SYNTHESIS & MECHANICAL PROPERTIES EVALUATION OF EPDM BASED ABLATIVE COMPOSITES

By

MUHAMMAD ARSHAD BASHIR

Supervisor

Dr. M. BILAL KHAN

Co-Supervisors

DR.SHAMSHAD AHMED

DR.NOAMAN UL-HAQ

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DEDICATED
TO
MY WIFE & CHILDREN

Without their cooperation and support it was not possible for me to complete my research work

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Praises to **ALMIGHTY ALLAH** who gave me the strength and courage to achieve my ambitions and thanks to the Prophet (PBUH) who showed the path of knowledge and light to human being.

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ABSTRACT

Ablative materials are heat shielding, protective materials which are used in aerospace industry to protect inner hardware and sensitive devices. It is required to develop light weight material with high modulus. EPDM is the best candidate for the synthesis of ablative materials by introducing different heating sink such as silica, glass fiber, carbon fiber, asbestos and carbon and their combinations.

The prepared materials were tested mechanically. It was found that tensile strength of materials containing carbon, carbon fiber, silica, asbestos was increased by increasing testing speed and decreased at the same speed, reverse behavior was observed in silica-glass fiber combination. In case of % Elongation, gradual decreasing behavior was observed with carbon, glass fiber and carbon fiber but there was opposite behavior in silica, glass fiber and carbon fiber.

Rheological investigations of these novel composites shows that moony viscosity of the materials containing glass fiber, carbon fiber, silica decreased in that order. The tested materials are used in wide variety of ablative applications. Parallel testing of thermal properties are in progress.

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Chapter – 1

INTRODUCTION

1. INTRODUCTION

1.1 GENERAL

Ablative composites are heat shielding sacrificial materials which protect inner hardware and sensitive electronic devices in the space vehicles at the time of reentry and during their flight due to air friction a tremendous heat is produced.

As the space vehicles move with very high velocity (five miles per second) so higher stresses are being applied on the outer materials so it becomes very important to study the mechanical properties of ablative materials. in this research we have tried to produce EPDM based ablative composites.

Since the beginning of the space age in the late 1950's, research and development of new thermally stable polymers has proceeded at an amazing rate. With this explosion of new effort have come new concepts and criteria for achieving thermal stability in plastics and elastomers. In this work, we attempt to describe

1. Some techniques for evaluating thermal stability.
2. Some basic molecular units which promote thermal stability in polymers.

We shall also try to draw comparisons between man-made and certain naturally occurring polymers which have long been used at elevated temperatures.

The increasing trend toward miniaturization and speed of the machines used in aeronautics and in the exploration and utilization of space has resulted in rapidly growing needs for thermally stable polymers. Prior to 1957, such polymers were employed only in terrestrial applications and were expected to retain useful properties in air for one to five years at temperatures in the range of 100° to 150°C (212° to 302°F). in the 1960's, the needs which coincided largely with aeronautical and aerospace developments – demanded from polymeric materials new levels of thermal, oxidative, and radiation stability. Polymers were required to function in air for one to three years in the temperature range from 150° to 200° C (302° to 392°F) and also for short times at temperatures above 500°C (932°F). in a few years, routine operating temperatures may be expected to be in the 250° to 350°C range (482° to 662°F). Higher temperature demands will be made on electrical insulation such as circuit boards, connectors, wire enamels, potting compounds, and slot insulation in motors. Organic adhesives, elastomers, structural composites (which are finding increased use on aircraft operating at supersonic speeds), and advanced ablation systems will also need organic materials with improved thermal stability. Further applications may occur in thermo electronic isotope generators, nuclear propulsion systems, heat pipes, and more efficient modes of subsonic transportation.

New demands for materials of light weight and high modulus – properties inherent in many thermally stable polymers- will arise as hardware is designed for large space stations and underwater exploration. Cryogenic applications are expected to increase, owing to very low transition temperatures of many of these new polymers. They can maintain useful properties at temperature extremes hundreds of degrees below and above ambient conditions.

Progress in the development of thermally stable polymers has been supported not only by defense and aerospace needs but also by terrestrial requirements, both industrial and commercial, for electrical and thermal insulation, coatings and films, fire-resistant fibers, adhesives and elastomers, structural foams, bearing races, vacuum valve seats, and coated cookware. Actually, the successful commercial development of the aromatic polyimides in the early 1960's stimulated research in this new area of polymer chemistry.

1.2 Reentry Condition

A space vehicle moving at orbital velocity possesses a tremendous amount of kinetic energy, which equals half the mass times the square of the velocity. This energy must be dissipated in reentry as the vehicle decelerates to its impact or landing velocity. In the passage through atmosphere, the kinetic energy is converted mostly into thermal energy, owing to atmospheric friction. Although very tenuous at high altitudes, the atmosphere presents a resistive medium to hypervelocity objects, as witnessed by incandescence and disintegration of meteors.

High velocities are described in terms of a Mach number (M) which is defined as the ration of the flow speed to the local acoustic velocity. In other words, an object flying at Mach 2 moves at twice the speed of sound. The speed of sound varies from about 750 mph at sea level to around 650 mph at very high altitudes. The usual classification of velocities is subsonic, $M<1$; transonic, $M\cong1$; supersonic, $M>1$; hypersonic, $M>5$. It should be noted at this point that the reentry of an orbital manned spacecraft, or of a high performance missile, involves velocities of Mach 25 to 30.

The behavior of hypervelocity bodies moving in air is the subject of gas dynamic. At $M>1$, noise will not precede a moving body, and the disturbances caused in the air are restricted to a roughly conical envelope trailing the object. The shock wave manifests self by the familiar supersonic boom.

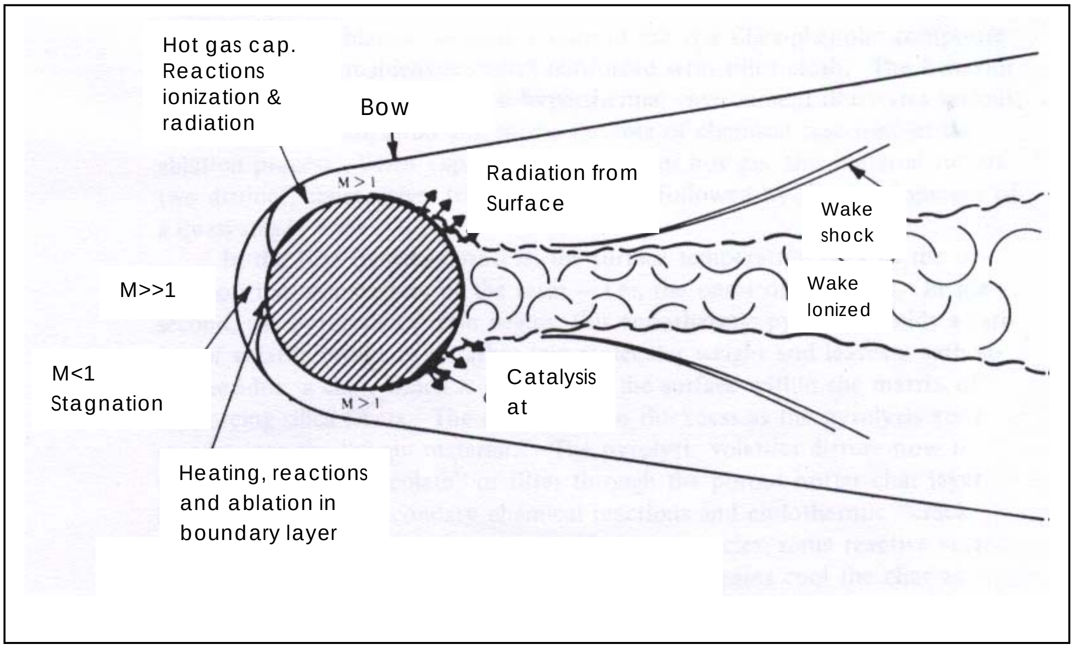


Fig. 1.1

1.3 Thermal Control in Reentry

To survive, the reentering space vehicle must have adequate thermal protection, particularly in the stagnation area. Thermal energy reaching the vehicle has to be diverted, blocked, dissipated, or absorbed in some way, so that only a tolerable amount penetrates the material.

Heat from the hot gas envelope is transferred to the surface of the body primarily by convection and, to a lesser extent, by radiation, and then through the material by transient conduction. The convective heating rate at the stagnation point on the spherical segment at the nose of a vehicle during reentry gives approximately by the following expression

$$q=17\left(\frac{\rho}{R}\right)^{1/2}\left(\frac{V}{1000}\right)^{3} \quad \text{Btu/ft}^{2}\text{-sec}^{*}$$

where ρ is atmospheric density, V is velocity in fps & R is the nose radius in feet

The rate is proportional to the cube of the velocity. The reduction in velocity would minimize the problem ; however, the slowing down of spacecraft by rockets cannot be used repeatedly because of propellant weight limitations. In the lifting reentry, utilization the glider principle, the velocity is lower than in the ballistic hyperbolic type of descent, and this results in a lower heating rate.

The heating rate is inversely proportional to the square root of the nose radius. The blunt body is heated less than the slender body because more energy is transferred to the ambient air via shock waves. The unexpected blunt-body concept revolutionized the shape of missiles and was kept secret for a time. A look at the shape of the mercury, Gemini, and Apollo capsules will show that their bases are surfaces with large radius of curvature. They have a blunt nose in order to maximize the heat carried away by the shock wave.

Although the heat transfer is reduced through the blunt-body design, the remaining heating rate is such that conventional methods of cooling are inadequate to save the payload. The term payload is borrowed from commercial aviation and means here astronauts, or thermonuclear warhead.

Many new schemes of cooling have been tried. One of the earliest approaches was the solid heat sink method, in which the heat is absorbed into a sufficiently thick outer layer of a material with high heat capacity.

1.4 Ablation Cooling

By ablation cooling, or simply ablation, is meant a cooling scheme involving a loss of surface material. It is mostly in this sense that the term ablation is now used.

The essential feature of ablation cooling is that the thermal energy reaching the body has to do work at the surface of an expendable protective layer, and thus is largely dissipated. The work at the surface involves endothermic processes, such as melting, vaporization, and thermal decomposition. Volatile products of these processes are injected into the boundary layer i.e. the shear region near the wall and decrease the heat transfer by the blocking action. The ablating mass carries away heat by virtue of its heat capacity. Since the surface takes the burnt of hyper thermal environment, high surface temperature are reached, and some heat is rejected by surface radiation. As a net result of all these processed, some surface material is lost, but the heat penetration to the vulnerable structure is limited and the payload is saved. Thus, in recent reentries of Apollo spacecraft, the surface temperature of the shield soared to about 5000°F, but the temperature inside the module remained comfortable.

Ablation cooling utilizes, to different extents, various modes of heat dissipation. Particularly it takes advantage of chemical reactions and phase changes; they are a distinguishing feature of the method. In a way, the loss of surface material may be largely regarded as a consequence, an effect attendant on chemical reactions and phase changes.

A typical ablative material in current use is a silica-phenolic composite i.e. phenolic formaldehyde resin reinforced with silica cloth. The behavior of this char-forming ablator in a hyper thermal environment illustrates various modes of heat dissipation and shows the role of chemical reactions in the ablation process. When exposed to a stream of hot gas, this material suffers two distinct, consecutive, transient processes followed by the development of a quasi-steady state.

In the first transient process, the surface temperature rises to the decomposition temperature of the resin. i.e. the onset of pyrolysis. In the second, the pyrolysis of resign begins; this endothermic pyrolysis yields a variety of volatile products of rather low molecular with and leaves a carbonized residue, a char, which is retained on the surface within the matrix of reinforced silica fibers. The char grows in thickness as the pyrolysis zone recedes into the virgin material. The pyrolytic volatiles diffuse now to the surface and percolate or filter through the porous hotter char layer. Here they undergo secondary chemical reactions and endothermic cracking.

As a result of the insulating effect of the growing char layer and the cooling action of the percolating gases, less heat reaches the moving interface and the pyrolysis slow down, while the surface temperature increases. Eventually the temperature rises to the point where the silica begins to melt and vaporize, thus absorbing heat. The glowing surface rejects some heat by surface radiation . The intimate contact between the molten silica and the embedded char particles facilitates the char-reinforcement interactions at and near the surface, at the prevailing high temperature. These reactions are highly endothermic. As a consequence of all these material consuming processes, the surface begins to recede. The loss of surface material is caused not only by phase changes and chemical reactions, but also by mechanical shear forces; runoff of molten silica, erosion and spallation. Spallation is an intermittent loss of large chunks of surface material due to the combined effect of shear forces, thermal stresses, and the buildup of internal pressure, since the viscous molten layer impedes the escape of pyrolatic gases.

The second transient stage terminates when the rate of the surface recession due to ablation equals the rate of the recession of the virgin material char interface. Now, a quasi-steady state exists, in which near equilibrium between the external heating and the heat dissipation by internal and surface processes is established. Provided a sufficient thickness of ablator is available for the duration of hyper thermal exposure, the underlying structure will survive.

Charring ablation, described above, is the most complex but also the most efficient type of ablation, since it involves many modes of heat dissipation. Other types are non charring melting ablation such as that of quartz, and non charring -non melting ablation, such as that of Teflon. The dissipative processes are here practically limited to the surface.

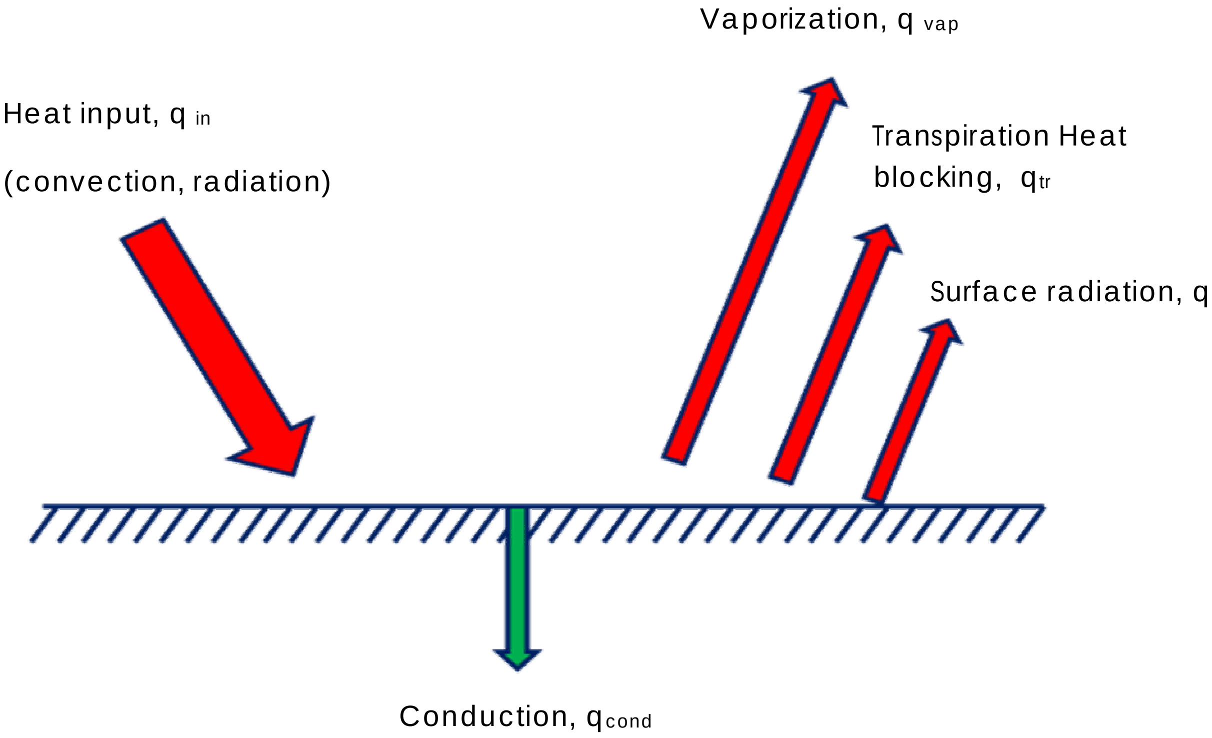


Fig. 1.2

1.5 OBJECTIVES OF STUDY

The main objects of the research work are :

1. To develop EPDM based ablative composites for space vehicles and rocket motors.
2. To study the mechanical properties with the variation of different heat sinks.
3. To obtain the materials with best mechanical properties by the addition of proper heat sinks.

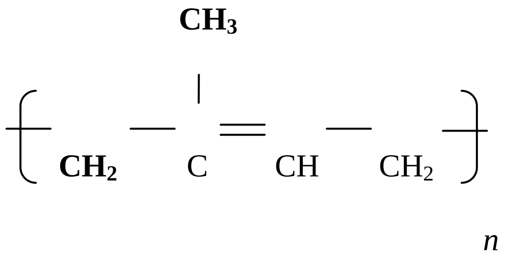
Chapter – 2

LITRATURE REVIEW

2.0 Types of Rubber

2.1 Natural Rubber (NR)

Formula



$$\left[\mathrm{CH_2} - \overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}} = \mathrm{CH} - \mathrm{CH_2}\right]_n$$

Latex, from which rubber is obtained, is found in a great variety of trees, vines, shrubs, and plants in many areas of the world. The production of latex is a characteristic feature of many plants, but latex containing rubber in large quantities occurs only in the species of the families Moraceae, Euphorbiaceae, Apocynaeceae, and Composite. Latex may be derived from many parts of the plant, such as the bark, roots, leaves, stems, and even tubers and fruits. The lattices from sources other than Hevea brasiliensis suffer some drawback or the other, as sources of rubber. They have a low content of rubber or/and a high content of impurities like resins and gums, or present difficulties in extraction of coagulation. In the early days of the rubber industry, it was profitable to collect “wild-rubbers” from these sources. Until the development of hevea plantations in Malaysia, Indonesia, Sri Lanka, and India, the chief source of rubber in Asia was

Ficus elastic. Hevea rubber became popular due to its high productivity and economics.

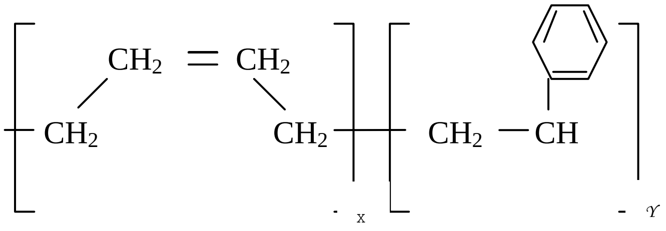
During the Second World War, uncertainty in the availability of natural rubber compelled manufacturers to look for synthetic rubber. However, synthetic rubber has not replaced natural rubber because of the unique properties of the latter.

Fresh latex, as it exudes from the tree, is slightly alkaline or neutral. It becomes acidic rapidly due to bacterial action. The formation of organic acids neutralizes the negative charge on rubber particles and the latex gets auto coagulated. Therefore, fresh latex has to be preserved usually with about 0.7% ammonia; a variety of preservatives may also be added with a low level of ammonia concentration to sieved field latex. After sieving and addition of preservatives, latex is fed into a bulking tank where settling and removal of the sludge takes place. Preserved latex concentrates are of tree types: centrifuged; creamed; or evaporated lattices; the first method predominates.

Uses

- Natural rubber is a general purpose rubber still very widely used. It constitutes approximately 30% of total rubber usage.

2.2 Styrene Butadiene Rubber (SBR)



SBR is a random copolymer of styrene and butadiene. This is a relatively high hysteresis rubber. Chemically SBR is a copolymer of styrene and butadiene. Polymerization can be carried out either in solution medium or in aqueous emulsion o the monomers. Cold or hot conditions (5°C or 50°C) can also be selected for polymerization, depending on the recipe. In addition, the ratio of styrene to butadiene, the type of emulsifier and anti-degradants, the use of extender oils, etc. can also be varied.

Commercial SBR is produced with basically one of three types of emulsifiers- fatty acid, rosin acids, or mixtures of the two. Fatty acid emulsifiers give a faster curing polymer but with some bloom from their insoluble salts; rosin acid emulsifiers are slower curing but have better tack, hence mixtures of the two are also used.

Four types of coagulants are used to precipitate crumb rubber from latex:

i. Salt-acid system introduces water soluble salts into the rubber, increasing its ash content.

ii. Alum-acid systems are not water soluble and they contribute to a smaller increase in ash content.

iii. Acid systems do not introduce ash.

iv. Glue-acid system introduces slight protein residues which may result in surface blemishes due to bacterial decay.

During the coagulation operation, the emulsifier is converted from the soap form of the rosin and/or fatty acid to the organic acid form. However, a small percentage of soap remains in the rubber as also water soluble salts, reflected in the ash content. The salts contribute to water swelling, decreased electrical resistance, and poorer ageing properties, and are usually controlled to an absolute minimum.

Uses

About 75% of the SBR used in the rubber industry goes into tyres. The remainder is used in general rubber goods that are not subjected to severe operating conditions e.g. belting, molded goods, shoe soles etc. Other forms of SBR, such as latex, are used in foamed backing for carpets.

2.3 Butadiene Rubber (BR)

Formula

$$\left(- CH_2 - CH = CH - CH_2 - \right)_n$$

Properties

- All the diene rubbers are polymerized from diene monomers.
- Double bond still present in the polymer molecule.

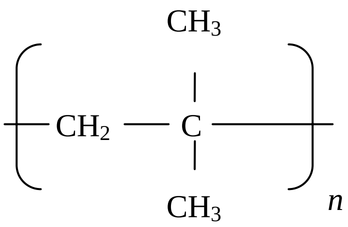
- Lowest hysteresis rubber.
- High resilience.

Uses

- Used in blends.

2.4 Butyl Rubber (IIR)

Formula



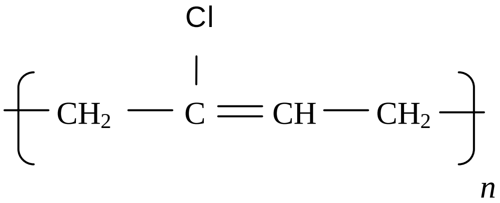
$$\left[\!-CH_2-\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}-\!\right]_n$$

Properties

- Saturated polymer.
- High hysteresis
- Low rebound

2.5 Chloroprene Rubber (CR)

Formula



$$\left[\!-CH_2-\overset{\overset{\textstyle Cl}{|}}{C}=CH-CH_2-\!\right]_n$$

this is another diene rubber. A chlorine atom substitutes for the hydrogen is butadiene. The best known rubber of this class is the Neoprenes manufactured by DuPont. The chlorine renders them self-extinguishing, hence their use in conveyor belting for coal mines.

Properties:

- Moderate Resilience
- Oil Resistance
- More fire resistant than non-helogenated elastomers like SBR and NR

2.6 Ethylene-propylene Rubber (EPDM)

Ethylene-propylene random, amorphous copolymers are prepared from higher vanadium halides and organo aluminium compounds in a solvent (hexane, xylene) at 50-80 °C.

$$VCl_3 \text{—} Al_2Et_3Cl_3$$

These saturated copolymers possess good resistance to heat ageing and to attack by ozone, but can only be vulcanized satisfactorily by means of peroxide systems. Owing to their excellent electrical insulation properties, they are widely used in cable manufacture.

In order to make these copolymers more suitable for conventional sulphur cures, some unsaturated sites must be introduced into or onto the EP polymer chain, e.g. by introducing a third monomer (Ca, 2%) to make an ethylene-propylene terpolymer called EPDM (ethylene-propylenediene-methylene, the methylene indicating that the polymer chain cosists mainly of CH_2 groups)

2.7 Manufacturing of EPDM

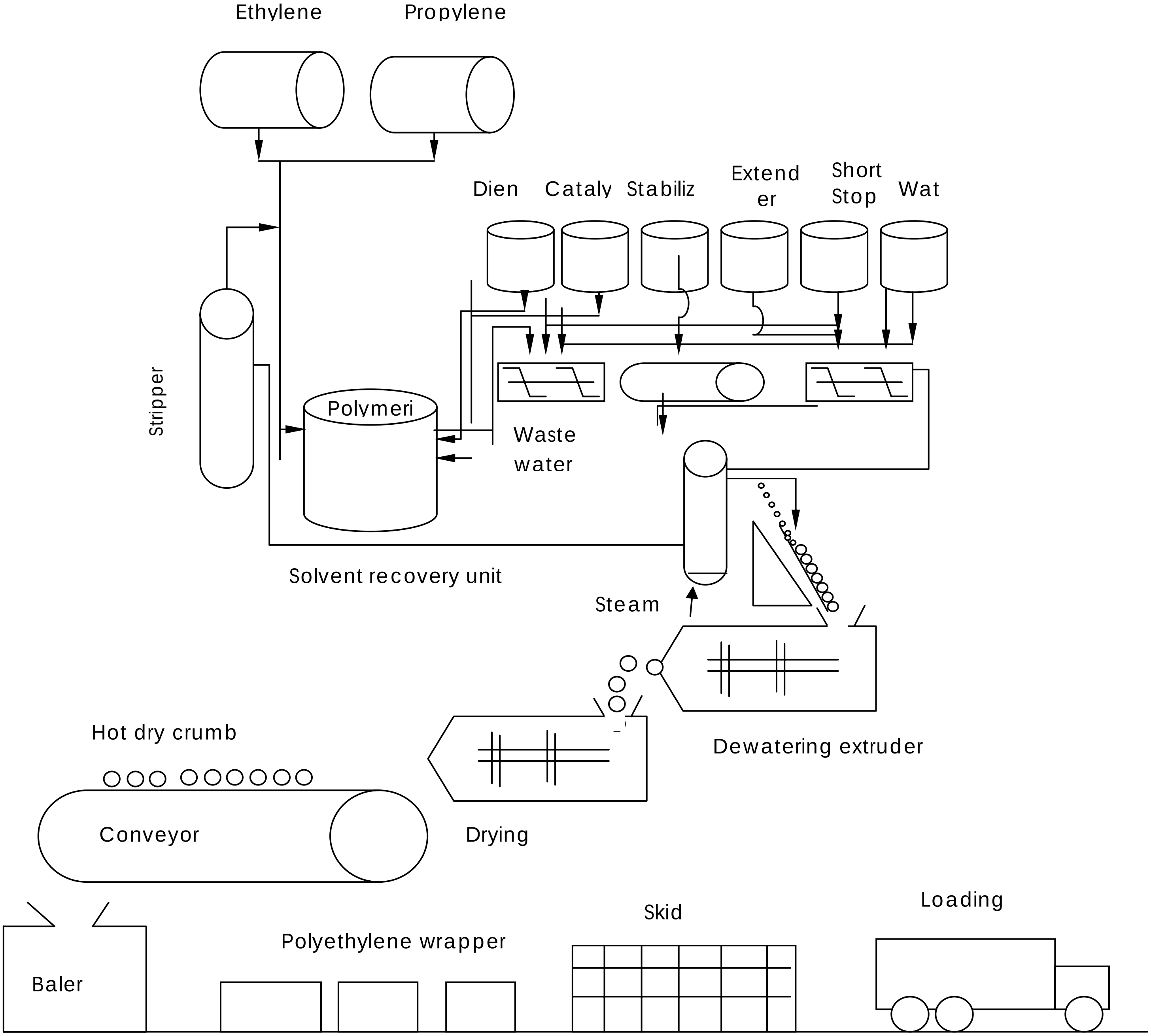


Fig. 2.1

EPDM is produced in a single stage process by polymerization of ethylene, propylene,, and the termonomer. A modifier is added to control the molecular mass. The heat of polymerization is removed by cooling the monomers and solvent, and by evaporative cooling. Polymerization is stopped and the solution is washed with water to remove catalyst residues. Emulsion, produced on washing, is led into a separating tank. A stabilizer, and if required, extender oils are added to the hexane solution of the polymer is a mixer. The solvent and un-reacted monomers are removed by multi-stage steam distillation and dried before recycling.

The hexane free polymer crumbs are separated from the aqueous suspension by filtration. Water is removed in dehydration and drying screw extruders. The dry rubber is pressed into bales, packaged in polyethylene film, and palletized.

The EPDM can also be produced by suspension polymerization. Polymerization occurs at near normal temperature with Ziegler-Natta Catalyst (aluminium alkyl in conjunction with an organic vanadium compound); the rubber particles form a suspension in propylene inert hydrocarbon medium. A stabilizers and, if appropriate, extender oil is added, the suspension is then stripped and the dry rubber packaged into bales, crumbs or pallets.

The commercial grades of EPDM differ in composition (ethylene and termonomer content), molecular mass, and amount of extender. They are broadly classified into the following categories:

i. Random polymers with roughly equal ethylene/propylene ratio.
ii. Sequential polymers with higher ethylene content. The ethylene is incorporated into the molecular chain partially in the form of sequences, thus producing a partially crystalline molecular structure.
iii. Oil extended polymers.

2.8 RUBBER VULCANIZATES

A typical rubber vulcanizate is a three dimensional polymeric matrix which incorporates carbon black or other additives and which is usually, but not always, bonded with or fabricated into composite articles. The major part of the world’s rubber consumption is in composite articles such as tyres, conveyor belts, v-belts, reinforced hose, cables, rubber-to-metal bonded parts etc.

Apart from natural rubbers whose properties have been known for many centuries, a multitude of synthetic rubbers have been developed since 1915, to meet the demands of the growing passenger and goods transportation needs of the twentieth century.

2.9 Types of Polymers

A polymer or macromolecule is a large molecule built-up by the repetition of small and simple chemical units. Polymer molecules consist of long chains of carbon atoms formed by covalent linking of monomeric units to which other atoms or groups are attached. The molecular mass may be 100,000-250,000, which represents a chain length of some 6,000-15,000 carbon atoms.

Polymerization is the process by which polymers are prepared. The mechanism of synthesis can be by chain addition, polycondensation or polyaddition. Polymers may have linear branched or cross linked structure. A linear polymer is one in which the units are connected to another in a linear sequence.

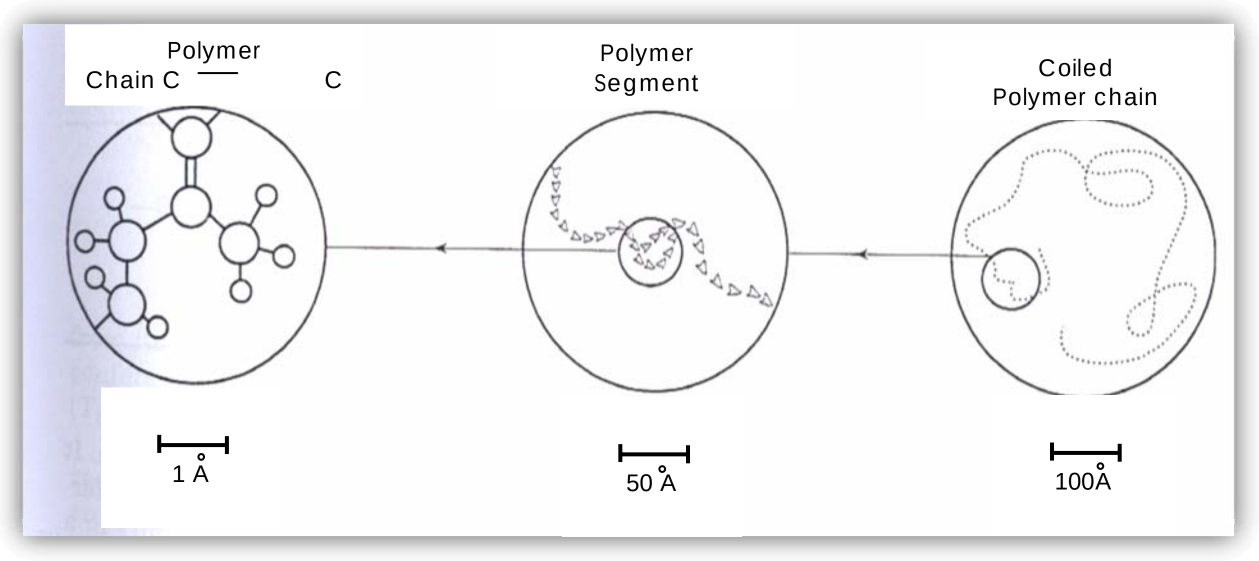


Fig. 2.2

A branched polymer is a nonlinear polymer with many ling side-chains at irregular intervals, a cross linked polymer is essentially a very large molecule of infinite relative molecular mass, the length of the chain between branch points being variable from 10-20 units in resinous and glass-like materials like phenol-formaldehyde resins, to 100-600 units in lightly cross linked rubber.

2.9.1 Star Polymer:

When three or more chains are linked at one end through a central moiety, it is known as Star Polymer.

2.9.2 Monomer:

The monomer is the starting material from which the polymer is formed. The repeat unit of the polymer is usually equivalent or almost equivalent to this monomer and is called “mer”. Pure hydrocarbons like butadiene, halogenated hydro carbons like chloroprene, or monomers with other functional groups such as acrylonitrile can be homopolymerized or terpolymerized to give end products.

Degree of polymerization (DP_n) is the number of repeat units in the chain.

“Homo polymer” is one which is made from only one type of molecule.

“Copolymer” is one which is made from two types of monomers.

“Heteropolymer” is a polymer that has atoms besides carbon as part of the chain backbone.

2.10 FUNCTIONALITY:

Functionality is the number of bonds a unit cab form with other units in a reaction. It determines the type of products which is formed in polymerization will occur at all. Polymer formation can occur only in a reaction where all participating molecules are bi- or poly-functional. Monomers with a functionality of 1 give only low molecular mass products, those with functionality 2 give linear polymers, while branched or cross linked polymers are formed with poly functional monomers.

2.11 THE STRUCTURE OF RUBBER VULCANIZATES

The different parts of a rubber vulcanizates molecule are described as:

2.11.1 Polymer molecules.

Rubber consists of long coiled polymer chains with rotatable segments and entanglement points. Under an external stress, the chains uncoil, partially straightens, and revert to the coiled condition on removal of the stress. In fact, the long range elasticity of rubber results from the distortion of the rubber molecule from its randomly coiled shape by rotation of the carbon-carbon bonds. The main chain confers properties on the vulcanizate dependent on the glass transition temperature, stereo regularity, chain length and chemical reactivity.

2.11.2 Crosslink

Permanent chemical bonds or cross links between the molecules are required in order to convert the tangled polymer molecules into a network. Vicinal cross links so close together that they act physically as one.

2.11.3 Network Chain

It is the length of polymer chain between two cross links. The primary chains are cross linked at many points along their length. For materials such as tyres and gaskets, the primary chains may have 10-20 cross links per primary molecules. The chain portions bond at both ends by cross linked junctions is called network chain segments, with an average molecular mass between cross links, M_{crl}.

2.11.4 Physical Cross links.

In physical cross links, the chains are not chemically attached to one another by valence bonds such as main chain bonds or sulphur-bridges, but are effectively pinned together in one of the three ways: (1) by chain entanglements due to a high relative molecular mass; (2) by the chains entering and leaving crystals and (3) by the chains entering rubbery domains from glassy domains from glassy domains. Irrespective of whether chemical or physical cross links are present, the macromolecules between cross links undergo extremely rapid molecular movements.

2.11.5 Extra network materials.

This term includes all substances in the vulcanizate which are not the part of the network. These comprise extractable non-rubber constituents in the raw rubber, fillers, anti-degradants and vulcanizing ingredient residues.

2.11.6 Chain end.

This is a length of elastically ineffective polymer chain bond at only one end by a cross link.

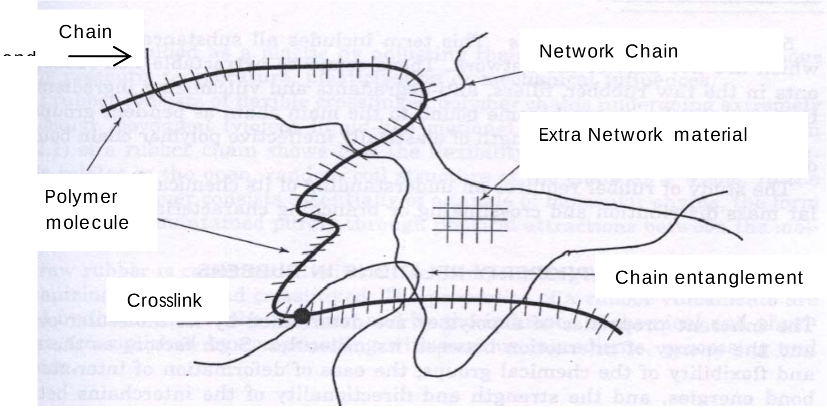


Fig. 2.2

2.12 STRUCTURE/PROPERTY RELATIONS IN RUBBERS

The inherent properties of a polymer are determined by its molecular organization and the energy of interaction between its molecules. Such factors as the size, shape and flexibility of the chemical groups, the ease of deformation of inter-atomic bonds, bond energies, and the strength and directionality of the interchains between molecules determine the physical and mechanical behavior of a polymer, especially properties such as tensile strength, modulus, stress relaxation and elongation at break.

Polymer molecules may be arranged predominantly at random or predominantly in regions possessing a high degree of geometrical order or, with a balance of crystallized and amorphous domains. In generals, rubbers exhibit an amorphous structure in the relaxed state, whereas fibers show a high degree of crystallinity.

Natural rubber (NR), for example, has weak forces of attraction between the chains. The very flexible chains tend to coil in a random fashion and can slide over each other readily on stretching, forming crystalline regions, which melt when the external stress is released. In the case of fibers, the linear polymer chains are held tighter by very large forces of inter-molecular attraction, resulting in high tensile strength and melting point. For example, nylon 6.6 has high intermolecular forces of attraction due to many polar groupings and hydrogen bonding forces. Strong forces between the individual chain molecules or molecular shapes which fit easily into a crystal lattice are typical of fibers.

In use, raw rubber is compounded with fillers and curatives, and cross linked. The properties of a rubber vulcanizates are determined by the nature of the polymer, and by the influence of chemical and physical changes accomplished by compounding with various ingredients, processing and vulcanization.

2.13 MOLECULAR MOTION IN RUBBERS

The two main types of molecular motion in high polymers are segmental motion and translational motion.

2.13.1 Segmental motion.

may involve (a) rotation of chemical groups about single covalent bonds in the chain backbone (b) vibrational and tensional movement of individual atoms or groups substituted on a polymer backbone (c) localized motions of short segments of the chain backbone and (d) crankshaft motion involving 4-6 bonds.

Segmental motion is associated with molecular and solid deformation. Above the glass transition temperature, molecular segments can move relative to adjacent segments and are subject to changes of position due to their thermal energy. The long chain molecules are entangled, and when lightly cross linked, from a deformable continuous network. Under equilibrium or reversible conditions, the amorphous network displays “rubber elasticity”, which can be substantially modified when fillers are added in large amounts, or at high strains, or when crystallization occurs. Under the application of an external force, segmental motion takes place. The molecules cannot become displaced in relation to one another as during viscous flow. The cross links do not interfere appreciably with the local freedom of motion of the molecular segments, but they do restrict bulk slippage of one molecule past another under stress.

2.14 Various States in Rubber Goods Manufacture

In the raw state, rubber should be easy to mix and has sufficient stiffness for conventional processing. Most rubbers contain some form of additive, introduced for some specific purpose, such as fillers, plasticizers, colourants, stabilizers against heat and oxidation, flame retardant, processing aids etc. the viscosity of the rubber should be such that initial mastication is not required or is done with minimum energy expenditure.

The process of working rubber on a mixing mill or in an internal mixer unit it becomes soft and plastic in known as mastication. The inventor of the first masticator was Thomas Hancock. The breakdown of rubber is air occurs much more rapidly at either high or moderately low temperatures that it does at temperatures around 100 °C. mastication in nitrogen, however, results in a small increase in viscosity or no appreciable change in molecular mss.

2.15 MOLECULAR MASSES AND SIZES

Molecular masses can be measured by various techniques which all have one point in common. The measurements are made in dilute polymer solutions wherein the molecules are isolated, one from another. The unit molecule in a solution is dynamic, its shape changing from instant to instant as it diffuses into the solvent. The timer-averaged shape is spherical, but at any instant, the actual shape will be approximately a random, but at any instant, the actual shape will be approximately a random, spherical tangle. The polymer chain conformations are dependent on temperature, solvent, structure, crystallization, extension and the presence of other polymers.

Many mechanical and rheological properties of polymers can be predicted from knowledge of their molecular mass and molecular mass distribution. Many commercial rubbers have molecular masses around 10^5 g/mol and with polydispersity indices of around 2-3. This is considered to be an optimum balance between good physical properties and processability. Low molecular mass portions of a rubber tend to weaken the physical properties, whereas the higher molecular mass portions increase the viscosity and cause processing problems. Therefore, a controlled distribution is preferred for many rubbers.

A polymer chain length may be expressed in the form of the relationship:

$$DP_n = \frac{L}{a} = \frac{M}{M0}$$

DP_n = degree of polymerization
L = length of the extended chain
a = monomer unit length
M = molecular mass of polymer
M_0 = molecular mass of monomer

2.16 Ablation Studies Process

Ablation studies can be divided into two broad categories:

(A) Those dealing with the mechanism of ablation, with associated basis experimentation.

(B) Those treating material behavior for a particular exhaust has or flight conditions with associated simulation experiments.

These categories overlap and are complementary. Both examine the behavior of ablators, the former in the generalized terms and the latter under specific use conditions. However, the approach and techniques differ.

Mechanism studies deal with individual steps in the process, effects of various parameters, interactions. They aim at elucidation of the mechanism, generalization and formulation of a theoretical framework, and prediction of performance. Simulation studies, or rather simulation testing, checks the overall effects under realistic conditions. Mechanism studies are of the interdisciplinary nature, while the simulation and flight or firing tests lie in the engineer's domain.

Chemists contribute to the elucidation of the mechanism of ablation by laboratory studies of the chemical reactions involved. These studies cover usually isolated steps, single components of the ablator or their simple combinations, and methodical changes of some parameter. Simulation testing under use conditions can also provide information of a chemical nature, at least by inference. It can verify laboratory finding or it may reveal unexpected behavior, necessitating special chemical investigation.

2.17 Chemical Environment in Reentry

Chemical and physical aspects of the atmosphere are treated in another chapter. A popular review of the present knowledge of the atmosphere has been prepared for chemists by Sanders. Here, some features which directly affect the ablators in reentry will be mentioned.

In the ionosphere (above 50 km) the radiation from the sun becomes very effective in producing atomic, ionic, and excited chemical species. The pressure, unlike the temperature, decreases monotonically with increasing altitude, down to about 10^{-4} torr at 100 km and to about 10^{-6} torr at 200 km. Hence, at high altitudes, the concentration of these reactive chemical species in a tenuous atmosphere is not so high. But in the compressed hot air behind the shock wave produced by the reentering hypervelocity body, the actual concentration of these species becomes large and is augmented by new species from thermal reactions. The species in the bow shock region and the wake determine the gas-gas reactions and the radiation effects. Such species as O_3, NO, N, O and others as well as free electrons are known to be present.

Of special interest to chemical ablation is the nature of the boundary layer near the surface of the body, since it governs the gas-solid reactions. Chemical composition of this boundary layer is complex, as discussed by Tirskyi. Gaseous ablation products and particulate matter are injected into the boundary layer, blocking the convective heat and also supplying new reactants. The injected gases may also block, at least partially, the access of reactive chemical species to the body.

2.18 Reactions at the Ablator Surface

Chemical processes at the ablator surface can be divided broadly into two classes:

1. Thermally induced processes, which would occur even in the absence of external gas. They include vaporization, dissociative vaporization, sublimation, and surface pyrolysis.
2. Chemical interactions of the ablator with a reactive chemical species or external gas i.e. gas solid reactions including combustion and chemical errosion. The gas-gas interactions in the boundary layer and in the wake can also be included here as an extension of surface processes.

2.19 Vaporization and Sublimation

The vaporization process in ablation is best illustrated by the case of quartz. i.e. silica. Quartz alone has been used as the ablator in nose cones. Any silica-reinforced plastic also leads eventually to a silica melt or silica-rich surface layer.

An extensive review of the high-temperature vaporization features of silica has been written by Schick. The straight vaporization absorbs

$$SiO_{2\,(1)} \rightleftarrows SiO_{(g)}$$

134 kcal/mole at 2000°K. This straight vaporization occurs to a small extent only and is overshadowed by the more endothermic dissociative vaporization of silica:

$$SiO_{2\,(1)} \rightleftarrows SiO_{(g)} + 1/2O_{2(g)}$$

The heat of this reaction at 2000 K is 179 kcal/mol. If the heats associated with various phase transitions in silica are included. i.e. if one considers ∝-quartz at 298K as the starting material. The thermal contribution increases to the estimated 222 kcal/mole. It is apparent that even at moderate rates, the vaporization of silica represents a major heat sink in the ablation of silica-reinforced resins. Since, however, it is molten silica that vaporizes, mechanical losses by liquid runoff and spallation limit the potential benefits of pure vaporization.

Ablation literature usually gives the behavior of Teflon as an example of sublimation.

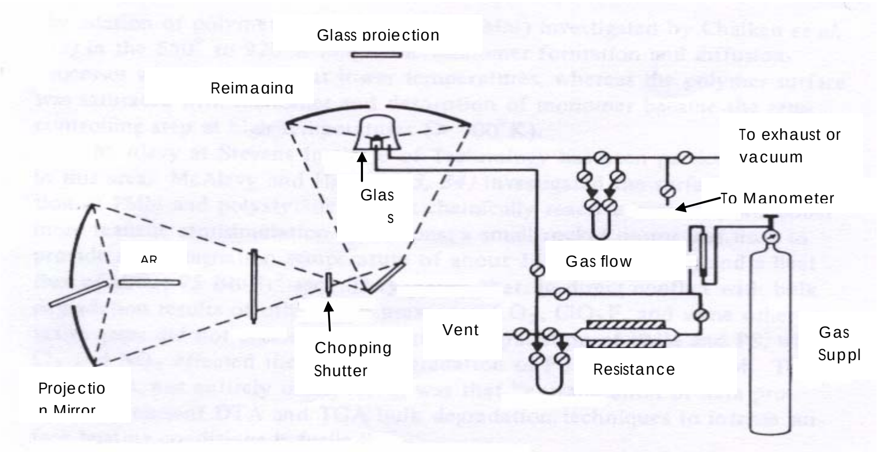


Fig. 2.3 Arc-imaging furnace adapted for ablation studies

However, true sublimation i.e. a solid to gas phase change is represented by carbon. Carbon sublimates at very high temperatures; below 3000 K the total vapor pressure is 0.489 atm. On sublimation, carbon forms gaseous atomic carbon and various polymeric carbon molecules, of which $C_{3\ (g)}$ is the most important up to 4000 K. carbon is likely to enter at an earlier stage into chemical reaction s, particularly the exothermic oxidation. In the sublimation regime, the carbon oxidation reactions are forced off the surface.

Practically all materials, including metals and refractories, will lose some surface material in hyper thermal, high-shear environment, by some type of vaporization or sublimation. Magnesia is interesting in that it will undergo a dissociative sublimation.

$$MgO_{(s)} \rightleftharpoons Mg_{(g)} + 1/2O_{2\ (g)}$$

The case is parallel to the dissociative vaporization of silica.

2.20 Surface Pyrolysis of Plastics

Ablation in practical situations may involve a rather special type of pyrolysis. Unlike the usual bulk pyrolysis in which samples are heated rather uniformly, the ablator surface is heated much more intensely that the rest, and degradation occurs just on the surface of the plastic. The phenomenon is termed surface pyrolysis or linear pyrolysis referring to the linear rate of surface regression. The term flash pyrolysis has a somewhat different meaning, implying a short duration exposure.

In practice, surface pyrolysis is applicable to non charring plastics. The usual degradation of charring ablative resins has the features of a bulk pyrolysis, since, after a brief initial period, decomposition takes place behind the char barrier. Non charring plastics used in ablation are exemplified by Teflon and low-melting infiltrants of ceramic matrices.

Completely volatizing non charring plastics provide copious gases, desirable for transpiration cooling. Those that depolymerise i.e. revert to their monomers are of special interest.

2.21 Surface Reactions in Reentry

The gas-phase chemistry of reentry has been covered extensively in a recent review by Heicklen. The most important gas-solid reaction during reentry is the oxidation of carbon, or combustion. This exothermic and ablator-consuming process has to be avoided or minimized. Reinforcing carbon, carbonaceous char, and organic components, all encounter the problem of air oxidation.

The oxidation of carbon at high surface temperatures has been studied extensively. Three regimes have been noted: the chemically controlled heterogeneous reaction, the diffusion controlled process and the sublimation regime. The transition from chemical to diffusional control occurs in the 1100 K to 1200 K range. The porosity of ablative chars may be an important factor. Thus, when combustion of porous and non porous carbon in the airstream at temperatures above 1000 K was directly compared, the rate for porous carbon approached the diffusion controlled value at the stagnation point but with nonporous carbon the reaction remained kinetically controlled. A diffusion controlled process is characterized by the dependence of rate on the square root of time.

At high altitudes and high surface temperatures, the reactions of carbon with various atomic and activated species occur. Atomic oxygen is considerably more reactive that O_2. Although nitrogen, which forms the bulk of the atmosphere at low altitudes, is considered an inert gas, it becomes active at high altitudes, is considered an inert gas, it becomes active at high altitudes. The reaction of microwave activated nitrogen with graphite in the 1694 K to 2365 K range was investigated by Goldstein. The product was $(CN)_2$ and the activation energy was estimated at 17 to 19 kcal/mole.

Comparative studies of the attack of pyrolytic and isotropic graphite by atomic and molecular oxygen at high temperatures were carried out recently by Rosner and Allendorf.

In addition to serving as a reactant, the ablator may behave passively as a third body, or a catalytic surface, for recombination reactions such as

$$O + O + M \rightleftarrows O_2 + M$$

$$N + N + M \rightleftarrows N_2 + M$$

These re-combinations of atomic species result in a considerable heat release. In recent years, because of military implications, considerable attention has been paid to the effects of ablation products on ionization in hypersonic wakes namely, detection of flying bodies by virtue of their wake observability.

A conical vehicle of 1-ft base radius flying at an altitude of 125,000 ft was considered. The following chemical species represented the wake:

Air: N_2, O_2, NO, N, O, NO^+, e^-

Ablation products: H_2, H_2O, OH, H, CO, CO_2

Other species: Na, Na^+, $Na(OH)^+$, H_3O+, O^-, O_2^-, OH^-

Theoretical analysis showed that ablation species exert significant influence on wake ionization. The temperature, important in infra red and optical detection, was lowered by injection of H_2, H, and OH but was slightly increased by CO and CO2. The electron density, of primary interest for radar observability of wakes, was increased considerably by the addition of sodium or other alkali metals, even at content levels associated with common ablators. The controlling mechanisms for sodium ionization were the reactions with O_2, O and OH. Much similar theoretical and experimental work on Flowfiel contaminants which enhance or suppress signature characteristic is now in progress.

2.22 Ablative Plastics & Composite Materials

2.22.1 General Features of Ablators

The desired properties of ablators, evident from previous considerations, are:

2.22.2 High heat-protective performance

Low thermal conductivity

High Specific heat

High (approaching unity) emissivity

High yield of low-molecular-weight gassed

High endothermicity of chemical reactions and phase changes

2.22.3 Good mechanical properties

Thermal stability

High strength and ability to absorb elastic stresses

Low mechanical erosion and dimensional changes

Low density

In specific applications, certain requirements are emphasized or relaxed and new demands arise. No single material can possess all these often-conflicting features, and combinations of materials called composites are mostly used. Homogeneous ablators, such as quartz, Teflon or a foamed plastic are sometimes employed but normally an ablator is heterogeneous and consists of polymeric components and a reinforcing agent or other modifier.

The performance of a composite will depend on the nature and ratio of its components and factors such as size, shape and form and orientation of fibers. It is obvious that even with a limited number of basic components a variety of final products are possible. A major effort in ablation technology is being spent on empirical experimentation to optimize various parameters; in this work a certain amount of compromises or trade-offs is unavoidable.

2.23 RUBBER MIXING

Mixing of raw materials in rubber industry is the essential and basic process.

2.23.1 MASTICATION

Raw natural rubber is dry, tough and quite unsuitable for mixing without mastication. Mastication is breaking down the long molecular chains of rubber to suitable lengths so as they make it more plastic. This can be done by mechanical shearing action either in open mills or in internal mixers. The process of mastication can be facilitated by adding a peptizers, usually produces a physical and chemical change reflected by a change in viscosity.

2.23.2 BANK MASTICATION

Bank mastication is the process of passing the rubber through the mill nip of a two roll-mill for a number of times. The process is entirely manual and the productivity is low. Moreover, effective control on plasticity cannot be achieved by this process, because of the length of time; the chain cession is generally quite high.

2.23.3 EFFECT OF PLASTICITY

The maximum effect of viscosity reduction is effected in natural rubber either at temp.55°C (in two roll mill) or above 130°C (in internal mixers). Very little break down is obtained in the 90-105°C region. Many synthetic rubbers are produced at viscosity levels that do not require pre-mastication. Similarly, natural rubber is produced in controlled viscosity grades that reduce the need of such mastication.

2.23.4 MASTERBATCHING AND MIXING

A masterbatching is an incomplete rubber compound having one or more compounding ingredients. Sulphur, accelerators, and anti-oxidants, used in relatively small proportions in the final mix, are first converted to masterbatches (commonly known as mother stocks) so that the mix is stiff enough for efficient mixing. By cutting off an appropriate weight of these masterbatches and blending them together with additional rubber, the required batches are produced. A compound mixed without the curing agents and accelerators is also called masterbatch, Such compounds may be mixed in two roll mills or internal mixers. Optimum dispersion of compounding ingredients is the primary factor of good quality. The level of dispersion required for any given rubber compound is pre-determined by specification or application properties, tensile, elongation, hardness, extrudability, mouldability, etc

2.24 MIXING EQUIPMENT

The selection of mixing equipment is made upon the basis of financial position, amount of rubber. Following equipments are necessary which are commonly used

(1) Mixing Mill
(2) Internal batch mixer
    (a) Interlocking
    (b) Non-Interlocking
    (c) High-intensity powder blenders
(3) Continuous Mixing
    (a) Interlocking (extruder type) twin screw.
    (b) Non-Interlocking twin screws
    (c) Single Screw (extruder type)
    (d) Static powder blenders

The choice of mixing equipment is dictated by production demands, type of compounds, length of production run, cost per unit weight of mix, and basic mixing philosophy.

2.24.1 MIXING MILL

Two roll mills usually consists of two hollow cast iron rolls, cylindrical in shape, with provisions for passing cold water or steam through the rolls, which are attached with bull gear, gear box, coupling and motor.

In the two roll mills, the mixing of powder takes place at the compressive zone of the roll nip. The compression produces a lateral shearing, i.e. the mixing takes place along the circumferential direction of the rubber bank on the mill. Effective incorporation of powders, thus, require the presence of a bank of rubber above the nip and the rubber bank should be squarely cut and folded back at the nip. Mixing in two roll mill is very much a manual skilled operation. Rolls should be smooth and free from nicks and burrs.

In mill mixing, temperature control is very important so, chilled water is passed through the rolls at a regulated flow rate to remove excessive heat, developed during mixing, and prevent scorching of compound. Heat is also necessary in some processes to warm up the rolls instead of cooling them.

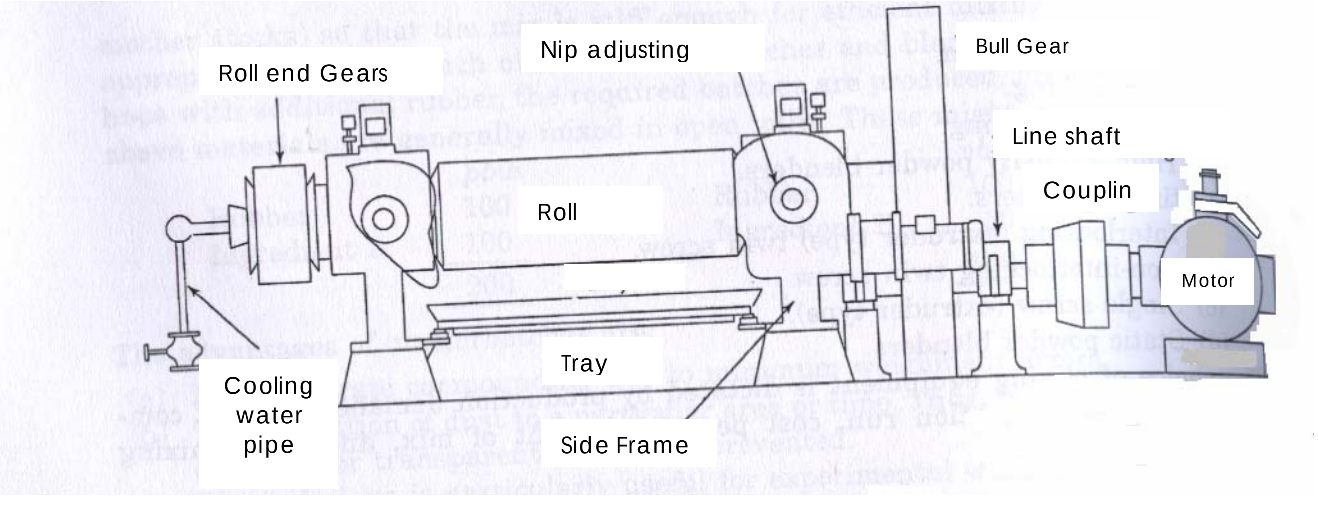


Fig. 2.4 .Mixing Mill

All types of compounds except those with very high filler loading can be mixed on open mills. Mixing time is very long, generally around 40 minutes. The normal mixing sequence is as follows:

i. Loading
ii. Warming
iii. Incorporation of powders and other ingredients such as oil and anti-degradant slowly as the rubber accepts them.
iv. Incorporation of curatives.
v. Sheeting off.

The mixing mill generally consists of two rools made of chilled iron and set in heavy frames. One roll has a driving gear or bull gear on one end.

Mixing take place at the compressive zone of the roll nip. The compression causes a lateral shearing. Effective incorporation of ingredients require the presence of bank of rubber above the nip and the rubber bank should be squarely cut and folded back at the nip. Manual skill is considered very important in two roll mixing. Rolls should be smooth and free from nicks and burrs, temperature control are important so, chilled water is passed through the rolls at a regular flow rate to remove excessive heat which is developing during mixing. In some cases warming is required, for this steam is passed through the rolls.

2.24.2 Kneader Mixer

Kneaders are pressure applied closed type of mixers. Mixing is undertaken in a closed chamber, therefore, material losses are avoided. Rubber and ingredients are forcibly mixed by two blades provided in an enclosed mixing chamber. The two blades are turned in reverse direction as the front and rear rotors are geared. A floating ram or pressure lid is also fitted into the kneader to exert pressure on the compound to hold it onto thr rotor. The mixing chamber itself can be tilted and cleaned. This is very helpful for mixing coloured compounds and for discharge of the batch.

2.25 MIXING PROCESS

To convert rubbers and compounding ingredients into a compound, there are several steps these steps include receipt of raw material, testing, storage, weighing feeding, mixing, batch off, cooling, testing, storage, and dispatch. All these stages are basically divided into three groups.

(a) Material flow to the mixer.
(b) Mixing
(c) Material flow away from the mixer

2.25.1 Material flow to the mixer

Rubbers and rubber chemicals should be stored properly to get the best products from the mixing process. Raw materials have to be prevented from deterioration and contamination. Following steps are to be followed.

i. Not to exposed the raw materials to the weather.
ii. Materials to be properly identified
iii. All polymers, specially natural rubber and polychloroprene, to be kept away from heat outlets and steam line

iv. Natural rubber, butyl and EPDM rubber should not be kept at very low temperature as this will make the viscosity of the polymers very high

v. Unsaturated polymers to be kept separately from butyl or EPDM

vi. First-in, first-out rule for using raw materials to be followed

vii. Ensure all powders are dry

2.25.2 Mixing Operation

During a mixing operation, simultaneously three processed take place: simple mixing; laminar mixing; and dispersion missing. In simple mixing, particles move from one place to another without physical change. This is also known as homogenization. When the shear force is large, particles break and polymer flows. This breaking of particles is dispersive mixing and flow of polymer is laminar mixing. The laminar incorporation means that the particles change their appearance but do not tear. With dispersive mixing, the single particles become smaller and the surface area larger; the agglomerates dissolve and all particles get homogeneously distributed.

The compounding ingredients which are added to rubber undergo the following stages of mixing

1) Incorporation of wetting stage: the rubber undergoes considerable shear, increasing the surface area for accepting filler agglomerates, and then sealing tem within. As mixing proceeds, the rubber further breaks down into small pieces and incorporates the powders.

2) Dispersion: the filler agglomerates are gradually broken down to their ultimate size and an intimate contact develops between the rubber and filler.
3) Distribution or mixing: it is increasing homogenization which takes place so that all parts of the batch possesses the same properties.
4) Plasticization: in this stage of mixing, the rheological properties are modified to suit subsequent processing operations.

These stages are similar to the preparation of a colloidal dispersion. With rubber, owing to the high viscosity compared with a liquid, the wetting and dispersion stages involves the expenditure of much energy, and the capital cost due to robust plants. The finally powdered solids do not soften or otherwise change when heat to temperatures normally attained during mixing. Consequently, they may be pictured as retaining their original form, remaining as individual small particles in a continuous matrix of rubber.

Mixing

2.26 MIXING SEQUENCE

Mixing time is generally very long up to 40 min. The sequence is as follows

(i) Loading (polymer and reclaim, if any)

(ii) Warming

(iii) Addition of powders and other ingredients such as oil and anti-degradant slowly as rubber accepts them.

(iv) Addition of curatives.

(v) Sheeting off.

The mixing mill generally consists of two rolls made of chilled iron and set in heavy frames. One roll has a driving gear or bull gear on one end.

These gears are usually of a different sizes or have a different number of teeth, so as to give a differential speed or friction to the front roll compared to the back roll. This ratio assists in forcing and mixing the compounding ingredients into the rubber. Thus the motion is transmitted to the front roll. The numbers of teeth on these two wheels determine the speed of the two rolls, usually called “friction ratio”

2.27 COMMON PROBLEMS IN MIXING

Problems usually experienced in mixing are dispersion, scorchiness, contamination, poor processibility, and batch to batch variation.

Reasons for the above problems are as follows:

- Dispersion
    i. Batch size in not proper
    ii. Mixing time is insufficient
    iii. Filler addition is not in proper time
    iv. Over-aged rubbers
    v. Moisture in fillers
    vi. Insufficient ram pressure
- Scorchiness
    i. Loading temperature is high
    ii. Insufficient cooling during mixing

    iii. Dump temperature is too high
    iv. Poor dispersion of vulcanizing agents
    v. Too high rotor speed
- Contamination
    i. Oil seepage from faulty oil seal in mixer
    ii. Contaminated ingredients
    iii. Residual compound sticking to rotor discharge door, hopper, and ram.
- Poor processibility at sheeter mill
    i. Ineffective control of mill roll temperature and friction ratio
    ii. Compound viscosity is either too high or too low.
    iii. Poor dispersion.
    iv. Too high loading of tackifiers.
- Batch to batch variation
    i. Variation in initial loading temperature.
    ii. Variation in ram pressure
    iii. Variation in dump time and temperature
    iv. Different level of dispersion

2.28 RUBBER RHEOLOGY

Rheology is the study of flow and deformation of materials. It seeks to derive relation among stress, strain, and time. For the rheological investigation, temperature is an additional parameter. Since rubber shows some of the properties of both a liquid and a solid (i.e visco-elastic behavior) so it is necessary to determine its rate of flow under various conditions of stress, temperature and time of application of stress, and elastic recovery on the removal of deformation, visco-elasticity, and rupture.

Rubber properties characteristics of the solid state or the liquid state can be emphasized by particular conditions of the test. The rate of deformation influences the time for the movements of the molecular chains. The slowest process (plastic flow or creep) involve the movement of the long chain molecules at intermediate speed, rubber shows high elasticity attributable to the rotation of the chains.

Owing to the complex visco-elastic behavior of rubbers, the various rheological tests do not necessarily define material parameters or predict the behavior of rubbers in processing and in use. Therefore, although many specifications and comparative evaluations are based on these techniques, their repeatability and reproducibility will bear improvement. These tests are highly sensitive to temperature, frequency and the amplitude of static or cyclic stress or strain. If different rubbers are being compared, their relative ranking may well depend on the test conditions used.

2.29 FLOW BEHAVIOUR OF UNVULCANIZED RUBBER COMPOUNDS

The flow behavior of un-vulcanized rubber compounds in extrusion and on mills, besides processing factors, depends on molecular mass and relative molecular mass distribution. In a polymer of broad molecular mass distribution, the higher molecular mass chains accept a disproportionately large amount of the total stress and show a delayed elastic response, compared to a sample of similar viscosity with a narrow molecular mass distribution. At low shear stress, the viscosity of a broader molecular mass distribution polymer is very much higher shear stress, the reverse is often true.

2.30 MEASUREMENT OF PLASTICITY

Plasticity is the resistance to flow which is caused by the application of shear stress. In general, there are five accepted test methods to determine the plasticity of rubber compounds.

1. Applying force on a pellet of standard dimensions and measuring deformation, after a given length of time at a prescribed temperature.
2. Extruding rubber through an orifice of known dimensions using a prescribed force and measuring the quantity of extrudate over a length of time at a definite temperature.
3. Rotating a specially designed knurled disk on a spindle inside a mould and measuring the resistance to rotation.
4. Shearing the rubber between two very wide angled cones or between a cone and a horizontal plate.
5. Using recording torque rheometers with miniature internal mixers and extruders for measuring torque versus temperature characteristics of unvulcanized compounds in flow.

2.31 RELAXATION PROPERTIES

The time dependent return to equilibrium of a system, which has been perturbed by an applied field, is known as relaxation. The applied field may be a mechanical stress or an electric field. In the stress relaxation process, the molecular chains shift to less stressed positions, each chain taking a time interval to relax, a characteristic of its size, shape and spatial arrangement.

2.31.1 VISCOELASTIC FRACTURE

Failure of visco-elastic solids is strongly affected by time dependent phenomena. The strength of real materials is reduced by flaws, dirt particles, bubbles, etc which randomly permeate the material. If there is a sufficiently deep flaw in relation to the bulk of the material, prompt fracture is certain. If there is no such flaw, the specimen will survive until one develops. Flaws may propagate through growth, stress increase or time dependent changes in bulk properties. The initial or slow growth portion of the fracture process is a time-consuming process, which, in effect, determines the time to break.

2.32 MEASUREMENT OF VISCOELASTICITY: DYNAMIC TESTS

In dynamic testing, both stress and strain vary periodically with time, for example, sinuso idally. The sinusoidal quantity may be stress, strain or energy. For a completely elastic material, the strain is in phase with the stress, and for a completely viscous material, the strain lags behind the stress by 90°.

Dynamic tests may be carried out in machines such as closed loop tester, forced vibrational tester, Rolling or Rheovibron. A typical test consists of a rubber cylinder of 25mm height, which is compressed by the test machine by 5%. A dynamic strain of ±2% is now imposed on the sample, so that it oscillates between 7% and 3% strain. The oscillation is applied sinusoidally and the rate is reported as the test frequency, usually in Hertz.

2.33 VULCANIZATION AND ITS EFFECTS

Chemical crosslink between macromolecules may occur in polymerization or in fabricating articles, resulting in polymers with network structures. The reaction which occurs during fabrication is known as vulcanization in the rubber industry, and curing or hardening in the plastics industry. Crosslink in rubber are formed by the reaction with a suitable “vulcanizing agent”, usually sulphur.

2.33.1 VULCANIZATION OF THICK RUBBER ARTICLES

Since rubber is a poor conductor of heat, long vulcanization times are required for thick sections to ensure that the vulcanization of the central portions is complete. In thick sections of rubber articles, the cure levels at the centre and at the surface of the block may be largely different on account of the temperature lag effect.

To obtain uniform vulcanization throughout thick sectioned articles, the following methods are used.

1. Increasing the moulding temperature step-wise. Thick articles should be heated slowly to allow penetration of heat before vulcanization beings. This is usually done by raising the temperature in steps or continuously over a period of time before starting the real cure time. Continuous temperature checks and state of cure checks are necessary.

2. Hand-building of the articles from different compounds. By adjustment to accelerator systems, compounds with substantially different rates of vulcanization can be prepared. A large section article can be hand-build using different compounds with the reaction rates increasing towards the centre of the rubber. Although time consuming, this techniques is still employed.
3. Preheating the blank in an oven at moderate temperatures. High frequency heaters, hot water baths and hot air ovens may be used to put in at least some of the required heat input into the compound before it is introduced into the mould.
4. Post-curing. In this case, the product is given a set cure is the press and final cure in an air oven or steam pan. However, it can cause porosity problems due to bubble formation. With thick articles, the time taken to cool to ambient can also affect the final properties.
5. Use of fillers with high thermal conductivity, e.g. zinc oxide.
6. Use of transfer or injection moulding techniques.

2.34 DETRMINATION OF STATE OF VULCANIZATION

The conventional methods for measurements of state of cure in rubber compounds are:

1. Physical property tests, e.g. tensile strength, elongation at break, modulus at 100% or 300% elongation, hardness.
2. Free sulphur determination.
3. Solvent-swell method.
4. Mooney-Revilin equilibrium modulus.
5. Differential scanning calorimetry.

2.34.1 PHYSICAL PROPERTY TESTS

There is a well-established increase in density on changing from the raw to the vulcanized state in rubber compounds; with 2-4% combined sulphur, the contraction in volume is around 1.6%. The effect is more pronounced in ebonite, where 5.5% increase in density is observed.

The change in these properties with cure time is relatively small. Careful preparation of test pieces from finished articles is essential; surface irregularities introduced in the sample preparation can affect the test results.

2.34.2 FREE SULPHUR DETERMINATION

Sulphur content of vulcanizates is an indicator of the state of cure and the type of vulcanization system employed. Sulphur can exist in vulcanized rubber compounds as under.

1. Free elemental sulphur
2. Bound sulphur
3. Sulphide sulphur
4. Sulphur in accelerator

2.34.3 SOLVENT-SWELL METHOD

In this method, the vulcanized rubber is immersed in a solvent until and equilibrium weight is reached. The volume fraction of a polymer in the swollen network is calculated by assuming addition of volumes and used to arrive at crosslink density by the equation.

$$\nu = \frac{\mathrm{In}\,(1-V_r) + V_r + X\,V^2_r}{V_s\,(V_r 1/3 - V_r/2)}$$

Where ν = cross link density, νs = molar volume of solvent, X = polymer solvent interaction parameter, Vr = Volume fraction of polymer in the solvent network.

2.34.4 Mooney-Rivlin Equilibrium Modulus

The Mooney-Rivlin equation states:

$$F=2A_0 (\lambda-\lambda^2) (C_1+\lambda^{-1} C_2)$$

Where F=force applied to sample, A_0 unstrained cross-sectional area, λ extension ratio, and C_1, C_2 empirical constants.

The extension ratio is measured for test samples and a graph is plotted of $\frac{F}{(2A0\ (\lambda\ -\lambda}$ versus λ^{-1} which gives slope C_2 and intercept C_1.

C_1 is proportional to crosslink density and C_2 is considered as an estimate of non-ideal behavior. It is usually found more convenient to estimate (C_{1+} C_2) at λ=1 and to define fractional conversion as

$$X_A = \frac{(C1+C2)}{(C1+C2)\ \mathrm{max}}$$

from which the time required to reach 80% or 90% conversion can be derived.

2.34.5 Differential Scanning Calorimetry

The differential scanning calorimetry method can be used with small (5mg) irregular samples and it measures the residual heat of vulcanization of a partially cured sample, provided the reactants do not volatilize or decompose during the test. The residual heat of vulcanization is assumed to be proportional to the amount of un-reacted cure system which remains in the rubber vulcanizate.

2.35 TECHNIQUES OF VULCANIZATION

Heat and pressure are commonly employed in vulcanization of rubber articles. Some times pressure and vulcanization take place simultaneously, while in other cases, heating of articles which are pre-shaped brings about vulcanization. For orderly and economical operation, continues curing processes have been developed, mainly for extruded goods.

2.35.1 PRESSURIZED VULCANIZATION

Moulding of rubber components is a complex process with many variables that must be controlled. It is the operation of shaping and vulcanizing the plastic rubber compound by means of heat and pressure in a mould of appropriate form.

2.35.2 ROTOCURE VULCANIZATION

This method is suitable for vulcanization of wide rubber conveyor belting and V-belts. By means of a steel belt, the sheeting is pressed against an internally steam-heated drum. The rate of rotation of the drum is adjusted to give a uniform state of cure along the length.

2.36 MOULDING

Moulds withstand the pressure necessary to cause a flaw in rubber, and transmit heat to the rubber. They are usually made f mild steel or cast aluminium alloy. There are three basic types of moulding – compression, transfer and injection moulding. In a compression type mould, the rubber blank is placed directly into the cavity of mould where it is heated by conduction and caused to flow by application of pressure. Transfer moulding use pre-warmed rubber which is heated during transfer and forced through holes into mould cavities in a tree part mould. In injection moulding processes, rubber compounds in pushed under pressure from an injection head, where it has been heated and plasticized, into a closed heated mould where cure is completed.

2.36.1 COMPRESSION MOULDING

This is the most common type of moulding used in the rubber industry. Essentially, it consists of pacing a pre-cut or shaped slug or a composite item into a two piece mould which is closed. The pressure applied by the press forces the materials to fit the shape of the mould and the excess flows out of the rim of the mould or through special vents. This excess in known as mould lash. There are three basic types of compression moulds.

i. Flash type moulds
ii. Semi-positive
iii. Positive moulds

i. Flash Type Moulds:

The simplest mould is the straight compression or flash type. It is loaded by placing an excess of uncured compound in the cavity. As the lid is closed under pressure, the compound conform to the shape of the cavity and after it is filled, the excess material is forced into overflow channels provided for the purpose.

Flash mould is the least expensive to manufacture and has the advantage of better heat transfer than other types. Such moulds are used for production of sheets, slabs, belting, tiling, etc. blanks do not have to be closely controlled in weight as any excess rubber will easily flow out of the cavity, air may also escape.

ii. Semi-Positive Moulds:

In its simplest form, the semi-positive mould consists of two parts, a plunger and a base. The plunger fitting loosely into the cavity which is at the base of a well whose contact, so that , as with flash moulding, the forces on the compound during vulcanization is not the full force exerted by that press. However, the pressure on the compound as it flows just prior the complete closing of the mould is greater than in straight compression moulding because of the restricted flow past the plunger to the overflow channels.

iii. Positive Moulds:

This type is n very little use today. In this case, the plunger fits tightly into the base, the full load of the press being applied directly upon the compound. Blank weight must be carefully controlled otherwise article thickness will vary. Air may also be trapped within the cavity. However, due to the great pressure which develops on the rubber in the positive type mould, gives it an advantage in moulding both extremely soft and extremely hard compounds. Disadvantages of positive moulding is the lesser heat transfer, because the top platen is insulated from the mould by an air space, except for the area in contact with the plunger.

2.36.2 TRANSFER MOULDING

Transfer moulding as the name implies involves the transfer of the uncured substance from one place to another within the mould. Rather than loading the mould by placing the stock directly in the moulding cavities, the mould is closed with the cavities empty. The compound is placed in a recess called transfer cavity on the top of the mould. The pot is fitted with a ram or piston which is inserted over the compound. As the force of the press is applied to the piston, the compound, softened from the heat of the mould, flows through suppress, channels, and gates.

2.36.3 INJECTION MOULDING

This process is normally used for plastic products, but in recent years, it has been adopted in an increasing scale in the rubber industry. The injection moulding process can be defined as automatic feeding, heating, and plasticization of rubber compound and its subsequent injection, in measured quantity, through a narrow orifice into a tightly closed hot mould in which vulcanization takes place. The entire operation is carried out by a single machine built for this purpose. The special features of this process are:

1. It is high speed, highly automated moulding technology. The machines are rugged and have a batch sequence which is preset injection pressure, time, mould cavity pressure.

2. Virtually all finishing operations are eliminated. Injection of pre-heated rubber in closed moulds ensure complete filling of all mould cavities and reduces injection rates to the minimum.

3. Uniform curing of variable thickness components can be accomplished with reduced cure times.

4. It is generally most efficient on medium-to small sized, high-volume parts using specially rubber compounds. Products are consistently of good quality with high dimensional accuracies.

5. Rubber compounds meant for injection moulding should have good flow characteristics; good tear resistance in heat, should have no tendency to reversion inside the closed mould, and should care as rapidly as possible.

2.37 MOULD SHIRINKAGE

All rubber products exhibit shrinkage after cure, mainly due to the thermal expansion which occurs at vulcanization temperature. Moulded rubber goods are never as big as the moulds in which they are cured. The difference between the dimensions at room temperature of the finished goods and of the mould, expressed as percentage, is called shrinkage from mould dimensions.

$$\text{Percentage moulding shrinkage} = \frac{(\text{dimension of mould}) - (\text{dimension of article})}{(\text{dimension of article})} \times 100$$

The amount of shrinkage depends mainly on the difference between the thermal expansion coefficient of the vulcanizate and mould material at the vulcanization temperature. Shrinkage is affected by factors such as curing temperature and the level of filler in a rubber compound. On cooling to room temperature, a rubber article contracts more than the mould because it has a considerably higher thermal coefficient. As a thumb rule mould shrinkage is about 2%, but this depends on the formulation.

Shrinkage of rubber as it cools down is desirable, for if the rubber and the mould had the same coefficient of expansion, it would be much more difficult to remove vulcanizates from the mould. In multi cavity moulds, the individual cavities may sometimes vary in dimensions and shrinkage, therefore, each cavity must be tested separately for acceptability of dimensions in the mouldings produced.

2.38 MOULD RELEASE AGENTS

Materials, which prevent the sticking of a moulding to the mould, facilitate the removal of the article from the mould and prevent the formation of a crust. They are applied to the mould, not to the rubber.

Silicon emulsions are the most widely used agents. They offer effective release properties and impart smooth shiny surfaces. They are most effective as they have a higher thermal stability so that longer use is possible. The silicone film withstands temperature of 200°C. neutral soaps are also popular. These solutions may be applied by brushing or by means of a spray.

Release agent application should always be minimum; otherwise number of moulding faults will result due to poor knitting of the compound. Presence of silicone and similar materials can be extremely detrimental to rubber to metal bonds and cause subsequent corrosion in some electrical applications.

Release agents may not be needed if lubricants are added to the mix and also moulds are extremely well finished.

2.39 Factors of Moulding

The following are the factors of moulding.

a) **Time:** In view of the high cost of mould and the relatively large consumption of steam and electricity, economy means the shortest possible vulcanization times. Moulding time is directly proportional to thickness of the article and inversely proportional to temperature.

b) **Temperature:** As a thumb rule foe every 10° rise, cure time is reduced by half. Temperature is obtained by using steam or electricity. Steam is easy to control ang gives uniform heating. Its disadvantage is the boiler pressure limitations.

c) **Flow Period:** Choosing the correct flow period is very important. Flow period depends on flow distances, the viscosity of the compound, and the bumping cycle.

d) **Scorch Control:** It plays an important role in moulding time reduction. The scorch time of the compound and the thermal conductivity of the moulds material are important. Aluminium moulds which are better conductors of heat probably give slightly shorter flow periods than steel moulds.

Chapter – 3

METHODOLOGY

3.1 FORMULATION OF MIXING

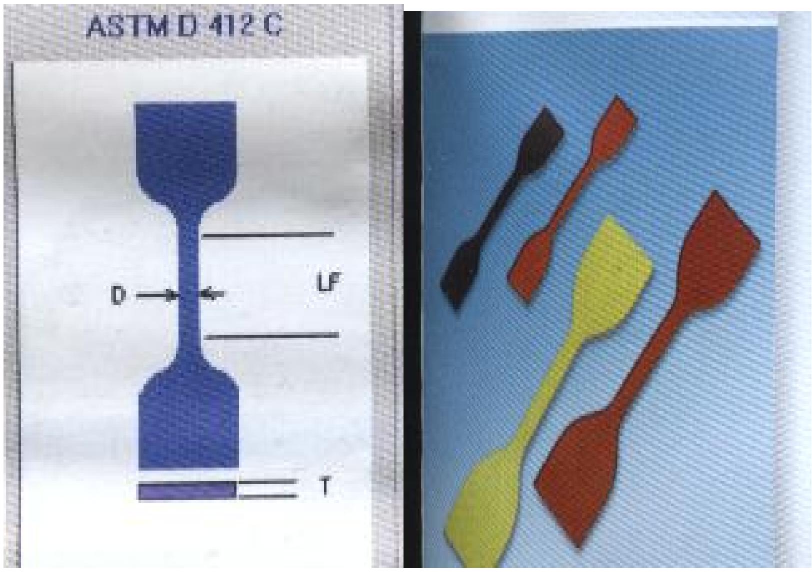
To develop any elastomeric based composite formulation is very necessary. In our case following seven types of formulations were prepared, sensitive balance with three digits accuracy was used for weighing the constituent’s materials.

#	Rubber (pphr)	Carbon (pphr)	C.Fiber (pphr)	G. Fiber (pphr)	Silica (pphr)	Asbestos (pphr)	S. Acid (pphr)	Zn.Oxide (pphr)	Wax (pphr)	PBN (pphr)	MBTS (pphr)	DPG (pphr)	Sulpher (pphr)
EP1	100	30	-	-	-	-	1	5	1	1	1	1	1.5
EP2	100	30	-	12	-	-	1	5	1	1	1	1	1.5
EP3	100	30	12	-	-	-	1	5	1	1	1	1	1.5
EP4	100	-	-	-	30	-	1	5	1	1	1	1	1.5
EP5	100	30	-	-	-	12	1	5	1	1	1	1	1.5
EP6	100	-	12	-	30	-	1	5	1	1	1	1	1.5
EP7	100	-	-	12	30	-	1	5	1	1	1	1	1.5

3.2 SAMPLE PREPARATION

To test the mechanical properties following types of samples were prepared according to ASTM standards.

Tensile Samples:



D=6mm
T= 2mm
LF=25mm

Fig. 3.1 Tensile Samples

Tensile samples were prepared to test the tensile strength, % elongation, elongation at break according to ASTM 412C as shown in above figure.

Hardness Samples:

ASTM= D2240
T=8mm
ϕ=62mm

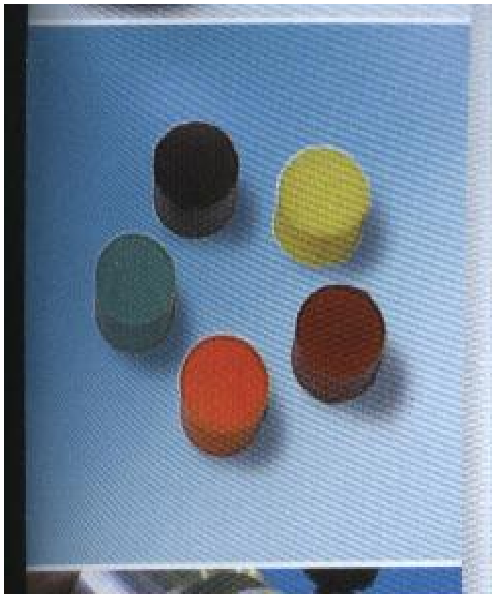


Fig. 3.2 Hardness Samples

Hardness samples were prepared to test the hardness of the ablative composites according to shore A as per ASTM D2240 as shown in above figure.

3.3 Tensile Strength Testing

To test the tensile strength, %elongation, elongation at break Tensor Check Gibitre Instruments (Italy) was used. Results are shown in the next chapter.

Fig. 3.3 Tensile Testing Machine

3.4 Rheological Samples

for the rheological investigation i.e. lowest moony viscosity, highest moony viscosity, tangent delta, curing time, curing behavior, 3 gms of unvulcanized rubber was used in the moving die, Rheo-check by Gibitre Instruments, Italy as shown in fig.

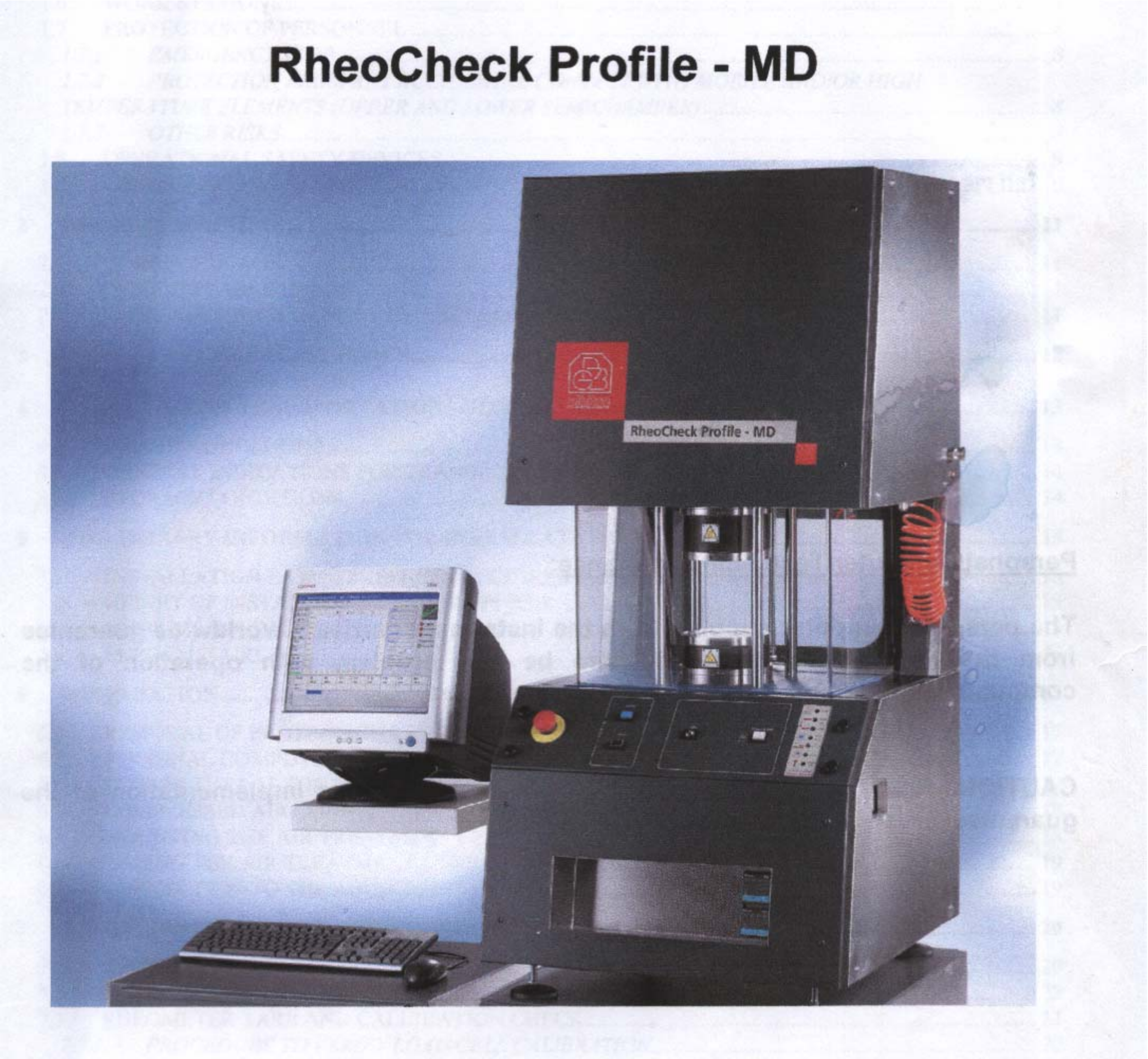


Fig. 3.4 Rheology Profile Equipment

3.5 MIXING

Mixing plays key and basic role in the manufacturing of elastomeric ablative composites. All the characteristics of mechanical properties depend on the proper and accurate mixing. We mixed our materials for 18 to 20 minutes on 2 roll mixing mill. Mixing is carried out due to friction ration (ratio of bigger roll dia to small roll dia). Proper water channels are provided to the rollers so the mixing temperature may not exceed 100 °C.

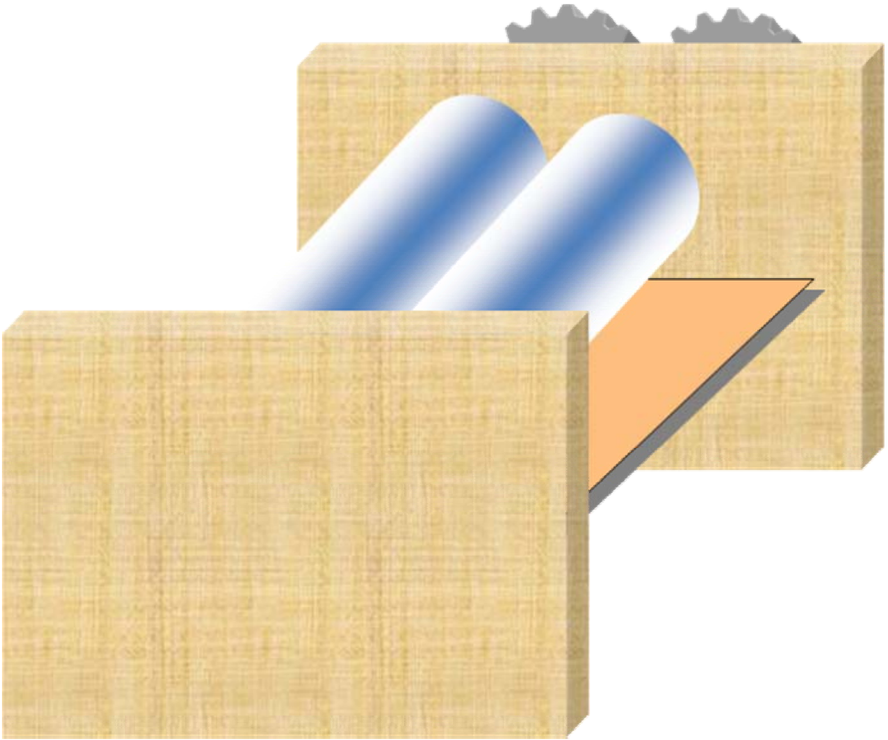


Fig. 3.5 Two Roll Mixing Machine

3.6 Vulcanization

Vulcanization is the final step in the manufacturing of elastomeric composites. Hydraulic presses, 50 Ton capacity (Shinto, Japan) were used to manufacture the samples which were heated electrically, 15 MPa pressure for 20 minutes applied to the moulds which were used for the samples between the two plates of the press as shown in figure below.

Fig. 3.6 Pneumatic Press for Vulcanization

Chapter – 4

RESULTS & DISCUSSION

4.1 Results

Results of experiments and mechanical testing like Tensile Strength, Hardness and Rheology are shown below.

4.2 FIGURES & TABLES

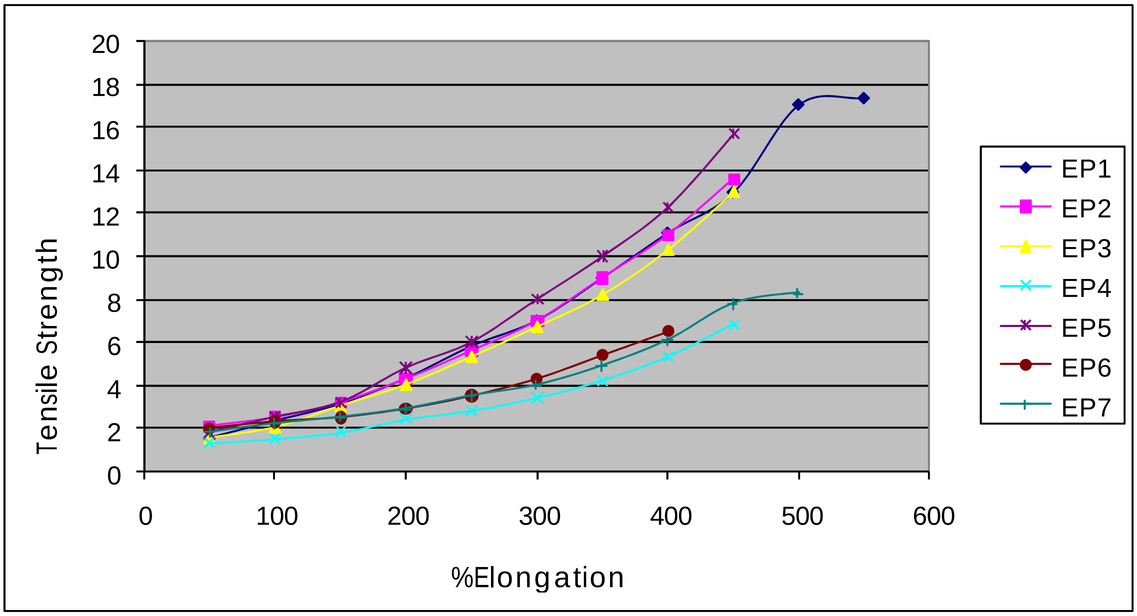


Fig-1 Tensor Check (speed 20mm/min)

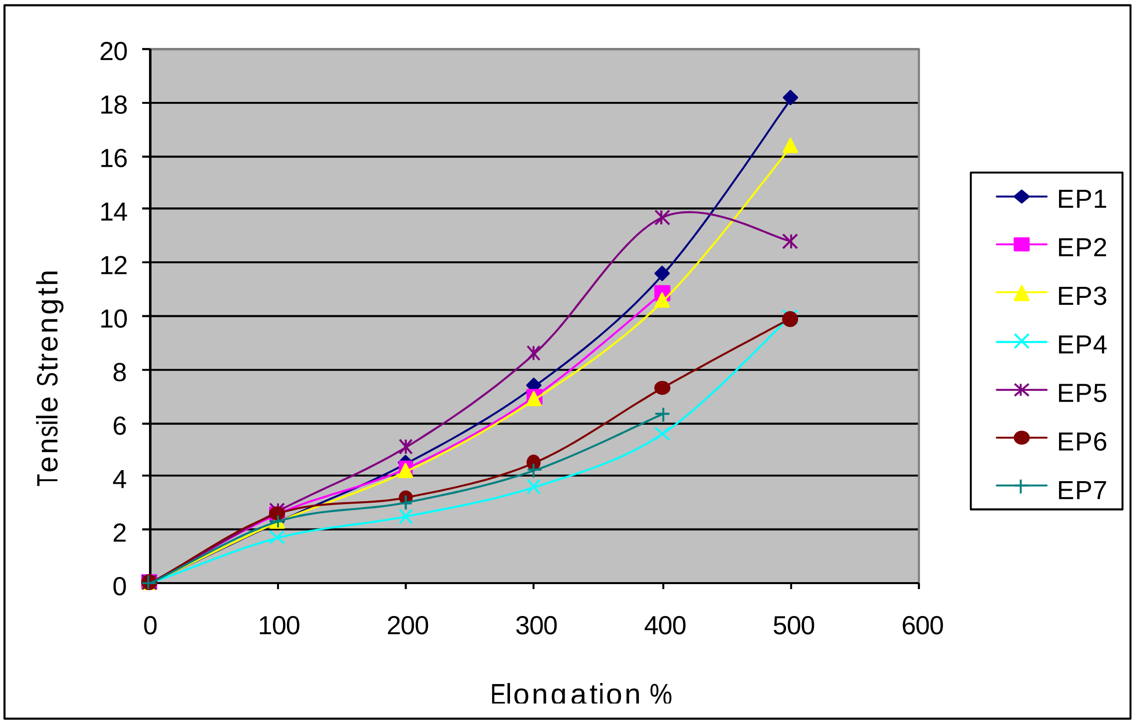


Fig-2. Tensor Check (speed 200mm/min)

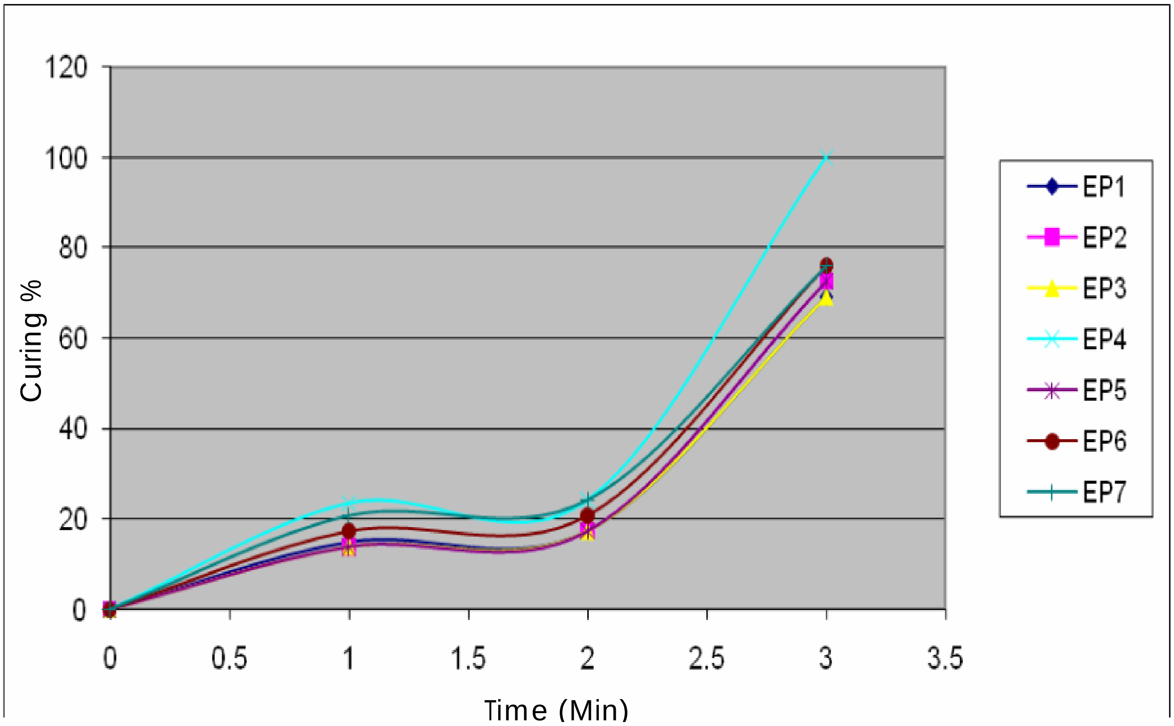


Fig-3. Curing Characteristics vs Time

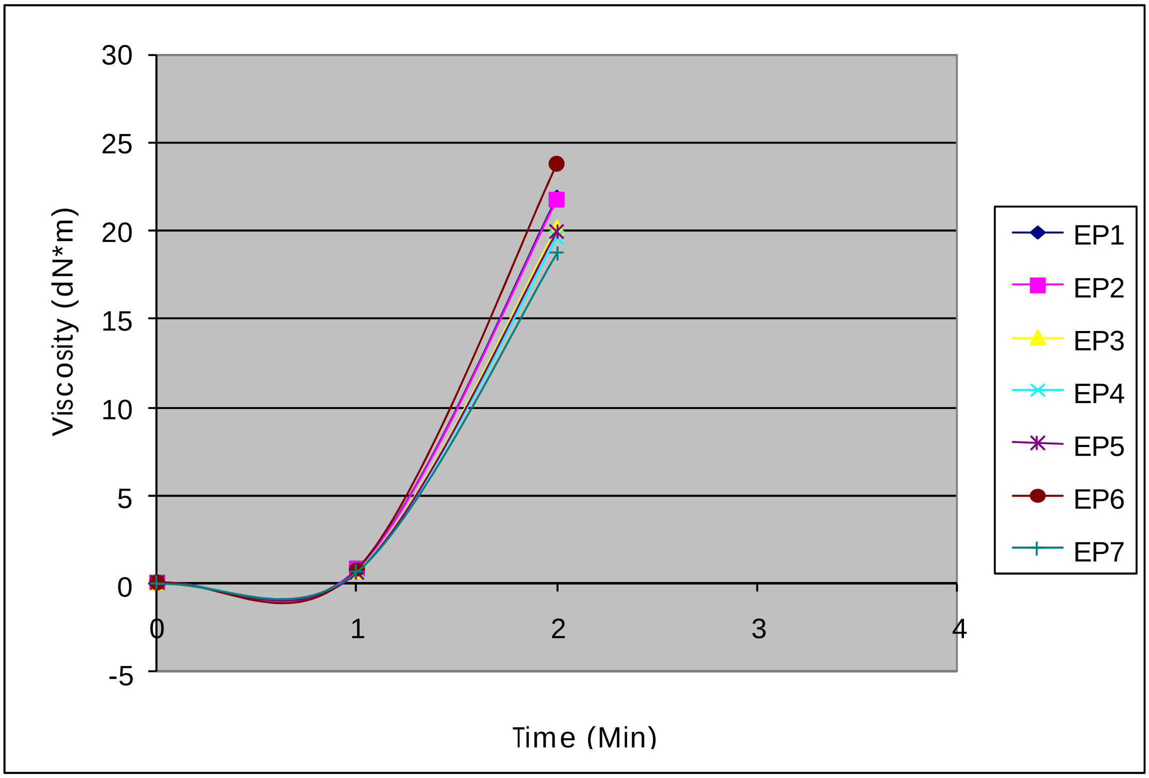


Fig-4. Viscosity Variation VS Curing Time

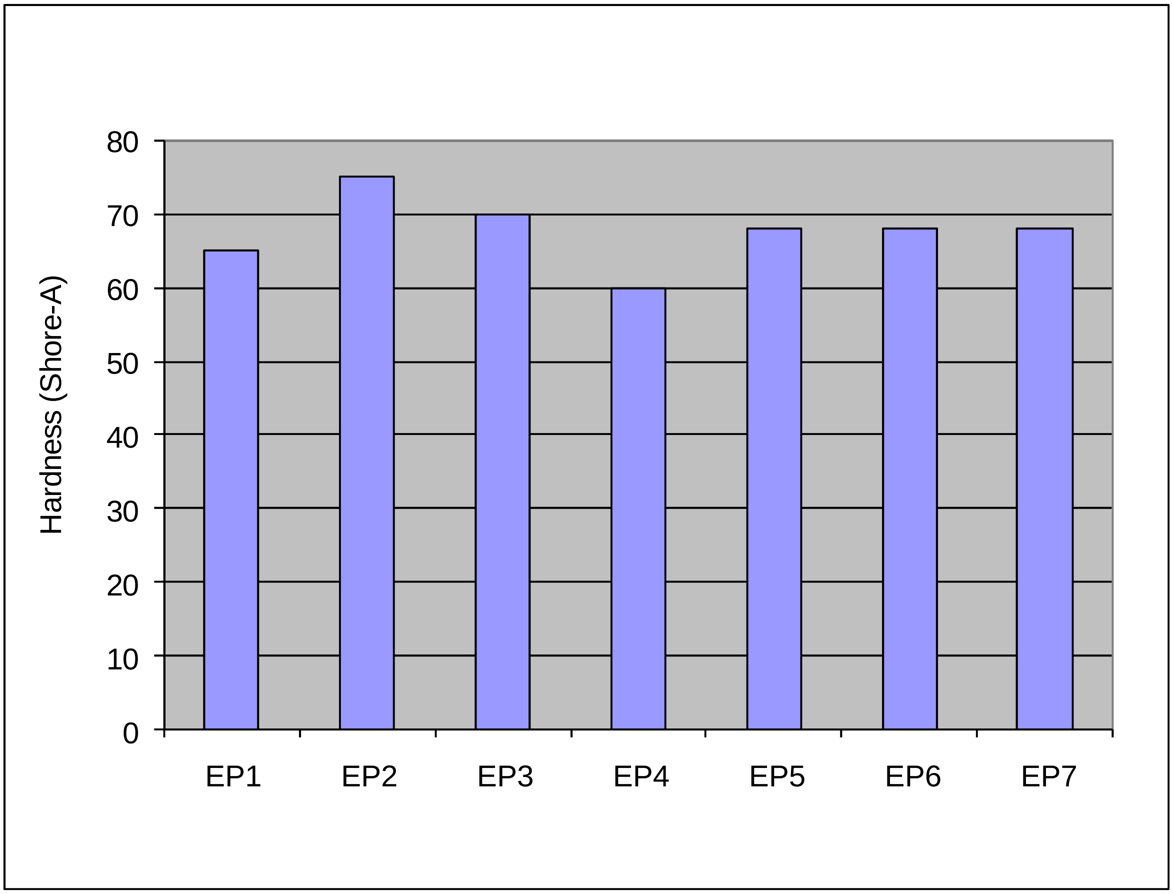


Fig-5. Hardness

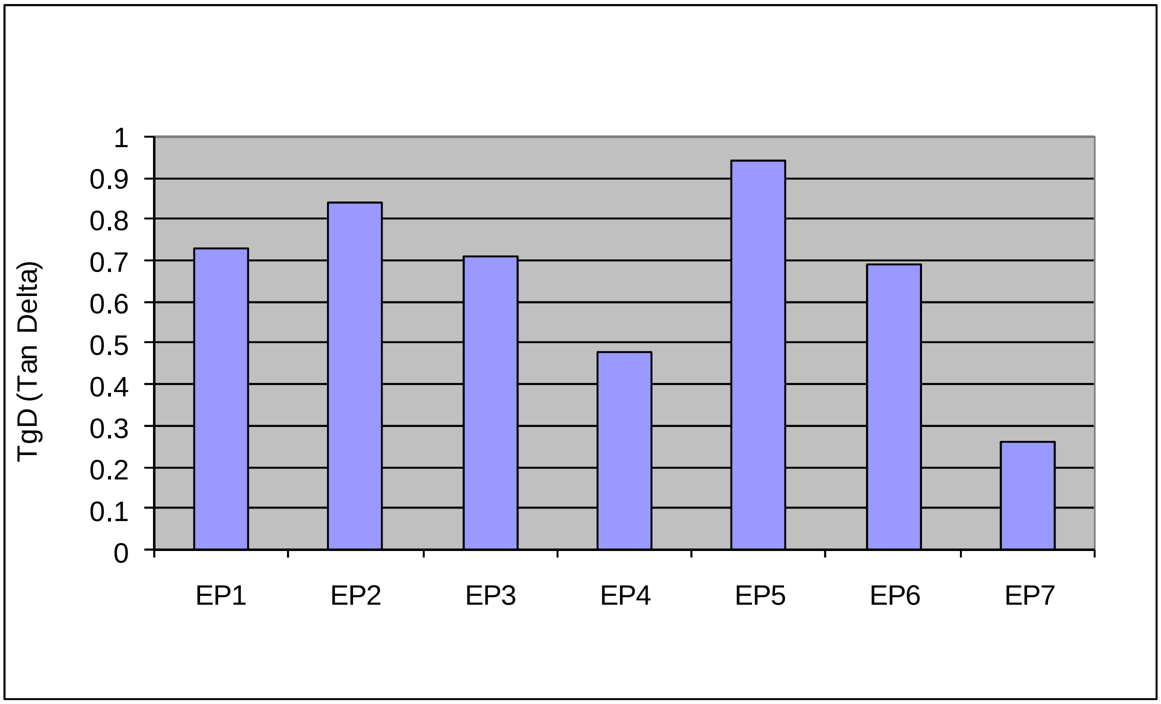


Fig-6. TgD (Delta)

DISCUSSION

In the process of formulation, Rheological Investigation and testing of mechanical properties of elastomeric ablative composites, it was observed that mechanical properties of ablative composites vary with the nature of fillers.

In case of tensile strength and % elongation, tests were carried out at different rates i.e 20mm/min and 200mm/min. Due to viscoelastic nature of the composites tensile strength of the samples containing re-inforcing fillers like carbon, silica and the combination C+carbon fiber and Silica+carbon fiber increased by increasing the test rate. While in case of non-reinforcing fillers like asbestos powder and glass fiber the tensile strength deceases on the increase of test speed, showing the low interfacial cohesion with the base polymer i.e EPDM and decrease in the viscolelastic nature of the composite, EP1 containing carbon as reinforcing filler showed the maximum tensile strength and % elongation but in case of EP5 containing asbestos powder as non re-inforcing filler showed the least tensile strength and % elongation. Comparing the mechanical testing at high and low rates between various specimens, normally a larger increase in the slope of stress-strain curve is expected. However since the EPDM matrix used in this study is highly cross-linked, therefore it shows a marginal creep.

All formulations showed the same behaviour during curing study by the Rheo-Check except EP4 containing silica. It is due to the reason that surface area of nano- sized particles of the silica which receive heat more quickly/efficiently thus fastening the curing speed.

Viscosity variation tests showed the lowest moony viscosity of all the samples in the same fashion because in the early stage reactions among the constituents of the composites are happening and large amount of heat is produced, the whole sample is converted into jelly like substance, so it exhibits lowest viscosity. This stage is very significant for the best curing of the elastomeric composites as all the ingredients move easily in the mould and permanent cross-linking of the composite take place, so the best product is formed through compression moulding. Thereafter cross-linking takes over the thermal aspect and the viscosity is primarily controlled by the polymer network formation (cross-linking) in a manner typical of exponential behaviour of viscosity curve.

So for as the as the hardness concerned EP2 containing carbon only has highest hardness and EP4 containing silica has lowest hardness depending upon the rigidity of the the fillers.

Tangent Delta which is ratio of the loss modulus to the storage modulus of the material is very important in the manufacturing of composites. In our case EP5 comprising of asbestos powder has highest tangent delta value due to less cohesion with base polymer and in EP7 the combination silica and glass showed the lowest TgD value representing the compatibility and cohesion with the base material-EPDM

4.4 CONCLUSION

Mechanical testing and Rheological investigations reveals that filler-matrix interaction are some of the salient features that plays an important role in the mechanical properties evaluations, curing characteristics, viscous behavior and tensile strength. By knowing characteristics of fillers (heat sinks) we can achieve the best mechanical properties of ablative materials.

The effect of heat sinks on the mechanical properties (hardness, elongation at break, tensile strength) at various speeds are shown in Fig. 1 and 2. Hardness increased gradually by adding glass fiber and carbon fiber along with carbon. It was affected in the same fashion by adding silica with glass fiber and carbon fiber.

Tensile strength and elongation at break at 20mm/min and 200mm/min were decreased gradually by adding carbon fiber and glass fiber along with carbon. But there is a drastic decrease in these properties by introducing glass fiber and carbon fiber along with silica because of their interfacial and cohesive attractions. Formulation having silica has lowest mechanical properties while mixture of carbon + asbestos has the highest at both rates of testing.

Rheological studies shown in Fig. 3, 4 and 6 revealed that loss modulus is low in silica + glass fiber while it is high in carbon + asbestos. Curing rate is high in EP4 while it is low in EP5. At the end we can conclude that

1. By the addition of non reinforcing fillers / heat sinks like asbestos powder, glass fiber, mechanical properties are not too good.
2. By the addition semi reinforcing fillers like carbon fiber mechanical properties are at the medium level.
3. By the addition of reinforcing fillers like carbon, silica and the combination of these with carbon fiber shows the best mechanical properties of the EPDM based ablative composites.

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