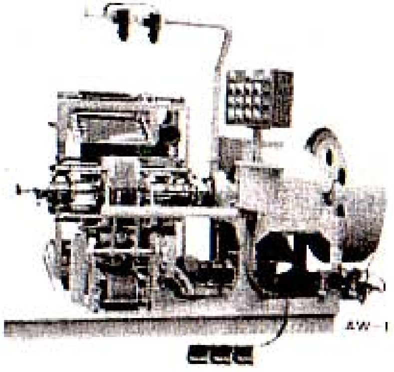


Fig. 8.2 (a) Tyre building machine

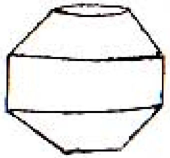


Fig. 8.2 (b) Sktched diagram of a 'green' tyre (before moulding)

Fig. 8.3 Bag -o- matic (bladder) curing press

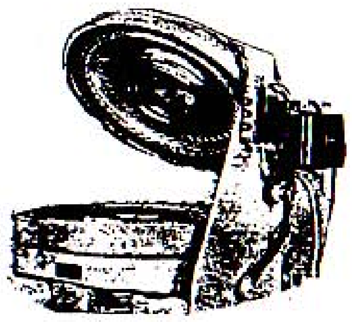


Fig. 8.4 (a) A watch case type tyre mould

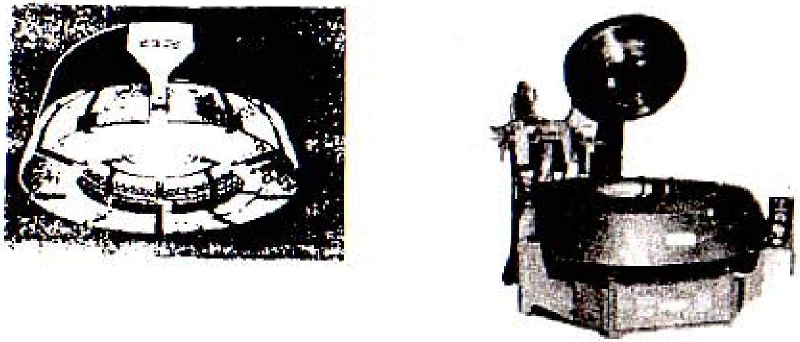


Fig. 8.4 (b) A segmented tyre mould

Tyre carcass construction

Cross - ply tyre

In a cross - ply tyre, two or more plies are applied alternatively in opposite directions. The cords in the plies cross at an acute angle 30° to 35° to the centre line of the tread. This arrangement gives strength to both sidewall and tread.

Radial tyre

In this tyre, the cords in the plies run substantially prependicular across the tyre from bead. The tyre has belt plies (breakers) which are arranged circumferentially around the carcass under the tread. This construction gives greater strength to the tread area, thus improving tread life, while the carcass remains flexible.

Belted bias tyre

This tyre has a carcass similar to that of cross - ply tyre together with two or more belts under the tread. This construction gives strength to the sidewall and greater to the tread. The belts reduce tread movement during contact with the road and thus improve the tread life.

The construction features of all three types of tyres are depicted in Figs. 8.5 a, b and c. Table 8.2 presents the carcass cord angles in each type.

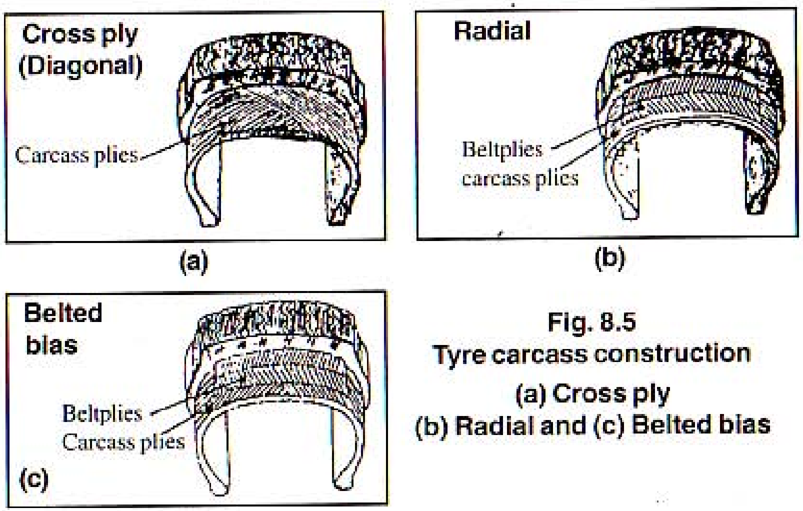
Table 8.2 Carcass cord angles in tyres

	Cross - ply		Radial		Belted bias	
	Casing	Belts	Casing	Belts	Casing	Belts
Green tyre	54 - 63°	--	80 - 90°	16 - 21°	58 - 61°	52°
Cured tyre	29 -36°	--	75 - 90°	12 - 18°	32°	26°

The angle of cord to the centre line of the tyre is also vital in tyre construction. The effects produced on the properties of a tyre, by the variation of angle of cord are illustrated in table 8.3

Table 8.3 Variation of cord angle on tyre properties

Properties of tyres	Cord angle	
	High	Low
Tread wear	Poor	Good
Road contact length	Long	Short
Lateral Stability	Poor	Good
Vehicle drive	Soft	Hard



(a) (b) (c)

Fig. 8.5
Tyre carcass construction
(a) Cross ply
(b) Radial and (c) Belted bias

Method of building of tubeless tyre :

The components of tyre such as beads, tread, casing components - plies, inner liner, sidewall, beakers, chafers etc. are assembled at the tyre building machine. This is an automatic machine which consists of a rotatable collapsible drum with edges shaped to receive the bead assemblies. Behind the drum is a set of racks for holding the strips of plies and rubber and lower down are power driven rollers and wheels for rolling the components into position. To right and left are supporting rings for beads so mounted that they place the beads in exactly the correct position on the drum.

At the beginning of building operation, the first ply with its attached inner lining is applied to the drum. The ply widths are such that they extend beyond the edges of the building drum. The beads are then set in place and the plies are turned up around the beads. When the plies and breakers have fitted and rolled on, the tread and sidewalls are applied and consolidated. The drum is then collapsed and the green tyre removed.

In an alternative method (especially for radial tyre construction) two building drums are employed. On the first drum bead, plies and sidewall and on the second, belts and tread components are built separately. Finally both these bonded units are assembled together to form the green tyre (See Fig. 8.6).

Typical formulations of rubber compounds used in pneumatic passenger car tyre are presented below.

(i) Tyre tread

Components	PHR
SBR (Oil extended)	60
Butadiene rubber (high cis)	40
ISAF - Black	50
Aromatic oil	10
Antioxidant (Amine type)	1.5
Zinc oxide	4
Stearic acid	1.5
CBS	1.0
Sulphur	2.0

Typical properties

Hardness	60 IRHD
Tensile Strength	19 MN/M^2
Modulus (300%)	9 MN/m^2
Elongation at break	500%

(ii) Side wall

Components	PHR
SBR (Oil extended)	100
FEF black	60
Aromatic oil	5
Antioxidant (Amine type)	2
Zinc oxide	4
Stearic acid	1.5
CBS	1.0
Sulphur	2.5

Typical properties

Hardness	58 IRHD
Tensile Strength	16 MN/m^2
Modulus (300%)	7 MN/m^2
Elongation at break	600%

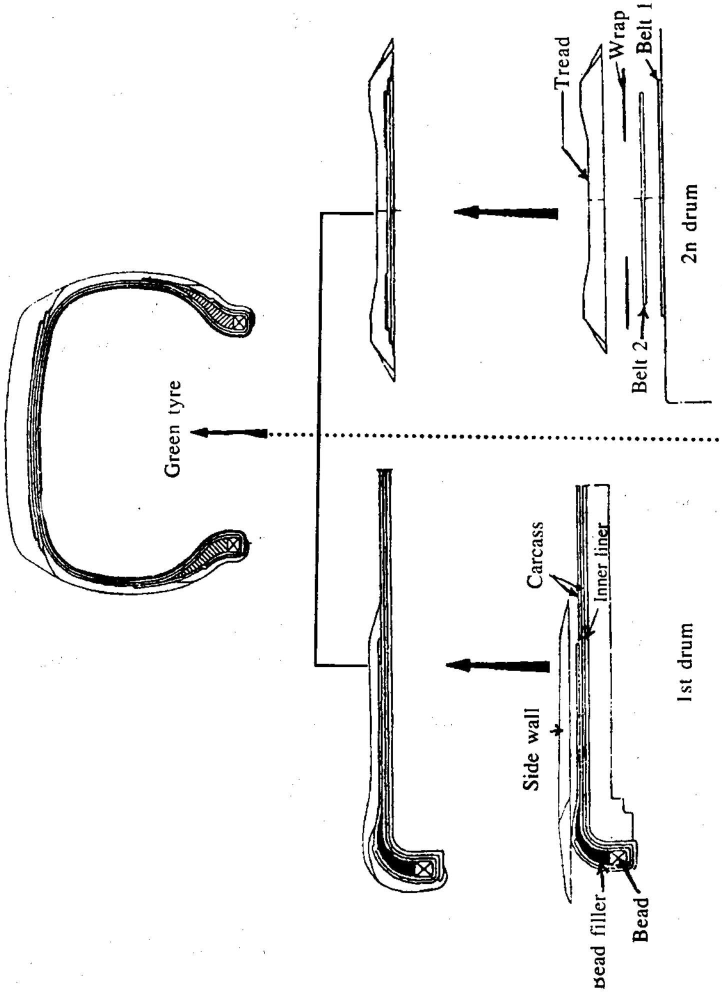


Fig. 8.6 Two - stage tyre building method

(iii) Inner liner (for tubeless tyre)

Components	PHR
Chlorobutyl rubber	90
NR	10
MT Black	50
HAF - LS black	30
C. I resin	10
Zinc oxide	5
Stearic acid	1.5
MBTS	1.0
TMTD	0.25
Sulphur	1.5
Antioxidant (Amine type)	1.0

A typical formulation for curing bag

Components	PHR
Butyl rubber (1.5 - 2% unsaturation)	100
Zinc oxide	25
FEF black	25
SRF black	25
Paraffin wax	5
Antioxidant (amine type)	2
Stearic acid	2
Dibenzoyl quinone dioxime	6
Lead di oxide	10
Sulphur	1.5

8.2 Retreading tyres

Tyres which are used in service are mostly retreaded for economic reasons. Before retreading, the tyres are checked for their suitability for the process. For, this, the tyre is first inspected and marked for all holes and other foreign substances. It is carefully sounded particularly at the shoulders to find any ply separation, If the tyre shows any defects such as ply separation, breaks in the bead reinforcement area, exposed bead wire or loose of broken cords, it is rejected for the retreading process.

Two process are mainly carried out for retreading tyres, namely (i) hot capping process and (ii) precured - tread retreading process.

Hot capping process

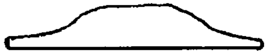
The operations performed in the process are as follows :

i. Preparation of tyre tread compound

ii. Extrusion or calendering of the compound in the form of rubber slab with beveled edges in camelback form

beveled edge slab

camel back form



iii. Buffing the worn - out tyre to remove tread portion

iv. Application of tacky rubber base (solution or a thin rubber sheet) on the buffed tyre.

v. Application of tread compound on the tacky rubber base

vi. Curing the whole tyre unit in a tyre mould (usually watch case type mould)

Formulation of tread rubber compound for retreading

The tread rubber compound for retreading process is very similar to that of tread compound used in the production of new tyres, however if the compound is not used immediately after its preparation, it requires good storage stability with non - blooming of its ingredients.

A typical formulation of tread rubber compound for good storage stability

Components	PHR
Natural rubber (RSS)	100
Zinc oxide	5
Stearic acid	1.5
Insoluble sulphur	2.5
CBS	1.0
PVI	0.3
HAF black	50
Aromatic oil	6
C. I. resin	4
Antioxidant (amine type)	1.5

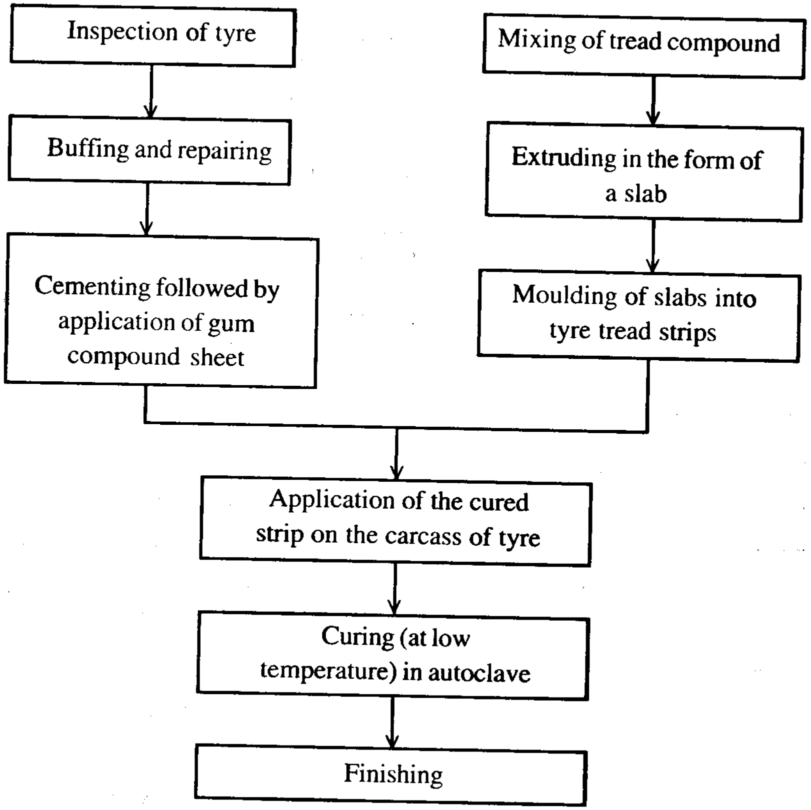
A typical formulation of rubber bonding compound

Components	PHR
Natural rubber (RSS)	100
Zinc oxide	5
Stearic acid	1.0
Insoluble sulphur	2.5
MOR (thiazole type accelerator)	0.8
FEF black	40
Blown asphalt	5
C. I. resin	5
Antioxidant (amine type)	1.0

ETMQ - 6, ethoxy - 1, 2 - dihydro - 2, 2, 4 trimethyl quinoline

Precured tread retreading process :

The process can be illustrated by the following flow line diagram :



In the process, the buffed tyre is inflated on an expandable hub and coated with vulcanizing cement. A layer of bonding cushion gum compound is then applied around the surface and the trapped air in the layer is removed. after this, the cured strip is applied and its ends are spliced and stitched. Following this operation, the expandable hub is collapsed and the tyre is removed for curing. Here the tyre is fitted on suitable rim and inflated using a tube. The inflated tyre is then slipped into a rubber envelope and cured in an autoclave at lower temperatures (110 - 120^0C)

Advantages of pre-cured tread rubber retreading process :

i. Low temperature curing enables the tyre in retaining its strength for many number of retreads.

ii. Process time is short

iii. Low labour charge

Vuculug process :

In the case of tyres having very big tread pattern as in farm tractor tyres, earthmover tyres etc., a different process called vuculug process is used. In the process, blocks of tread pattern in the worn - out tyres are removed and then uncured rubber blocks approximately in rectangular cross - section and of same sizes are applied in their places. Curing process is then carried out in a horizontal autoclave in open steam. During curing the tyre is rotated to prevent deformation of shape. Tyres up to 100" x 30" may be retreaded, by this process.

8.3 Bicycle tyre

Bicycle tyre is a simple composite structure. It consists of only tyre tread, ply, and bead components. The wide edges of the tread component become the sidewall of the tyre.

Methods of manufacture of bicycle tyres are summarized below :

Monoband method :

In the method, the tyre cord fabric coated with rubber is slit in the warp direction and is wound up over two rotating bead wire hoops in a building machine, at bias angle 45^0. After this, the body of the tyre is removed and tread component is applied on a collapsible drum.

Drum building method :

The method of building is similar to that of car tyres.

On the collapsible building drum grooves are provided for bead settling. First the bias cut rubber coated fabric is placed around the drum and joined by overlap of 1/2" to 3/4" by giving a slight stretch to the fabric.

Then bead wire hoops are placed in their positions and the fabric edges are folded over to cover completely and to make 1/2" overlap in centre. A hand roller is then applied to consolidate the ply parts and finally the tread component is applied with bevel joint. The green tyres thus produced are then hung on a bar to prevent their distortion during the storage.

Curing process:

For curing the cycle tyres, usually multiple daylight presses are employed (Fig. 8. 7). In each daylight, a cycle tyre mould is fixed. The mould is jacketed for steam supply and is provided with air line at the centre. The green tyre with a curing bag (tube) is first placed in the mould and the nipple of the curing bag is then connected to air supply line for inflating the bag. Normally the cure time is about 5 to 8 mins, at 150°C. After the cure, the air line is disconnected and tyre with the curing bag is removed form the mould. The air bag is then stripped off from the cured tyre.

8.4 Bicycle tube

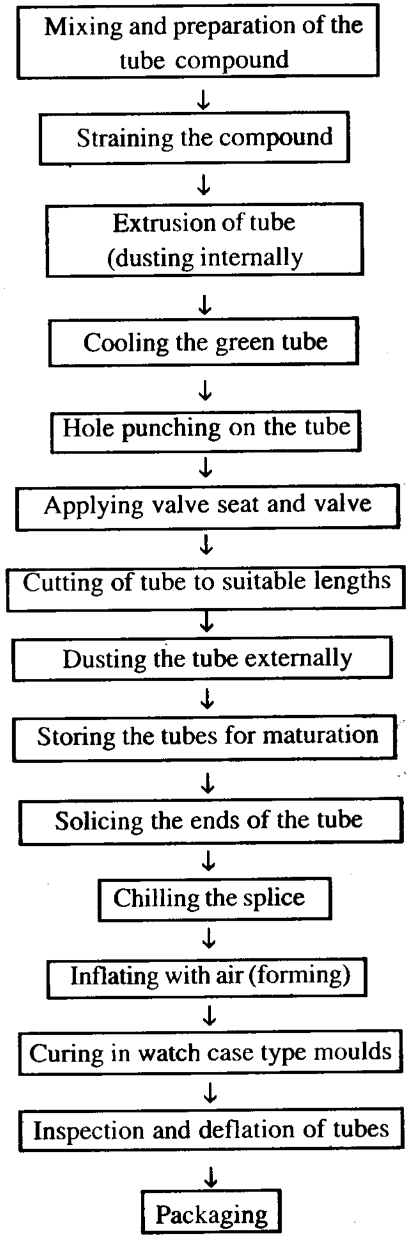
Bicycle tubes are manufactured by two methods, namely (i) Moulding method and (ii) Mandril curing method.

Moulding method (for production of seamless tubes)

The main stages involved in the method are illustrated in following flow chart.

In the method, the compound which is prepared in the form of sheet is cut into thin strips and then conveyed to an extruder machine fitted with a metal wire mesh for straining. (i.e to remove by foreign coarse particles). Following this, the compound is fed into an extruder for extrusion of tube (see Fig. 8.8). The machine has a device to dust the extruded tube internally with talc powder. The green tube thus produced is then cooled by passing through a water - bath. Then hole is punched on the tube and valve - seat as well as valve fittings is applied. In the next stage, the tube is cut into appropriate length according to tube size and dusted externally. The tube is then stored for about 24 hours (to obtain good green strength). After this, the ends of the tube are jointed using a special type of splicing machine, followed by inflating the tube with air (to give the form). Finally the formed tube is moulded in a watch - case type vulcaniser. The vulcanised tube is then inspected, deflated and packed.

Flow - chart for production of bicycle tube by moulding method



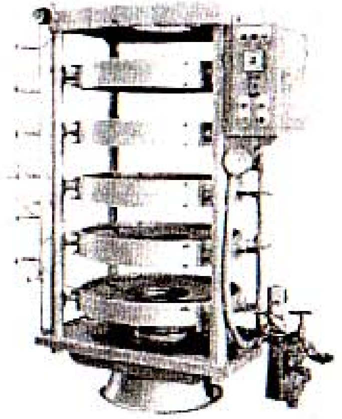
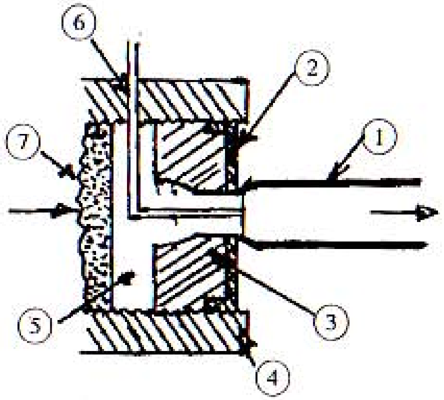


Fig. 8.7 Bicycle tyre curing press with 5 - daylights



(1) Extruded tubing

(2) Die

(3) Spindle

(4) Head

(5) Supporting arm

(6) Passage for dust powder

(7) Rubber mix leaving screw

Fig. 8.8 Schematic arrangement for tube extrusion

Mandril curing method

As the name implies, the method differs from the previous method in curing operation. The green tube which is cut into size, is mounted on a mandril, (a light metal pole) by applying compressed air. The ends of the tube are then fastened by rubber bands to prevent any distortion of the tube during curing.

In a similar manner, many mandril-inserted tubes are produced and are loaded on a metal frame for curing operation in an autoclave. After curing, the tubes are stripped from the mandrils by means of a special demounting cylinder, using compressed air. The tubes are then cut into appropriate lengths and valve seats together with valve - fitting are patched on the tubes at right positions. Finally the ends of each tube are joined.

To make the point between the two ends, first a rubber compound based adhesive is applied at both ends. Then one of these end is dipped into a solution of sulphur monochloride solution and after semi - drying the end is pressed with the other end for bonding. The bonding in this method occurs due to the cross - linking reaction between sulphur monochloride and rubber in the adhesive at room temperature. Although this method is health hazardous (due to sulphur monochloride vapour) it is still employed in some industries.

As an alternative to this bonding method, a method in which both ends of the tube are joined with a hot temperature - curing adhesive in a tiny press in also employed. Unlike seamless tube, the tubes produced by this manufacturing method show joint marks on their surfaces.

8.4 Hose

Hose consists of three components namely (i) lining (tube) (ii) reinforcement (carcass) and (iii) cover, as illustrated in Fig. 8.9

The lining is a tube like innermost rubber component which meets the requirements needed for a material passing through it.

The reinforcement imparts strength and flexibility. It is based on textile material, which may be applied to the lining in yarn by knitting, braiding, spiralling or circular loom weaving. In some hoses, wrapping the lining with rubber coated fabric at bias angle is also used as reinforcement.

The cover protects the reinforcement and the lining from the environmental conditions such as weathering, temperature extremes, oil and chemical contamination as well as cutting and abrasion when the hose is dragged on the ground.

Types of hoses

Moulded hose

The moulded hose has lengths up to 500 m and is used for delivering liquid material at low pressure. The main stages involved in the production method are as follows :

i. Extrusion of lining

The lining should be hard and firm in the green uncured state.

ii. Application of reinforcement

Generally, textile material cotton or rayon finds use as reinforcement. It can be applied by braiding or spiralling method.

iii. Application of outer cover

An appropriate rubber compound is applied on the reinforcement as outer cover, by means of a cross - head extruder machine (Fig 8.10)

iv. Curing

For curing, a thin lead sheath is applied on the green hose by means of a lead press. The lead covered green hose is then wound on a drum and filled with water, followed by sealing its ends with metal clamps. The drum with the hose unit is subsequently, placed in an autoclave for curing.

v. Finishing

After curing, the clamps are cut and lead sheath is removed by slitting along its length in a special stripping machine. The hose thus produced is then coiled up, tested and inspected for any defects.

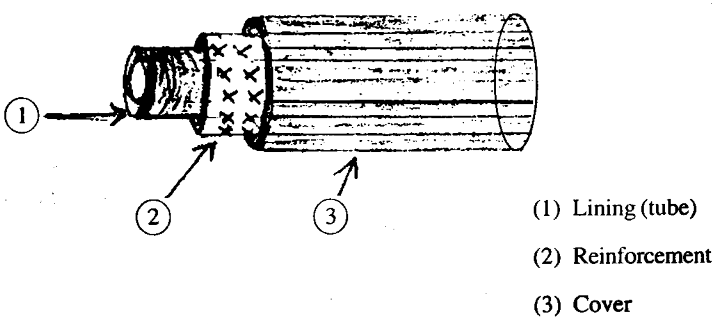


Fig. 8.9 The components of a hose

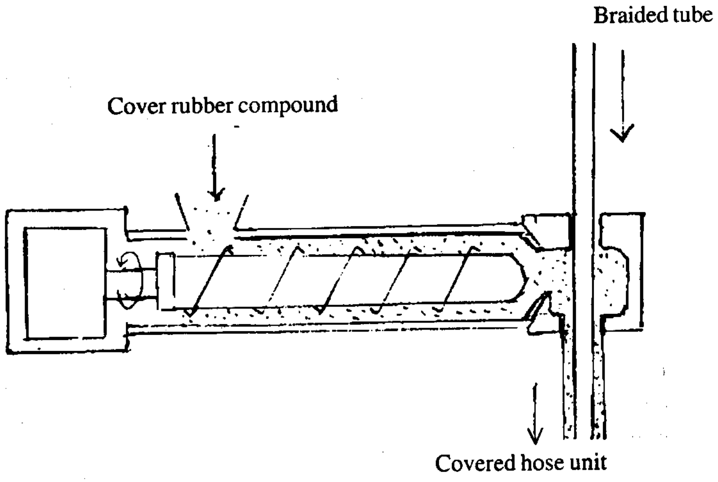


Fig. 8.10 Illustrating the application of cover on a braided tube by a cross - head extruder

Hydraulic hose

The hoses of lengths up to 40m (rigid type) and 300 m (flexible type) are commonly used as hydraulic hoses, for application in air - crafts, automobiles, mining and petroleum industries.

For lining, either nitrile rubber or chloroprene rubber is chosen. As the reinforcement, textiles material like rayon or steel wire is used. The textile cord or steel wire is generally applied on the lining in horizontal position by means of a spiralling or braiding machines. The outer cover of the hose is based on chloroprene rubber compound, on account of its good weather resistance and strength properties.

The method of production of hydraulic hose consists of the following steps:

i. Extruding the lining

ii. Blowing the lining on to a steel mandrel with compressed air for hoses of short lengths. Flexible plastic cores are used for long hoses.

iii. Braiding and / or spiralling with reinforcement.

iv. Covering (a) by means of a cross - head extruder for long hose (b) with rubber compound strip for short hose, manually.

v. Wrapping the cover with cloth, before curing :

A nylon cloth previously wet with a soap solution is wrapped spirally around the cover. This is done for short length hoses. In the case of long length hoses, lead sheath is applied by means of a lead extruder, as done in the production of moulded hose.

vi. Curing of hose unit

Autoclaves of appropriate length and size are chosen to cure the hose unit.

viii. Finishing.

On completion of cure, cloth wrapper/lead sheath is removed and the hose is tested for any defects.

Machine made wrapped hose

For building of this type of hose, a machine consisting of three rollers, with their centres on the corners of an equilateral triangle is employed. The base of the machine is formed by two of these rollers as shown in Fig. 8.11. In the method of manufacture, the following operations are carried out.

i. Extruding the lining

ii. Blowing the lining on to a mandrel. In this case, the length of the mandrel is nearly same as the length of three roll machine (up to 40 m).

iii. Applying fabric reinforcement.

To do this, the following procedure is carried out :

The mandrel together with its blown - on lining tube is placed between the two bottom rollers, and the third top roller is brought down in contact with the lining. Then with the help of revolving rollers, the fabric reinforcement is applied on the lining lengthways in strip form. The fabric used for this purpose is a bias -cut (angle45^0) rubber coated textile which can impart good flexibile strength to the hose.

iv. Application of rubber cover :

The cover rubber is next applied lengthways and is pulled into position and consolidated by the rollers of the machine.

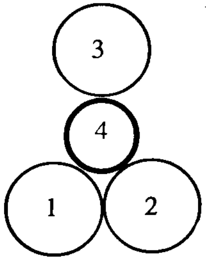
v. Wrapping the cover with nylon cloth :

The procedure is same as that of hydraulic hose wrapping, as given earlier.

vi. Curing in an autoclave

vii. Finishing : The hose, after the removal of wrapped cloth and mandrel, is inspected and tested.

Hose, which are used at high operating pressure in hydraulic systems, are essentially fitted with end - fittings. These end - fittings must be made to close dimensional tolerances to resist high fluid pressures. The proof pressure test is conducted at twice the working pressure.



1,2	Bottom rollers (rotatable)
3.	Top roller (rotatable and vertically movable)
4.	Mandrel inserted lining (tube)

Fig. 8. 11 Three - roller machine for production of a wrapped hose

8.6 Belting

Belting may be classified into three types :

i. Conveyor belt

ii. Flat transmission belt

iii. V-belt

Conveyor belt

The conveyor belt is designed for the transport of material. It is flat and consists of two components namely carcass and cover. The carcass provides strength to the belt and the cover protects the carcass from the abrasive wear and environmental factors such as weather, chemical contaminants, etc., to which the belt may be subjected in service. The carcass is a laminated structure which contains several plies of rubber frictioned and / or skimmed fabrics. The construction of the carcass varies and depends upon the purpose of use. Typical constructions used are illustrated in Fig. 8.12.

The carcass is built on a long table. The number of plies and the choice of fabric are determined by the load to be carried. Generally cotton, rayon, nylon or terylene finds as the fabric material in the carcass. The compound used as cover is designed to meet the following requirements :

i. good flexibility combined with strength.

ii. resistant to abrasion, tearing, cutting and impacts.

iii. good ageing properties

iv. good grip on driving pulley

v. ability to dissipate static charges

Rubbers chosen for cover are commonly NR, SBR, NBR and CR. Plasticized PVC, Butyl rubber, and EPDM are also used in special cases.

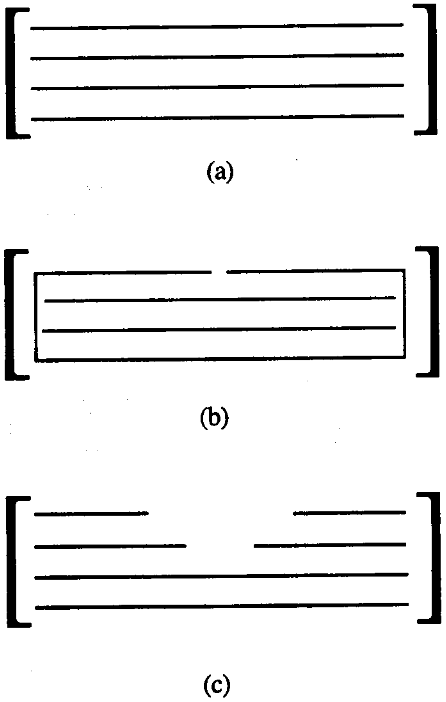


Fig. 8.12 Construction features in conveyor belt

(a) Straight laid

(b) Folded jacket

(c) Stepped ply

Curing of the green belt is carried out by means of a series of presses or by rotocure method as described in the chapter 6.

Formulations of typical conveyor belt compounds :

Component	Belt cover	Fabric skimming	Fabric frictioning
NR (RSS)	100	100	100
ISAF Black	40	-	
FEF Black	-	30	20
GPF Black	-	30	30
Petroleum oil (dark)	5	7.5	7.5
Pine tar	5	7.5	7.5
Zinc oxide	4	10	10
Stearic acid	2	1.5	1.5
Sulphur	1.75	0.5	0.5
CBS	0.75	–	–
MBTS	–	1.5	1.5
TMTD	–	2.5	2.5
TMQ	0.5	1	1
IPPD	1	–	–

CBS	N - Cyclohexyl - 2 - benzothiazole sulphenamide
MBTS	Dibenzothiazyl disulphide
TMTD	Tetramethyl thiuram disulphide
TMQ	1. 2 - Dihydro - 2, 2, 4 - trimethyl quinoline (polymerised)
IPPD	N - isopropyl - p - phenylenediamine

In the case of passenger conveyor belting, the carcass is further reinforced with steel cords. The rubber coated textile is usually sandwiched between two outer layers of transverse steel cords. Besides this, the outer cover rubber is made with ribs along its length to facilitate its movement on the comb like platform at the entry and exit points.

Flat - transmission belts

These belts are used for transferring power from one shaft to another and operate at high speeds round smaller pulleys or shafts, as compared with conveyor belts.

In the method of production of flat transmission belts, widths of frictioned and skimmed rubber coated fabrics are laminated together in the form of a slab and then cured in a press or a rotocure machine, a high percentage stretch being applied during cure to ensure that minimum amount of distortion occurs in service.

Cut - edge type belt

This type is produced from the moulded slab by slitting on a multi - slitting machine to the required widths and lengths.

Folded - edge type belt

In the construction of this type of belt, the outer plies are folded round the centre core of the laminated plies, to form a jacket. This gives better edge wear than the cut - edge type belt, but production method is slow.

V - belts

These are endless belts, cut in V - shape. The belts are also used for power transmission. They find applications as fan - belts for automobiles and frictional horse power drives for domestic and industrial machines.

V - Belts consist of four components such as ;

i. base rubber component
ii. cord fabric component
iii. top rubber component
iv. outer cover (fabric component)

Shorter - V - belts

For the manufacture of shorter belts, collapsible building drums are employed. First, the layers of base rubber component are applied on the drum and then the cord is wound on at touch pitch. After this, top rubber layers are applied. The individual belts are then cut off by means of circular knives and transferred to a skiving machine to produce them in V - shape. Each belt is then covered with fabric jacket/s and finally vulcanised in open stem pans.

Long - length belts

A method similar to the above is employed for the production of long - length belts. In the construction, a weftless cord fabric is used instead of individually wound cord and the belts are vulcanised endlessly by moulding in a press, under stretched controlled conditions.

8.7 Cable

Cable is constructed with the following three components (see Fig. 8.13)

i. Metallic conductor

ii. Insulator

iii. Sheath (jacket)

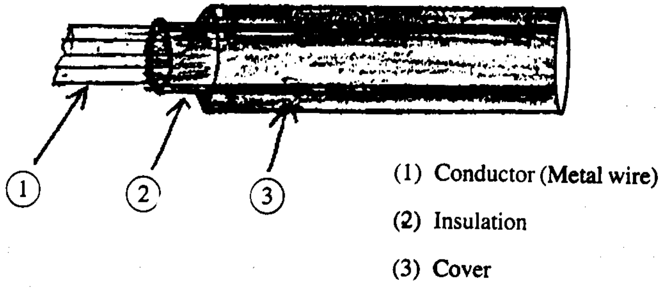


Fig. 8.13 The components of a cable

Insulator is a rubber formulated to have a very high order of electrical resistance. It must have the ability to retain the electrical resistance under the adverse conditions of ageing, moisture, and elevated temperature, Sheath is also a rubber which is formulated primarily with regard to its mechanical properties and service life.

Compounds used for insulator are commonly based on NR, SBR, IIR or EPDM and sheath compounds on CR, CSM (chlorosulphonated polyethylene rubber) or NBR / PVC blends.

Manufacturing method

The method of manufacture involves with the following stages :

i. Preparation of suitable rubber compounds of insulator and sheath.

ii. Application of insulation and sheath compound layers on metallic conductor, by means of extruder machines fitted with cross - head units.

iii. Curing

a. Batch process : the curing method is somewhat similar to that of flexible hose; in the method lead sheathing can be used as the mould.

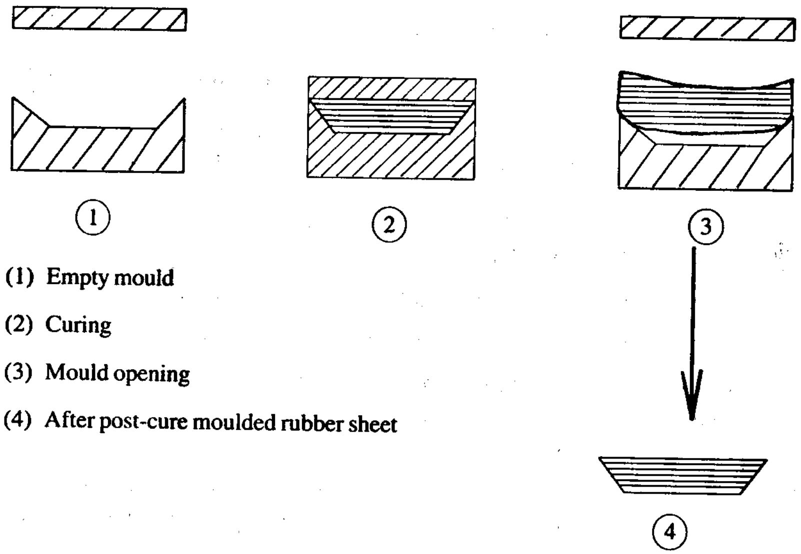
b. Continuous process : For continuous method of curing, most often, steam tube curing unit is used, steam pressures in excess of 2000 psi is commonly applied to cure the cable at temperatures of over 200°C. Instead of steam tube vulcanising method, fluid bed or fluidized bed continuous methods of curing may also be employed (refer chapter 6.)

8.8 Cellular rubber products

Microcellular sheet

Microcellular sheet is a cellular rubber product which contains non - inter connecting closed cell structure. It is produced by the use suitable rubber compound containing a blowing agent (a gas liberating chemical). The proportions of filer and softener in the sheet compound are varied to obtained different values of specific gravity and degree of hardness. The soft grade microcellular sheet with low specific gravity contains low proportion of filler and high proportions of softener and blowing agent.

The manufacture of microcellular sheet requires very careful control in mixing and moulding. In the moulding process, the mould should be loaded with a slight excess of compound and applied with full pressure. Since the sheet expands and jumps out of the mould cavity as soon as the mould is opened, the edges of the mould are angled. This will help the release of the cured sheet without any distortion or surface defects (see Fig. 8.14)



(1) Empty mould

(2) Curing

(3) Mould opening

(4) After post-cure moulded rubber sheet

Fig. 8.14 Production of microcellular rubber sheet

Post - curing

Since the moulded sheet shows gradual shrinkage over along period, due to gas permeation from the cells of the sheet, it is generally post - cured in a hot air oven at 120° - 130° C, for about an hour.

Sponge rubber

As compared with microcellular sheet, sponge rubber contains inter connecting open cell structure. The rubber compound used for making sponge, is formulated with same ingredients as that of microcellular sheet. However the proportions of softener and blowing agent are relatively high in sponge rubber compound.

During moulding, the mould cavity is partially filled with rubber compound and an air space is left in order to give open - cell structure to the expanded rubber.

Typical formulations of rubber compounds for the production of microcellular sheet and sponge rubber :

	Microcellular sheet	**Sponge rubber**
Component	**PHR**	**phr**
NR (RSS)	100	100
Sulphur	2	2
ZnO	5	5
Stearic acid	2	2
TMTD	1	1
DPG	0.5	0.5
Whiting	75	40
C. I. resin	6	6
Petroleum oil	4	20
Phenolic antioxidant	1	1
Blowing agent (DNPT)	5	5
Colour (Pigment)	As required	As required

8.9 Rubber to metal bonded products

Rubber to metal bonding involves the formation of an adhesive joint between rubber and metal, so that the composite is strong enough to withstand the service conditions, without failure. The bond can be formed simultaneously with vulcanisation or using suitable bonding agents between the metal and previously vulcanised rubber. Since the latter method is less commonly employed, the former method is considered. The method of bonding of rubber to metal involves with the following stages:

i. Metal preparation

ii. Application of bonding agent

iii. Application of rubber blank/s

iv. Vulcanisation (Moulding)

Metal preparation

To prepare metal, all traces of oil, grease or solid lubricant must be completely removed, from the metal surface. Although a number of processes are available for cleaning, the metal surface is first decreased, and then grit or shot blasted. Degreasing is usually done by exposing the surface in the vapour of neutrial stablised trichloroethylene. In the grit or shot blasting, grits of steel or sand or glass powders of 40 - 60 mesh particle size are used. Instead of this mechanical cleaning, chemical cleaning can also be performed. These processes usually consist of acid cleaning bath, water phosphating bath, water wash and a chromate rinse. Chemical cleaning method especially, phosphate treatment is gaining greater acceptance as a cost effective process and gives the added benefit of improved corrosion resistance.

Bonding with bolymeric bonding agents

After cleaning, the metal surface should be coated with bonding agent as soon as possible to avoid surface oxidation and contamination. Bonding agents are chosen to suit particular rubber mixes, metals, vulcanisate temperatures and service requirements. In some cases a primer (corrosion resistant coating) is used on the metal, followed by a second bonding agent.

A protective cover coat of rubber solution is usually applied over this bonding agent.

Typical bonding agents are based on the following materials :

i. Rubber derivatives - chlorinated rubber, cyclised rubber, epoxidised rubber etc.

ii. Isocyanates - both polyfunctional and polymeric types of isocyanates.

iii. Cynoacrylates

iv. Epoxy resins

Bonding with rubber to brass - plated metals

An excellent bond is formed when rubber is vulcanised in contact with brass - coated metal. However brass plating has many disadvantages, the greatest of which is the difficulty of controlling the plating operation. The brass deposit must be of a definite type and composition requires considerable expertise to maintain consistently. The reaction rates of sulphur to rubber and sulphur to brass must be suitably balanced. Thus low sulphur and sulphurless mixes cannot be blended without high sulphur intermediate layer. A rubber cover coat is necessary to protect the brass surface during storage and handling.

Bonding of rubber to ebonite coated metals

In this method, the clean metal is coated with an ebonite solution to which the applied rubber mix adheres during vulcanisation. A disadvantage of this method is that the high sulphur content of the ebonite layer vulcanised in contact with an accelerated low sulphur mix results in poor physical properties at the interface. This may be reduced to some extent by a thin intermediate layer of a low sulphur mix. Further the ebonite bond is not applicable for high temperature service because of its thermoplastic nature.

Application of rubber blank

The blank should be free from bloom and dust. For compression moulding, freshly milled blanks are preferred, although freshening by a solvent wipe may be sufficient.

Moulding

Transfer and injection moulding methods are preferable since these techniques ensure a fresh surface at the bonding interface. The metal inserts should have no sharp corners. Stress concentrations at rubber boundaries can be relieved by reducing all sharp angles. Care should be taken in designing moulds that the flow of rubber does not sweep the bonding agent off the metal.

8.10 Rubber lining of chemical process plants

Rubber linings and coverings are used to protect chemical process plants and equipment against corrosion. In addition to chemical resistance, they also provide resistance to abrasion and changes in temperature, during the service. The most popular rubbers used for rubber linings are as follows:

- Natural rubber (soft and ebonite)
- Butyl or Halogenated butyl rubber
- Polychloroprene rubber
- Chlorosulphonated polytheylene rubber (Hypalon)
- EPDM rubber
- Nitrile rubber

Natural rubber (soft) is widely used for lining storage tanks, reaction vessels, pipe work, etc., particularly for abrasive conditions.

Natural rubber ebonite is preferred as lining material where chlorine is encountered.

Butyl rubber and halogenated butyl rubber are superior to natural rubber for chemical resistance and high temperature use.

Polychloroprene rubber is preferred to other rubbers for lining reaction vessels, pipes and valves in marine environments as well as riser pipes in oil rigs.

Chlorosulphonated polyethylene rubber is specially used for lining storage tanks and vessels for storing oxidising acids such as concentrated sulphuric acid and chromic acid.

EPDM rubber is most suitable for potable water applications, because of its resistance to microbiological growth.

Nitrile rubber is the outstanding rubber to resist petroleum hydrocarbon oils and it is the best choice for lining oil tanks and vessels.

Manufacturing method

The steps involved in the method are similar to those described rubber to metal bonding process.

i. Preparation of metal surface

ii. Application of bonding agent

iii. Preparation of rubber lining.

A suitable rubber compound in the form of sheet with required thickness is prepared by calendering or extrusion process. The compound sheet should be homogeneous and blister free. Generally, sheets of one meter wide and up to 6 mm thick are required.

iv. Application of rubber sheet on metal sheet

Rubber sheet is carefully positioned on the metal surface and rolled or pressed down, taking care to remove air between the two surfaces. The joints in linings are usually made by overlapping adjacent layers of rubber, the edges of which have been skived before, to facilitate the bonding. The other types of joints such as (i) bevel joint and (ii) strapped joint are also used in some cases. (see Figs. 9.15 a, b and c)

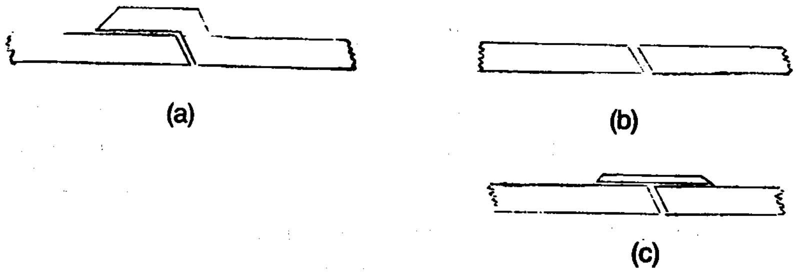


Fig. 8. 15 Common joint types in rubber linings
(a) overlap joint **(b) Bevel joint**
(c) Strapped joint

iv. Vulcanisation

The preferred method of vulcanisation is steam cure method, using steam pressure 50 psi, in an autoclave.

Vulcanisation can also be carried out using atmospheric steam at 100°C or with boiling water, Self - vulcanising linings capable of vulcanising at ambient temperatures are also used.

Inspection and testing

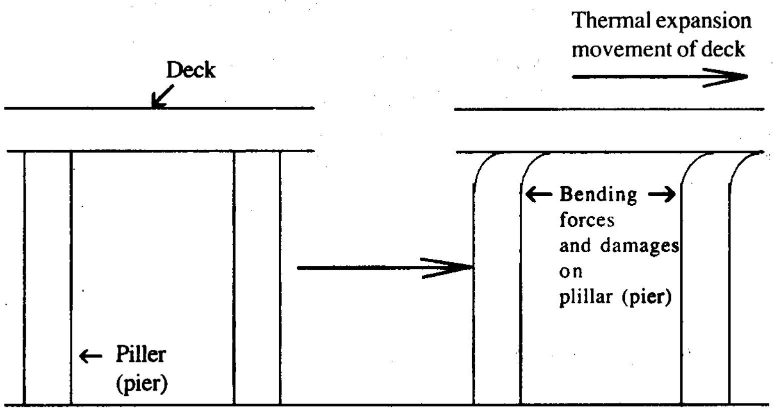
Stringent inspection and testing are essential during the lining operation to ensure a satisfactory finished product. Tests carried out, include (i) visual inspection for defects (ii) high frequency spark testing to confirm that the required degree of vulcanisation has been achieved and (iv) qualitative or quantitative assessment of bond strength.

8.11 Bridge bearing

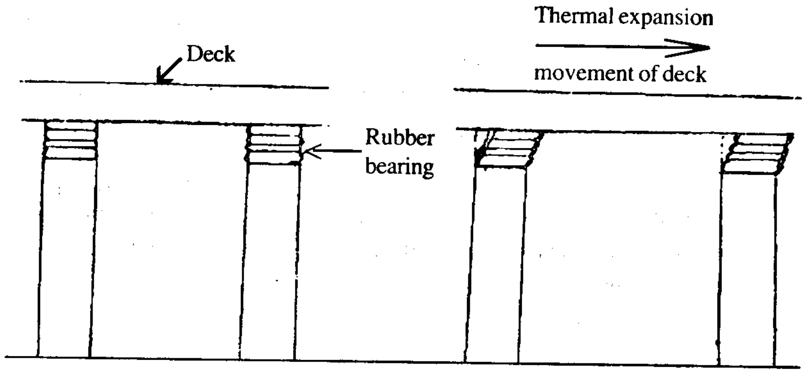
Bridge bearing is a rubber to metal bonded product, in which rubber blocks are interleaved with wide sheets of metals. It has a high vertical stiffness and relatively a low horizontal stiffness. The specified allowable strain limits for design of bridge bearing are 15% in compression and 50% in shear.

The greater shear strain limit allows the movement of a bridge deck on its supporting piers, when changes in length occur due to thermal expansion and contraction. As the deck can move, considerable bending forces on the piers are avoided (see Fig. 8.16). Bearings must also support the considerable weight of the bridge and varying loads imposed by traffic.

Rubber bridge bearings are now in widespread use and two types of rubber are commonly used - Natural rubber and Polychloroprene rubber. Both rubbers are strain - crystallising rubbers. This property may be essential for long term strength. Natural rubber performs better in sub - zero temperatures and it is less prone to stiffening, as compared with polychloroprene.



(a) Deck on pillar without rubber bearing



(b) Deck on pillar with rubber bearing (bending forces and damages on pillar are avoided)

Fig. 8.16 Illustrating the advantage of using rubber bearings

A typical formulation of bridge bearing based on natural rubber :

	PHR
Natural rubber (RSS grade)	100
Zinc oxide	5
Stearic acid	2
Microcrystalline wax	3
Sulphur	1.5
CBS	1.5
SRF - Black	60
IPPD - amine antioxidant	1
Petroleum oil	5

Cure time at 140°C	60 mins
Tensile strength (MPa)	22
Elongation at break (%)	450

To design the bearings with required shear stiffness and compression stiffness values, the following mathematical expressions are considered.

Fig.: 8.17 illustrates the modes of deformation of a bridge bearing unit.

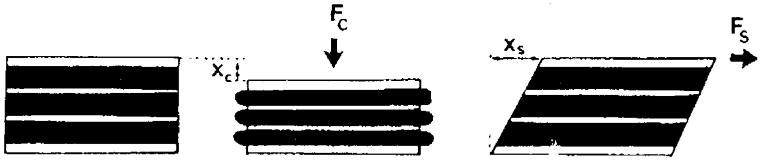


Fig. 8.17 Modes of deformation in rubber bearing

Shear siffness :

The shear stiffness of the bearing is given by

$$K_s = \frac{F_s}{X_s} = G\frac{A}{T} \quad \text{-----------} (1)$$

Where G is the shear modulus of the rubber, A is the cross - sectional area of the bearing and T is the total thickness of rubber.

Compressive stiffness :

A similar equation like (i), can be written for compressive stiffness of the bearing.

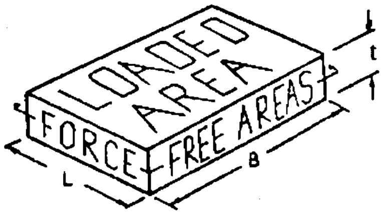
i. e. $$K_c = \frac{F_c}{X_c} = \frac{E_c.A}{T} \quad \text{-----------} (2)$$

but E_c, the effective compressive modulus in this case, is dependent upon the geometry and is given by : ---------------

$$E_c = E_o(1+2kS^2)$$

where E_o is the Young's modulus of the rubber, k is a numerical factor which decrases form 0.93 to 0.53 with increasing hardness of the rubber over the range 30 to 70 IRHD and S is the shape factor of the bearing defined as the ratio of the cross - sectional area of the bearing to the force - free surface area of one layer of rubber and expressed as :

$$K_c = \frac{L.B.}{2t\,(L+B)} \quad \text{(see Fig. 8.18)}$$



$$\text{Shape factor} - = \frac{\text{loaded area}}{\text{force free area}}$$

$$\text{i.e. } S - = \frac{LB}{2t\,(L+B)}$$

Fig. 8.18 Illustrating the loaded area and force free areas for expressing shape factor

In connection with the design of natural rubber bearings, the data of engineering properties of the rubber as presented in table 8.4 are of great importance.

Table 8.4 Data of engineering properties of natural rubber bearing containing various amounts of SRF blacks, hardness range from 40 to 60 IRHD

Hardness IRHD ± 2	Youngs modulus Eo MN/m²	Shear modulus G MN/m²	k (numerical factor)
40	1.50	0.45	0.85
45	1.80	0.54	0.80
50	2.20	0.64	0.73
55	3.25	0.81	0.64
60	4.45	1.06	0.57

For further understanding of the design features, a worked out problem is given below :

A steel laminated rubber bearing, 300 mm long and 300 mm wide is interleaved with three rubber layers, each 25 mm thick. If the young's modulus and shear modulus of the rubber are respectively 4.45 MN/m^2 and 1.06 MN/m^3, Calculate the horizontal shear and the vertical compressive stiffnesses of the bearing. (Take the numerical factor k = 0.55)

If the compressive strain is limited to 10%, what is the maximum load applicable on the bearing ?

The rubber bearing as depicted in Fig. 8.17 can be referred to for solving this problem.

Shape factor (one layer) $= \dfrac{300 \times 300}{2 \times 25\,(300+300)}$

$= 3.$

Compressive modulus $E_c = E_0(1+2\,ks^2)$

$= 4.45\,(1+2 \times 0.55 \times 3^2)$

$= 4.45 \times 10.9\ MN/m^2$

Shear stiffness $K_s = G\dfrac{A}{T}$

$= \dfrac{1.06 \times 300 \times 300}{3 \times 25} \times \dfrac{10^{-6}}{10^{-3}}\ MN/_m$

$= 1.27\ MN/m$

Compressive stiffness $= \dfrac{E_c\,.\,A}{T}$

$= \dfrac{4.45 \times 10.9 \times 300 \times 300 \times 10^{-6}}{3 \times 25 \times 10^{-3}}$

$= 58.21\ MN/m$

Since the allowable strain = 10% $T = \dfrac{10}{100}\,.\,T$

Then the maximum compressive

deformation (Xc) $= \frac{10\ T}{100}$

$= \frac{10 \times 3 \times 25}{100} = 7.5\ \text{mm}$

but, compressive stiffness $= \frac{F_c}{X_c} = 58.21\ \text{MN}$

Maximum load (applicable) $F_c = 58.21 \times 7.5 \times 10^{-3}\ \text{MN}$

$= 436.6\ \text{KN}$

Chapter 9

Physical Testing of Rubbers

Physical tests on rubber are generally carried out to determine its suitability for a particular application, for quality control purposes or for research and development. The tests are essential in all phases of ruber technology and can be classified into two groups, as given below.

i. Tests on raw rubbers and unvulcanized rubber mixes and

ii. Tests on vulcanisates

Since the results obtained from the tests are very dependent upon i) the shape and size of test-piece, ii) the method of production of test-piece, iii) storage conditions and, iv) exact conditions of tests, these factors should be carefully controlled in a laboratory. This would enable the laboratory to get reproducible test results or to compare the test results with those obtained from the other laboratories. In view of this, standardisation of tests are dealt with by standardising bodies of particular countries as well as international standard organisation. Rubber products of international trade may have to confirm to these standards.

9.1 Tests on raw rubbers and unvulcanised rubber mixes

Determination of Plasticity

A compression type plastimeter is used to determine the plasticity of a sample of raw rubber mix. In the determination, a test-piece of the rubber sample is pressed between the parallel plates of the instrument and its compressed thickness is measured after a specified period of time.

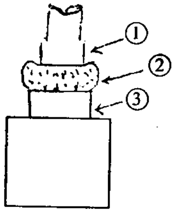
The commonly used instrument is Wallace rapid plasti meter. It is simple to operate and can be used for quick determination (see fig. 9.1).

Wallace rapid plastimeter

This is a parallel plate plastimeter containing of two parallel circular platens, of which the lower platen having a large diameter than the top platen. Both platens are provided with a suitable means of heating and jacket to maintain the specified temperature (100°C). In the plastimeter, there are means of (i) moving the top platen normal to its surface to compress the test-piece to a thickness of 1 mm (ii) applying to top platen a test force of 100N, normal to its surface to compress the test-piece and (iii) indicating the thickness of test-piece to the nearest 0.01 mm, when it is between the platens.

Procedure

A cylindrical test-piece of volume of $2cm^3$ is punched out from the given rubber sample and placed on the lower platen of the instrument. It is precompressed to a height of 1mm at 100°C, for 10 seconds and then applied continuously with a compressive force of 100N. After a time of 15 seconds, the plasticity which indirectly corresponds to the compressed height of the test-piece (in 0.01 mm) is measured in W.R.P.N. (Wallace rapid plasticity number) from the dial gauge of the instrument. The dial gauge is graduated form 0 to 100 W.R.P.N. It should be noted that the greater the W.R.P.N. reading, the lower the compressive deformation and hence the plasticity of the test-piece.



1. Upper platen
2. Rubber sample under compression
3. Lower platen

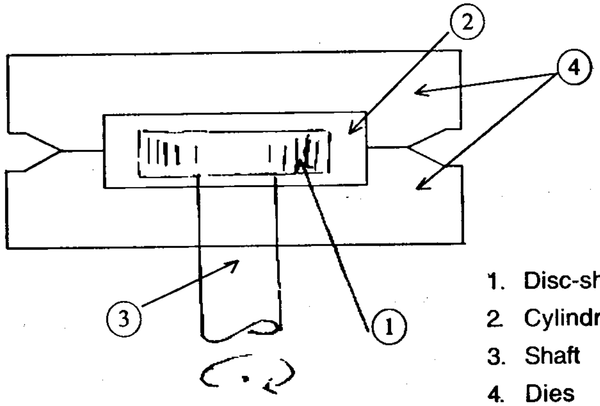
Fig. 9.1 Wallace rapid plastimeter

Determination of viscosity

A rotation instrument known as Mooney viscometer is used to measure the viscosity of raw rubbers and rubber mixes. The main features of the instruments are shown in fig. 9.2.

For the measurement of viscosityof a rubber sample, the sample is first introduced into the heated die cavity and then sheared rotationally with a knurled disc rotor. Since the torque developed on the rotor varies with the time of shearing and viscosity of the rubber sample, the torque indicated on the scale after a specified time is measured as viscosity of the the rubber sample.

For the division of dial scale, a torque of 8.3 N.m is considered as equivalent to 100 Mooney viscosity units.



1. Disc-shaped rotor
2. Cylindrical chamber
3. Shaft
4. Dies

Fig. 9.2 Diagram of the mooney viscometer

Test conditions for determining mooney viscosity

i. Test-piece : Two cylindrical test-pieces of diameter 4.5 cm and thickness 3mm should be punched out from the rubber sample.
ii. Test temperature : 100°C
iii. Precheating time of the test-piece in the die cavity : 1 min, before starting the rotor for its motion.

iv. Viscosity reading : Reading should be taken, after 4 minutes of shearing action in the case of NR, SBR, NBR (see fig. 9.3), for butyl rubber a time of 8 minutes should be given for shearing action.

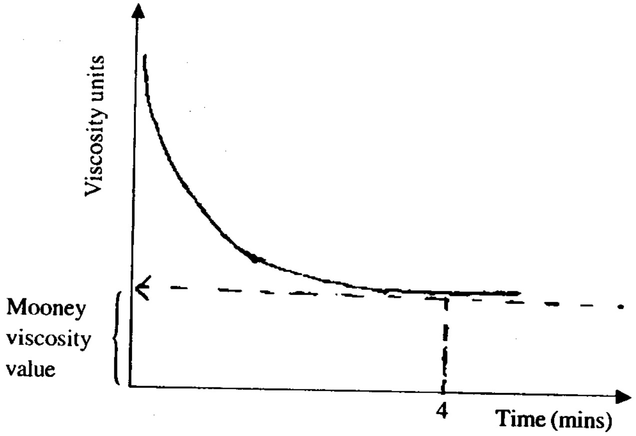


Fig. 9.3 Typical mooney viscosity curve for NR-compound

Mooney viscosity value of a rubber sample is generally expressed as

$$ML_{1+4}^{100^\circ C} = x \text{ Mooney units}$$

Preheating Time (1 min) ↗ ↖ Reading Taken (after 4 mins)

Cure properties of rubber mixes

The most obvious changes in a rubber mix on vulcanization are :

i. Stiffenening
ii. Increase in elastic property
iii. Reduced solubility in solvents

All these changes have been used to assess the degree of vulcanization. Mooney viscometer is widely used to assess the stiffening character of the rubber mixes, at processing temperatures. The results enable an estimate of processing safety to be made. In the practical determination, the instrument is run at a temperature of 120° C and the results are interpreted from the autograph (Mooney viscosity units versus time) as illustrated below. (see fig. 9.4)

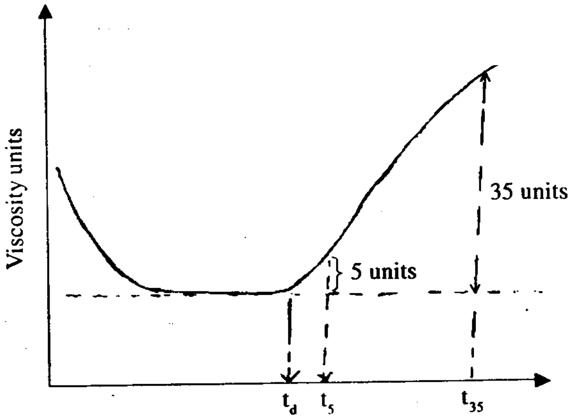


Fig. 9.4 Mooney viscosity readings with time of curing

Data of results to be reported :

a. Delayed time t_d
ii. Scorch time t_5
iii. Cure rate index t_{35}-t_5

The application of the mooney viscometer has been found to be somewhat limited to assess the cure at high practical moulding temperatures (140° - 180° C) because of the slippage of rotor from the rubber surface after some degree of vulcanization.

For this reason, oscillating disc rheometer and similar related equipment are employed to find the complete cure properties of a rubber compound.

Oscillation disc Rheometer

The main features of the instrument are shown in fig. 9.5 (a) and (b). The instrument also measures the change in shear modulus of rubber as the cross-links form during vulcanisation.

Unlike mooney viscometer, the oscillation disc rheometer consists of a biconical disc of diameter 35.5 mm. During operation, this disc is oscillated at 1.7 H_z through a small rotary amplitude 1°/2°/3°, in the rubber mass.

The test-piece used in the instrument is one cylindrical piece of rubber of diameter 30 mm and thickness 12.5 mm which is generally punched out from the sample (a rubber mix sheet).

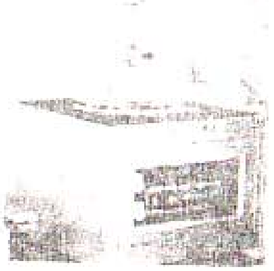


Fig. 9.5 An oscillation disc rheometer

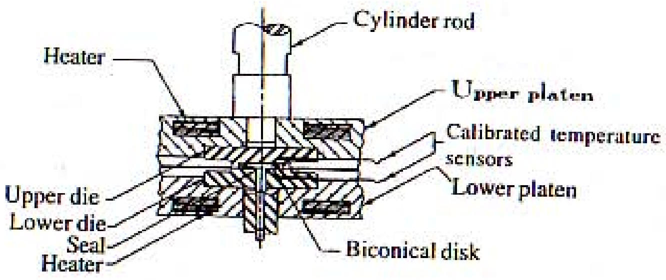


Fig. 9.5 (a) Oscillation disc cure meter assembly

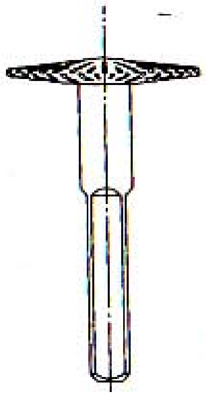
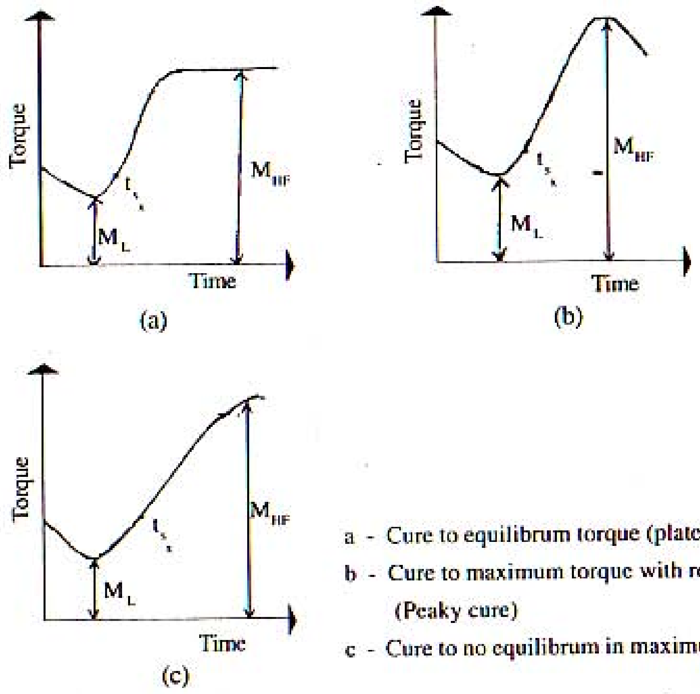


Fig. 9.5 (b) Biconical disk

Typical rheographs (cure curves) and interpretation of cure characteristics are given below :



a - Cure to equilibrum torque (plateau cure)

b - Cure to maximum torque with reversion (Peaky cure)

c - Cure to no equilibrum in maximum torque

Fig. 9.6 Typical oscillation disc rheographs

Interpretation of cure characteristics

i. Minimum torque (M_L)

ii Plateau torque (M_{HF})

iii. Maximum torque (M_{HR}) - for reverting curve

iv. Highest torque value (M_H) attained in a curve

v. Scorch time (t_{s_x}) time in minutes, to x units of torque increase above M_L. For example : t_{s_3} for 3° oscillation, t_{s_2} for 2° oscillation.

vi. Cure time ($t_c 90\%$) = time in minutes to 90% of full torque development (see fig. 9.7)

vii. Cure rate index $= \dfrac{100}{t_c 90\% - t_{s_x}}$, the parameter proportional to the average slope of the cure curve in the steep region.

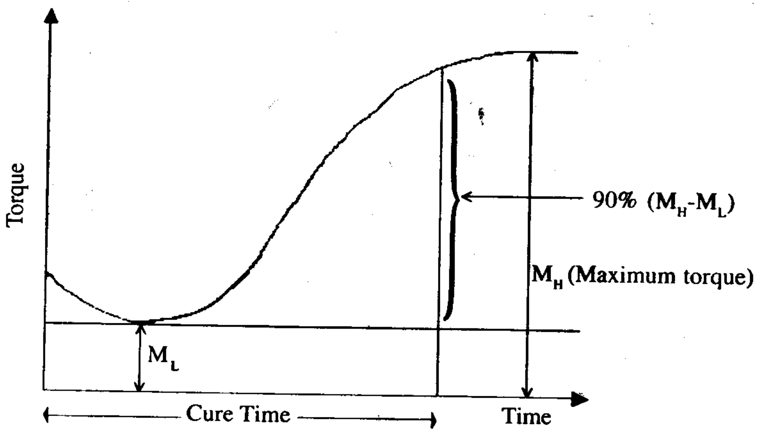


Fig. 9.7 Illustrating the measurement of cure time (optimum) from cure curve

Determination of specific gravity of rubber and its importance in rubber industry

The specific garvity of a rubber can be determined by two ways as illustrated below:

i. By practical determination (using Archimede's principles): In laboratories, instruments based on Archimede's principles such as specific gravity balances, densimeters, e.t.c. are used to measure the specific gravity of rubber, directly.

ii. By theoretical calculation from the formulation that is used for preparing the rubber mix.

For example :

Suppose the mix formulation used for preparing SBR based tyre tread is given as follows:

Components	Parts by weight	Specific gravity	Parts by volume
SBR 1500	100	0.94	106.40
HAF black	50	1.80	27.77
Zno	4	5.57	0.72
Stearic acid	2.5	0.92	2.72
Petroleum oil	5	1.10	4.55
Sulphur	2	2.05	0.97
MBTS	1.5	1.5	1
TMTD	0.2	1.42	0.14
Antioxidant (DOPPD)	1.5	1.2	1.25
Total	166.7		145.52

The specific gravity of the mix (Calculated) $= \dfrac{166.7}{145.52} = 1.145$

Importance of determining specific gravity (SG) in rubber industry

i. To control laboratory work (i.e. For consistency in rubber mix properties, SG determined by theoretical calculation should be very close to the SG determined by a practical instrument)

ii. To obtain the cost per volume of rubber articles (This can be found by multiplying the cost per weight of the rubber mix used for producing the articles by the SG)

iii. To calculate the internal mixer load for the mix (For example if the volume of an internal mixer for efficient mixing is V, then the appropriate load of the mix is V.SG)

iv. Percentage increases in volume of rubber in oils, in motor fuels or in organic solvents can be found.

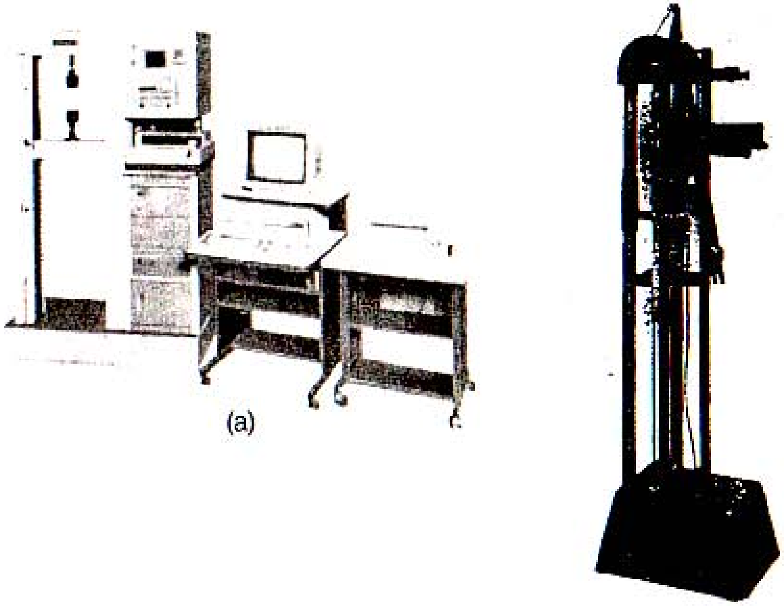
9.2 Tests on rubber vulcanisates

Tensile test

Tensile test is easy to carry out and has become established in the rubber industry as a measure of the quality of rubber within a short time. In the test, a test-piece prepared from vulcanized rubber is stretched by means of a tensile testing machine and the relationship between the applied force and the deformation produced is determined.

Different types of test-pieces are used to determine tensile properties. They are in the shape of dump-bell or ring, or straight test-pieces.

Both (i) pendulum type and (ii) electronic transducer type tensile testing machines are employed for the determination (see fig. 9.8. a&b).These machines are designed to provide constant rate of traverse of the moving grip or pulley of 500 ± 50mm/min for all test-pieces. The pendulum type machine is involved with inertia; the results of which are not as correct as that of the inertia less electronic machine.


(a)

(b)

9.8 Tensile testing machine
a) Electronic Transducer type b) Pendulum type

Conditioning

The test-pieces are conditioned generally at the test temperature either 23 ± 2°C or 27 ± 2°C, for not less than 16 hours immediately before testing.

Measurement on dumb bell test- piece

Thickness is measured by a micrometer gauge the foot of which exterts a pressure of 20kpa on the rubber. Width can be assumed to be equal to the width between the cutting edges of the narrow central part of the die. Test should be carried out on at least three test-pieces.

Procedure

The dumb bell test is placed centrally in the grip and the following measurements are taken while the test-piece is stretched:

i. The force on the test-piece

ii. The elongation of the test-piece as shown by the distance between the gauge marks on the test-piece (as given in the dimensions of the test-piece fig. 9.9)

Expression of results

i. Tensile strength $= \frac{F}{A}$ (given in megapascals)

where F is the breaking force in newtons
A is the initial cross-sectional area in square metres.

ii. Percentage clongation at break is given by $= \frac{L - L_o}{L_o} \times 100$

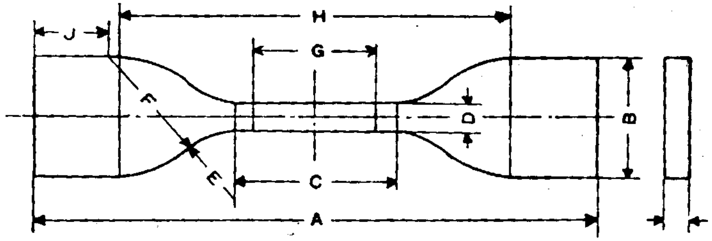
where L is the length in mm, between gauge marks at break
L_o is the initial length, in mm between gauge marks.

iii. Modulus is given by $= \frac{f}{A}$

where f is the force, in Newton at the required elongation (usually 300%)

A is the initial cross-sectional area in square meters

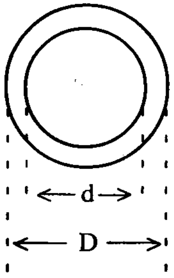
Dimensions of a standard dumb bell test-piece



Unit : mm

A.	Overall length, minimum	115
B.	Overall width	25 ± 1
C.	Length of narrow section	33 ± 2
D.	Width of narrow section	$6^{+0.4}_{-0}$
E.	Radius of fillet	± 1
F.	Outer radious	25 ± 2
G.	Gauge length	25 ± 1
H.	Distance between grips	80 ± 5
I.	Thickness	
J.	---------	15.5 ± 1

Dimensions of standard ring test-piece



Internal diameter (d) = 44.6 mm
External diameter (D) = 52.6 mm
Thickness (T) = 4 ± 0.2 mm

Fig. 9.9 Standard test-piece for tensile testing

To report the results of (i) (ii) and (iii) the middle value should be considered for an odd number of test-pieces and the average of the middle two values for an even number of test pieces.

Measurement on ring test-piece

The machine used for testing the ring test-piece, consists of two rotatable pulleys, each 25 mm in diameter. One of which is movable and is automatically rotated by the machine to equalize the strain in the ring while the test-piece is being stretched. The test results are obtained as follows:

i. Tensile strength $= \dfrac{F}{2A}$

where F is the breaking force in Newtons
A is the initial cross-sectional area in square millimeters

ii. Elongation at break (%) $= \dfrac{l - l_o}{l_o} \times 100$

where l is the internal circumference in mm at break (it can be measured directly from a scale attached to the machine)
l_o is the initial internal circumference in mm

iii. Modulus $= \dfrac{f}{2A}$

Where f is the force, in Newton at the required elongation
A is the initial cross-sectional area in square meters

iv. The initial internal circumference is taken as the mean circumference

$$= \left[\frac{52.6 + 44.6}{2}\right] \pi$$

$$= \frac{97.2}{2} \pi = 48.6\pi \text{ mm}$$

Report of tensile tests

The test report should include the following

i. the values for tensile strength, elongation at break and modulus (at 300%).
ii. Type of test-piece used.
ii. Method of determining cross-section (for rings only)
iii. Number of test-pieces used
iv. Number of tests
v. Temperature of test
vi Direction of grain (for dumb-bell)

The test results generally depend upon the following :

i. Rubber
ii. Compounding ingredients and method of mixing
iii. State of cure
iv. Time and condition of storage before test.
v. Type of test-piece
vi. Pre-stretching of test -piece
vii. Rate of stretching
viii Temperature of test

Hardness test

Hardness of rubber means resistance of the rubber to any deformation. The hardness test is based on a measurement of the indentation of a rigid ball into a rubber test-piece under specified conditions. In the normal test, the measured indentation is converted into international rubber hardness degree (I.R.H.D), the scale of which is so chosen that zero represents the hardness of a material having an elasticity modulus of zero and 100 represents the hardness of a material of infinite elasticity modulus.

To express the elasticity modulus (Young's modulus) in terms of indentation, the following mathematical equation is considered.

$$\frac{F}{M} = 0.0038\, R^{0.65}\, P^{1.35}$$

where P is the indentation expressed in $\frac{1}{100}$ mm,

M is the young's modulus of rubber expressed in MN/m^2

R is the radius of the ball of the indentor expressed in mm

and F is the indenting force, expressed in Newton.

To derive hardness in I.R.H.D a graph or a standard table of values relating I.R.H.D and Young's modulus may be used.

Generally I.R.H.D is directly read on a scale fitted to the indentation - measuring instrument. The commonly used laboratory instrument for this measurement is Dead-load hardness tester. The instrument can be used to determine the hardness of vulcanised rubbers preferably of a hardness range between 30 and 85 IRHD. (fig.9.10)

Fig. 9.10 A dead-load hardness tester

The essential parts of the instrument are as follows:

i. Vertical plunger : It has a rigid ball or spherical surface on the lower end, and means of supporting the plunger so that the spherical tip is kept slightly above the surface of the annular foot prior to the applying contact force.

ii. Means for applying a contact force and an additional indenting force to the plunger.

iii. Means for measuring the increase in depth of indentation of the plunger.

iv. Flat annular foot. It is normal to the axis of the plunger and having a central hole for the passage of the plunger. The foot rests on the test piece and exerts a pressure on it of $30 \pm 5^{KN}/m^2$.

v. Means of gently vibrating the apparatus : An electrically operated buzzer to overcome any slight friction. The appropriate dimensions and forces applied are given in table 9.1.

Test-piece

The standard test-piece is 8 to 10mm thick. Non standard test-pieces should not be less than 4mm.

The latest dimensions of both standard and non-standard test-pieces should be such that no test is made at a distance from the edge of the test-piece less than appropriate distance as indicated in table 9.2.

The depths of indentations varies with the thickness of the sheet and with a sheet thickness of less than 4mm, there is an undesirably large effect.

Table 9.1 Forces and dimensions of apparatus used for normal test

Diameters	Force on ball			
	contact	Indenting	Total	on foot
mm	N	N	N	N
Ball 2.5 Foot 20 Hole 6	0.30	5.40	5.70	8.3

Table 9.2 Minimum distance of impact from test piece edge

Total thickness of test-piece mm	Minimum distance from point of impact to edge of test piece mm
4	7
6	8
8	9
10	10
15	11.5
25	13

Conditioning

Tests should not be carried out less than 16 hour, after vulcanisation. Temperature of the test should be a standard laboratory temperature either 23 ± 2° C or 27 ± 2° C.

Procedure

The upper and lower surface of the test pieces are dusted with talcum powder and the test-piece is supported on a horizintal rigid surface. The foot is brought into contact with the surface of the test-piece. The plunger and indenting ball is pressed for 5 secs on to the rubber, the force on the ball being the contact force.

The pointer of the gauge is adjusted to read 100 at the end of 5 secs period. The additional indenting force is then applied and maintained for 30 secs, when a direct reading of the hardness in IRHD is obtained. During the loading periods, the apparatus is gently vibrated to overcome any friction.

Expression of results

Hardness is reported to the nearest whole number as the median of three or five measurements in IRHD. (the middle value when these are arranged in increasing order).

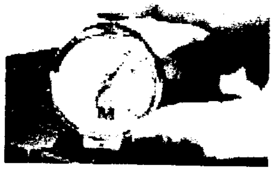
Pocket size hardness testers (Durometers)

These are more convenient for general use. The force on the indentor is applied by spring loading. The instruments used in common are shore A and D type durometers. The indentor in type A is frustoconical and in type D, pointed conical (see fig. 9.11 (a) and (b)). Shore A - scale varies from 0 (soft) to 100 (completely rigid)- and is most applicable to soft rubbers and Shore D finds apllication for hard rubbers and thermo plastics.

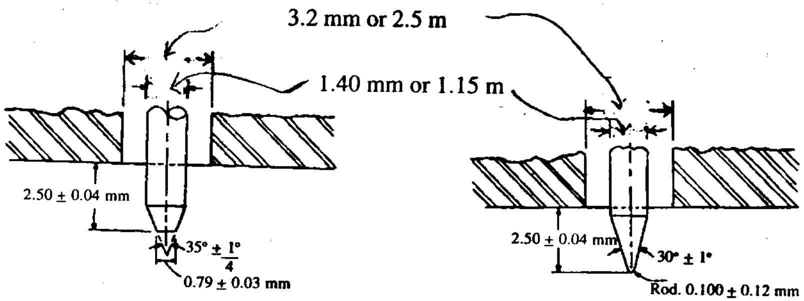
Readings with Shore A are nearly equal to IRHD for most work (fig. 9.12) but they are subject to variations as the springs are liable to incorrect settings, fatique and the indentors prone to wear or damage. The time of application of load is also not carefully controlled and this can lead to errors.

Method of measurement

The rubber sample is first placed on a hard horizontal surface and the durometer is held in vertical position with the pointer at least 12 mm from any edge of the sample. The pressure foot of the indentor is then applied on the sample surface rapidly as possible without shock. Following this, just sufficient pressure is applied to obtain firm contact between press foot and sample. Final reading is taken after 15 secs (as per ISO method).



DUROMETER
Rubber Hardness Tester



(a) Indentor for type A Durometer (b) Indentor for type D Durometer

Fig. 9.11 Shore durometers (a) type a and (b) type D

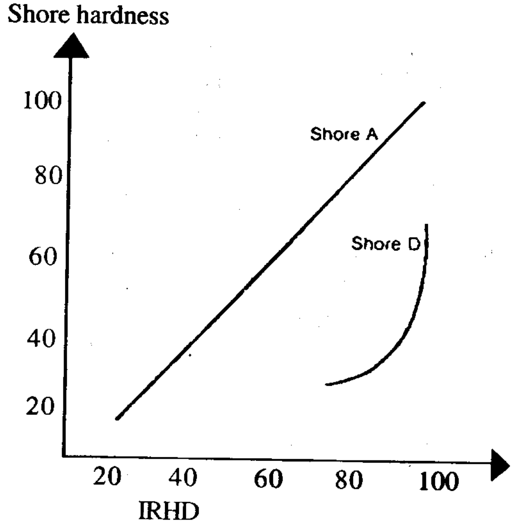


Fig. 9.12 Relationship between IRHD scale and shore A and shore D scales

Rebound resilience

Resilience is the ability of a rubber to return the energy used to deform it, during its recovery from the deformation. The property is mathematically expressed as the percentage ratio of the energy returned during an impact to the energy input.

$$\text{i.e. Resilience} = \frac{\text{Energy returned}}{\text{Energy input}} \times 100\%$$

A certain proportion of the energy used in the deformation is dissipated as heat, and thus is not returned during the recovery. This loss in energy is termed hysteresis of the rubber. If the deformation of rubber is an indentation due to single impact, the resilience measured is said to be rebound resilience.

Methods of determining rebound resilience

These methods are generally applicable to rubber vulcanisates of hardness in the range from 30 to 85 IRHD. In each method, an apparatus consisting of a pendulum like oscillatory device is used. The oscillatory device has a rigid body or hammer with an indenting spherical surface at the end. It is supported so as to oscillate linearly or circularly under the action of a restoring force. A system of pointer and fixed scale is provided to follow the motion of the striker body.

The test result obtained in each method is not of the same value, because of its dependence on the design of pendulum in the method. Further, it has been found that the resilince for a given rubber is not a fixed value, it varies with (a) temperature, (b)strain distribution, (c) strain rate and (d) strain history.

Lupke pendulum method

Of all the available standard methods, the Lupke pendulum method is the best known, because of the following reasons:

i. Due to the smallness of the moving parts, damping by air resistance is negligible.

ii. There are no bearings to cause friction.

iii. Vibration in the apparatus is negligible.

Lupke pendulum apparatus

The apparatus consists of a pendulum which is released from a given height to strike the test-piece. The rebound of the pendulum is the measurement of the resilience.

The pendulum consists of a horizontal rod of mass 350g, which is suspended on four strands of fine wire so that it maintains a horizontal position when describing an arc of a circle when falling under gravity. The pendulum strikes the test piece which is located in a holder of low heat conductivity. The pendulum rebounds from the test piece and the extent of rebound is indicated by a pointer which travels over a scale positioned concentrically with the path of the rod. The scale is divided into one hundred divisions, representing percentage rebound (see fig. 9.13).

Test-piece

This is a disc with thickness 12.5 ± 0.5 mm and diameter 29 ± 0.5 mm. It can be prepared by moulding or by cutting from a vulcanised product. It should have flat smooth and parallel surfaces. If stickness is shown on surface, dusting with talc powder is recommended.

Conditionning

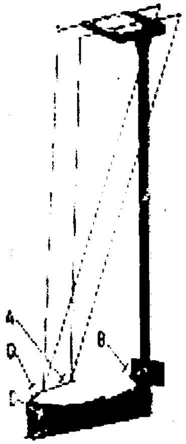
i. Thermal conditioning : Test - piece in the holder of the device, should be at the test temperature for at least 20 mins. prior to testing.

ii. Mechanical conditioning : The test should be given not less than three and not more than seven successive impacts with the striker member of the pendulum before noting test rebounding readings. This conditioning is required in carbon filled rubber to homogenise the carbon black filler dispersion in the rubber.

Determination of rebound resilience

Three rebound readings are noted successively. The readings are then expressed in percentages and their median value is taken as the rebound resilience.

To report rebound resilience, the average of rebound resilience values of two test-pieces should be considered.



A. Metal rod (pendulum)
B. Test piece
C. Scale
D. Pendulum release point

Fig. 9.13 Lupke Pendulum

Abrasion resistance

Rubber products that rub against another surface in service deteriorate from wear. There are many laboratory tests devised and investigated, but none correlates with service. Unless the nature of the abrasive surface and the manner in which abrasion takes place are identical to those found under service conditions, abrasion resistance tests are at best comparative.

Most tests involve a flat specimen, a disc or a moulded wheel and the abrasive is rotated against the specimen. Loads and angles can be adjusted in some tests.

The results obtained as abrasion loss are best compared with a standard or control rubber vulcanisate. If the laboratory abrasion test shows that trial compound gives less abrasion loss than the standard rubber, it is usually safe to expect a better result in service for products - tyres, belts and foot wear etc.

Of all the available abrasion testers, the DIN abrasion tester is best known. The main features of the tester is shown in fig. 9.14. The instrument consists of a drum diameter 150 mm and length 500mm, the outer surface of which is attached with a sheet of specified abrasive paper.

The test-piece used is a cylindrical piece of diameter 16 mm and thickness 6 mm - 16mm. It is inserted into the sample holder and its protrusion is adjusted.

During the test, the drum rotates at 40 rpm, and the test-piece holder travels over the surface of the abrasive paper no longer in one track, at a rate of 0.32m/sec, under a loading of 10 Newtons or 5 Newtons, for a distance of 40m. The test-piece holder is automatically lowered to and raised from the drum by means of a cam, at the begining and end of test. Upon completion of the test, the test-piece is removed and its volume loss is determined by weighing and calculation. The abrasive resistance of the rubber can then be determined by relating the test results to those of a control rubber.

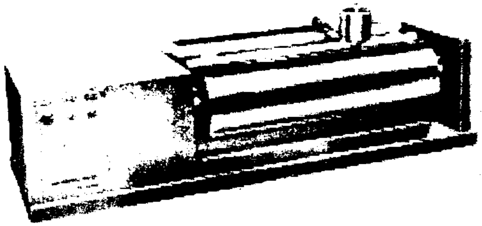


Fig. 9.14 DIN - Abrasion tester

Tear resistance

Some rubber vulcanisates tear easily when nicked or cut, whereas others are tough and tear with difficulty. Various tests are devised to measure this property with only fair success. Resistance to tearing depends on several factors such as speed of tearing, crystalisation of the rubber on stretching or amount and type of fillers in the rubber compound , type of specimen depth of nick or cut, etc. For the reasons, results obtained by different methods are not in agreement and no method correlates well with service. However, the test method in which a crescent shaped specimen is used, is now commonly accepted as the most reliable method.

Procedure

A test-piece in the shape of a cresent (fig. 9.15) is punched from the sample of vulcanised thin rubber sheet of thickness 2mm. A cut (nick) of depth 1 ± 0.2 mm is made at the center of the concave inner edge of the test-piece by means of a sharp razor blade or a sharp knife free from ragged edges. The test-piece is mounted in the testing machine (Inertialess electronic type tensile testing machine is preferred to pendulum machine) and stretched at a rate of separation of 500 ± 50mm/min, until the test-piece breaks. The maximum force to break the test-piece is then recorded.

The tear strength is given in kilonewtons per metre of thickness by the formula.

$$T = \frac{F}{d}$$

Where F is the maximum force in newtons
d is the thickness in mm

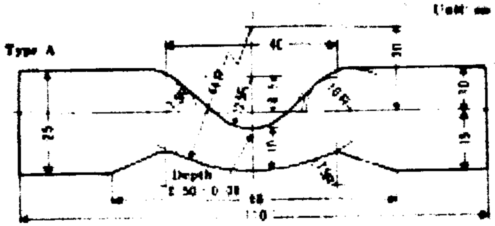
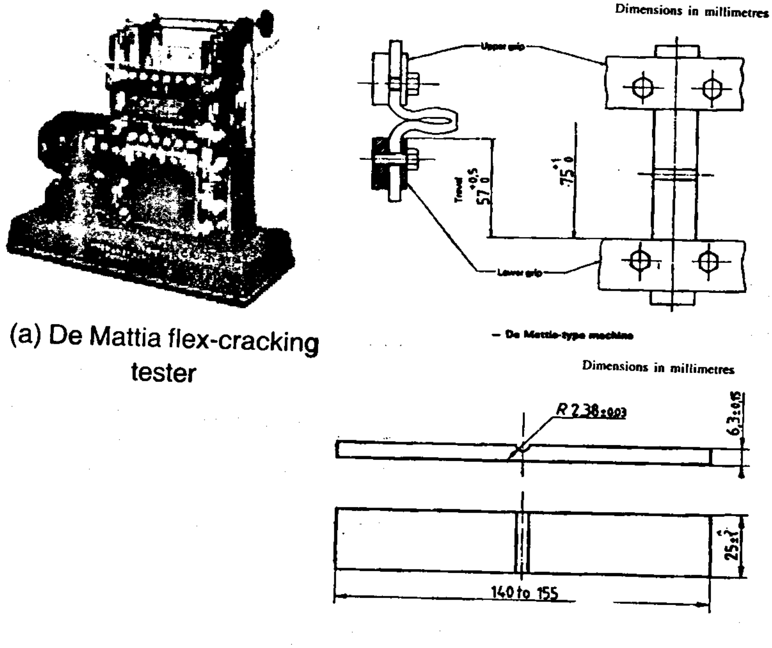


Fig. 9.15 The form and dimensions of cresent test-piece

Flex - cracking and crack growth

When rubber is repeatedly flexed so that the surface ubdergoes cyclic variations in strain, cracks slowly develop or if a crack or cut already exists, it will grow in a direction perpendicular to the strain. To assess the rubber resistance in such situations different tests are employed. Most of these tests based on the ISO recommendations use the De Mattia Machine and measure the spontaneous development of cracks by repeated flexing or the growth of a deliberately made cut through the test piece.

The test-piece is a flat strip, with a moulded transverse semi -circular groove in which the strain is concentrated when the test-piece is bent by bringing its ends nearer togrther as shown in fig. 9.16.



(a) De Mattia flex-cracking tester

(b) Test piece

Fig. 9.16 a) De mattia flex-cracking tester b) Test-piece-shape and dimensions

Test procedure

The test-pieces are inserted in the grips of the machines so that they are flat and not under tension, with the groove in each test-piece in midway between the two grips in which that the test-piece is held and on the outside of the angle made by the test-piece when it is bent.

The machine is then started and continued the test with frequent inspection until the first minute sign of cracking is detected. The number of flexing of cycles at this point is recorded and the machine is restarted. It is stopped after intervals in which the number of flexing cycles is increased in geometric progression, a suitable ratio being 1.5 on each occasion. The inspection of the flexed test-piece is made each time, with the grips separated to a distance of 65 mm.

Temperature of test : Tests are normally performed at standard laboratory temperature.

Expression of results

Cracking is graded according to the following scale:

Grade	Appearance of cracks
Grade	1 pinpricks < 10
Grade 2	10 < pin pricks or pin pricks <10 with one or more cracks having perceptible length but < 0.5 mm.
Grade 3	1mm > crack length > 0.5 mm
Grade 4	1.5 mm > crack length > 1mm
Grade 5	3mm > crack length > 1.5 mm
Grade 6	Crack length > 3 mm

Flex cut growth

The flex cut growth test differs from that of flex cracking in that the test-piece is first punctured at the base of the groove, by a chisel-shaped tool with a blade 2 mm wide. The length of the resulting cut (parallel to the grooe axis) is measured before and after various periods of flexing, the test result being the numbers of flexing cycles for predetermined increases in this length.

Accelerated ageing (Heat resistance) tests

These tests are designed to asses the relative resistance of rubber vulcanisates to deterioration with passage of time. For this assessment, the test methods that ISO recommends are (i) Air oven ageing method and (ii) Oxygen pressure method.

In both methods, tha values of physical properties such as (i) tensile strength (ii) modulus at 300% extension, (iii) elongation at break or (iv) hardness of aged and unaged rubber test - pieces are compared for the assessment of age resistance of rubber.

Air oven ageing method

In an air oven ageing method, the test - pieces suitable for the above measurement are heated at constant temperature when renewed air is slowly circulated in the oven.

The oven used for this method is either a cell type oven or a normal oven. The cell type oven consists of one or more cylindrical vertical cells, having height of 300 mm and of such domensions that the space occupied by the test pieces does not exceed 10% of the capacity of the cell (see Fig. 9.17). The cells are thermostatically controlled and air is circulated through the cells for not less than 3 and not more than 10 changes per hour.

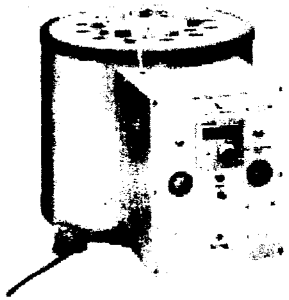


Fig. 9.17 Cell type oven for ageing test

In the normal oven, the test - pieces are suspended so that they are alteast 10 mm from each other and 50 mm from the sides of the oven. As in the case of cell type oven, the volume of the test - pieces does not exceed 10% of the free space of the oven and a slow circulation of air is provided during the test.

The advantage of the cell type oven is that the vulcanised rubber test pieces of different formulations can be aged together by placing individually in each cell of the oven.

Duration of air oven ageing test

The period required to obtain any given degree of deterioration of the test pieces depends upon the type of rubber under examination. It is recommended that test period be 1, 3, 7, 10 or a multiple of 7 days.

Temperature of test

The oven is maintained at one of the collowing temperatures :

For conventional rubbers - 70 ± 1°c
85 ± 1°c
100 ± 1°c
125 ± 2°c
150 ± 2°c

Oxygen pressure method

This method was intended to accelerate the ageing of rubber. Unlike air oven ageing method, the oxidation of rubber is uniform in the method. The oxgen pressure chamber used in the method consists of a vessel of stainless steel designed to retain an internal atmosphere of oxygen under pressure with 2 MPa. The chamber is maintained at temeprature 70 + 1° C by means of a thermostat.

As in the air oven ageing test, the total volume of the test pieces does not exceed 10% free space of the pressure chamber. During the test, the test pieces are exposed to the elevated temperature and pressure for a specified period ot time. The selection of suitable peiod of time depends upon the rate of deterioration of the particular rubber being tested. Time periods frequently used are 24, 48 and 96 hours.

Expression of the results :

The test results of both the unaged and the aged test pieces are reported together with the percentage in the value of the property measured as calculated from the expression -

$$\frac{X_a - X_c}{X_c} \times 100$$

where X_c is the value of the property before ageing

X_a is the value of the property after ageing.

Permanent set

Permanent set tests are intended to measure the ability of rubber vulcanisates to retain elastic properties after prolonged action of compressive and tensile stresses.

Compression set at constant strain

Test detalis : A cylindrical rubber test piece of specified diameter and thickness is compressed between two polished plates separated by spacer bars to ensure the constant strain of 25%. The test - piece is strained for 72 hours at 20 C or 24 hours at 70°C, 100°C or 150° C (depending upon the type of rubbers), removed from the test device and allowed to recover for 30 mins. at room temperature. The compresson set, measured as the difference in thickness of the test piece is then expressed as the percentage of the initial strain [see Figs. 9.18 (a) and (b)].

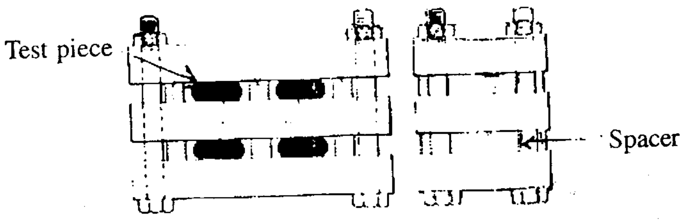


Fig.9.18 a. Compression set apparatus, constant deformation (strain)

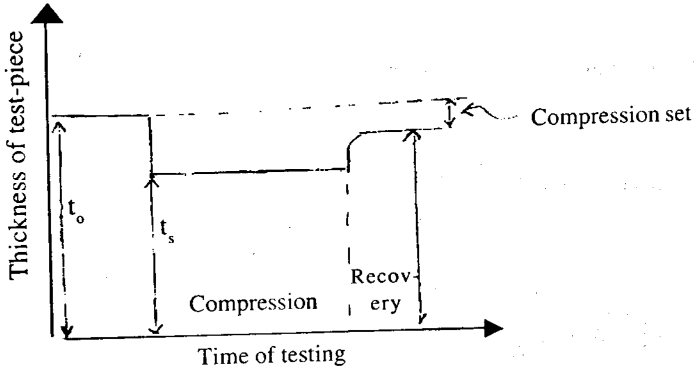


Fig.9.18 b. Variation of thickness of test - piece during the compression set test

Standard dimensions of test - pieces used as follows:

a. Diameter = 13 mm, Thickness = 6.3 mm.

b. Diameter = 29 mm, thickness = 12.5 mm

Expression of Result :

$$\text{Compression Set (at constant strain, 25\%)} = \frac{t_o - t_r}{t_o - t_s} \times 100\ \%$$

where t_o--- Original thickness of test - piece

t_s --- Compressed thickness of test - piece

t_r --- Recovered thickness of test - piece

Compression set (at contant stress)

In this test, a constant compressive stress (400 psi) applied on the test piece for an specified time (24 hours) at constant temperature (70°c). After recovery period of time (30 mins.), at room temperature, the final thickness of the test - piece is measured. The compression set in this case is expressed as the percentage change in thickness of the test piece.

$$\text{i. e. Compression Set (at constant stress)} = \frac{t_o - t_r}{t_o} \times 100, \text{ where}$$

t_0, is the original thickness of the test piece and t_r, the thickness of test piece after recovery.

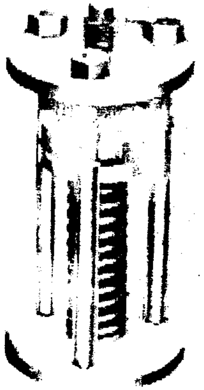


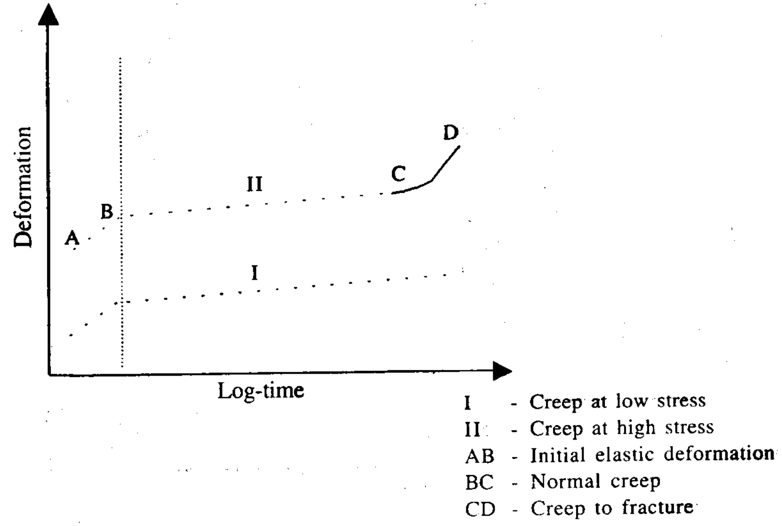
Fig. 9.19 Compression set apparatus, contant stress (load)

Creep

When a rubber is applied with a constant stress, it shows a slow continuous increase of deformation beyond the relatively large initial deformation that occurs. This phenomenon is termed creep. Unlike the initial elastic deformation, the additional deformation represented by creep is not recoverable, after removal of the stress.

Creep will occur whenever rubber is subjected to stress under compression, tension or in shear. For most gum and filled rubber vulcanisates, creep varies approximately linearly with the logarithm of time under load. Fig. 20) For example, the amount of creep occuring in the decade of time from one minute to ten minutes after loading is the same as the amount in much longer decade from one week to ten weeks after loading. Thus, creep rate of rubber is measured as the change of strain in one decade of time and is usually expressed as the percentage of initial strain. From the practical point of view the initial strain is considered as the strain, one minute after the deformation is imposed.

$$\text{Thus, the rate of creep (\%)} = \frac{\text{Change in strain in one decade of time x 100}}{\text{Strain, one minute after the deformation is imposed}}$$



I - Creep at low stress
II - Creep at high stress
AB - Initial elastic deformation
BC - Normal creep
CD - Creep to fracture

Fig. 9.20 Typical creep curves

Stress relaxation

When rubber is held at constant deformation (strain), the stresses set up gradually decrease with time as the molecular crosslinked network approches an equilibrium condition. This is said to be stress relaxation. Like creep property, the stress relaxation of a rubber also varies approximately linearly with the logarithm of time under deformation (Fig. 21). So, the measurement of the property is very similar to that of creep property and the result is also usually expressed in percentage value.

Thus, the rate of stress relaxation (%) =

$$\frac{\text{Change in stress in one decade of time}}{\text{Stress, one minute after the deformation is imposed}} \times 100$$

Tests to evaluate creep and stress relaxation in rubbers

Creep and Stress relaxation measurements can be made in tensile, compressive or shear deformation of rubber. For measurement of creep, a constant load is applied on the sample of rubber and the gradual increase in its strain per decade of time is noted. In the case of stress relaxation test, the sample of rubber is held at constant strain and the stress (load) needed to maintain the strain per decade of time is determined.

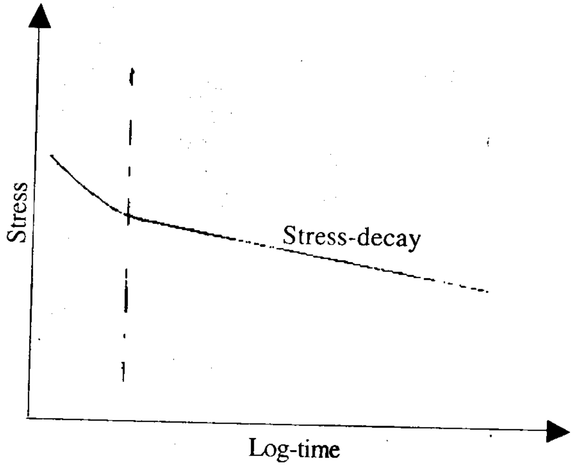


Fig. 9. 21 Typical stress relaxation curve

Main causes for creep and stress - relaxation in rubbers

The occurance of both creep and stress - relaxation phenomena is attributed to the occasional failure of the cross - links, especially those of the physical entanglement kind and to the breakage of the molecules themselves in atmospheric oxidation.

In tension, the creep rate may reach double the rate of stress - relaxation; in shear it is about the same and in compression it is lower.

Chapter 10

Latex Technology

In comparision to the manufacture of dry rubber products, the manufacture of products direct from latex has some distinct advantages as given below :

i. Relatively simple machinery are required.
ii. Low power is consumed
iii. Simple methods of preparing latex compounds are involved
iv. Environmental pollution is reduced.

However, the major disadvantage of latex product manufacture is that a high proportion of water content in latex compound has to be removed at one stage during the manufacturing process. By reason of this, only products having thin walls and cellular structures are produced in common.

10.1 Natural rubber latex

Natural rubber field latex is a thin fluid and used only in its concentrated form for the manufacture of latex articles. In the concentration method, the dry rubber content of field latex is generally raised to about 60%, and this level of concentration is found to be most economical for transportation and product manufacture.

The concentration of natural rubber field latex can be effected by one of the following methods :

i. Centrifuging
ii. Creaming
iii. Evaporation

Of these, the method of centrifuging is most commonly employed. The method accounts for ninety percent of the total production of concentrated natural rubber latex, at present. There are two kinds of concentrated latices produced by this method, namely high ammonia latex and low ammonia latex.

Centrifuged latex

High ammonia centrifuged latex (HA - Latex)

To produce this type of latex, field latex is first preserved with high proportion of ammonia (0.7 - 0.8 % by weight on latex) and then treated with diammonium hydrogen phosphate. This reduces the Mg^{++} ions present in the latex and enhances the resistance of the latex to bacterial action.

$$(NH_4)_2 HPO_4 + Mg^{++} \rightarrow MgNH_4 PO_4 + H^+ + NH_4^+$$
$$\downarrow$$

The latex is then centrifuged at high speed, around 7000 - 10,000 rpm in a centrifuge machine. During the centrifuging process, the concentrated latex of dry rubber content of about 60% by weight centrifuges inwards towards the axis of the rotation and the skim latex containing about 5% dry rubber content flows outwards away from the axis of rotation. Thus, the two kinds of latices are separately collected from the same machine.

The skim latex is generally converted into dry skim rubber which is blended with other grades of dry natural rubber for use in low cost rubber goods.

Low ammonia centrifuged latex (LA - Latex)

As the name implies, this type of latex is produced with low ammonia content of about 0.2% by weight on latex. Compared to HA - latex, LA - latex has more advantages which include :

i. enhanced resistance to bacteria growth in latex

ii. better storage stability of latex compounds

iii. low level of ammonia concentration in factory atmosphere

Low ammonia latex is produced in various grades, each of which differs in the type of secondary preservatives it contains (see table 10.1)

Table 10. 1 Different grades of low ammonia centrifuged latex

Grade	Preservatives used (% by weight on latex)
LA - SPP	Ammonia (0.2)
	Sodium pentachlorophenate (0.2)
LA - BA	Ammonia (0.2)
	Boric acid (0.25)
	Lauric acid (0.05)
LA - ZDC	Ammonia (0.2)
	ZDC (0.1)
	Lauric acid (0.05)
LA - TMTD/ZDC	Ammonia (0.2)
	TMTD (0.05)
	ZNO (0.02)
	Lauric acid (0.05)

Creamed latex

Creamed latex concentrate is also produced from high ammoniated latex (about ammonia concentration of 1% by wt. on latex). Like in the centrifuging method, the level of Mg^{++} ions are first reduced in the field latex, by treating with diammonium hydrogen phosphate. The latex is then added with creaming agent such as ammoniam alginate (about 0.15% by wt. on latex) and left to stand without agitation. This slows down the brownian movement of the latex particles and brings about their buoyant movement towards the surface. After a period of about one week, the latex particles thus concentrated on the top region (creamed latex) is separated from the rest of the latex.

Evapourated latex

To produce evaporated latex concentrate, field latex is first stabilised with alkali solution (eg. KOH) and then concentrated by passage through film evaporators at a high temperature. The concentrate has a greater total solids content about 75%.

Characterisation of Natural rubber latex

Natural rubber latex is characterised by the following :

i. Total solids content (TSC)

ii. Dry rubber content (DRC)

iii. Alkalinity (ammonia content)

iv. KOH number

v. Mechanical stability time (MST)

vi. Volatile fatty acid number (VFA number)

Total solids content (TSC)

The total solids content is the fraction of the latex, which is relatively non - volatile at temperatures in the region of 100°C. By determining this value, the water content of the latex can also be estimated. The method of determination involves with evapourating of a known weight of latex (1.5 g to 2.5g) to dryness at 100°C for two to three hours and then weighing the residue. Total solids content is then expressed as a percentage mass of residue in the latex.

ie. $$\text{TSC}(\%) = \frac{m_1 \times 100}{m_0}$$

where m_0 - mass of test portion of latex and m_1 - = mass of residue in the form of dried sheet.

Dry rubber content

Dry rubber content is the fraction of latex which is coagulated under controlled conditions. The dry rubber content taken in conjunction with the total solids content provides information regarding the fraction of the non - rubber constituents in the latex. The method of determination constitutes coagulating a known weight of latex (10g) with acetic acid (2%) and ethanol (95% v/v), under standard conditions and then separating, drying and weighing the coagulum.

The dry rubber content is then expressed as a percentage mass of rubber in the test portion of the latex.

ie. $$\text{DRC}(\%) = \frac{m_1 \times 100}{m_0}$$

where m_0 = mass of test portion of latex and m_1 = mass of coagulum in the form of sheet.

Alkalinity (ammonia content)

Alkalinity is the concentration of ammonia in the latex. It is generally expressed in one of the following ways :

i. As a percentage weight of ammonia content in the latex, or

ii. As a percentage weight of ammonia content in 100g of water in the latex.

In the method of determination, the alkalinity is estimated by titration with an acid. The course of the reaction can be followed by means of a pH meter, or using the indicator methyl red.

KOH - number

The KOH number of ammoniated latex is defined as the number of grams of potassium hydroxide equivalent to the acid radicals combined with ammonia, in latex containing 100 grams of solids.

The KOH number includes all acids which are present as ammonium salts, whatever their nature (both volatile and non - volatile fatty aids). By determining the KOH number the extent of hydrolytic degradation of protective cover components of latex particles, such as proteins and lipids could be assessed. It is therefore considered as a measure of age and general condition of latex.

Mechanical stability time (MST)

The mechanical stability time is measured in seconds. It is a measure of the resistance of the latex sample towards mechanical agitation, To determine this value, the latex sample is stirred at a high speed about 1400 ± 200 rpm, by means of a standard instrument called mechanical stability tester. In the test, the time required to initiate visible flocculation in latex (appearance of specs of latex particles) is noted.

Volatile fatty acid number (VFA No.)

The volatile fatty acids which present as ammonium salts in normal natural rubber latex are low molecular weight organic acids such as formic acid, acetic acid, and propionic acid. These are formed in latex as a result of degradation of sugars, and tend to reduce the stability of the latex, by increasing the ionic strength.

In the method of determination of VFA, the serum is separated from a known weight of latex, acidified strongly and then subjected to steam distillation. The steam - volatile acids are then estimated by titration.

The specified values of the above parameters for HA - centrifuged latex and HA - creamed latex are indicated in table 10.1

Table 10.1 Specification for HA - centrifuged latex and HA - creamed latex

	HA - centrifuged latex	HA - creamed latex
Total solids content TCS (min. %)	61.5	64
Dry rubber content DRC (min. %)	60	62
Total alkalinity (min% ammonia in 100g of water in latex)	1.6	2
KOH number (max.)	1.0	0.8
MST. (min.) seconds	540	540
VFA number	0.2	2

10.2 Synthetic latices

The development of synthetic latices has also contributed greatly to the growth of latex industry. Synthetic latices are prepared largely by emulsion polymerisation. The latices generally differ from natural rubber latex in the following :

Particles

(a) They are more or less spherical in shape.

(b) Average particle size of synthetic latices is smaller than that of the natural rubber latex, approximately of the order of 10.

(c) Synthetic latex particles are more uniform in size than are those of natural rubber latex.

Specific surface area

By reason of smaller particles, the total interfacial area per unit volume of a typical synthetic latex, is larger than that of natural rubber latex. As a result of this, the surface free energy of synthetic latex is relatively high and the latex generally shows greater affinity for added surface active substances. This may cause viscosity problems if it is to be blended with natural rubber latex.

Wet - gel strength

The term wet - gel strength means the mechanical strength of gelled latex films, before they have dried out. Films or deposits from synthetic latices have very low wet - gel strength, especially if the films or deposits are hot. This property is particularly, important in processes where the cured products have to be stripped from their moulds while still in a wet condition. For such process (eg. foam manufacture), synthetic latices are unfavourable.

Mechanical stability

Although synthetic latices show high mechanical stability time, they are very sensitive to the coacervating effect of mechanical pressure. Even light hand rubbing is sufficient to cause rapid destablisation.

Chemical nature

The chemical compositions of the synthetic latexes are relatively simple. Because of the absence of proteins and other natural substances the latices do not undergo spontaneous coagulation and putrefaction. The latices are also found to be less prone to attack of micro - organisms.

10.3 Compounding ingredients to latex

Latex compounds generally consist of the following groups of substances :

i. Surfactants

ii. Modifiers of rubber properties such as vulcanising system, softener, fillers, antidegradants.

iii. Auxillary ingredients such as flame retardants, colourants, heat sensitisers. etc.

Surfactants

Surfactants are incorporated into latex to lower the surface free energy of latex. Besides this, they may also function as (i) dispersing agents (ii) wetting agents (iii) emulsifiers (iv) stablisers (v) foam promoters etc.

Types of surfactants

1. Anionic surfactants

Anionic surfactants are water soluble and their surface active components carry negative charges.

Examples : Carboxylates, Sulphonates, Sulphates, and Inorganic polyphosphates.

Carboxylates :

These ionise to give anionic surface active component RCOO - where R is a non - polar hydrocarbon chain group. The hydrocarbon group may be saturated or unsaturated. Examples : Ammonium salt of lauric acid ($C_{11}H_{23}COO\ NH_4$) where $C_{11}H_{23}$ is the R group.

Potassium Oleate ($C_{17}H_{33}COO\ K$) where $C_{17}H_{33}$ is the R group.

Carboxylates are sensitive to acids and heavy metal ions. In the presence of these chemicals, carboxylates are unstable and may precipitate out from the latex system.

Sulphonates

Sulphonates ionise into RSO^-_3 active ion, where R may be aliphatic, aromatic or alkyl - aryl hydrocarbon group.

Examples : Sodium isopropyl naphthalene sulphonate.
Sodium naphthalene formaldehyde sulphonate.

Sulphonates are very much less sensitive to acids and heavy metal ions than are the carboxylates. Their surface activity is therefore retained over a wide range of pH and metal ion concentration.

Sulphates

The surface active ions for these types are RSO^-_4 ($RO.SO_3$) where R is straight chain hydrocarbon group (saturated or unsaturated). Examples : Sodium lauryl sulphate, sodium cetyl sulphate.

These are more soluble in water than the corresponding sulphonates. They are strongly surface - active and find application as wetting agents, dispersing agents and stabilisers.

Inorganic polyphosphates

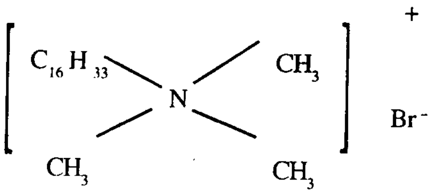
Examples : Tetra sodium pyrophosphate
Sodium polymetaphosphate

Inorganic polyphosphates are mildly surface - active substances, which find extensive application as deflocculating agents in pigment dispersions. These polyphosphates also function as heavy metal ion sequestering agents and thereby improve the stability of the latex colloidal system.

II. Cationic surfactants

These ionise in water to give cationic surface active components. The surfactants are generally salts of primary, secondary or tertiary amines. They can be sub - divided into (i) ammonia types and (ii) quartenary ammonium salts. The most commonly used cationic surfactant in latex work is cetyl trimethyl ammonium bromide. Cationic surfactants find application essentially for the preparation of cationic synthetic latices and sometimes as foam stabilisers.

Example : Cetyl trimethyl ammonium bromide.



III. Amphoteric surface active agents

In this group of substances, the surface - active component of the molecule may be a dipolar ion (zwitter ion) or it may be either an anion or a cation according to the prevailing conditions of pH.

Examples : Water - soluble proteins (mildly surface active). These are used as protective colloids and viscosity modifiers.

IV. Non - ionic surfactants

These surfactants do not give rise to ions in aqueous medium. The types which are used in latex work, are generally the products of ethylene oxide with fatty acids, fatty alcohols or phenols. These have the general structure as follows :

$$R\,[(CH_2CH_2O)_n]_m\mathbf{H}$$

Where R is hydrophobic radical which is derived from the fatty acid, fatty alcohol, or phenol. The hydrophilic component in the structure is polyethonoxy chains $(CH_2CH_2O)_n$.

Typical examples : Vulcastab L W (Polyethylene oxide condensate)

The condensates are very useful as emulsifying agents and stabilisers (for both latices and dispersions of insoluble powders). However they have the unusual property of being less soluble in hot water than in cold. The effect of temperature upon solubility is reversible and is due to the tendency of polyethonoxy chains to dehydrate on warming. The temperature at which this reversible change occurs is said to be cloud point. The other substances which behave like polyethylene oxide condensates in latex compounds are polyvinyl methyl ether, poly - 1 , 2 - propylene diols and methyl celluloses.

Modifiers of rubber properties

The modifiers are added to change the physical and / or chemical properties of the rubber. They are,

i. Vulcanising system :
  a. Vulcanising agent
  b. Activators of accelerators
  c. Accelerators

ii. Softeners :
  a. Resins
  b. Petroleum oils
  c. vegetable oils
  d. Organic esters eg. Dioctyl phthalates

iii. Fillers : Mineral fillers such as Clays, Whiting, Talc. etc.

iv. Antioxidants : Phenolic antioxidants

Auxillary ingredients :

These are incorporated into latex compounds for special purposes :

a. coagulants

b. Heat sensitizers

c. Flame retardants

d. Colourants (pigments and dyes)

Preparation of compounding ingredients

Since most of the rubber compounding ingredients are insoluble in water, (in latex medium), it is important that these substances be prepared in the form of aqueous dispersions or emulsions, before incorporating into latex. However there are practical limitations such as

(i) The pH of the dispersion / emulsion should be similar to that of latex.

(ii) The dispersion / emulsion should not be so concentrated that it has a destablising effect on the latex.

(iii) The dispersion / emulsion should not contain destablising polyvalent metal ions (M^{++} or M^{+++})

Dispersions

Water - insoluble powdery ingredients are prepared in the form of dispersions before mixing into latex. In the dispersion, the particles of the ingredients are suspended through out the watery medium.

Preparation of dispersions

In the general method of preparing dispersions for latex work, a coarse slurry of the powder containing small amounts of dispersing agent and stabiliser with water is first made. Then the slurry is ground in a suitable mill to produce a dispersion of small particle size. The commonly used grinding equipment fall into two categories as follows :

(i) Those which merely breakdown aggregates of fine particles but do not effect any reduction of ultimate particle size. Example : Colloid mills.

(ii) Those which do effect a reduction of ultimate particle size as well as dispersing any agglomerates which may present. Examples: ball and pebble mills, ultrasonic mills, attrition mills.

The first category mills are used for the dispersion of such powder as zinc oxide, kaolinite clay, precipitated whiting etc., whose particles appear in loose aggregates of much finer particles. The latter category mills are used for solids such as sulphur, accelerators and antioxidants, all of which consist of rather coarse particles and hence a reduction of ultimate particle size is essential.

Ball mill

The mill consists basically, of a steel or porcelain cylindrical container mounted horizontally and is capable of being rotated about its axis. Before operation, the container is charged with small pebbles or balls with various sizes, to about one - third the capacity of the container. Then it is added with equal volume of slurry powder to be ground. An air space of one - third capacity is left in the container for efficient grinding.

Dispersive action takes place mainly by shearing, resulting from the relative movement of the balls and to a lesser extent by impact.

It is vital importance that these mills should run at the correct speeds. The optimum speed is about 50% to 60% of the critical speed, which can be calculated from the expression $\frac{54.18}{\sqrt{r}}$ where r is the internal radius of the mill in feet

Ball mills continue to be used extensively for batch production.

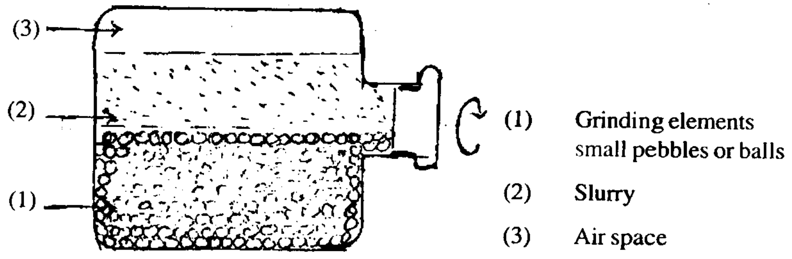


Fig. 10.1 Illustrating the principle of the ball mill

Attrition mill

This mill can be regarded as a development of the ball mill, in which the grinding chamber is fixed vertically and the balls are agitated by a vertical shaft fitted with arms in rotatory motion. The grinding chamber is usually of a stainless steel and the stainless steel balls range in diameter from 3mm to 12mm, according to the type of material being processed. It has been found that the attrition mill is about ten times as fast as the ball mill in producing a dispersion. The mills range in size from 25 liters to 400 liters. In the operation, the slurry of the powder is charged directly into the machine, and then re-circulated through the chamber by means of an external pump system, until required degree of dispersion is obtained.

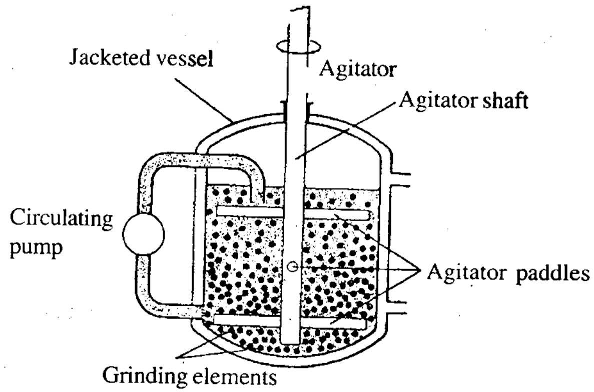


Fig. 10.2 Illustrating the principle of an attrition mill

lloid mills

These mills do not effect any reduction of ultimate particle size but they merely breakdown the aggregates of fine particles of the powder. A typical colloid mill is shown in the Fig. 10.3. The mill consists of two closely set carborundum parts, one of which is stationary and the other is rotatable at high speed. When the slurry is passed into the mill, the aggregates of the powder particles are broken - down into finer particles due to the rotational shearing action.

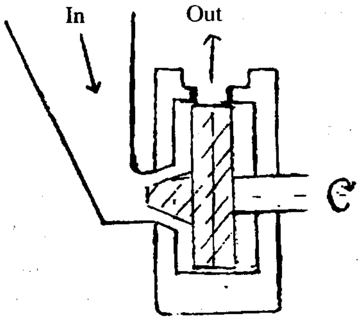


Fig. 10.3 A colloid mill

Preparation of emulsions

Only emulsions of the oil - in - water type are needed in latex compounds. For preparing such emulsions, there are generally two methods employed. In the first method, dispersing aids, stabilisers thickeners, etc. are dissolved in water and then added with oil under high - speed stirring. The second method, referred to as the soap - in - situ method, is more effective than the first method. In the method, a soap is used as the main dispersion aid. As initial step, the fatty acid component of the soap is dissolved in the oil and the alkali component of the soap, in water, together with any stabilisers and thickeners. The oil phase is then poured into the aqueous phase with rapid stirring, whereupon emulsification takes place spontaneously.

For intense shearing and disintegration of oil droplets colloid mills or ultrasonic mills may be used.

Table 10.3 Composition of liquid antioxidant emulsion (50%)

		Wet
Component A	Antioxidant (liquid)	100
	Oleic Acid	5
Component B	Ammonia solution (S. G.0.88)	5
	Soft water	90

Component A is first warmed to 75°C and then component B is added into it, using a high speed stirrer or a homogeniser.

10.4 Latex compounds

Compounding ingredients prepared in the form of solutions, dispersions or emulsions having similar pH values to that of latex are chosen. After incorporating the ingredients into the latex, the latex compound thus prepared is generally left to stand with slow speed of stirring for a period of 24 hours. This brings about an equilibrium state called matured state, to the latex compound, which is normally preferred for production of good quality latex rubber products.

Traditionally the compounds find applications in the production of dipped products, (balloons, gloves etc.) foam products (mattress, cushions etc.) cast articles (toys), extruded latex goods (thread), carpet backing and water based adhesives and surface coatings. They are also used for rubberising bitumen and stabilising soil against erosion.

Typical compositions of dispersions.

(i) Vulcanising agent -

Sulphur is generally prepared as a 50% dispersion.

	Dry	Wet
Sulphur	100	100
Dispersal LN (10%)*	2.5	25
Ammoniam caseinate (15%)	1	7
Bentonite clay (5%)	1	20
Soft water		48

Ball milled for 72 hours.

(ii) Accelerator - ZDC, ZMBT (prepared as a 50% dispersion)

	Dry	Wet
Accelerator	100	100
Dispersal LN (10%)	2.5	25
Vulcastab LW (20%)	1	5
carboxy methyl cellulose (10%)	0.5	5
Water		65

Ball milled for 24 hours.

* Sulphonate type dispersing agent.

Typical compositions of oil emulsion

Softener - Paraffin oil (prepared as an emulsion 50%)

		Wet
Component A	Paraffin oil	50
	Oleic acid	5
Component B	Triethylamine	1.5
	Soft water	43.5

Components A & B are mixed in an emulsifier, at high speed stirring.

10.5 Methods of destablisation of latex compounds

In the method of production of a latex article, the colloidal nature of latex system is destablised at one stage. The technique of destabilising latex is generally, carried out in one of the following ways :

i. Dehydration of latex (Removal of water molecules associated with surfactant molecules by means of air drying, addition of alcohol, etc.)

ii. Neutralisation of charges of latex particles (For instance, negative charges on latex particle are neutralised with hydrogen ions, by the addition of organic or inorganic acids) .

iii. Depletion of the surfactant from the latex particle surface (By mixing with colloidal silica having high surface area)

iv. Addition of divalent metal ions (For instance, addition of calcium chloride or nitrate gives rise to insoluble soap molecules)

10.6 Latex articles

Of all the latex based rubber articles, the dipped and foam rubber articles find applications widely and are in increasing demand. Thus, in this section, the methods of production of these two types of articles will be discussed in particular.

I. Dipped articles

The main steps involved in the manufacture of latex dipped articles are as follows :

Preparation of latex compounds
Pretreatment of formers
Dipping methods
Drying
Vulcanisation
Finishing
Inspection and testing

Preparation of latex compounds

Natural rubber latex compounds based on LA - latex or deammoniated HA - latex are commonly used. However, latex compounds formulated with prevulcanised natural latex are also chosen for some types of dipped products. In the case of prevulanised latex - based compounds, the process does not require the vulcanisation step, which is considered as an advantage.

Preparation of prevulcanised latex

To prepare prevulcanised latex, LA - latex is generally chosen. It is then incorporated with sulphur, accelerator, and zinc oxide, each being taken a little in excess of the normal quantity. These three ingredients are added generally as a coarse slurry into the latex. The latex mix is then heated to 60^0 to 80^0 C while it is stirred slowly to attain desirable degree of vulcanisation. The time taken for this reaction varies from two to three hours. The degree of vulcaninsation is normally monitored by testing the elastic modulus of a small portion of coagulum obtained from the mix, from time to time. The prevulcanised latex thus prepared may be added with other ingredients such as softener, antioxidants, fillers, pigments, etc. as required prior to the dipping process.

Pretreatment of formers

Porcelain formers are generally preferred to other formers made with materials like aluminium, wood, glass etc. These formers are glazed and made hollow. For cleaning, the formers are first scrubbed, with mild alkaline detergent and then rinsed well with water.

Dipping methods

The methods employed are named as straight dipping, coagulant dipping, and heat - sensitised dipping.

i. Straight dipping method

This method involves with first immersing a former into a suitably compound latex, then allowing it to dwell for a specified time and finally withdrawing from the latex compound. By this technique a thin deposit of latex (ca. o. 2mm) can only be obtained in a single dip. However, thickness of the deposit may be increased by increasing the number of dipping, The advantage of this multi - dip process is that if any pin holes are formed on the surface of the deposit (coating), those can be eliminated (see Fig. 10.4a.)

ii. Coagulant dipping method

Coagulants chemicals are employed in this method, to obtain the latex deposit on the former. Both wet and dry coagulants find applications.

(a) Method using wet coagulants

There are two techniques adopted in this method. In the first technique, the former is dipped into the coagulant solution, before immersing into the latex compound. The disadvantage of this technique is that the latex coating may slip off from the former due to the presence of residual coagulant solution film on the surface of the former.

In the second technique, former is first immersed into the latex compound and then dipped into the coagulant solution. After this, the former with the first coating and coagulant solution film, is again immersed into the latex compound. This technique also suffers from the disadvantage that the two coatings formed on the surface of the former may not cohere due to the residual coagulant solution film, entrapped between them.

An example of wet coagulant-dilute acetic acid (2%)

(b) Dry coagulant dipping method

In this method, the former is first dipped into a coagulant solution, withdrawn and allowed to dry. This produces the deposition of coagulant chemical on the surface of the former. After complete drying, the former is then immersed in the latex compound for a specified dwell time to obtain the required thickness of latex deposit.

A typical composition of dry coagulant soution is as follows :

	pwt
Anhydrous calcium chloride	15
Calcium nitrate tetrahydrate	15
Industrial methylated spirit	50
Water	20

The variation of thickness of latex deposit with dwell time in coagulant dipping method is depicted on Fig. 10.4 b.

Typical formulations of latex compounds used for production of (i) household gloves and (ii) balloons by coagutant dipping method are given in table 10.4

Table 10.4 Typical formulations of latex compounds for coagulant dipping

Components	Formulation 1 eg. Household gloves		Formulation 2 eg. Balloons	
	Dry	Wet	Dry	Wet
Centrifuged NR latex (60%)	100	167	100	167
Potassium hydroxide (10%)	0.5	5	0.5	5
Potassium oleate (10%)	0.25	2.5	0.25	2.5
Sulphur (50%)	1.5	3	0.5	1
Zinc diethyl dithio carbamate (50%)	1	2	0.75	1.5
Zinc Oxide (50%)	1	2	1	2
Phenolic antioxidant (50%)	1	2	1	2

iii. Heat - sensitised dipping method

In the method, a heated former is employed and the latex is compounded in such a way that it is heat - sensitive. Heat sensitivity of latex is generally induced by compounding with polyvinyl methyl ether, because this substance is very effective and yet tends to enhance the room - temperature stability of the latex compound. The other substances which function in similar manner to polyvinyl methyl ether are polypropylene glycol, polysiloxane ethers, Zinc ammine complex ($ZnNH_4^{++}$) formed from zinc salt and ammonia or ammonium soaps.

Under normal conditions, the chemicals do not affect the stability of latex, but as the temperature is raised, they precipitate out and permit coacervation of latex. By suitably heat sensitising the latex, it is possible to obtain very thick deposits.

Steps involved in the method

a. Preparation of heat sensitive latex compound.

b. Raising the temperature of former's surface temperature for effective deposition of latex.

c. Immersing the heated former into the latex compound for required dwell time.

d. Withdrawal of former with the deposit of latex.

e. Drying, curing and stripping the product from the former.

Tables 10.5 and 10.6 present the typical formulation of latex compounds that are used for heat sensitised dipping method.

Table 10.5 Typical formulation based on centrifuged NR latex (60%) for heat - sensitised dipping

Components	Dry	Wet
Centrifuged LA - NR latex (60%)	100	167
Non - ionic stabiliser (25%)	0.25	1
Formaldehyde solution (40%)	To bring down pH to 7.5 - 8	
Water	–	30
Sulphur dispersion (50%)	1.25	2.5
ZDC dispersion (50%)	1	2
Zinc oxide dispersion (50%)	1	2
Phenolic antioxidant (50%)	0.5	1
Polyvinyl methyl ether (10%)	2	20

Table 10.6 Typical formulation based on prevulcanised NR - centrifuged latex for heat - sensitised dipping

Components	Dry	Wet
Prevulcanised - NR latex (60%)	100	167
Non - ionic stabiliser (25%)	0.25	1
Formaldehyde solution (40%)	To bring down pH to 7.5 - 8	
Water	–	30
Polyvinyl methyl ether (10%)	2	20
Phenolic antioxidant (50%)	0.5	1

It has been found that the thickness of latex deposit increases steadily with rise in temperature of the former (Fig. 10.4. c)

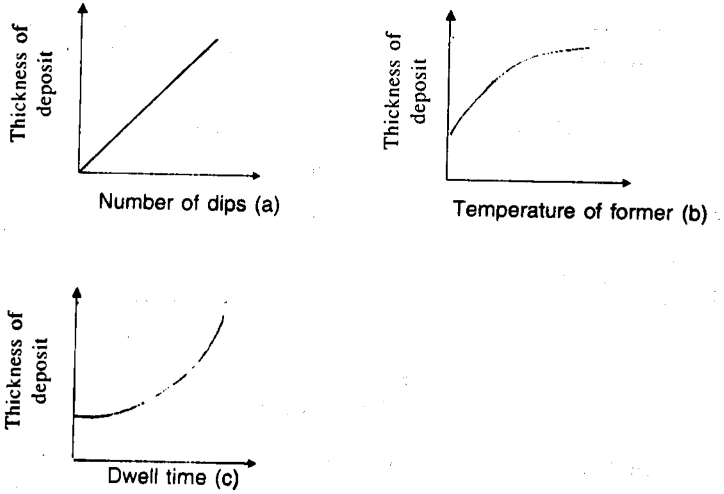


Fig. 10.4 Illustrating build - up of deposit in (a) Multiple straight dipping, (b) coagulant dipping (c) Heat - sensitized dipping

Dipping tanks

In the production - scale dipping tank, the latex compound is kept in motion and circulated from the top to the bottom of the tank and back again. Such motion is given in order to prevent skinning, creaming, and sedimentation. The speed of agitation is controlled just sufficient to prevent these effects. Generally, a suitable motion is obtained by means of a slow speed mechanical stirrer and a suitable combination of baffles and false bottoms. Screening or other means of filtration is usually provided in order to retain air bubbles and traces of coagulum which have formed in the latex compound. (see Fig. 10.5)

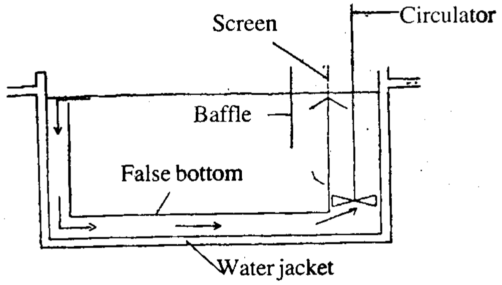


Fig. 10.5 Illustrating a typical dipping tank

II. Foam rubber articles

Latex foam rubber consists of open and interconnecting cells. It has a porous surface skin, which allows air to pass through readily. Foam rubber is widely used in applications requiring soft and comfortable cushioning material.

Examples : Latex foam - mattress, Carpet backing, Foam - toys etc.

Among all the methods available for the production of foam rubber articles, the Dunlop method is most popular in industry and the method is considered here. The method of production can be carried out either as a batch or continuous method.

Methods of production

The main stages involved in each method can be listed as follows :

i. Deammoniation of latex (if HA - latex is used)

ii. Initial compounding with vulcanising agents frothing agents and antioxidants

iii. Maturation

iv. Further compounding with vulcanising agents, frothing agents, secondary gelling agents and if required fillers.

v. Foaming

vi. Addition of zinc oxide and gelling agent (sodium silicofluoride)

vii. Moulding and gelation

viii. Vulcanisation

ix. Washing

x. Drying

xi. Finishing and inspection

The sequence of operations involved in each method is illustrated in Fig. 10.6 (a) and (b)

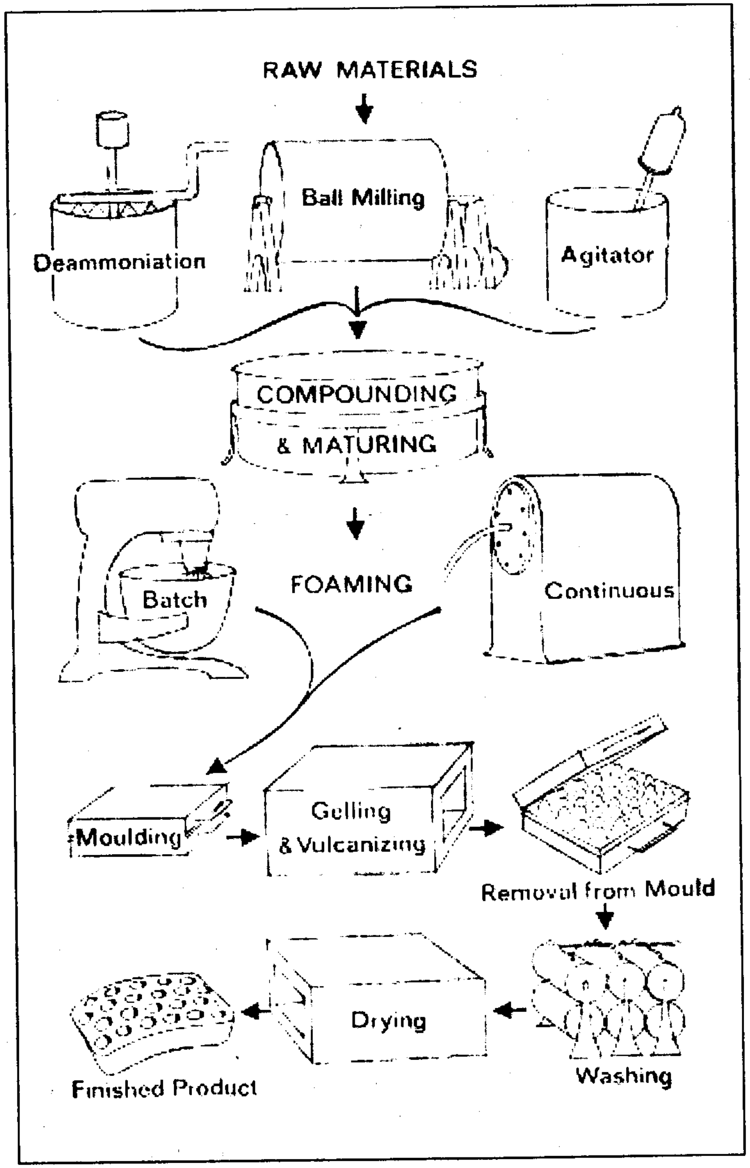


Fig. 10.6 (a) Sequence of operations in latex foam manufacture (batch method)

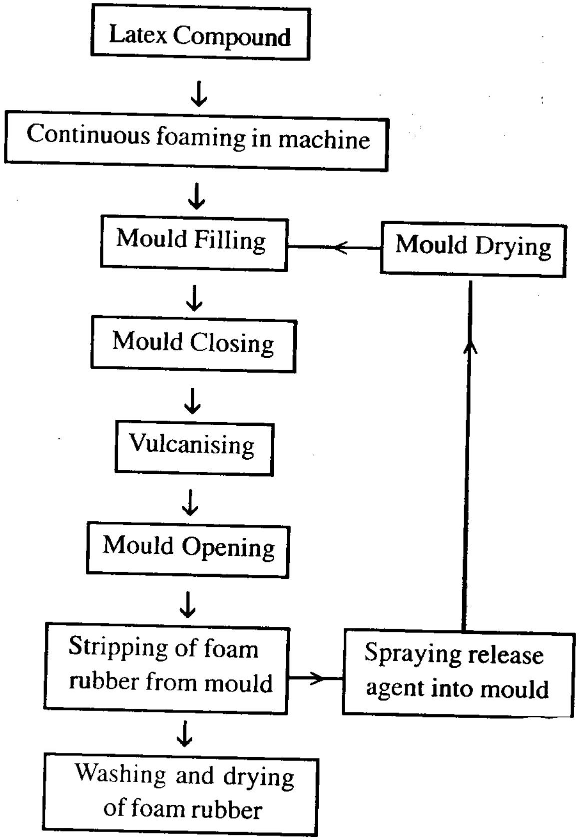


Fig. 10.6 (b) Sequence of operations in production of latex foam by continuous method

(i) Deammoniation

In the case of HA - latex, the ammonia content of latex is reduced to 0.12 - 0.22%, by blowing a current of moist air over the surface of the latex while it is stirred at about 50 rev / min. During this process, a small amount (0.25 - 0.5%) of potassium oleate can be added to minimise any risk of destablisation.

(ii) Initial compounding

Initial compound consists of the following components (table 10.7). The potassium oleate solution is added to the latex, followed by sulphur, accelerators and finally the antioxidant. When all ingredients are incorporated, stirring should continue for approximately 10 mins. to ensure through mixing.

Table 10.7 Initial compound

Components	Dry	Wet
Deammoniated centrifuged NR latex (60%)	100	167
Potassium oleate (20%)	0.5	2.5
Sulphur dispersion (50%)	1.5	3
ZDC dispersion (50%)	0.75	1.5
ZMBT dispersion (50%)	0.75	1.5
Phenolic type antioxidant (50%)	1	2

(iii) Maturation

When mixing is completed, the compound is kept at 30°C and maintained at the temperature for a period of 16 hours, with continuous stirring at slow speed (50 rev/min.). After this, the compound temperature is reduced to about 20° C for the next operation.

(iv) Further compounding

To the matured and cooled compound, the following ingredients (table 10.8) are added with stirring.

Table 10.8 Additional compounding ingredients

Components	Dry	Wet
Potassium oleate (20%)	1	5
sulphur dispersion	1	2
ZDC dispersion (50%)	0.25	0.5
ZMBT dispersion (50%)	0.25	0.5
Vulcafor EFA or DPG dispersion (50%)	0.8 - 1.0	1.6 - 2.0

If fillers are to be incorporated, they are also added at this stage.

(v) Foaming in batch method

This is carried out in a foam mixer consisting of a metal bowl and a wire whisk stirrer which can rotate at three or four different speeds. The rotating wire whisk whips the latex to froth. Control of the volume to which the latex is foamed is essential and is achieved by using a measure to check the distance of the foam from the top of the bowl, when the whisk is stopped.

The initial foaming is carried out at high speed, when the foam is approaching the final volume, the speed is reduced to medium rate.

(vi) Addition of Zinc oxide and gelling agent

Just before the required volume is reached, zinc oxide dispersion is added. Stirring is continued for 45 - 60 seconds and the speed of the mixer is again reduced to the slowest rate and sodium silicofluoride dispersion is slowly added. The quantities of zinc oxide dispersion and sodium silicofluoride dispersion required for the mixing are given below.

	Dry	Wet
Zinc oxide dispersion (50%)	5	10
Sodium silicofluoride (20%)	0.8 - 1	4 - 5

(vii) Moulding and gelation

When the foaming operation is completed, the latex foam is immediately transferred into preheated two - piece mould (30 - 40°C) for gelation. The time required for gelation is normally 10 to 15 mins. Gelation is found to occur at pH 8 - 8.5 due to hydrolysis of sodium silicofluoride.

$$Na_2SiF_6 \rightarrow 2Na^+ + SiF_6^{--}$$

$$SiF_6^{--} + 4H_2O \rightarrow Si(OH)_4 + 4H^+ + 6F^-$$

The contributing factors for gelation are :

(a) The fall of pH due to the presence of HF acid

(b) The adsorptive effect of $Si(OH)_4$ - silicic acid

(c) The destablisation effect of zinc ammine formed from the reaction of Zinc oxide with ammonium fluoride (NH_4F)

The mould employed for the latex foam product is usually made of light cast aluminium alloy. If the product is large in size, the top - piece of the mould is fitted with tapered metal pins for efficient heat transfer and easy removal of the products.

Foaming in continuous method

In a continuous mixer (e. g. Oakes machine) the latex compound and air metered under pressure, into a forming head consisting of a rotor enclosed by two stators. Both rotor and stators have a large number of protruding lugs with small clearances small enough to provide sufficient shear to foam the latex when the rotor revolves (see Fig. 10.7). The foam passes, through a length of hose, to a blender into which the dispersions of zinc oxide and sodium silicofluoride gelling agent are metered and mixed with the foam. From the blender, the fully compounded foam is discharged into moulds again by way of a flexible plastic hose. By using two foaming heads and two blenders in the system, the foam output may be switched from one to other, thus allowing for cleaning without breaking the continuity of production.

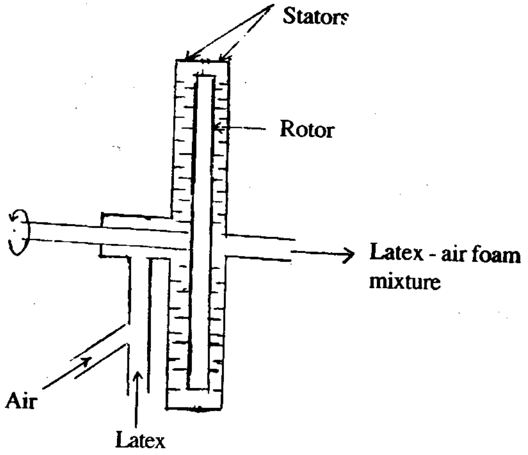


Fig.10.7 Illustrating the foaming of latex in Oakes machine

Vulcanisation

After gelation, the foam is vulcanised by heating for 20 - 30 minutes at 100°C. The time will depend upon the thickness of the product. Vulcanisation is usually carried out in a steam chamber. Hot air or hot water may also be used. To minimise, shrinkage in the products, vulcanisation should follow gelation as soon as possible.

Washing

After vulcanisation, the mould is opened and the wet cured foam is removed and washed in running water. This is effected by passing the foam articles through a series of water sprays and squeeze rolls, with a final pass through dry rolls to remove excess water. Alternatively a centrifuge machine (hydroextractor) may be used with a flow of water passing through until washing is complete.

Drying

Drying may be completed either batch - wise in an oven with circulating air at about 80°C, or continuously in a tunnel oven. A temperature gradient is often maintained through the tunnel oven, the temperature of the air being highest at the tunnel entrance and progressively lower throughout the oven length. Generally, a temperature range from 90°C down to 70°C is normal.

Finishing and inspection

After drying, the products are trimmed and examined. Defects such as tears and small surface blemishes can be repaired using latex as an adhesive. Products are then tested against the specification to which they are being produced.

Quality control tests

The following tests are carried out to control the quality of the foam rubber products :

(i) Hardness or Indentation Index

The hardness expressed as the indentation index is checked on each day's production by determining the load required to compress the foam to the specified indentation depth.

(ii) Indentation set

This is determined periodically, by measuring the change in thickness when a static load is imposed on the product for a specified time at a specified temperature.

(iii) Pounding test

This test involves submitting sample to continued pounding with a indentor for a given number of cycles (eg. 25 x 10 cycles at rate of 4 per second). The loss in hardness and any permanent deformation is measured.

(iv) Other physical tests

Elongation at break, measurements and accelerated ageing tests should be made periodically as a means of detecting any marked variation in the quality of production.

Faults and remedies

Fault	Possible cause	Suggested remedy
Coarse Structure	Gelation at too low a pH	Increase secondary gelling agent (Vulcafor EFA).
Rat holes	- do -	- do -
Loose surface skin	a. Insufficient gelling agent	Increase sodium silicofluoride and / or secondary gelling agent.
	b. Mould too cold	Use warmer mould
Thick skin	Mould too hot	Use cooler mould
Flow marks on surface	a. Mould too hot	Use cooler mould,
	b. Gelation too fast	Reduce sodium silico fluoride
Surface lakes	a. Excess mould release agent	Reduce mould release agent
	b. Mould release agent not dry	Ensure that mould release agent is dry
Splitting in centre	c. Gelation too fast	a. Reduce sodium silicofluoride b. Use cooler mould

---

Review_questions

Chapter I

1. Give reaction schemes to illustrate the mechanisms of (a) free - radical addition polymerisation (b) condensation polymerisation. How relative molecular mass (molecular weight) control be achieved in each case ?

2. Compare the advantages and disadvantages of polymerisation

   (a) in bulk (b) in solution and (c) in emulsion.

3. Write an account of the mechanism of polyesterification reactions involving glycols and dicarboxylic acids.

4. Describe the principal features of free radical emulsion polymerixation, showing in what ways it differs from other of free radical polymerisation.

5. How is the molecular weight of polymer homologues characterised and what is meant by the molecular weight distribution (MWD) of polymers ?

6. List the main structural characteristics of polymer molecules. What is the existence of a large number of structural isomers in polymers due to ?

Chapters 2 and 3

1. Outline one scheme for producing and marketing comminuted natural rubber. What is the PRI (plasticity retention index) test that is used for grading of natural rubber?

   What is the purpose of this test and what are its limitations?

2. Discuss the chemistry of the reactions of natural rubber with each of the following ?

   i. Chlorine
   ii. Sulphuric acid
   iii. Hydrogen chloride
   iv. Butadiene sulphone

   Indicates briefly any changes in the physical and chemical properties of the polymer which these reactions brings about.

3. Explain why the equilibrium modulus of cross - linked elastomer increases with elevation of the temperature.

Chapter 4

1. Outline the manufacture of "hot", "cold", and "solution" SBR. How may the structure of the copolymer vary and what effect does this have on processing and properties ?

2. Describe the various types of thermoplastic rubbers (TPRs) available, indicating the main applications of each.

3. Discuss the structural features of the polymer which account for each of the following :

   i. the low gum - vulcanisate strength of styrene - butadiene rubbers.
   ii. the oil resistance of acrylonitrile - butadiene vulcanisates and
   iii. the oxidative ageing resistance of chloroprene rubber vulcanisates.

4. Discuss the technological differences between -

   i. butyl rubber and halogenated butyl rubber
   ii. styrene - butadiene rubber and cis - 1, 4 poly isoprene
   iii. thermoplastic rubber and raw natural rubber

5. Describe typical applications where each of the following are used

   i. Chlorosulphonated polyethylene
   ii. Fluoroelastomers
   iii. Silicone elastomers
   iv. Ethylene propylene terpolymers

Chapter 5

1. What changes in structure and properties take place when natural rubber is vulcanised ?

   State briefly the differences you would expect to find in vulcanisation characteristics when the following accelerators are used separately in a natural rubber mix containing the necessary activators and sulphur :

   - i. MBTS (dibenzthiazyl disulphide)
   - ii. CBS (N - cyclohexyl - 2 - benzothiazyl sulphenamide)
   - iii. TMTD (tetramethyl thiuram disulphide)
   - iv. DPG (diphenyl guanidine)

2. Outline the production and classification of thermal and furnace carbon blacks.

   Discuss a. Applications where the various types are used and

   b. the type suitable for use in a petrol resistant hose liner.

3. Explain the term "structure" as applied to carbon black. How does "structure" affect processing and vulcanisate properties ?

   Give an application of (a) a high structure black and (b) a low structure black.

4. State briefly the functions and use each of the following :

   - i. triallyl cyanurate
   - ii. dicumyl peroxide
   - iii. N - tert - butyl benzthiazyl sulphenamide
   - iv. N - isopropyl - N - phenyl - P - phenylene diamine

5. Give three important reasons why zinc oxide is used in rubber compounding. Indicate the approximate proportions used for each purpose.

6. Write an essay on the use of antioxidants in diene rubbers.

7. Write notes on the production and use of (a) factice and (b) reclaimed rubber.

8. Discuss the characteristics of precipitated hydrated silica as used in the rubber industry. Give and account of the major areas of applications of this material.

9. Discuss the reasons for the use of processing aids in the manufacture of rubber products. Your answer should include reference to specific materials used as processing aids.

10. Discuss the use of textiles in rubber products.

11. Many of the ingredients used in rubber mixes are partially hazardous. Discuss this statement, indicating the types of hazard that could occur. What precautions should be taken in storage, weighing and mixing areas to minimise the risks. Refer to specific materials in your discussion.

Chapter 6

1. Describe, giving labelled diagrams, the principal features of a two roll mill. Detail a typical mill mixing specification for a loaded rubber mix.

2. Describe the safety devices which may be used on -

   i. a laboratory two roll mill

   ii. a factory two roll mill

   iii. a steam pan

3. Discuss recent advances in polymer processing obtained by internal mixer developments by the use of continuous mixers and by the introduction of mill room automation.

4. Outline some special uses of the extruding machine in the rubber and allied industries, thus demonstrating its versatility. Point out the features of the ram type of machine which might render this type preferable in some instances and undesirable in others.

5. What is the origin of 'die swell' ? Trace its effects on the design of extruding dies. What connection has this phenomenon with the process of calendering ?

6. Using diagrams, explain the principles involved in compression, transfer and injected moulding of rubber mixes.

   Discuss two processing problems that may be encountered with each moulding technique.

7. Summarise the advantages of the injection moulding process, compared with other moulding processes, when applied to elastomers. Discuss problems which arise and their possible solution by suitable machine design, compound formulation and operation technique.

8. Discuss those features of rubber mould design that directly concern the practising rubber technologist.

8. Various forms of continuous vulcanisation processes have been applied to the manufactures of a range of rubber products. Describe the process now available for continuous vulcanisation and indicate product to which they are applicable. Describe any changes in compounding made necessary by the adoption of a continuous vulcanisation.

9. Outline the production of a rubber dough for use in a spreading process. What factors determine the viscosity of the dough produced ? Describe a spreading process, including plant details that could be used in the large volume production of a single - sided rubber coated fabric.

   Give two reasons why spreading may be preferred to calendering for the rubber coating fabric.

10. Discuss some of the problems commonly encountered during the processing of rubber compounds and describe how they may be minimised by suitable compounding technique.

Chapters 7 and 8

1. Describe current methods of bonding rubber to (a) metals and (b) textiles. What precautions are necessary to ensure good bonding ?

2. Describe the construction of a rubber conveyor belt and discuss the functions of the rubber and the fabric components.

3. You are required to rubber - line a chemical plant to resist concentrated sulphuric acid in a phosphate fertiliser factor. The plant operates at a temperature of 95 C. Some of the plant will have to be lined on site and low pressure steam will be available. Draw up a procedure for this lining work. Suggest a formula for the rubber lining, giving reasons for the choice of polymer and for the use of the other main ingredients in the mix.

4. Outline the manufacturing steps involved in the production of the following :

   a. High pressure braided hose

   b. Low pressure braided hose

   c. Fabric reinforced hose

5. Discuss the factors that influence the design of mixings. Illustrate your answer, or parts of your answer, by suggesting mixings suitable for TWO of the following products :

   a. a food sealing ring, for home bottling

   b. a translucent blood transfusion tubing

   c. a car tyre tread

   d. a green eraser for ink, hardness 70 - 75 IRHD.

6. Write a typical rubber mix for a styrene - butadiene rubber (SBR) tyre tread and explain the choice of ingredients.

   How would the mix formula be altered to produce (a) a tyre tread with lower heat build - up characteristics and (b) a tyre tread with improved tear resistance ?

7. Discuss modern trends in the design of passenger and truck tyres with emphasis on carcass construction. write a mix formula for an earth mover tread giving reasons for choice of polymer and each compounding ingredient.

8. Describe the types of crack which may appear in tyre treads and sidewalls during service and indicate the steps taken during manufacture to minimise their occurence.

9. Radial tyres are gradually replacing the older cross ply type in the car tyre market. What are the difference in construction and manufacture between the two types ? What factors in performance have encouraged this development ?

10. i. Discuss the advantages of natural rubber when used as a spring in engineering applications and suggest how the stiffness of the rubber can be improved for such applications.

    ii. Determine the Young's modulus of the rubber which is required to produce a cylinder of radius 0.03m and height 0.01 m.

    You may assume

    (a) the compression modulus of the rubber is 6.5 MN/m^2

    (b) the numerical factor k is 0.75 and

    (c) $E_C = E_0 (1 + 2 ks^2)$ where the symbols have their usual meanings.

Chapter 9

1. Discuss what is meant by the "scorch time" of a rubber mix and explain its technological significance.

   Describe how this parameter is determined experimentally giving essential details of the equipment used.

   In what respect does this test differ from the determination of viscosity of an uncured mix using the same equipment.

2. Briefly describe TWO types of test equipment used to measure hardness of rubber.

3. Describe a standard test method for determination of the tensile properties of rubber vulcanisates. Include in your answer definitions of all quantities to be measured.

4. Define the term "Rebound resilience"

   Place the following gum - vulcanisates in order on increasing rebound resilience at 25 C :

   a. SBR b. BR

   c. NR d. IIR

   Give a diagram of a pendulum type resilience tester and describe how it is used for the determination of the rebound resilience of a rubber vulcanisate. Your answer should include reference to the factors which must be standardised in order to ensure reproducible results.

5. The following physical tests have been employed in the rubber industry for many years :

   a. tensile strength b. hardness

   c. abrasion resistance d. hysteresis and resilience

   Discuss the usefulness of these tests to predict service behaviour of rubber articles.

6. A rectangular prism of vulcanised rubber has a square cross - section of side 4 cm and is 10 cm long. This prism has a weight of 32 g in water of density 1000 kg/ m^3. Calculate the specific gravity of the material of the prism

   The mix for the prism is as follows :

	Parts by weight	S.G.
Rubber	100	0.93
zinc oxide	3	5.55
whiting	30	2.62
stearic acid	2	0.92
antioxidant	1	1.2
accelerator	0.8	1.4
sulphur	2.5	2.06

Together with some china clay of specific gravity 2.70.

Find the number of parts by weight of china clay in the mix

Chapter 10

1. Describe methods used commercially to produce (a) dispersions of water insoluble powders and (b) emulsions of liquids for addition to latex. Suggest possible test methods you would use to determine the stability of these preparations.

2. Describe briefly the manufacture of latex foam. Discuss factors which influenced the shrinkage of latex foam mouldings. Compare the properties of latex foam with those of polyurethane foam.

3. What do you understand by the terms (a) volatile fatty acid number and (b) potassium hydroxide number as applied to rubber latex.

   Discuss in detail the technological significance of these two properties.

4. Discuss ONE function of each of the following in natural rubber latex technology :

   a. sodium silicofluoride
   b. HAF black
   c. Octyl alcohol
   d. casein
   e. potassium oleate
   f. zinc oxide
   g. zinc salt of MBT
   h. mineral oil
   i. acetic acid
   j. sodium bisulphite

5. Compare the properties of synthetic rubber latices with those of natural rubber latex, giving examples of the main applications of synthetic rubber latices. Discuss the modifications to processes and formulations where natural rubber latex has been partially or completely replaced.

6. Give the composition of natural rubber latex and explain how the rubber particles exist in liquid phase in latex.

7. Give the chemistry of autocoagulation of natural rubber latex and explain how it is prevented or delayed by adding various types of anticoagulants.

Subject Index

ABOUT THE BOOK :

The book provides a broad general framework of essential information on the subject-Rubber Technology and will be of greatest practical value to students of polymer technology courses at all levels and to all concerned in the rubber industry.

ABOUT THE AUTHOR :

Kanthappu Subramaniam is serving as the Head of the Division of polymer, Chemical and Textile Engineering Technology, Institute of Technology, University of Moratuwa, Sri Lanka. He earned post-graduate qualifications in polymer Technology from the National College of Rubber Technology, Northern Ploytechnic, London. He has worked as a technologist, researcher, and teacher and has over three decades of experience in the rubber technological field. He holds five national patents for his research work on Balata polymer material in British Guyana, South America and has authored several research papers on rubber technology.