STUDIES ON RUBBER COMPOSITIONS AS PASSIVE ACOUSTIC MATERIALS IN UNDERWATER ELECTRO ACOUSTIC TRANSDUCER TECHNOLOGY AND THEIR AGING CHARACTERISTICS

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CERTIFICATE

This is to certify that this thesis entitled ***"Studies on rubber compositions as passive acoustic materials in underwater electro acoustic transducer technology and their aging characteristics"*** *is a report of the original work carried out by Shri. Velayudhan Blalakrishna Pillai. in Naval Physical and Oceanographic Laboratory, Kochi. No part of this work reported in this thesis has been presented for any other degree from any other institution.*

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DECLARATION

*I hereby declare that thesis entitled "****Studies on Rubber Compositions as Passive Acoustic Materials in Underwater Electro Acoustic Transducer Technology and their Aging Characteristics****" is the original work carried out by me under the supervision of Dr. J. Narayana Das, Scientist G, Naval physical and oceanographic laboratory, Kochi 682021, and no part of this thesis has been presented for any other degree from any other institution*

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Velayudhan Balakrishna Pillai

Preface

Rubber has become an indispensable material in Ocean technology. Rubber components play critical roles such as sealing, damping, environmental protection, electrical insulation etc. in most under water engineering applications. Technology driven innovations in electro acoustic transducers and other sophisticated end uses have enabled quantum jump in the quality and reliability of rubber components. Under water electro acoustic transducers use rubbers as a critical material in their construction. Work in this field has lead to highly reliable and high performance materials which has enhanced service life of transducers to the extent of 10-15 years. Present work concentrates on these materials. Conventional rubbers are inadequate to meet many of the stringent functional of the requirements. There exists large gap of information in the rubber technology of under water rubbers, particularly in the context of under water electro acoustic transducers. Present study is towards filling up the gaps of information in this crucial area.

The research work has been in the area of compounding and characterisation of rubbers for use in under water electro acoustic transducers. The study also covers specific material system such as encapsulation material, baffle material, seal material, etc. Life prediction techniques of under water rubbers in general has been established with reference to more than one functional property.

This thesis is divided into 6 chapters.

Chapter 1 presents a review of under water engineering rubbers with particular reference to rubbers used in electro acoustic for electro acoustic transducers.

Chapter 2 deals with theoretical studies on rubber compounding, compounding materials and their characterisation techniques.

Chapter 3 covers the experimental studies on diverse parameters affecting water intake through diffusion and permeation mechanism. This also deals with specific material system for encapsulation, baffles, seals etc.

Chapter 4 presents theoretical investigation on aging and life prediction techniques as well as investigation on Viscoelastic parameters of under water rubbers.

Chapter 5 gives a consolidation of experimental results and the observations are discussed for better understanding of the underlying phenomena emerging out of theoretical and experimental works covered in Chapters 3 and 4.

Chapter 6 presents important conclusions arrived at as a result of the research work.

CONTENTS

Chapter 1

INTRODUCTION

The use of rubber in engineering applications dates back to mid nineteenth century. In 1850 rubber springs were used for dray wagons. A more spectacular application is the use of 12 mm thick rubber blocks in 1889 to support a railway viaduct in Melbourne. Today the original Natural Rubber (NR) parts are still functioning. Innovations driven by technological requirements and environmental protection issues have led to several strides in rubber technology. Some of the most striking examples of such innovations relate to applications in offshore engineering and underwater acoustic systems. Offshore oil platform design has transformed from rigid towers of steel and concrete to compliant structures capable of deep-water oil production. Elastomeric flex joints form an intrinsic part of the structural design. The ride comfort and safety of modern passenger vehicles, trucks etc. depend on advanced suspension systems, which often use a large number of rubber components. Modern aircrafts, helicopters and the space shuttles use engineered rubber components for key functions, where the failure may be catastrophic. Ocean environment is extremely aggressive in terms of marine corrosion, salt laden atmosphere, waves, tides, ocean currents, temperature variations, pressure variations etc. Particular merit of rubber is its ability to function in such aggressive environments for long years. A unique feature of rubber is very low shear modulus which is more than a thousand times lower than its bulk modulus and its ability to deform elastically several hundred percent. A wide range of engineering applications has been developed on the basis of these properties. Rubber components capable of very different stiffness in different directions have been designed. In structural engineering they find applications such as bridge bearings, compliant foundation against seismic disturbance, offshore mooring system assemblies where flexible connections are provided by rubber flex joints etc. Rubber plays crucial roles in underwater acoustic systems, such as acoustic windows, acoustic baffles encapsulation materials, shock and vibration absorbers. Rubber components are extensively used as seals, energy absorbers, environmental protection materials, electrical insulation etc in most underwater engineering applications. The range of versatile applications has been possible due to the large scope for tailor making of properties in rubber compounds.

1.1 Rubbers in underwater Engineering

1.1.1 General considerations

Rubbers are used in a verity of components and devices starting from rubber seals, to sonar dome baffles. Performance requirements are specific to each component. For example, for a deepwater seal retention of sealing efficiency demands compression stress relaxation to be minimum. On the other hand for anti vibration applications damping behaviour is paramount. For rubbers used in acoustic applications, wave propagation characteristics assume greater significance. Rubbers employed for encapsulating electro acoustic transducers must have both electrical and acoustic properties as desired. However, in all underwater applications, the interaction of rubber with the water medium, determines the reliability and service life. Reliability is always the over riding priority.

1.1.2 Mechanical Properties

Mechanical properties of rubbers are unique. Stresses, for example are dependent on time and temperature and non linear with strain. Rubbers also have unique Poisson's ratio, frictional properties, Gough-Joule effect, and very high -energy storage. Hysteresis is high.

Rubber and rubber products are tested for initial and continued performance of the unique functions that are enabled by their viscoelastic properties.

Static or low deformation tests for the common stress -strain properties of modulus, tensile strength and elongation are usually made only for quality control since rubber products are seldom elongated in service. Low rate tests for creep, stress relaxation, and set, reflect the limitation of service because time dependent properties are peculiar for rubbers because of the time dependent properties are peculiar to rubbers. Examples are anti vibration mounts, seals and gaskets. The amount of static deformations also affects such other properties permeability, electrical properties, and low temperature behavior. Flexibility is important in coatings, encapsulation materials, acoustic baffles transducer mountings etc. Hardness is a function of modulus.

Elastomers are usually deformed dynamically in service. Deformation is thus resisted by elastic and damping forces. The principal purpose of dynamic mechanical tests is to evaluate these forces and attendant loss of energy.

Physical testing of rubber often involves application of a force to a specimen and measurement of the resultant deformations. Two common modes are tensile and shear. Concept of stress and strain is used to denote the results. Stress is the force per unit cross sectional area i.e., F/A Strain is the deformation per unit original length ($\Delta L/L_o$) in tensile tests or deformation per unit distance between contacting surfaces (S/D) in shear tests. Stress is expressed as Pascal (Pa). Strain is often expressed as a percentage rather than a ratio. The term extension ratio is the length at a given point in the test sample divided by its original length Young's modulus E is given by

$$E = \frac{F / A}{\Delta L / L_O} \qquad 1.1$$

Same equation applies when a bar is decreased in length by a compressive force. The rigidity or shear modulus G is defined as the ratio of shearing stress to shearing strain:

$$G = \frac{F/A}{S/D} \qquad 1.2$$

A third type of modulus is the bulk modulus B. It is defined as the ratio of hydrostatic pressure to volume strain.

$$B = \frac{\text{Hydrostatic Pressure}}{\text{Vol. change/unit Volume}}$$

When a material is stretched its cross sectional dimensions decrease Poisson's ratio v is the constant relating these change in dimensions;

$$v = \frac{\text{Change in width per unit of width}}{\text{change in length per unit of length}}$$

The stress-strain test in strain is the most widely used test in rubber industry. Among the purpose of the tests are to determine effects of liquid immersion on aging, to ensure that all compounding ingredients have been added in proportions, to determine rate of cure and for optimum cure for experimental compounds. Standard methods for tensile testing of vulcanized rubbers are given in ASTM-D-412

1.1.3 Electrical Properties

Underwater electro acoustic transducer as the name implies are electrical devices, often handling heavy power in kilowatt ranges. Rubber components used in their construction such as encapsulation, cable chains, connectors etc should have adequate electrical insulation characteristics. Permanence of. insulating capacity under long water submergence conditions is an essential requirement. In rubbers electrical insulation behaviour is largely a function of compounding ingredients and their distribution within rubber itself. Design of the material must cater for high and stable electrical resistivity. Effect of different types of carbon black and their quantity needs to be known for designing rubbers with optimum electrical behavior

1.1.4 Viscoelastic Properties

Rubber molecules are characterised by long chains with a coiled morphology in an unstrained condition. When stressed, these coils unfurl and give rise to large strains before rupture. Within elastic limits the molecular chains retract to at equilibrium once external load is removed. In the case of an ideally elastic material the strain goes to zero. An ideal linear elastic solid obeys Hooks law: which can be written in the form

$$F = kx \qquad (1.3)$$

Where F is force, x is deformation and k is the spring constant.

On the other hand, in a purely viscous material, the molecules rearrange in the new geometry permanently. An ideal viscous liquid obeys Newton's law: stress is proportional to rate of change of strain with time.

Newton's law may be written in the form:

$$\tau = \eta_c (d\gamma/dt) \qquad (1.4)$$

η_c is a viscous damping coefficient and $d\gamma/dt$ is the shear strain rate. The laws above may be written alternatively as

$$\sigma = G\varepsilon \qquad (1.5)$$

for an elastic solid and

$$\sigma = \eta_e(d\varepsilon/dt) \qquad (1.6)$$

for a Newtonian fluid.

where σ is shear stress, ε is strain, G is the modulus and η_e is the Newtonian viscosity. Behaviour of rubber is a combination of such ideal elastic solid and a purely viscous fluid.

This behaviour can be represented as

$$\sigma = G\varepsilon + \eta_e(d\varepsilon/dt) \tag{1.7}$$

This combination viscous and elastic behavior makes rubbers viscoelastic materials. Viscous properties are desired in rubbers for shock absorption and acoustic damping. Many practical problems like stress relaxation creep, compression set etc are manifestations of viscous properties.

Underwater acoustic transducers are typical dynamic devices operating over a wide frequency band and temperature range. Since acoustic wave imposes periodic stress in material mechanical properties becomes a function of exciting wave. The term dynamic mechanical properties refer to the behaviour of materials when subjected to stresses and strains that change with time. Traditionally viscoelastic behaviour has been described by means of Maxwell and Voigt elements (Fig.1.1and Fig.1.2)

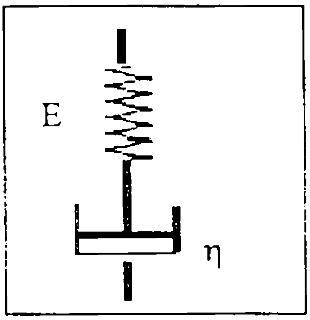

Fig.1.1 Picture presentation of Maxwell model

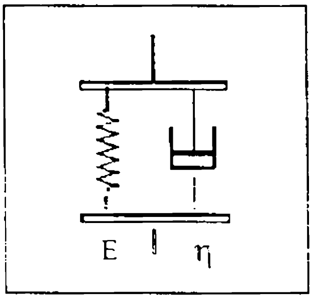

Fig.1.2.Picture presentation Voigt model

Most materials exhibit behaviour that is more complex than either of these two simple models.

The Voigt element in terms of stress and strain is written as (Eqn.1.7)

A sinusoid ally varying strain can be expressed as

$$G = \varepsilon_o \sin\omega t \tag{1.8}$$

Introducing the complex notations,

$$G= \varepsilon_o \exp(i\omega t) = \varepsilon_o(\cos \omega t + i \sin\omega t) \qquad (1.9)$$

where $i = (-1)^{1/2}$

Rate of change of strain with time is given by

$$d\varepsilon/dt = i\omega\, \varepsilon_o \exp(i\omega t) = i\omega\varepsilon \qquad (1.10)$$

Substituting in the equation, we get,

$$\sigma = (G+ i\omega\eta)\, \varepsilon \qquad (1.11)$$

The term in parenthesis represents modulus because it is a ratio of a stress to strain. It is denoted by the complex dynamic modulus G.* Denoting G_1 is the real part of the complex number. Likewise, $\omega\eta$ is defined as the imaginary dynamic modulus given by symbol G_2.

Thus these terms are rewritten as follows :

$$\sigma=(G_1+i\, G_2)\, \varepsilon =G^*\varepsilon \qquad (1.12)$$

Eqn. 1.12 defines real, imaginary and complex modulii. Absolute value of complex modulus is given by the ratio of stress amplitude σ_0, to strain amplitude ε_o.

Thus, $G^* = \sigma_0/ \varepsilon_o = (G_1^2 +G_2^2)^{1/2} = G_1[1+ (\tan \delta)^2]^{1/2}$ (1.13)

Where $\tan \delta$ is the ratio G_2/G_1.

A typical dynamic mechanical evaluation involves applying a sinusoidal stress or strain to sample and measuring the resulting strain or stress. Because of the energy dissipation in material the stress and strain will not be in phase. The lag between the two is monitored and calibrated to yield elastic and viscous components of the complex modulus. The complex elastic modulus will have two components

As shown in Eqn.1.13, we have

$$G^* = G' + i\, G'' \qquad (1.14)$$

Real part of the complex modulus denotes the energy stored in the material due to its elastic nature, whereas the imaginary part corresponds to the energy lost due to viscous behaviour. Ratio of the two components is the mechanical loss factor of the material

$$\tan \delta = G''/G' \qquad (1.15)$$

δ is the angle by which the strain lags behind the stress in such cases. Polymers are characterized by wide variation of stiffness and damping properties with frequency and temperature. Thus it is imperative that they must be optimized for specific dynamic mechanical behaviour within the operating band. Selecting a rubber for a particular application requires an accurate knowledge of its dynamic mechanical properties.

Like other functional behaviour, acoustic behaviour also undergoes drastic change around glass transition zone, in polymer. Glass transition in amorphous polymer materials marks the onset of cooperative thermal motions of individual chain segments, involving large scale conformational rearrangements of the chain backbone. Below the glass transition large scale motion becomes frozen. Major changes in physical properties, including acoustic properties, take place at the glass transition. According to the free volume theory [1] the total macroscopic volume of a polymer is considered to be the sum of the actual volume of the polymer chains (the occupied volume) and the holes or voids that constitute the free volume. Glass transition occurs when there is enough free volume for large scale molecular motions associated with the transition to take place. It is assumed that the occupied volume increases linearly with temperature throughout but free volume undergoes a discontinuous increase in expansion coefficient at the glass transition when the number of holes increases. A number of factors have been shown to influence glass transition temperature(Tg), such as backbone flexibility, steric effects, polarity, pendent groups, crystallinity, presence of plasticizers, cross link density etc.

Table1.1Glass transition temperatures of some common rubbers

Rubber	Formula	Tg (°C)
Natural Rubber	$-CH_2-C(CH3)=CH-CH2-$	-72
Polychloroprene	$-CH_2-C(Cl)=CH-CH_2-$	-50
Styrene butadiene Rubber	$[-CH_2-CH=CH-CH_2-CH_2=CH(C_6H_5)]$	-65
Butyl Rubber	$-(CH_3)_2 C-CH_2.CH_2-CCH_3=CH-CH_2-$	-70
Nitrile rubber	$[-CH_2-CH=CH-CH_2-CH_2-CN]$	-20
Poly *cis*-1,4-Butadiene	$[-CH_2-CH=CH-CH_2]-$	-108
Polydimethyl Siloxane	$(CH_3)Si-O-Si(CH_3)- O-$	-123

The table illustrates the effect of some of the factors that influence the glass transition. Poly dimethyl siloxane has the lowest Tg because of two flexible backbone components. Comparing Poly butadiene with Natural Rubber, it is seen that substitution of a methyl group for a hydrogen atom raises Tg as a result of the steric hindrance caused by the larger size of the methyl group. Steric effects are important because glass transition requires certain free volume to be available. Comparing natural rubber with Polychloroprene the methyl group is comparable in size to chlorine atom but the Tg of neoprene is higher because of the greater polarity of the chlorine atom. Polarity increases inter chain attraction, which decreases free volume and hence raises Tg. In SBR copolymer large pendent phenyl group in styrene is effective in raising Tg of copolymer to -65°C though Tg of poly butadiene itself is -108°C. Other factors influencing the glass transition are, cross link density, Co-polymerization and additives such as fillers and plasticizers.

The linear viscoelastic properties of polymers are both time and temperature dependent. For underwater transducer applications visoelastic properties of interest is spread over several decades of frequency. Experimental estimation of viscoelastic properties over bands of frequencies can be achieved by use of time temperature super position technique. This technique is based on an empirical relationship between the time and temperature dependent properties of viscoelastic materials. The relaxation process of a polymer at a particular temperature will be enhanced at elevated temperature i.e. the relaxation time will be shorter at any higher temperature. In essence, the time- temperature superposition principle assumes that by changing the temperature the complete relaxation spectrum is affected to the same degree. Hence increasing temperature shortens all relaxation times by the same factor. In the actual experiment the temperature is held constant, the frequency and time is varied. By repeating the experiment at different temperature a set of isothermal dependencies of E′ or E″ on frequency, ω can be obtained. Any of the viscoelastic parameters can be shifted along the time/ frequency axis such that they are superposed on one another to generate a master curve at a particular temperature.

According to amount of shift of a frequency scan that is associated with a particular temperature will be different from that of a frequency scan associated with any other temperature [2-7]. Therefore for every temperature, there is a characteristic shift-factor. The William-Landel-Ferry (WLF) equation [2,8]

1.1.5 Underwater properties

Diffusivity of water in rubber, presents a picture much different from that of other liquids. Absorbed water affect physical, mechanical and electrical properties of rubbers. Rubber compounds contain varying quantities of water-soluble ingredients that act as sinks which absorb water as it diffuses through the rubber phase. The process is diffusion controlled. Diffusion of water through rubber is an important consideration in underwater application [9,10,11]. A number of theoretical treatments have appeared in the literature on the problem of estimating diffusion coefficient from absorption data [12-14]. Tester [15] derived an equation from the consideration of an osmotic mechanism to represent absorption for vulcanised rubber immersed in water. The relationship was tested on a vulcanised rubber and the results are in good agreement with theory in the absence of air. Deviations found in the presence of air were explained to be caused by aging resulting from oxygen dissolved in water. Accelerated aging was shown to be responsible for the marked increase of the rate of absorption. Aminabhavi et al [16] suggested simple ways by which diffusivity could be determined from water absorption experiments. They estimated activation energy of diffusion processes in CR, SBR and EPDM rubber. Their study showed lower diffusion coefficient for all materials in salt water as compared to distilled water though solubility coefficient(s) and permeability (p) are higher. Amerongen [17] reviewed diffusion of matter in rubbers. The survey covered the fundamental background, including mathematical models required to understand experimental approach to diffusion, and for interpretation of measurements. The subjects discussed include diffusion, solubility and permeation of organic liquids, water and solids such as sulphur and other compounding ingredient in and through rubber. Paper also discusses temperature dependence of diffusion; effects of modification of the rubber vulcanisation, crystallisation etc which are of great relevance in the present study.

Theoretical aspects of diffusion have been well studied since Ficks [18] laid foundation in 1855. Solution to the diffusion equation has been obtained for simple geometric shapes (cubes, rod, sheet etc)[12-14]. Mathematical solution based on the semi- infinite medium has been found to be adequate for many situations [19]. In this case it is assumed that the liquid extends to infinity on one side of the interface and that rubber extends on the other side. In a sheet of finite thickness diffusion behavior is the same as this until the liquid reaches the centre of the sheet. When a plane polymer sheet is exposed to fluid, the changes in concentration (C) of the diffusing substance as a function of time (t) and position (x) is given by Fick's second law.

$$\frac{\partial c}{dt} = D\left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{dz^2}\right] \qquad (1.16)$$

where 'D' is the diffusion coefficient. If the material has a uniform initial diffusion concentration (C_0) and the surface is kept at a constant concentration (C), the solution [12-14] of Eqn.1.1 is

$$C\text{-}C_0/C_\infty\text{-}C_0 = 1 - 4/\pi \sum_{n=0}^{\infty} [(-1)^n / (2n+1)]$$

$$\times \exp[-D(2n+1)^2 \pi^2 t/h^2] \cos(2n+1)\pi x/h \qquad (1.17)$$

where 'n' is an integer from 0 to ∞. The total amount of substance diffusing into the polymeric material (Mt) as a function of time is given by the integral of the Eqn. 1.17 across the thickness (h):

$$M_t / M_\infty = 1 - 8/\pi^2 \sum_{n=0}^{\infty} 1/(2n+1)^2 \exp[-(2n+1)^2 \pi^2 Dt]/h^2 \qquad (1.18)$$

where M_∞ is the equilibrium value of the diffusing substance at infinite time and is estimated from the diffusion plots by extrapolation. The diffusion process will show an initial linear increase and then asymptotic saturation associated with plasticization effects.

For long times, Eqn.1.18 may be approximated by

$$M_t/M_\infty = 1 - 8/n^2 \exp[-(\pi^2 Dt]/h^2] \qquad (1.19)$$

and the approximation for short time is:

$$Mt/M_\infty = 4/h[Dt/\pi]^{1/2} \qquad (1.20)$$

Eqn.(1.20) is a valid representation of the time dependence of the water uptake.

It follows from Eqn.1.20 that $D = \pi[h/4M_\infty]^2 [Mt/t^{1/2}]^2$

When diffusion proceeds, the boundary between swollen and unswollen matrix advances with a rate 'P'. P is related to the diffusion coefficient 'D', by the relation [20]

$$P = \sqrt{(4D/\pi} \qquad (1.21)$$

Eqn.1.20 implies that swollen boundary movement is proportional to square root of time.

Diffusion of water in rubber is complex due to hydrophilic impurities present in rubber [20,21]. Several workers [22-24] studied the osmotic effects in water absorption. Fedors [22] described the absorption of liquids by polymers which contain liquid soluble inclusions. It was shown that the equilibrium uptake of water can be calculated if several properties of the inclusion such as solubility as well as modulus of the polymer were known. Muniandy and Thomas [21] tested the hypothesis that hydrophilic impurities cause rubber vulcanisates to absorb high amount of water than pure hydro carbon rubbers and time to reach equilibrium absorption in such cases is very high. They carried out experiments on model compounds incorporating known amount of sodium chloride in a pure rubber. Based on the results they developed a theory to explain the amount and rate of water absorption in rubber vulcanizates. Hydrophilic impurities may originate from natural sources in natural rubber and from emulsifying agents and catalysts in the synthetic rubbers. Water diffuses through rubber phase in which it is only slightly soluble and collects around the hydrophilic impurities forming droplets of solution. The droplets of solution will exert osmotic pressure on the rubber, which acts as semi permeable membrane. Resulting elastic stress in the rubber, arising from enlargement of the cavity containing the impurity will resist dilation. When elastic forces are sufficient to balance the osmotic pressure no further enlargement of the droplet will occur. The equilibrium condition is given by

$$\pi_0 = \pi_1 - p_r \qquad (1.22)$$

where π_0 is the osmotic pressure of the external solution in which the rubber is immersed π_1 is the osmotic pressure of the droplet solution and p_r is the elastic pressure exerted on the droplet by rubber.

Classically the osmotic pressure is given by

$$\pi = CRT/M \tag{1.23}$$

where C is the concentration of the solute of molecular weight M. R is the gas constant, T the temperature.

Elastic pressure p_r, exerted on the spherical cavity in an infinite block of rubber is given is given by

$$p_r = E/6[5\text{-}4/\lambda\text{-}1/\lambda^4] \tag{1.24}$$

Where E is the Young's modulus of the rubber and λ is the extension ratio of the rubber at the surface of the cavity.

$$\pi_0\text{-}\pi_1 = E/6[5\text{-}4/\lambda\text{-}1/\lambda^4] \tag{1.25}$$

Impurities act like sinks of water, producing pockets of higher concentration within the rubber matrix which will reduce the rate of diffusion.

The study of water permeation through elastomers has attracted much attention owing to its wide technical applications [13]. The aim of such studies has been to collect information to the packaging industry, to develop liquid - liquid separation processes or to study diffusion mechanisms and morphology of polymer membranes. Water permeation through elastomers and plastics have been comprehensively reviewed by Cassidy and Aminabhavi [25]. They summarized the available data for the period from1968 to1982 on, diffusivity, solubility and permeability of water and water vapour into and through elastomers and plastics. Kosyanon and McGregor [26] analysed diffusion data from literature and found that the diffusion coefficient of gases in elastomers can be accounted for by the WLF equation [8]. Parameter $K=B_d/B_f$ of Frisch and Rogers [27] is used as a correction factor. K and log (D_g) are shown to vary with the penetrant. From the values of K and log D_g of the gases their diffusion coefficient in any elastomers of known T_g could be estimated. From Arrhenius equation and the WLF relationships, an equation is derived to predict the activation energy of diffusion directly from temperature at which diffusion is taking place, T_g of the polymer, value of K and universal constants A and B. Cassidy [28] and others have studied several elastomers such as neoprene, styrene butadiene rubber, nitrile rubber and their binary composites for fresh water and salt water permeation. Diffusivity data have also been collected on a few elastomers. Arrhenius activation parameters for the transport processes involved in the experiments have been estimated at 3 temperatures. Cassidy and Aminabhavi [29] in another work studied permeability of SBR/EPDM single and binary laminates for directional flow behaviour of distilled water and salt water. Result of the study supported activated transport mechanism. Under activated transport mechanism temperature increase causes water absorption rate to increase. For all elastomers, salt water exhibited higher permeation rates than did distilled water. Distilled water showed greater directional behaviour compared to salt water. In most cases it was found that diffusion coefficient D decreases as the total concentration C of water absorbed is increased. The effect is more pronounced in elastomers containing water- soluble salts such as sodium chloride. Barrie et.al [30] measured the sorption, diffusion and permeation of water in cis polyisoprene and natural rubber. They found that at higher relative pressures the diffusion coefficient in all cases decreased with concentration and activation energies for diffusion increased with concentration. Their findings were to be expected since with increased clustering of the sorbed penetrant increases at higher relative pressures.

Molecular. diffusion of water through elastomers is an important consideration in underwater applications. In most practical situations moisture content is monitored from the weight gain of the material. The percent moisture content (Mt) at time t is defined by

$$M_t = (W-W_d)*100/W_d \tag{1.26}$$

W and Wd are respectively the wet and dry weight of the polymer membrane. When a material is immersed in a liquid, absorption takes place and this process can be described by relation (1.19)

Diffusion coefficient, D, in x, y, z direction is given as

$$D = D_x[1+h/l(D_y/D_x)^{1/2}+h/n(D_z/D_x)^{1/2}] \tag{1.27}$$

l = film length, n = film width, h = thickness D_x, D_y, D_z are diffusion coefficient in x,y,z directions.

For homogeneous materials, $D_x = D_y = D_z$ so that

$$D = Dx\ [1+h/l+h/n]^{1/2} \tag{1.28}$$

Since M_t is a linear function of $t^{1/2}$ the slope θ of the plot allows the calculation of D and D_x, from Eqn1.28 and Eqn.1.29

$$D = [\theta^2 h^2\ \pi/16Ms]^{1/2} \tag{1.29}$$

and

$$D_x = [\theta^2 h^2\ \pi/16M_s]^{1/2}[1+h/l+h/n]^2 \tag{1.30}$$

Diffusion coefficient can be estimated from permeability [31-34] Q, using the equation

$$D = Q/S \tag{1.31}$$

Alternatively D can be calculated from the absorption vs time curve using the Eqn.1.29. Some general observations can be made from the above discussions. The amount of water taken up by a given sheet is proportional to the square root of time. The time required to reach a given stage of decomposition is proportional to the square of thickness of the sample. The percent increase in weight after exposure to water for a definite period is inversely related to sheet thickness of sample. This method of determining diffusion coefficient at vapour pressures above 0.75RH is not reliable.

Water absorption rates are observed to be higher than what the water vapour pressure increase suggests. Also at higher vapour pressures attaining equilibrium absorption, takes a long time.

The permeability or permeation coefficient (P) of a material depends on solubility (S) and diffusivity (D) of penetrant liquid through elastomer, and is a product of D and S [35]

$$P = D^*S \tag{1.32}$$

Many of the additives when used in the compounded rubber increase the solubility of water in the rubber. Also an increase in temperature usually increases both D and S in most polymers. An increase in cure usually decreases P.

The amount (Q) of the permeant (in mg) transported through the polymer membrane is given by relation [35]

$$Q = P(p_1 \text{-} p_2)At/L \tag{1.33}$$

Here $p_1$and p_2 are the vapour pressures (in cm Hg) of water on the wet side and dry side of the barrier respectively: A is the area (in cm^2) of the membrane exposed to the permeant. L the thickness of the membrane, t is the time duration of exposure in sec. and P the permeability constant. Thus it can be seen that the rate at which water is transported through the membrane depends on the water vapour pressure differential across the membrane, permeability constant and the membrane thickness.

1.1.6 Sealing properties

Elastomeric seals used in the deep sea applications demand special design considerations to meet challenges of operating environment, dynamic response. Major issues include sealing efficiency, compression set, stiffness, and long term behavior. Studies on compression stress relaxation behavior under different environmental conditions enable estimation of long term performance.

1.1.7 Acoustic properties

For a plane wave propagating in x direction through a homogenous elastic medium the wave equation is [7]

$$p = p_0 \cos(kx - \omega t + \phi_0) \tag{1.34}$$

p where p_o is the amplitude and is the initial phase. The total phase ϕ at position x and time t is $\phi = kx - \omega t + \varphi_0$

The wave number, k, and angular frequency, ω, are related respectively to the wave length, λ, and frequency f, of the wave are as follows:

$$k = \frac{2\pi}{\lambda}, \qquad \omega = 2\pi f \tag{1.35}$$

The complex number representation of the wave equation is given by

$$p = p_0 e^{i(kx - \omega t + \phi_0)} \tag{1.36}$$

In a loss less medium sound waves propagate with constant sound speed. For a sound wave, which has the single wavelength, the sound speed and the frequency are related as follows

$$c = f\lambda = \omega / k \tag{1.37}$$

The increase in the wave length of sound with decreasing frequency has important implications for attenuation of sound.

An elastic wave can be launched in a material like rubber by applying a sinusoidally varying force into the material surface. A longitudinal wave is launched if the force applied is perpendicular to the surface. As this longitudinal wave propagates into it, the rubber molecules are forced back and forth by the oscillation of the wave. This gives rise to local pressure and density fluctuations. Wave properties such as, speed and attenuation are characterised in terms of corresponding modulus. Thus longitudinal wave is defined by complex elastic modulus, shear wave by complex shear modulus etc. Jarzynski [7] discusses the basic nature of sound propagation, the equations governing sound interaction in materials properties and gives an insight into the nature of sound absorption in the material. Under water acoustic transducers use rubbers in three major roles: Acoustic absorbers, Reflectors, and acoustic window materials. Acoustics absorbers are important for sonar transducers, acoustic baffles, acoustic calibration facilities and also for reduction of sound radiation and echoes from ships and submarines. Acoustic reflectors are used as decouplers as well as in sonar dome wedges. Acoustic window materials act as the coupling medium between the transduction material and water. Rho-c rubber [36] is a widely used material because its acoustic properties are close to that of water. When ρc, the product of density of a material and the velocity of sound in the material is equal to that of the medium, the material is loosely called as Rho-c material. The product of density (ρ) and sound velocity(c) is the characteristic acoustic impedance. This parameter is the ratio of sound pressure to particle velocity. Sound energy transmission between adjacent media takes place without reflection losses if the acoustic impedance matches. But in a viscoelastic medium like rubber there is a certain measure of sound energy dissipation as the wave propagates through the solid. Since acoustic waves are pressure waves supported by the particles of the medium, particles in the medium participate in the oscillatory motion; sound wave propagation is directly linked to the density as well as elastic properties of the medium. If the acoustic impedance of the propagating medium is z_1

$$z_1 = \rho_1 c_1 \qquad (1.38)$$

and that of the receiving medium

$$z_2 = \rho_2 c_2 \qquad (1.39)$$

The intensity of reflection

$$R = \frac{\rho_1 c_1 - \rho_2 c_2}{\rho_1 c_1 + \rho_2 c_2} = \frac{z_1 - z_2}{z_1 + z_2} \qquad (1.40)$$

Where acoustic wave is incident on viscoelastic material like rubber due to the dissipative mechanism within the material acoustic impedance gets modified as

$$z_2 = \frac{\rho_2 c_2}{1+r^2} + \frac{ir\rho_2 c_2}{1+r^2} \tag{1.41}$$

where $r = \frac{\alpha c_2}{\omega}$ $\quad i = \sqrt{-1}$

Since acoustic impedance of rubber is a complex parameter, while it is possible to provide a perfect match for the real part of the impedance, there will always be a residual mis- match due to imaginary component. Reflection free transmission of acoustic energy from rubber to water is not possible. However, by careful material selection and optimization, pressure reflection coefficient close to zero and pressure transmission coefficient close to unity could be achieved. The propagation of an acoustic wave through a solid polymer is determined by a number of parameters, which define the reflection, transmission and energy absorbing properties. Sound wave is incident at a boundary interface. Reflection and transmission occur as shown in Fig 1.3 The pressure reflection coefficient, R_p describes the reflective properties, correspondingly the pressure transmission coefficient, T_p and acoustic power dissipation (PD). These relationships can be expressed as

$$R_p = (p_r/p_i) \tag{1.42}$$

$$T_p = (p_t/p_i) \tag{1.43}$$

$$PD = [1-(R_p^2+T_p^2)] \tag{1.44}$$

where p_i, p_r, p_t are incident, reflected and transmitted pressure respectively.

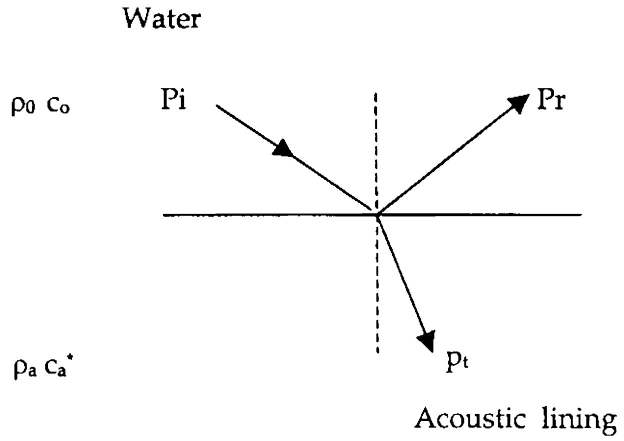

Fig.1.3 Reflection and transmission of sound at a water polymer interface.

For efficient anechoic function both R and T must be close to zero. Using the terminology of echo reduction (ER) and transmission loss (TL)

$$ER = -20 \log R_p \tag{1.45}$$

$$TL = -20\log T_p \tag{1.46}$$

Transmission loss quantitatively describes the weakening of sound between a point 1 metre from the source and a distant point. Similarly echo reduction is the weakening of the intensity of reflected signal. In a lossless medium sound waves propagate with a constant speed. Speed of sound is related to the wavelength and frequency as per Eqn(1.37.)

It follows from Eqn.1.37 that the sound wave length is inversely proportional to the frequency. Typically an acoustic window material with sound speed around 1500 m/sec will have the wave length λ=15m at 1000Hz. Hence at audio and low ultrasonic frequency range the encapsulation thickness of 3mm is small compared to wave length of sound and hence acoustic impedance mismatch is less severe. Sound absorption,α, in units of dB/cm, is a measure of the loss in energy of the sound wave as it travels through the solid. The energy of the sound wave is converted into random thermal motion or heat. Acoustic attenuation between two positions is usually expressed in terms of logarithm of amplitude at the two positions, expressed in decibels. In practice, because the polymer is viscoelastic, sound speed 'c' is related to complex modulus. In an unbounded, isotropic solid there are two independent modes of acoustic propagation longitudinal and shear. In the longitudinal mode, the particle motion is parallel to the direction of propagation, while in the shear mode; the particle motion is perpendicular to the direction of propagation.

For characterizing a solid four parameters namely longitudinal sound speed c_l, shear sound speed, c_s, longitudinal absorption, α_l and shear absorption, α_s. One important experimental technique gives a modulus values rather than sound speed. The relationship is particularly simple [7]. Thus

$$c^* = (G^*/\rho)^{1/2} \qquad (1.47)$$

[37] The modulus and velocity may be expressed in complex form as

in Eqn.1.14 and

$$c^* = c_1 + ic_2 \qquad (1.48)$$

Thus,

$$(c^*)^2 = \frac{(G' + iG'')}{\rho} \qquad (1.49)$$

$$= c_1 - c_2 + 2ic_1c2 \qquad (1.50)$$

Separating and identifying real and imaginary parts gives:

$$G = \rho(c_1^2 - c_2^2) \qquad (1.51)$$

and

$$c^* = c\frac{[1 + i\alpha c/\omega]}{[1 + \alpha^2c^2/\omega^2]}$$

$$G'' = 2\rho c_1c_2 \qquad (1.52)$$

Consideration of the normal complex exponential form for a progressive wave [38,39] allows one to relate c_1 and c_2 to the observed phase velocity c and the amplitude of attenuation constant by the relations

$$c_1 = \frac{c}{(1+\alpha^2 c^2/\omega^2)} \tag{1.53}$$

and

$$c_2 = \frac{\alpha c^2}{\omega\left[1+\alpha^2 c^2/\omega^2\right]} \tag{1.54}$$

$$c^* = c\frac{\left[1+i\alpha c/\omega\right]}{\left[1+\alpha^2 c^2/\omega^2\right]} \tag{1.55}$$

since $$G^* = G' + i\,G'' = [c^*/\rho]^2 \tag{1.56}$$

Equations can be used to solve for the magnitude of the phase velocity and attenuation.

Doing so yields

$$c^2 = \frac{2\left[(G')^2+(G'')^2\right]}{\rho\left[[(G')^2+(G'')^2]^{1/2}+G'\right]} \tag{1.57}$$

and

$$\alpha^2 = \frac{\omega^2\rho\left[[(G')^2+(G'')^2]^{1/2}-G'\right]}{2\left[(G')^2+(G'')^2\right]} \tag{1.58}$$

Therefore by substituting the appropriate storage and loss modulus, G, K or E the acoustic parameters, sound velocity and attenuation can be estimated from dynamic mechanical properties

1.2 Underwater electro acoustic transducers

Electro acoustic transducers are widely used in underwater surveillance and detection. In the civilian sector they include fish finders, sea bottom profilers, ocean depth sounders, and seismic exploration devices while in the military sector applications ,they are found in mine hunters, torpedo nose cones, homing heads and anti submarine detection systems.

A transducer is a device that converts one form of energy into another. If a transducer converts mechanical energy into electrical energy and vice versa, it is called an electro mechanical transducer, a particular class of the electro mechanical transducer is the electro acoustic transducer. Acoustic radiation in the form of an acoustic wave arises from the vibrations of the transducer, which is energized, by a voltage source. The transducer vibration of the transducer imparts a periodic motion to the particles of the medium in contact with it: the periodic motion of the particle of the medium about their equilibrium position along the line of energy propagation constitutes the acoustic wave. Such a transducer is said to function in transmission mode. When the sound wave is incident on a transducer the pressure variation in the medium in contact with the transducer surface imparts a vibratory motion into it. The mechanical energy is converted by the transducer into electrical energy, resulting in a voltage out put. Such a transducer is functioning in the reception are known as acoustic receivers, or hydro phones.

Transducers can be designed to operate at over wide range of frequencies starting from a few Hertz to several thousand Mega Hertz. Frequencies between 20 Hz and 20 kHz is known as audio frequencies and those between 16 kHz and10^9 as ultra sonic frequencies.

Acoustic systems are operated with a wide range of power- from microwatts to kilowatts. The minimum acoustic power needed to be detected in a system is set by the thermal noise of the system or medium. The upper limit is set by practical design problem such as break down limit and mechanical strength in the transduction material. Maximum power that can be transmitted in water is only 0.33 watts per cm^2 without distortion.

The geometry of a transducer varies depending upon the application. It may be planar, spherical, or cylindrical. Its dimensions vary from a few millimeters to a few meters. It is difficult to manufacture large transducers in single element. It is common practice to fabricate either mosaics of closely spaced elements or arrays with inner spaced elements of the required size and shape.

The majority of transducers fall into two categories-those which employ electric fields in their transduction process and those which employ magnetic fields. Some are inherently linear, while others have to be polarized to produce linear action. This arises from the fact that the force producing acceleration of the active mass of the transducer, which in turn causes acoustic radiation, can be directly proportional to the square of the applied signal, depending upon the physical mechanism employed for transduction.

1.2.1 Acoustic transduction

Under water electro acoustic transduction is accomplished by either of the two phenomena: Electrostriction and magnetostriction

Electrostriction refers to the conversion of energy between acoustical and electrical forms by means of a dependence between electrical fields and particle displacements in ferroelectric or piezo electric materials.

Magnetostriction denotes conversion of energy between acoustical and electrical forms by means of a dependence between magnetic fields and particle displacements in ferro magnetic materials. In the electrostriction phenomenon, there is a distinction between piezo electric effect and ferroelectric effect. Piezoelectric transducers use crystals in which the dimensions change according to the applied electric field. If the field is alternating, the crystals vibrate and give an acoustic radiation. Typical piezoelectric materials used for this purpose are quartz, ammonium hydrogen phosphate, Tourmaline and Lithium sulphate.

Ferroelectricity is an electrical phenomenon analogous to the ferromagnetic phenomenon. Ferro electricity can be defined as reversibility in a polar crystal, of the direction of the electric dipoles by means of an applied electric field. Most popular Ferro electrics or piezo electric ceramic used in electro acoustic transducer fabrication are Barium Titanate and Lead Zirconate Titanate

1.2.2 Transducer Materials

Transducer materials can be broadly classified into two categories namely active transduction materials and passive acoustic materials. Both are equally important in the efficiency and reliability of the transducer system performance. A brief discussion of these materials will be relevant in the context

Piezo- electric effect was discovered in 1880 by Jacques and Pierre Curie in quartz. It is based on the observation that a mechanical strain results from a voltage applied to a piezoelectrical material and voltage produced is proportional to the strain. The inverse effect was discovered in the following year by Lippman in quartz. It relates to the appearance of electric charges on the opposite surfaces of the crystal, proportional to the stress. This unique property of certain crystalline material has been exploited in the design of piezo electric transducers.

1.2.2.1 Active Materials

Piezoelectricity is the property possessed by some materials of becoming electrically charged when subjected to a mechanical stress. Such materials also exhibit the converse effect. i.e. the occurrence of mechanical deformation on application of an electric field. The piezoelectric effect was first observed in naturally occurring single crystal compounds e.g. quartz and Rochelle salt. The occurrence of piezoelectricity in such compounds is due to the lack of a centre of symmetry in the unit cell and consequently distortion of the unit cells produces electric dipoles

Certain compounds can be made piezo electric by the application of a high electric field (polarization), these are termed Ferro electric materials examples of such materials are Barium titanate and Lead Zirconate Titanate which can be produced as single crystals or as poly crystalline aggregates by the ceramic process The polarization process involves the application of an electric field across the ceramic, usually at an elevated temperature, causing switching or realignment of the dipoles in the direction of the field. After removal of the electric field there is a remnant polarization in the ceramic, which is responsible for its piezo electric properties. The resulting ceramic is now anisotropic and can be returned to its unpolarised iso tropic condition by raising its temperature above the Curie point or by mechanically over stressing.

These piezo electric materials are the actual energy converters used in the construction of underwater acoustic transducers. Poly crystalline Ferroelectric has been extensively used for fabricating transducer elements. Most favored transduction material for underwater electro acoustic transducers are polarised ferroelectric ceramics like Barium Titanate and Lead Zirconate Titanate. The applications of ceramic transducers fall basically in two broad categories-High power sources and high sensitivity receivers; specific ceramic compositions are recommended for the two applications.

1.2.2.2 *Passive Materials*

There are a number of materials, other than active transduction materials, used in the construction of underwater electro acoustic transducer system. They are, in general, referred to as passive acoustic materials. Passive materials include a range of metallic and non-metallic materials with well defined and carefully controlled acoustic properties. Their role in the construction of the transducer are diverse, like sounder absorbers, acoustic baffles, window materials, acoustic reflectors, de-couplers, acoustic fill fluids, seals, o' rings etc.

Acoustic reflector materials are used in transducer arrays for reflecting and isolating the noise generated by the propellers. Acoustic reflectors are fabricated of rubber sheets into which holes have been moulded and open end covered. The air trapped in the holes provide the necessary compliance for effective low frequency isolation of underwater sound, reflector materials are also designed with syntactic foams and various micro balloons. The visco elastic polymer air micro bubbles composites are particularly useful in the design of anechoic coatings. Various inclusion-viscoelastic polymer matrixes have been investigated for use as sound absorbing material. Among the inclusions are sawdust [40], metal oxides, metal oxide micro particles, phenolic micro particles, metal powders [41] etc.

Acoustic baffles are used in large high performance underwater transducer arrays for the purposes of isolating ship's noise as well as for improving directivity and sensitivity of the transducer elements. The baffle forms a major element contributing to better performance of the system. The materials used for construction of baffles are therefore required to possess specific acoustic and dynamic mechanical properties. As the application of baffles is in deep marine environment baffle rubber must also be compatible with marine water, temperature pressure and dynamic loading condition. Rubbers show unique combination of stiffness and damping capability. A major consideration is the constant modulus over wide range of the operating frequency. Frequency - modulus relationship of SBR rubber has been studied to achieve an optimum combination of properties. Results of the study are reported in the present work.

1.3 Rubbers as passive acoustic materials

Rubber forms a major class of passive acoustic materials. Rubber components in underwater electro acoustic transducers rank as one of the most sophisticated applications due to the additional functional requirement namely propagation of acoustic waves. Because of the constraints imposed by ocean environment coupled with application specific performance requirements, conventional engineering rubbers can hardly meet the performance standards envisaged. There exists a need to study and develop application specific passive acoustic rubbers with balance of performance and long service life. Good amount of information is available in literature on the rubbers used in general underwater engineering applications. But in functionally specific cases like passive acoustic components used in underwater transducer technology there exists large gaps in information. The present study pays attention to such critical technologies. In these function-specific applications the rubbers are required to possess critical combinations of commonly referred engineering properties as well as desired acoustic properties. In several cases the intended underwater service life is of the order of a decade and more. Rubber is extensively used in the construction of underwater electro acoustic transducers. The major applications include, transducer encapsulation, acoustic baffle materials, under water seals, junction box.

Primary function of an encapsulation material is the protection of electro acoustic transduction devices from water. In this positive role encapsulation material should not adversely affect the acoustic transmission efficiency of the transducer. Because of the close acoustic impedance properties of rubber with water, ease of fabrication, sealing efficiency, and versatility to tailor make properties; rubbers are the most favored material chosen for this application. However, the performance requirements reliability and service life demanded of the underwater transducers call for rubbers with more stringent performance specifications.

The important properties considered in the design of encapsulation materials for underwater electro- acoustic transducers are (1) Water absorption and permeation (2) Electrical resistivity (3) Dynamic mechanical properties (4) Acoustic impedance (5) Ease of processing and (6) Permanence of properties. Of the above parameters water absorption and permeation and consequent changes in other properties determine the service life of underwater devices

1.4 Scope of the study

Foregoing review brings out the need for function specific rubbers for optimum performance in underwater electro - acoustic transducers. There exist large gaps of information in the functional properties for specific application areas such as encapsulation rubbers, baffle rubbers, seal materials. The above rubbers must function in an operating environment characterized by dynamic stresses from cyclic mechanical forces, temperature variation, electrical field, and corrosion etc. Water ingress causes unacceptable changes in properties. Present investigations aim at filling gaps in the system and evolving compound design approaches for performance improvement and added service life. A major part of the work is devoted to studying the long term properties of the selected vulcanizates based on CR, BIIR and NBR with the aim of generating viable life estimation model.

1.5 Structure of the thesis

The thesis comprise of six chapters

CHAPTER 1

This chapter introduces the topic of the work starting with a general introduction to the engineering applications of rubbers, discusses role of rubbers in underwater engineering. Chapter gives a description of underwater electro acoustic transducers, materials used in their construction and goes on to describe the role of rubbers as the major passive component. Chapter discusses in some detail the important properties, pertaining to the application of rubber as encapsulants, namely water ingress through diffusion and permeation, viscoelasticity, dynamic mechanical testing, acoustic wave propagation through rubbers, electrical properties and processing techniques The chapter also gives an introduction to specific end use in acoustic baffles and under water seals.

CHAPTER 2

Chapter 2 deals with theoretical aspects of rubber compounding. The chapter includes detailed discussions on the compounding materials used in this work. Compounding principles and techniques adopted for achieving specific properties have been discussed. The chapter addresses in detail theoretical aspects of important properties, including processability testing, static mechanical properties, dynamic mechanical testing, environmental properties with particular reference to action of liquids, cause of ageing in rubbers, mechanism of thermal degradation, thermal analysis techniques etc.

CHAPTER 3

This chapter covers the studies conducted on Neoprene rubber, Bromobutyl rubber, Styrene butadiene rubber, Nitrile and Natural rubber, on properties relevant to underwater electro acoustic transducer technology. The properties dealt with, include water intake characteristics: diffusion and permeation, static and dynamic mechanical properties, cure characteristics of conventional and low temperature curing systems, thermal behavior, electrical resistivity. Studies conducted on the specific material systems: viz encapsulation material, acoustic baffle material, under water seal material etc have also been included in this chapter.

CHAPTER 4

This chapter gives a brief account of the theoretical and experimental studies conducted on the degradation behavior of rubbers with particular reference to the controlling properties such as water intake, static mechanical and dynamic mechanical properties and electrical properties.

CHAPTER 5

Results of experimental studies arrived at on compounding techniques and the life prediction techniques are consolidated and presented in this chapter. Trends are discussed and conclusion of the present work is presented.

CHAPTER 6

This final chapter gives the summary of the theses

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Chapter 2

RUBBER COMPOUNDING: THEORETICAL STUDIES

2.1 Introduction

This chapter discusses the underlying principles employed in compounding application specific rubbers and the functional properties of various compounding materials used in the study. The chapter also reports the theoretical studies on the important properties relevant to present investigations.

In the design of rubber compounds one must take into account not only the properties of the vulcanisate essential to satisfy service requirements and cost of raw materials but also the process by which raw rubber will be transformed into final products. The principal task of compounding is therefore concerned with arriving at an acceptable balance between the demands arising from these three considerations.

The raw rubbers, whether natural or synthetic, vary from soft plastic material to tough gristly substance. They are not suitable for use in the form in which they are supplied. Their elastomeric properties have to be developed by compounding. The possibilities are many.

The addition of various chemicals to raw rubber to impart desirable properties is termed rubber compounding. Typical ingredients include cross linking agents, activators, and accelerators, reinforcements, anti-degradants, process aids, and extenders.

2.2 Rubber polymer

In rubber compounding although the type and amount of additives can give considerable variation to the end product, the main characteristic is determined by the kind of rubber used.

Present work concentrates mainly on Polychloroprene (Neoprene-w) rubber. Better balance of properties like, seawater compatibility, weathering resistance, bonding with metal, amenability to build in desired static and dynamic mechanical properties favour Neoprene over other rubbers for this application.

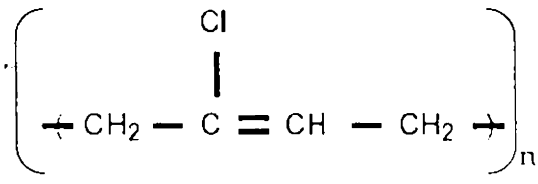
Apart from Neoprene rubber, following additional polymers have been included in the study for specific properties of interest. These rubbers are

1. Bromo butyl rubber
2. Styrene butadiene rubber
3. Acrylonitrile butadiene rubber
4. Natural rubber.

A Brief review of properties of rubbers covered in the present investigations is given in following sections.

2.2.1 Poly chloroprene rubber

Neoprene is the popular name for polymers of chloroprene, 2 chloro-1, and 3-butadiene.This is one of the favoured materials for underwater application. It has a combination of desirable properties as discussed. Neoprene consists mainly (88-92%) of *trans*-1,4-chloro-2- butenylene units. A poly Chloroprene unit is shown in Fig 2.1



$$\left(-CH_2-\overset{\overset{\displaystyle Cl}{|}}{C}=CH-CH_2- \right)_n$$

Fig 2.1 Polychloroprene structure

The *cis*1, 4 addition accounts for 7-12%, and the 1, 2 around 1.5%. The allylic chlorine facilitates vulcanisation in Neoprene [1].Neoprene owes its resistance to ozone attack, oxidation, or weathering to the electro negative chlorine on the 1, 4 *Trans* double bond. Its weather resistance surpasses that of other diene rubbers such as SBR or NR but requires aging resisters to give best service. This polymer has flame resistance. Because of the regularity of structure neoprene crystallises easily, especially when stretched.

Among different grades of neoprene, W and GRT grades are generally used in underwater application. Neoprene-W is more crystallisation resistant. It is mercaptan modified to give C-C link in the polymer. W grade has better storage stability and heat resistance [2]. Their better molecular weight distribution imparts better processability. GRT grades are sulphur modified to give C-S-C link. They have lower storage stability due to wide molecular weight distribution. GRT grade is suitable for low temperature vulcanisable formulations. Neoprene GRT contains co monomers for improved resistance to low temperature crystallisation and hardening.

Neoprene is generally vulcanized using metallic oxides. A combination of 5 parts of zinc oxide and 4 parts of magnesium oxide is the most commonly used. Zinc oxide increases the rate of cure during its early states and ensures good aging properties. Magnesium oxides serve as mild peptizer for neoprene and help to improve storage life and resistance to scorch. For minimum water absorption red lead (Pb_3O_4) is generally recommended. A typical basic Neoprene rubber compound shall consist of ingredients listed in Table 2.1

Table 2.1 Basic neoprene compound

Ingredient	Amount	(pphr)
Neoprene G	100	-
Neoprene W	-	100
Phenyl beta naphthyl amine	1	1
Magnesium oxide	4	4
Zinc oxide	5	5
NA 22	-	0.5

The selection of fillers is very important in properly compounding neoprene stocks. In general, all types of carbon black exert greater reinforcing effects in neoprene-w compounds than in the G types. Channel and furnace blacks provide greatest reinforcement and impart weathering resistance, abrasion and tearing resistance. Where high resilience and flex crack resistance are required the furnace and thermal black grades are recommended. Mineral fillers such as clay do not in general, exert reinforcing action but act as diluents, thereby modifying the physical characteristics. Among non black fillers clays provide superior resistance to weathering, while barites impart mineral acid resistance. Whiting is the preferred filler for heat resistant compounds. Three types of acceleration system have been developed for the w types. First is the use of sulphur with accelerators like thiuram disulphide. Second is with neoprene accelerators like mercapto imidazoline (NA-22) with a retarder like Di Benz thiazyl disulphide (MBTS). Thirdly, the use of NA-22 alone or in conjunction with the safe processing combination like Tetra Methylene Thiuram disulphide (TMTD). Neoprene G type can be cured without organic accelerators.

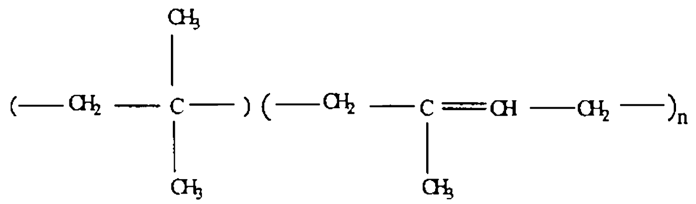
2.2.2 Bromobutyl Rubbers (BIIR)

Bromobutyl rubber is the brominated modification of butyl rubber (IIR). Butyl rubber is a general purpose, non oil resistant elastomer resulting from the co polymerisation of isobutylene.

$H_2C=C[CH_3]_2$

and isoprene.

$H_2C=CCH_3-CH=CH_2$ to yield Butyl rubber (Fig.2.2)



$$(-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-)(-CH_2-\underset{CH_3}{C}=CH-CH_2-)_n$$

Fig 2.2 BUTYL RUBBER

During bromination a molecule of bromine reacts with each available isoprene unit in the rubber molecule. The sterically hindered nature of the unsaturated unit directs the reaction towards substitution. The primary microstructure is represented as

$-C[CH_3]_2-CH_2-CCH_2-CHBr-CH_2-$

Many of the physical properties of butyl rubber are a function of the crosslink density, which is directly proportional to the isoprene content of the polymer. Proportion of isoprene may be varied from low for good ozone resistance, chemical and flex resistance to higher values for improved tensile and abrasion resistance. Commonly used fillers and reinforcing agents include both carbon black and mineral fillers. Carbon blacks provide superior reinforcement compared to mineral fillers with smaller particle size providing higher tensile strength and hardness. BIIR has been selected for the present study on the basis of its outstanding permeation resistance to both water and gases. It can be compounded for excellent dielectric strength and insulation resistance. BIIR has high damping and abrasion resistance at room temperature. Tg of this rubber is about -70°C. BIIR has enhanced cure compatibility as compared to IIR. The material used in this study (POLYSAR X2) has been obtained from M/s Polysar, UK

2.2.3 Styrene -Butadiene Rubber (SBR)

SBR is a general purpose, non oil resistant rubber manufactured by the co polymerisation of butadiene

$CH_2=CH-CH=CH_2$

and styrene (i.e. vinyl benzene)

$CH_2=CH-C_6H_5$

Unreinforced SBR has poor tensile properties, therefore carbon black or inorganic fillers such as silica, calcium silicate or clay are added to improve the strength. Carbon black filled compound have lower densities, high strength and lower water absorption than mineral filled compounds. SBR formulation deteriorates quickly in contact with oils and solvents. The grade selected is 1502 which contains about 23.5% by wt., styrene and has a glass transition approx.-65°C.

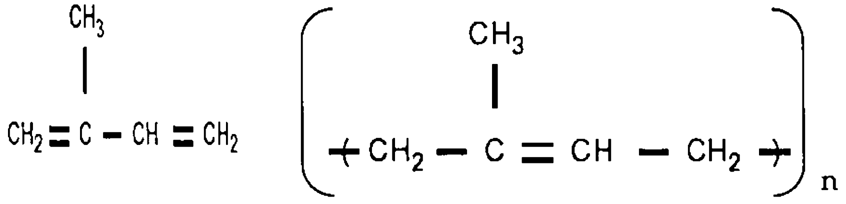
Polymer properties of the grade used for studies are given in Table.2.2

Table 2. 2 Polymer properties

Property	Value
Arrangement of monomers	Random
CIS -1-4 Butadiene (% by wt.)	9
Trans-1, 4-Butadiene (% by wt.)	76
1,2- Butadiene (vinyl) ((% by wt)	15
Intrinsic viscosity (dl/g)	2.0
Mooney viscosity [ML(1=4)100°C]	50
Specific gravity	0.94

2.2.4 Natural rubber (NR)

Natural rubber is a product coagulated from latex of tree, *Hevea brasiliensis.* It is chemically polyisoprene. Isoprene and poly isoprene chemical structures are represented as Fig.2.3 (a) and (b) respectively.



$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}-CH{=}CH_2$$

$$\left(-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH-CH_2-\right)_n$$

(a) (b)

Fig.2.3 (a) Isoprene monomer unit (b) Poly isoprene

It must be blended with inorganic or carbon black reinforcing agents and sulphur and then vulcanised to exhibit maximum physical properties. Physical properties depend on the extent of vulcanisation which in turn depends upon the amount of sulphur contained in the final product. NR has poor oil resistance as well as poor oxidation and weather resistance. Its Tg is about -70°C.Technically specified grade ISNR5 obtained from RRII, Kottayam, India was used for studies.

The specification of the material is given in Table 2.3

Table 2.3 Specification of ISNR -5

Dirt content (% max by mass)	0.05
Volatile matter (%max by mass)	0.8
Ash (% max by mass)	0.5
Nitrogen (do.)	0.6
Initial plasticity (min)	30
Plasticity retention index(min)	60

2.2.5 Acrylonitrile-Butadiene rubber (NBR)

NBR, Nitrile rubber,is an emulsion copolymer of acrylonitrile, (CH_2=CH_2-CN,) and butadiene, (CH_2=CH-CH=CH). Acrylonitrile functionality imparts excellent fuel and oil resistance to the rubber. Grades differ according to their acrylonitrile content, which is the determining factor in final vulcanisate.

Nitrile Rubbers offer excellent resistance to oils and hydro carbon solvents. The grade used in the present study is 34% ACN obtained from Korean synthetic rubber company, Korea.

2.3 Compounding of rubber

None of the rubbers discussed have useful properties until they are properly formulated. Various processes involved in compounding are discussed in the following sections.

2.3.1 Vulcanization and vulcanising agents

A Raw rubber is a high molecular weight liquid with low strength. In spite of entanglement they can readily disentangle upon stressing leading to rupture or viscous flow. Vulcanisation is an irreversible process during which a rubber compound through a change in chemical structure (cross-linking) becomes less plastic and more resistant to swelling by organic liquids while elastic properties are conferred, improved or extended over a great range of temperature. This process can be brought about by a variety of agents.

2.3.1.1 Sulphur Vulcanisation

Sulphur is combined in the vulcanization net work in a number of ways as illustrated in Fig.2.1.

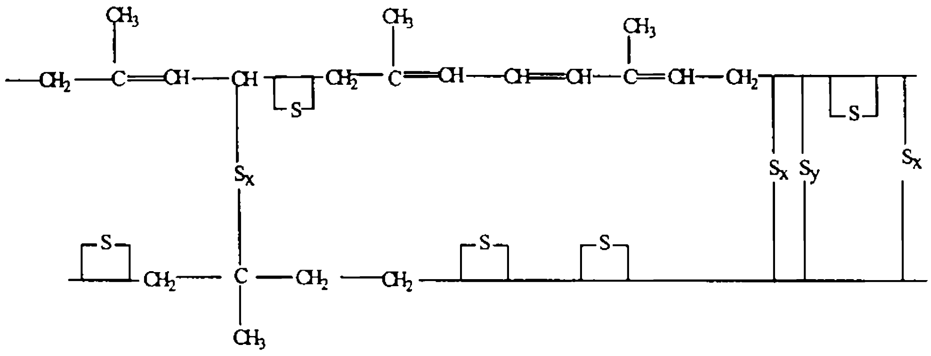


Fig.2.4 Probable combinations of sulphur in vulcanised NR net work

As cross-link it may be present as mono sulphide, disulphide or polysulphide. It could be forming pendent sulphides, or cyclic monosulphides and disulphides. The number of sulphur atoms in each has been estimated. An unaccelerated rubber vulcanisate may have 40-45 atoms. In a conventional accelerated vulcanizates this figure may drop to10-15. An efficient vulcanising system this number could reduce to 4-5. Sulphur less system could have even lower values. The general course of vulcanization could be deduced from the estimates of nitrogen and sulphur, relative amount of inefficiency and degree of cross linking, pendent and intra molecular sulphur.

The initial step in the vulcanisation seems to be the reaction of sulphur with the zinc salt of the accelerator to give Zinc per thio salt XS_xZnS_xX where X is a group derived from the accelerator. This salt reacts with the rubber hydrocarbon RH t o give rubber bound intermediate

$$XS_xZnS_xX + RH \rightarrow XS_xR + ZnS + HS_{x-1}X$$

and a perthio-accelerator group. This group with another Zinc oxide molecule will form a per thio-salt of lower sulphur content. This may further be an active sulphurating agent, forming intermediates of varying degree of poly sulphidity. The hydrogen atom which is removed is likely to be attached to a methylene group in the α position to the double bond. The intermediate X S_xR then reacts with a molecule of rubber hydrocarbon RH to give a crosslink and more accelerator is be generated:

$$XS_xR+ RH \rightarrow RS_{x-1}R+XSH$$

On further heating the degree of poly sulphidity further declines. This process is catalysed by XS $_x$Zn S_xX. Cross links which were initially at position 4 and 5 undergo an allylic shift, with the result that new configurations appear.

2.3.1.2 *Major compounding ingredients*

Vulcanization is only one aspect of tailoring the properties of a rubber product. there are several other ingredients added to the base polymer for building specific properties into the product rubber each one with a specific role to play.The major ingredients involved in compounding of rubber can be divided into cure system filling agents, anti degredants, process aids and softeners.

2.3.1.3 *The cure system*

The cure system for a rubber consists of curing agents or vulcanising agents, cure accelerators accelerator activators and retarders. The most commonly used vulcanising agents are sulphur and sulphur bearing compounds. Organic peroxides such as dicumyl peroxides are also used as vulcanising agents. Organic compounds currently used as cure accelerators include carbamates, thiuram and thiazoles. Several different types of chemical compounds function as accelerator activators. Zinc oxide is a necessary accelerator activator for sulphur vulcanisation. A fatty acid such as stearic acid is a useful cure accelerator.

2.3.1.4 *Sulphur*

Almost all commercial products of natural rubber, styrene butadiene rubber, nitrile rubber and butyl rubbers are cured with sulphur. Relative requirement of sulphur for normal vulcanization have been established empirically. General quantities of sulphur requirement are given in Table 2.4.

Table2.4 General Requirement of sulphur

Rubber Type	**General sulphur Requirement (pphr)**
NR	1.75-2.75
SBR	1.50-2.00
NBR	1.00-2.00
IIR	1.00-1.50

In semi-efficient vulcanisation, efficient and sulphur less curing, the proportion of sulphur used are, 0.8 to1.5 phr, 0.3 to 0.8 and 0 to 0.3 respectively. Normal sulphur vulcanization generally produces polysulphidic crosslink. Low sulphur and sulphur less cures leads to mono or disulphide cures. The presence of sulphur increases the tensile strength, elongation at break and resilience but aging properties deteriorate.

2.3.1.5 *Sulphur donors*

Thiuram disulphide and di morpholyl disulphide are examples of sulphur donors. Main advantages of sulphur donor curatives are that the vulcanizates produced have only mono and disulphide cross links. Poly sulphidic cross links are liable to degradation. Mono and disulphide cross links impart high heat resistance, better mechanical properties and aging properties.

2.3.1.6 *Metallic oxides*

Because of the deactivating influence of chlorine atom on the chloroprene unit normal sulphur vulcanisation is impractical in poly chloroprene rubbers. Metallic oxides are necessary for vulcanising chloroprene rubber. Most often used is a combination of zinc oxide and magnesium oxide, zinc oxide acts as cross-linking agent and magnesium oxide as acid acceptor. The dosage is generally MgO: 4 pphr, ZnO: 5 pphr.

2.3.2 Accelerators

Vulcanisation with sulphur alone is an extremely slow process. Relatively large amount of sulphur and longer vulcanisation time are necessary. The compound has a strong tendency to revert and their resistance to aging is poor and mechanical properties are also poor. Sulphur exists as S_8 ring and is relatively stable. To make sulphur reactive a considerable amount of activation energy is to be expended. The sulphur ring has to split. The process of activation occurs at high temperature and it can be promoted by certain organic substance called accelerators and metallic oxides. Important accelerators fall into following major groups (1) Dithiocarbamates (2) Xanthates,(3) Thiurams, (4) Thiazoles.

2.3.2.1. *Dithio Accelerators*

(A) Zinc diethyl dithio carbamate (ZDC)

This is most important dithio carbamate. It is particularly suitable for hot air and steam vulcanization. Dosage is-0.3-0.6pphr.

2.3.2.2 *Xanthate Accelerators*

The most important ones are: 1. Sodium isopropyl xanthate 2.Zinc isopropyl xanthate. These are extremely fast accelerators are used mainly in latex industry.

2.3.2.3 *Thiuram Accelerators*

These form a group of ultra accelerators with higher processing safety than dithio carbamates. Most important accelerators of this group are Tetra methylene thiuram disulphide (TMTD) and Tetra methylene thiuram monosulphide(TMTM). When used as primary accelerators in normal sulphur vulcanization, they impart to the vulcanizates relatively high modulus, good mechanical properties and aging properties. Dosage is 0.5 pphr. The onset of vulcanization of compounds containing thiuram accelerators can be retarded with small amount of MBTS and the rate can be increased by adding small amount of basic accelerators such as di phenyl guanidine's (DPG.)

Generally, thiuram accelerators are used as secondary accelerators to raise rate of vulcanization of thiazole accelerators.

2.3.2.4. *Thiazole accelerators*

These are most popular class of accelerators. The following derivatives are more commonly encountered.

(A) Mercapto accelerators

Compared with dithio carbamate and thiuram, mercapto accelerators have to be used in somewhat larger proportion and with somewhat larger amount of sulphur. The most important accelerators in this group are mercpto bens thiazole(MBT), zinc salt of mercapto bens thiazole(ZMBT) and mercapto bens di thiazole(MBTS).

(B) Sulphenamide Accelerators

The most important ones are

1. Cyclo hexyl benz thiazyl sulphenamide -CBS
2. Di cyclo hexyl bens thiazyl sulphenamide-DCBS

These are typical delayed action accelerators. They can be used in combination with mercapto accelerators. Mechanical properties of articles produced with these are superior to those produced with mercapto accelerator alone.

2.3.3 Fillers and reinforcements

For many service applications, it is necessary to incorporate into rubber relatively large amounts of reinforcing materials in order to increase its hardness, stiffness, tensile strength and resistance to abrasion and tear properties of the products. These filler materials include various carbon blacks, fine particle calcium carbonates, clays and silica. Use of these filler materials in compounding requires knowledge of properties obtained through their use. Carbon black is commonly used filler.

2.3.3.1 *Carbon black*

Carbon blacks are essentially elemental carbon prepared by converting liquid or gaseous hydrocarbon into elemental carbon. They are prepared by partial combustion or thermal decomposition. Depending on the process adopted for the preparation, carbon blacks are grouped as furnace blacks, thermal blacks, and channel blacks. The properties imparted by carbon blacks to the rubber vulcanizates depend on several factors like particle size, structure, physico chemical nature of the particle surface, and chemical nature of the particle surface and particle porosity of the carbon blacks. Carbon blacks are actually fused clusters of individual carbon particles. The particle size of the blacks range from10 to 25nm for the channel black, 20 to 80 nm for the furnace blacks and 180 to 470 nm for the thermal blacks. The aggregation of carbon of carbon particles into long chains is referred to as structure of the blacks. Compared with the other processes, the furnace process gives high structure blacks. The physico-chemical nature of the particle surface is indicated by the degree of orientation of the particles in the layer planes. Those which are less reinforcing, are found to have highly oriented layers whereas the reinforcing ones,.are irregular in shape and have less crystalline orientation. The carbon particles contain very small amounts of hydrogen, oxygen and sulphur on the surface as phenolic, ketonic and carboxylic groups. The presence of these groups affects the rate of cure of the mixed compound.

The physical properties of carbon blacks used in this work are given in Table 2.5.

Table 2.5 Physical properties of carbon black

Name	Abbreviation	ASTM Design.	Particle Dia(nm)	Iodine No.	Structure (cm^3DBP/ 100g)
High Abrasion Furnace	HAF	N-330	32	80	105
Fast Extrusion Furnace	FEF	N-550	47	42	120
General Purpose Furnace	GPF	N-660	70	35	90
Semi ReinforcingFurnace	SRF	N-770	83	26	70
Medium Thermal	MT	N-990	300	-	33

Depending on the particle size and structure of carbon black, processing properties of the mix varies. On the processing side the black decreases loading capacity, dispersability, scorch time and extrusion rate decreases and incorporation time, mill bagging, viscosity and surface finish increases. As the structure in black increases, loading capacity, scorch time and extrusion smoothness increase. Similarly particle size and structure of the black affect the vulcanisate properties also. As the particle size of the black decrease rate of cure, strength, modulus, hardness, abrasion resistance, tear resistance, heat build up and electrical conductivity increase. As the structure of the black is increased, tensile strength, elongation, cut growth resistance and flex resistance decrease and modulus, hardness, abrasion resistance and heat build up increase.

2.3.3.2 *Non black fillers*

In compounding rubber for a specific application, there are a variety of factors to be considered and controlled. It is essential to know how the various properties are affected by the addition of non-black fillers. Some of the important properties to be considered are strength, stiffness, elongation, hardness, permanent set, resistance to tearing, flexing and abrasion, resistance to deterioration, time and temperature of cure, compatibility with adjacent materials, and adhesion. Most of these properties are affected to varying degrees by the non black fillers.

Factors other than fillers that affect the tensile properties are the type and quality of rubber, amount of softeners, degradation resulting from mixing, degree of vulcanisation. The effect of filler itself depends on the quantity used. There is an optimum quantity for every filler. Physical parameters factors mentioned under carbon black hold here as well. Chemically it is important to know whether the material is acidic or alkaline and whether it will react with accelerators. Generally the best reinforcing action is achieved with fine particle fillers. Presence of agglomerates and coarse particles reduce the effect. Dispersability of the filler is equally important. Surface area of the filler has an effect on curing because of the possibility of adsorption of accelerator. Additionally the ability of the filler to wet the rubber is dependent on the surface activity of the filler regard less of whether that activity is chemical or electrical. Chemical activity of the filler may cause under cure or over cure. In either case the strength will be poor. Alkaline filler increases the rate of cure and an acidic one retards it. In cases like calcium silicate MBT accelerator will be chemically converted so that the resulting product may not be an accelerator.

Among non-black fillers precipitated silica is maximum reinforcing. The next in line is calcium silicate, and chemically altered clay followed by zinc oxide and ultra fine carbonates. Effect of filler is to reduce elongation of the vulcanisate. For high elongation it is best to use medium particle precipitated calcium carbonate. The resilience of compounds containing different fillers is generally inversely proportional to the reinforcement imparted to them. Whiting stocks have good resilience while calcium silicate is relatively poor in this respect. Precipitated silica is an exception in that they impart both resilience and reinforcement. This unique behaviour has been investigated on SBR based acoustic baffle material. Hardness is generally increased by increasing the proportion of filler in rubber. It also depends on the shape and size of particles. Needle shaped or lamellar particles tend to arrange themselves in parallel lines during mixing, tubing or calendaring and will produce harder stokes than spheres of the same material. Thus calcium carbonate from ground shell is result harder stokes than ground lime stone. Size and shape of the filler particle also determine how much tear resistance it imparts. The best tear resistance is obtained from fine particle size, spherically shaped fillers. Lamellar shaped particles give poor results. Among non black fillers highest tear resistance is given by Precipitated silica followed by calcium silicate and chemically treated clays. Precipitated calcium carbonate gives only marginal tear resistance. Ground whiting, clay magnesium carbonate and similar fillers give poor tear resistance. Fine particle size fillers give the best resistance to flex apparently because coarser particles act as nuclei from which crack will spread. Fillers that produce grain effect and overloading with any type are to be avoided. Zinc oxide, precipitated silica and calcium silicate are good fillers for resistance to flexing. The highest resistance to abrasion is given by the finest particle size fillers. Precipitated silica gives best results. Calcium silicate, zinc oxide, and clay follow in that order. Calcium carbonate is poor in this respect. To obtain the best electrical properties one should use fillers which are free of water soluble materials and which are not hydrated. Some carbonates are good in this respect. Individual types of non black fillers used in the present study are reviewed.

2.3.3.3 Precipitated Calcium carbonates

Precipitated calcium carbonates are made from limestone. The carbonate is first converted into another calcium compound. And this is later converted back into the carbonate under conditions that permit control of particle size. Precipitated calcium carbonate imparts reasonably good tear resistance.

2.3.3.4 Precipitated Silica

Precipitated silica is the best non-black reinforcing filler. They have a particle size as low in 20nm. They also have an extremely reactive surface. Precipitated silica is easily mixed and excellent dispersion is obtained. Silica stiffens rubber compounds to a considerable extent. The stiffness can be modified with plasticizers. Since silica is highly adsorptive in rubbers like NR additional quantities of curatives are needed. The precipitated silica imparts very good tensile and tear resistance to synthetic rubbers particularly nitrile rubbers.

2.3.4 Plasticizers

Plasticizers are added in rubber compounds for meeting following objectives (1) increasing plasticity and workability of the compound (2) for better wetting and incorporation of fillers (3) to provide lubrication (4) to improve moulding operation and to modify the properties of vulcanised product. There are two classes of plasticizers; chemical plasticizers and physical plasticizers. The chemical plasticizers act by reducing the molecular weight of the rubber by chain scission. Physical plasticizers act as intermolecular lubricants. Chemical plasticizers are appropriate for modifying the properties of the uncured stock rather than those of vulcanised. The type of rubber being used is one which responds to such agents. Physical plasticizers are used when modification of the vulcanizate properties is desired and when processing requires the lubricating, tackifying and other special properties. Available chemical plasticizers are quite different from one another. Aromatic mercaptan, certain petroleum sulphonates, penta chloro thiophenol are typical chemical plasticizers. It is important to note that in NR chemical plasticizers are effective at higher temperatures. Important physical plasticizers come from among the following sources. Petroleum, pine tree, coal, synthetic organic compounds. Petroleum oils are most common among these. They range from highly aromatic to naphthenic and paraffinic oils. These are available in various viscosity grades. For small dosages aromatic oils are suitable. For high dosages particularly with high quantities of fillers, naphthenic oils are preferred from the point of view of compatibility and age resistance.

2.3.5 Antidegradants

Rubbers undergo change in properties with passage of time. Oxidation by atmospheric oxygen is the major cause. A number of external and internal factors influence aging. Type of rubber, cure system and antioxidant are among these. More saturated rubbers show better resistance, possible reason being that oxidation is primarily a free radical process. The general class of anti degradants include substituted phenol, p-Diphenyl amines, Phosphites etc. Materials used for protection during storage and processing are referred to as stabilisers. Stabilisers may be destroyed or rendered ineffective during vulcanisation. Thus, they do not always serve as antioxidants in the vulcanised product. The minimum amount of stabiliser necessary is normally added, with the assumption that additional anti oxidants will be added during compounding to give the desired aging characteristics. There are number of factors external to the polymer itself that affect aging. These factors are heat, oxygen, fatigue, ozone and metal catalysts.

Generally heat is an important factor in rubber aging. This is due to the temperature dependence of rate process. Accelerated tests are thus helpful to the extent that they give general aging trends. Though heat aging is not a major concern in the underwater applications, temperature dependent activation of water diffusion is relevant in the context of present investigation. The effect of oxygen on an elastomer will depend upon the type of rubber and the aging condition to which it is subjected. In general two competing processes take place; chain scission and cross linking. Chain scission results in the breaking of bonds. Cross linking results in the formation of bonds as a result of sites of unsaturation. Net effect of chain scission is a reduction of tensile strength. NR and IIR are more susceptible to chain scission than other rubbers. Crosslinking typically results in a loss of elasticity that is characterised by increase in modulus. Neoprene, SBR, NBR is most susceptible to crosslinking. Cyclic loading may lead to serious reduction in useful life. It is important to use anti oxidants to prevent flex cracking and fatigue failures.

The effect of ozone on rubbers is typically a surface effect. The mechanism of reaction of ozone is believed to proceed through ozonolysis [3]. The reaction is believed to proceed as shown in Fig. 2.4

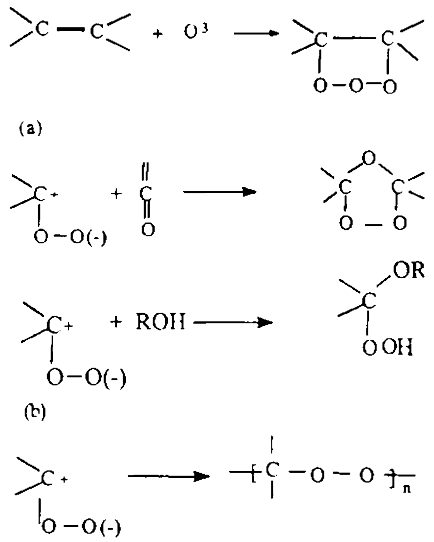


Fig.2.5 Ozonolysis reaction

The ozonide intermediates decompose to cause chain scission, resulting in the formation of cracks in a stressed rubber. The characteristic feature of ozone cracking is that cracks are at right angles to the direction of strain.

In unstressed rubbers ozonolysis will give a bloom like appearance called frosting. The formation of cracks is dependent on the degree of elongation of the rubber. The degree of elongation necessary for cracks to begin forming will depend on the type of rubber and compounding ingredients. Usually the range is 5 to 10 percent. At a high elongation large, deep cracks are found. These large cracks lead to failure. The type of rubber will also affect cracking. NR forms fine cracks, SBR forms large cracks. Neoprene shows much better crack resistance. Protection against ozone often involves surface coating or waxes that bloom to the surface, certain combination of polymers give better ozone resistance such as nitrile rubbers and PVC.

2.3.6 Principles of compounding

The mixture of rubber and ingredients used for manufacturing of a rubber product is known as compound. The process of making such a compound is called compounding. The process consists of the selection of the type and amount of various compounding ingredients used in a mix, the manner of mixing, processing of the finished mix and the method and details of vulcanisation.

2.3.7 General compounding formulation

Major constituents of a technical rubber vulcanizates have been listed in Table 2.6

Table 2.6 Major constituents of technical vulcanisates

Ingredient	Types
Base polymer	Natural or Synthetic rubber
Aids and means of curing	(i) Cross linking agent (ii) Accelerator for the cross linking reaction (iii) Activator and retarder eg. Zinc oxide, Stearic acid
Aids to processing	(i) Peptising agents (ii) Softeners
Aids to quality	(i) Fillers-reinforcing type (ii) Anti degradents
Diluents	(i) Non reinforcing fillers
Special materials	(i) Colour, (ii) Blowing-agent, (iii) Antifouling agents

2.3.8 Compounding for specific properties

For a particular application, the basic polymer or a blend of polymers is to be selected first according to the broad pattern of final properties required. This must then be combined with an appropriate crosslink system, carbon black or a combination of carbon black and non black reinforcement if any, process aids being included to ensure satisfactory mixing and processing. Reinforcing fillers of finer particles size are as a rule difficult to incorporate during mixing, and they yield stiffer stocks. Protective agents are selected depending on service conditions and the nature of the base polymer.

Compounding considerations for different vulcanisate properties differ in approach. Following is a brief discussion on each vulcanisate property vis a vis compounding procedure.

2.3.8.1 *Hardness and modulus*

Hardness gives a measure of the modulus at low strains. Hardness and modulus of a vulcanizate are normally increased by the use of particular fillers, greatest effect being obtained with finer carbon black and silica. The extent of hardness increase per part of filler for different carbon black types in CR.IIR, NR and SBR are given by Jacques [4] Highest influence is found with CR among the above rubbers. For the same quantity of carbon black NR is shown to give higher tensile strength. The reinforcement pattern of non black fillers is less clear. Varying chemical nature of materials concerned in addition to their varying particle shape and surface state, influence the hardness. In effect the broad picture of finer particle resulting in greater hardening remains. Data relating to the influence of calcium carbonate of known particle size have been published [5]. Compounding which increases hardness also produces increase in the higher strain moduli values. Use of silane coupling agents to improve the bonding of rubber to silica and silicate fillers during vulcanisation have been investigated [6] Elastic modulus in a filler-rubber system could be increased by using heat treatment during mixing. Sulphenamides tend to produce slightly harder vulcanizates than thiazoles. Softeners and plasticizers reduce hardness.

2.3.8.2 *Viscoelasticity*

Vulcanised rubber shows visco elasticity, and is different from elastic materials. High elasticity property can be imparted to vulcanised rubber by reducing its visco elastic properties like loss modulus, creep and stress relaxation. Glass transition event dominate the viscoelastic in polymers. This decides the frequency and temperature at which damping maximum occurs as also the intensity of damping. Compounding which contributes to a more tightly knit cross linking, occupying the maximum possible volume proportion of the vulcanisate will enhance the elastic properties. A stable cross linking system can minimise stress relaxation and creep in rubbers. Such vulcanizates should be able to resist degradative influences of the service environment as well. The Highest strength is given to rubbers by using fine particle size carbon blacks or reinforcing silica and to obtain higher levels, it is essential that these are well dispersed. Selection of type and quantity of carbon black significantly influence the dynamic mechanical properties [7]. Low structured carbon black is the choice for higher elasticity. Certain resins like phenolic resins are also capable of producing increased strength levels.

Rubbers such as CR and NR, which crystallise on stretching yields high tensile strength hardness value below 50 IRHD. Other polymers such as SBR, NBR of low gum strength., require fine particle size reinforcing fillers to develop maximum strength. And this reinforcement is accompanied by increased modulus and hardness.

In both cases highest strengths are achieved by the use of fine particle size carbon black or reinforcing silica. To obtain highest levels it is essential that these are well dispersed. Optimum levels vary according to the polymer filler- system, but generally lie in the range of 30-60 pphr.

2.3.8.3 *Resistance to abrasion*

Compounding of rubber for improving abrasion resistance often gives confusing results. In general fine particle size blacks improves abrasion resistance. Optimum level of filler for maximum reinforcement is found to be 50 pphr. Abrasion resistance can also be improved by adjusting polymer types. Thus it is established that a blend of NR and poly butadiene gives better abrasion resistance than NR alone in a similar compound. A good level of anti oxidant protection is also needed for getting abrasive wear properties.

2.3.8.4 *Tear*

Unlike abrasion resistance use of reinforcing blacks does not result in a noticeable effect in tear properties. Natural rubber and poly isoprene give some response, but SBR and Neoprene show much reduced effect. Coarse fillers of mineral origin particularly those with relatively large particle fractions generally reduce tear values. Certain resinous processing aids like coumarone indene resin, petroleum resins and Phenolic resins are capable of improving tear resistance. It is believed that these resins can wet the surface of fillers and improve rubber to rubber particle contact. In low hardness stocks the high gum strength polymers such as NR or CR give higher tear levels than low gum strength types such as SBR or NBR. In CR small particle size non carbon black fillers such as aluminium silicate give high tear strength figures. Silica is capable of producing superior tear resistance than that given by reinforcing carbon blacks. Tear resistance falls appreciably with increasing temperature.

2.3.8.5 Resistance to cyclic stress, flex cracking cut growth

The initiation and development of crack in rubber vulcanizates is a frequent cause of failure. The nature and stability of cross linking system, the choice of protective agents and the degree of dispersion of curatives, reinforcing and other fillers are factors influencing performance in flexing. If compounding reduces resilience additional heat will be liberated during flexing resulting in failures. Apart from the choice of base polymer, compounding variation can have quite complex effects on crack development. Crack growth rate is high for SBR, BR and CR but low for NR. The Goodrich flexometer data reported in literature show 7°C temperature rise for 4.1% reduction in resilience. The effect of polymer choice can be seen from the data provided by Beaty [8]. Results on moulded test pieces stressed at 12kHz, show that good resistance to crack initiation need not be accompanied by good crack growth resistance.

2.3.8.6 *Electrical properties*

Electrical properties depend not only on the nature of polymer but also on the type of filler and platiciser. NR, SBR and IIR are all capable of giving good electrical properties. PVC, neoprene and NBR are useful for low voltage resistance applications, but are more useful as outer protective coatings over insulating layers for weather or solvent resistance depending on service conditions. Reinforcing furnace blacks are used in production of anti static or conductive rubbers, being used in special applications like in oxygen masks used in operation theatres. Mineral fillers (whitings, clays) coated silica with low water soluble contents give appreciably higher electrical resistance and dielectric characteristics. Some synthetic aluminium silicates are conductive in nature and are used in white antistatic products. Other compounding ingredients used should be such that they have minimum water absorption properties.

2.3.8.7 Bonding with adhesives

For successful rubber to metal bonding highly polar polymers like CR, NBR are better than NR or SBR of lower polarity. These in turn bond more readily than IIR. There are several other factors than the type of polymer which determine bonding performance. These include type and level of plasticizers used, carbon black, cure system etc. TMTD/Sulphur less sulphur donor systems have been known to give rise difficulties with certain bonding systems.

2.3.8.8 Resistance to Liquids

All rubbers can absorb liquids to a greater or lesser degree. The action of liquid on vulcanisates may result in physical swelling of the polymer, degradation of the polymer and fillers, and the leaching of or attack on, plasticising agents. Cross linked rubbers prevent rubber molecules from becoming completely surrounded by the liquid and restrict deformation of rubber. Amount of liquid absorbed by a given rubber depends on the number of crosslink per unit volume. The shorter the average length of the rubber chain between cross links lowers the degree of swelling. For optimum resistance to a particular liquid, the polymer should be chosen so that its solubility parameter is as far apart from that of the contact liquid [9]. Chemical attack on the polymer is most likely to arise from oxidising substance, and in this event polymer having a relatively inert backbone structure should be chosen, IIR, CSM, or EPM. In addition to the intrinsic swelling and chemical resistance of the polymer, volume content of the polymer in the vulcanisate should be kept as low as practicable since this will minimize its contribution to any volume change. Fillers chosen, should be as inert as possible under the service condition. Plasticizer stability is also important.. Ester plasticizers should be avoided where hydrolysis could occur. Extractable plasticizer or additives are undesirable where shrinkage effects cannot be permitted, for instance in certain seals, unless swelling of polymer by liquid in which it operates compensates for this. A high state of crosslinking in the final vulcanisate will also assist in reducing ultimate swelling. Where resistance to water or aqueous solutions is required, the presence of water soluble salts in the vulcanisate is detrimental as they facilitate the ingress of water. CR which is cross linked using magnesia-zinc oxide systems produces traces of water soluble chlorides; so for better water resistance lead oxide cures are preferred.

2.4 Rheology of Rubbers

A significant factor favouring the choice of rubber for transducer application is its processability. Rubber lends itself for easy fabrication by compression moulding, transfer moulding and injection moulding operations. Parameters like scorch safety, viscosity, cure temperatures etc could be adjusted in judicious compounding. Cure parameters can be conveniently studied using rheometers. Conventional moulding temperature of rubber is around 150 °C. For transducer fabrication lower processing temperature is desirable, for preventing accelerated thermal aging. Lower vulcanisation temperature also facilitates insitu moulding with thermoplastic structural components and cables. In literature and patent no practical curing system have been reported for effective cross linking of rubbers particularly neoprene.

2.4.1 Viscosity control

When raw polymer are selected it is necessary to select the correct Mooney viscosity level to ensure acceptable mixing and processing characteristics synthetic rubbers are available in several viscosity values. For blending operation rubbers of same viscosity grades are recommended. When high green strength is required high viscosity grades are required

2.4.1.1 Mooney viscosity

The Mooney Viscometer was introduced by Melvin Mooney in the1930's. It still remains very popular process ability tester. The Mooney viscometer is a shearing disc viscometer. The standard test is carried out as per ASTM D-1646-80. Under this test method, two measurements can be made.

1. Mooney Viscosity is a measure of shearing torque averaged over a range of shearing rates. The rotating disc is used to determine the Mooney viscosity of various types of rubber or of the fully mixed compound. Test temperature is normally selected based on rubber type.
2. Mooney scorch- the viscosity of the compound containing all curatives/ is monitored in Mooney units, over a given test time. Minimum viscosity at the scorch test temperature and time required for specific change in minimum viscosity are used as a measure of the beginning of vulcanisation and the rate with which the vulcanisation proceeds.

Both the rotor and die are serrated. That is a crosshatch pattern is milled into the surface. This pattern mechanically grips the rubber. Two rotors are available one is 1.2 inches in diameter; the other is 1.5 inches. The rotor revolves at 2 rpm. Rubber fills the remainder of the cavity and shearing action of the rotor revolving in the rubber sample provides a thrust which mechanically deflects a U shaped spring which in turn turns a micrometer type gauge thus permitting measurement.. Test temperature is selected. Sample is loaded and given one minute to warm up. The motor is turned on and the test is completed in four, six, or eight minutes depending on the type of rubber.

Scorch or processing safety is determined with small rotor and the dies preheated to test temperature. The rotor driven by a motor revolves at 2 rpm through the rubber sample. The rubber offers resistance to the tuning rotor. This resistance is measured in the same manner as for viscosity determination. Test temperature is higher in scorch safety determinations. With fully compounded stock the accelerators and sulphur interact and vulcanisation begins. Scorch safety is the time until vulcanisation is apparent on the scorch curve.

2.4.2 Rheometers

The Monsanto oscillating disc rheometer is the most popular. In this method a biconical disc is embedded in a sample of fully compounded rubber. Dies are heated to appropriate curing temperature to effect vulcanisation. The rotor is oscillated sinusoidally through an arc of 1, 3, or 5° at 100 rpm and it exerts a shear strain on the rubber sample. The torque at the maximum required to oscillate the rotor is proportional to the stiffness on the rubber. Torque is recorded as a function of time. Since the stiffness of the rubber compound will increase during vulcanization, a complete curing curve can be generated which actually represents a finger print of the compound during curing.

The dies are electrically heated to temperature is based on the application. The typical temperature range is 100-200°C. A rubber sample is placed on the rotor and the dies are closed and held closed by the air driven arm. The rubber sample then flows to fill the cavity formed by the closed dies and the rotor is then embedded in the rubber. The rotor then gets oscillated through a pre selected arc of 1, 3 or 5°. The force required to oscillate the rotor is measured electronically by a strain gauge which are mounted on the torque arm. An electronic signal is sent to the recorder which then plots the curve.

The rheograph is typically divided into three separate regions the phase 1, is the processing area on which a judgement can be made on the flow characteristics and a general viscosity level prior to vulcanisation. Phase 2 gives the rate of cure. This phase begins after passing through the induction point. Phase 3 represents the maximum torque developed or the maximum state of cure. The important parameters derived from cure include minimum torque, maximum torque, scorch time and cure time. These are useful input for quality control and product development.

2.5 Engineering properties of rubber vulcanizates

2.5.1 Static mechanical properties

Rubber is unique among engineering materials in the diversity of physical properties that can be achieved through compounding. Because the physical properties of the rubber material are crucial to the service performance of a component, significant efforts have gone in to the development of physical testing methods. Engineering properties of direct relevance to the present work include static mechanical properties, dynamic mechanical properties, acoustic properties, electrical properties, environmental properties and age associated changes in properties

2.5.1.1 Tensile stress -strain

Tensile strength is the maximum tensile stress reached in stretching a test piece, usually a flat dumb-bell shape to its breaking point. By convention the force required is expressed as the force per unit area of the original of the test length. Elongation is the extension between bench marks produced by a tensile force applied to the test piece and is expressed as a percentage of the original distance between the marks. Elongation at break is the elongation at the moment of rupture. Unlike metal stress is not proportional to strain and therefore modulus is the stress at some strain. It is neither a ratio nor a constant but merely the coordinates of a point on the stress- strain curve.

The tensile stress strain properties of rubbers are measured with a tensile testing machine. The early heavy pendulum dynamometers have largely been replaced by inertia -less transducers which convert force into an electrical signal. Measurement of stress and stain are taken continuously from zero stain to breaking point. Dum-bell shaped test pieces are die cut from flat sheet. The ends are placed in the grips of the testing machine and the lower grip is power driven at 50 cm per minutes so that the piece is stretched until it breaks. Tensile strength and elongation are useful for compound development, manufacturing control and for determining and compounds resistance to attack by various chemicals. Tensile tests are universally used as a means of determining the effect of various compounding ingredients and are particularly useful when such ingredients affect the rate and state of vulcanisation of the rubber. Similarly tensile tests are excellent for controlling product quality one compound has been selected. The tests are sensitive to changes in manufacturing condition and can be used to identify under or over vulcanisation and presence of foreign matter. Tensile tests can be made before and after exposure to determine the relative resistance of a group of compounds to deterioration of a group by heat, oil, ozone weathering chemicals etc. Even a small amount of deterioration causes appreciable changes in tensile properties.

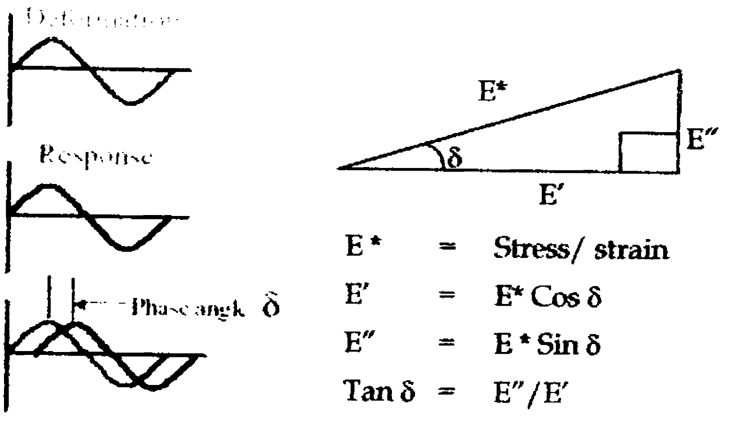
2.5.1.2 *Compressive stress -strain tests*

Elastomers for engineering applications are more often used in compression than in tension and ISO 7743 provides a method for determining the compression stress-strain relationship. The test piece is a cylindrical disk of 29 ± 0.5 diameter and 12 ± 0.5 mm in thickness. The test piece is compressed axially in a universal tensile testing machine used in its compression mode, with auto graphic recording of force and deflection. The test piece is placed between two sheets of fine glass paper with the abrasive side against the elastomer, in order to resist lateral slip. Two conditioning cycles are made in which the test piece is compressed to 5% greater than is required for the standard. The results from the third compression are expressed either as the compression stress at a specified strain or a series of strains or as the compression strain at a specified stress or series of stresses.

2.5.2 Dynamic mechanical properties

In a cyclic or dynamic situation such as in underwater acoustic applications, viscoelastic nature of materials having both elastic and viscous behaviour is very important. Energy required to deform a perfectly elastic material is completely recovered when the force is removed. But the viscous element which is caused by internal molecular friction retards elastic deformation and energy is lost. The lost energy is dissipated in the form of heat and the consequent temperature rise in the elastomer is called the heat build up. The percentage energy loss per cycle of deformation is known as hysteresis. If force is plotted against deflection for one cycle of deformation a hysteresis loop is obtained. The area under the unloading curve is proportional to the energy returned. Resilience is the term used to define the energy returned on recovery and is expressed as a percentage. Rebound resilience is used as a test of dynamic properties the difference is the hysteresis energy loss. If the relationship between stress and strain were perfectly linear the loop will be elliptical. And if the sample were perfectly elastic the ellipse will collapse to a straight line. If the loading and unloading cycle is repeated the shape and position of the hysteresis curves change. In a rubber containing carbon black filler, most of the break down occurs in the first cycle.

In phase stress is due to the elastic component of in the rubber. Because of the hysteresis losses, the stress lags behind the resultant of the two stresses by an amount which is known as the phase or loss angle, δ. Fig.2.6 demonstrates resolution of complex modulus into viscous and elastic components.



$E^* = \text{Stress/ strain}$

$E' = E^* \cos\delta$

$E'' = E^* \sin\delta$

$\tan\delta = E''/E'$

Fig.2.6 Resolution of complex modulus into elastic and viscous components

The more viscous the material the greater is the loss angle. The tangent of the phase angle, tan δ in the simplest terms is the viscous modulus. For mathematical convenience the viscous modulus is some times considered to be imaginary.

2.5.2.1 Measurement of dynamic properties

Dynamic Mechanical Analysis (DMA) is a technique used to measure the mechanical properties of a wide range of materials. Many materials, including polymers, behave both like an elastic solid and a viscous fluid, hence the term viscoelastic. DMA differs from other mechanical testing devices in two important ways. First, typical tensile test devices focus only on the elastic component. In many applications, the inelastic, or viscous component, is also important. It is the viscous component that determines properties such as impact resistance. Second, tensile test devices work primarily outside the linear viscoelastic range. DMA works primarily in the linear viscoelastic region and hence it is more sensitive to structure.

DMA measures the viscoelastic properties using either transient or dynamic oscillatory tests. Transient tests include creep and stress relaxation. In creep, a stress is applied to the sample and held constant while deformation is measured vs. time. After some time, the stress is

2.5.2.2 *Dynamic mechanical analysis*

Dynamic properties of a rubber are depended upon the method of measurement especially if fillers are present. It is therefore important to define the test parameters used when testing the general requirements are outlined in ISO 2856 but the standard does not give any details of the machine. These may be classified as follows

(a) Free vibration

(b) Forced vibration

(c) Propagation

Machines using free vibration set the test piece in oscillation and the amplitude is then allowed to decay due to the damping in the system. With forced vibration oscillation of the test piece is maintained by external means and the frequency is adjusted either to be non resonant or resonant. Methods based on propagation of ultrasound operate at much higher frequencies. Rebound resilience and torsion pendulum and Yerzly oscillograph methods are based on free vibration principle.

TA Instrument 983 dynamic mechanical system is has been used for characterisation of dynamic mechanical properties in the present investigations. The test piece is clamped between the ends of two parallel arms, which are mounted on low-force flexure pivots which only allow motion in the horizontal plane The distance between the arms is adjustable by means of a precision mechanical slide. An electro magnetic motor attached to one arm drives the arm/test piece to a strain selected by the operator. As the arm/test piece system is displaced, the test piece undergoes a flexural deformation as depicted schematically in Fig.2.8

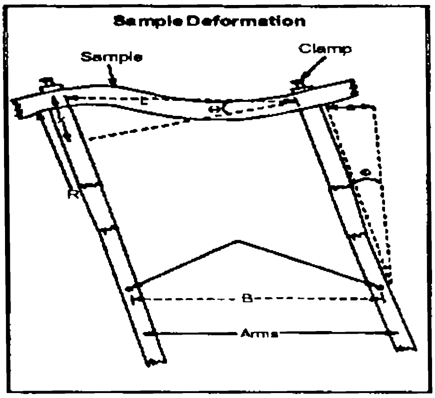


Fig.2.8 Flexural deformation of sample

A linear variable differential transformer mounted on the driven arm measures the response to the applied stress and provides feed back control to the motor. The test piece is positioned in a temperature controlled chamber which contains a radiant heater and a coolant distribution system.

The unit can be operated in a number of modes. When operating in fixed frequency mode the test piece is subjected to a sinusoidal oscillation at a selected frequency and amplitude. The unit can be programmed to measure the viscoelastic characteristics at 57 frequencies during a single test. The test piece is allowed to reach mechanical and thermal equilibrium at each frequency before the data is collected. After all the frequencies have been scanned, the test chamber temperature is automatically stepped to the next temperature and the frequency scan is repeated.

In the resonance mode, the unit operates on the mechanical principle of forced resonant vibratory motion at a fixed amplitude (selected).The arms and test piece are displaced by the electro magnetic driver, subjecting the test piece to a fixed deformation and setting the system into resonant oscillation.

In free vibration, a test piece will oscillate at its resonance frequency with decreasing amplitude of oscillation. The resonant mode differs from the free vibration mode in that the electromagnetic driver puts energy into the system to maintain fixed amplitude. The make up energy, oscillation frequency and the test piece geometry are used by the DMA software to calculate the desired viscoelastic properties.

2.5.2.3 Application of DMA

A common measurement on polymers is the glass transition temperature, Tg. It can be measured with various techniques, but DMA is by far the most sensitive. Tg can be measured by the E′ onset point, by the E″ peak, or the peak of Tan δ. In addition to the Tg, the absolute value of the various viscoelastic parameters is also useful. Because Tg has a kinetic component, it is strongly influenced by the frequency (rate) of deformation. As the frequency of the test increases, the molecular relaxations can only occur at higher temperatures and, as a consequence, the Tg will increase with increasing frequency. In addition, the shape and intensity of the Tan δ peak as well as the slope of the storage modulus in the transition region will be affected. Assessing the effects of plasticizer and other additives such as fillers, on modulus and transition temperatures is common among the use of DMA. Based on end-use conditions, it is important to understand the temperature and frequency dependence of transitions. DMA is the only technique that can measure β and γ secondary transitions. Secondary transitions arise from side group motion with some cooperative motion from the main chain as well as internal motion within a side group. The transitions are below the Tg and typically sub-ambient. They are very important as they affect impact resistance and other end-use properties.

2.5.2.4 Time-temperature super positioning (TTS)

The TTS technique, well grounded in theory, is used to predict material performance at frequencies or time scales outside the range of the instrument. Data is usually generated by scanning multiple frequencies during an isothermal step-hold experiment over a temperature range. A reference temperature is selected and the data shifted. A shift factor plot is can with stand such attacks to different extent. If a rubber absorbs a large volume of liquid, it will generally become weak and useless for most engineering applications. Moreover, chemical attack can cause further deteriorations: in either case, weakening will be progressing. It is clear from these observations that the durability of an elastomeric component is influenced by its environment. Elastomer selection therefore needs to take account of the service fluid composition. Organic liquids tend to weaken elastomers by physical means only, whereas corrosive liquids such acids alkalies and marine waters tend to attack chemically as well.

Rubbers are used as coatings and lining to protect the chemical plant equipments, pipes, and underwater systems so on against corrosion and abrasion. The physical processes associated with the phenomenon have already been considered in chapter 1. The absorption process is governed by thermodynamic parameters.

$$\Delta G = \Delta H - T\Delta S \tag{2.1}$$

Thus the requirement is that $T\Delta S$ be greater than ΔH. Enthalpy change is largely influenced by solubility parameter ψ values for liquid and polymer [11] where ψ^2 is the cohesive energy density- a measure of the energy of attraction between like molecules. ΔH will be less than $T\Delta S$ only when certain conditions for ψ are met: such as ψ values are within about1 $(cal/cm^3)^{1/2}$ each other. Then considerable swelling will occur. If the liquid is a moderately viscous oil, this maximum difference in ψ reduces to about $0.8(cal/cm^3)^{1/2}$. Application of solubility parameter becomes more complex at values of solubility parameter greater than about 15-23 $(cal/cm^3)^{1/2}$.

The final concentration $M\infty$ is lower for a highly cross linked elastomer even for liquid of similar ψ. A more important parameter governing the rubber-liquid interaction is viscosity of the liquid.

2.6.2 Rubber water interaction

Effect of the interaction of water with rubber forms key issue of the present investigation. The basic parameters governing these interactions have been already discussed in chapter1. Stevenson and Campion [12] discuss effects of the phenomena and give some typical water absorption values of elastomers exposed for 2 year in salt water. Equilibrium water absorption by NR is about 4%, NBR about 5 %, and poly chloroprene cured with magnesium oxide cure is more than 32%. However, according to the authors salt water is not generally a deleterious environment for rubber. They cite the examples of neoprene based protective coatings used in offshore installations, fracture mechanical analysis of NBR based flex joints used in tension leg platforms in North sea and the case history [13] of a rubber tyre after 42 years of exposure to sea water.

2.6.3 Hydrocarbon liquids

In hydrocarbon liquids, diffusion dominates the movement of liquid into the rubber bulk. Individual molecules move by jumping into adjacent holes formed momentarily in the elastomer matrix during random motion, arising from kinetic energy. The thermodynamic drive is a tendency to equalise chemical potential of the diffusing liquid throughout the rubber matrix. The rate of migration is governed by Ficks laws of diffusion. The amount diffusing across an area A as per the above laws can be expressed as

$$[1/A](dm/dt) = -D(dc/dt) \qquad (2.2)$$

By considering incremental increase in concentration along the path of the species Fick's second law is obtained:

$$(dc/dt) = D(d^2c/dx^2) \qquad (2.3)$$

As diffusion progresses, the average distance travelled by a particle in time t from x=0 is $(2Dt)^{1/2}$. This expression indicates that a diffusion-related phenomena increase with the square of rubber thickness.

Mathematical solutions of Fick's second law are complex but have been obtained for many situations [14]. An easy means of measurement of D is by determining mass uptake. Sheet samples are immersed into the liquid of interest. Samples are removed at appropriate intervals and increase in weight noted.

To determine D for the sheet sample the solution of Fick's second law is applied with appropriate boundary conditions:

$$Mt/M\infty=2/h\,(D\,t/\pi)^{1/2} \qquad (2.4)$$

Eventually D becomes concentration dependent as, after awhile liquid that has entered can contribute to the rate at which fresh liquid diffuses. One convenient method of obtaining a diffusion coefficient is to measure D_{av}, an average D at the point of 50 % mass uptake so that:

$$0.5 = (2/h)(D_{av}t_{av}/\pi)^{1/2} \qquad (2.5)$$

From the equation it follows that a plot of mass uptake vs sq root of time should be informative.

2.7 Acoustic properties

Rubbers exhibits extreme versatility for tailor making acoustic properties; be it for acoustic window performance or an absorber in sonar dome, baffle or a reflector for acoustic decoupler device. The parameters governing the acoustic wave propagation are the density and sound speed in the material. But sound speed in viscoelastic materials is a complex quantity owing to the fact that the dynamic modulus of rubbers is a super imposition of viscous and elastic components of modulus. The encapsulation material while meeting the primary function of protecting sensor material from sea water must also posses the requisite acoustical properties for transmitting the maximum acoustic power from transducer to water mediüm. Acoustic impedance of the rubber has an inherent reactive component. Mathematical relationship between the specific acoustic impedance of water and rubber has been already discussed in chapter 1. It is brought out that it is practically impossible to get completely reflection free transmission across rubber. However, by adjusting the density and modulus it has been possible to achieve optimum acoustic transmission through rubbers. Another important aspect is the frequency and temperature response of rubber. Practical implication of constant acoustic wave velocity is extremely important in acoustic baffle design. Glass transition in the material determines damping maximum of rubber. Tg in the material could be tailored to modify the frequency response [15].

2.8 Thermal analysis of Rubber

Thermal analysis is a generic term for a series of techniques that measures some physical change in a material as a function of temperature. All materials as they experience changes in temperature, undergo changes in their physical and or chemical properties. These changes are sensed by suitable thermo couples and converted in into equivalent electrical signals which are collected and analysed to give thermo grams showing the property change as function of temperature. Among the various techniques following three are used in the present work.

2.8.1 Thermogravimetric Analysis (TGA)

TGA measures weight changes associated with thermal events. This technique is commonly used for compositional analysis, determination of thermal stability and for evaluation of thermal decomposition kinetics in order to predict long term as well as short term thermal stability. Usual working temperature range is from ambient to1200°C

2.8.1.1 Applications of TGA

TGA provides information about the gross composition of polymer formulations. Using programmed heating and a change in the atmosphere over the sample, it is easy to determine the weight loss associated with light or heavy oils, bulk polymer and carbon black or other reinforcing agents. By heating elastomers in TGA under nitrogen and then switching to oxygen at 800 ° C, It is possible to determine the amounts of oils, polymers, carbon black and organic filler present.

One widely used technique for predicting the resistance to oxidation involves heating polymer sample in an oven and periodically testing for the weight gain due to oxygen uptake. TGA allows the same measurements to be made continuously. The sample is heated to the temperature of interest in an inert atmosphere, then purge gas is changed to oxygen. The time from oxygen introduction to the onset of weight gain is a measure of the oxidative stability off the polymer system.

TGA provides a method[16] for accelerating the life time testing of polymers so that short term experiments can be used to predict life time. The procedure consists of recording TGA curves of the sample at different heating rates. The temperature (T) for a selected value of conversion (say 5%) is noted from the TG curves. The slope of the plots of heating rate (Θ) versus 1/T the activation energy E′, is evaluated by the method proposed by Flynn and Wall [17]using the equation.

$$E= -R/b[d \log\theta / d(1/T)] \qquad (2.6)$$

where E= activation energy, R= gas constant T = temperature at constant conversion, K. θ = heating rate,(°C), b= constant 0.457 evaluated from Flynn and wall method.

Estimated time of failure t_f can be evaluated by using Toops [18]equation

$$\ln t_f= E/ RTf + \ln[(E/ \theta R^{*}p(X_f)] \qquad (2.7)$$

where t_f = estimated time of failure(min),Tf= failure temperature(K).P(Xf) = a function whose value depends on E at the failure temperature

2.8.2 Differential Scanning Calorimetry (DSC)

DSC measures the heat flows associated with transition in materials. Such measurements provide qualitative information about physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity. In addition to the determination of heats and temperature of physical and chemical transitions, DSC has specific use in finding out calorimetric purity and second order transitions.

2.8.2.1 Applications of DSC

DSC is routinely used to measure glass transition temperature Tg; melting point, degree of cure, degree of crystallinity, heat of fusion and /or crystallisation; decomposition temperature and numerous other parameters. The area under the curve in DSC is proportional to the heat of transition and the mass of the reactive sample.

$$\Delta H\, m = KA \qquad (2.8)$$

Where ΔH is heat of transition (or reaction), m is the mass of reactive sample, K heat is the calibration constant and A is area under the DSC curve. The calibration coefficient, K is determined using compounds of known heats of transition. Thus from the knowledge of the characteristic peak, sample mass and known heat of transition it is possible to estimate the amount of polymer in the blend. DSC is an effective technique for rapidly evaluating the oxidative stability of polymers. The oxidative degradation is seen as an exothermic peak in DSC and extrapolated onset temperature of the peak gives an idea about the relative thermal stability. As already defined, glass transition temperature, T_g is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states. Since cooling causes the polymer to freeze into an unordered solid, this process is also referred as vitrification. T_g is a secondary thermodynamic transition related to flexibility of a polymer (rubber) back bone, the secondary inter chain forces acting on it and the free volume of the system.

2.8.3 Modulated DSC (MDSC)

MDSC [19] is an extension modulated DSC offers unique advantage of providing quick and accurate determination of thermal events. In modulated DSC a different heating profile is applied to the sample and reference by the furnace. Especially, a sinusoidal temperature oscillation is over laid on the conventional linear temperature ramp to yield a heating profile in which the sample temperature is still continuously increasing with time but not in the linear fashion. Rather, the temperature increases at a rate which is sometimes faster than the underling linear heating rate and some times slower than the under lining heating rate. Consequence of this over laid heating profile is that sample experiences a rapid instantaneous heating/cooling and a slower underlining heating rate. This result in improved sensitivity without loss of resolution. The actual variation in the heating rate obtained depends on: the underlying heating rate, the amplitude of modulation, and frequency of modulation.

One way to mathematically represent DSC heat flow is

$$dQ/dt = dT/dt\ (Cp+F_R(t,T)+F_A(t,T) \qquad (2.9)$$

This equation shows that the total DSC heat flow is comprised of two components- one which is heating rate dependent ($Cp+F_R(t,T)$ and another which is dependent only on absolute temperature, $F_A(t,T)$. Thus there is one component that directly follows the modulated heating rate (Reversing) and one component which does not (non reversing). MDSC measures the total DSC heat flow as well as two components of heat flow.

2.8.3.1 Direct Measurement of Heat capacity

MDSC provides the unique ability to measure heat capacity directly in a single experiment and to measure it even at very low underling heating rates. In theory heat capacity should decrease as a monomer polymerises because polymerisation, or cross linking, causes material's free volume for internal molecular motions to decrease. However, the onset of heat capacity decrease occurs after the exothermic peak in the non reversing heat flow curve. This means that heat changes more drastically during cross linking than during linear polymerisation.

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Chapter 3

COMPOUNDING STUDIES

This chapter discusses conventional and exploratory compounding studies carried out on common engineering rubbers namely Neoprene rubber, Butyl rubber Bromobutyl rubber, Styrene butadiene rubber, Nitrile rubber and Natural rubber. Their short term and long term properties relevant to underwater electro acoustic transducer technology have been discussed.

3.1 Introduction

Rubbers in general has been widely accepted material for use in marine applications. The notable attributes include its compatibility with salt water, weathering, resistance to oil, oxidation, ozone resistance, and amenability to adhesive bonding as well as high mechanical properties. A major limitation of poly chloroprene rubbers is their rather high water absorption. Absorbed water interact with rubber leading to undesirable changes in physical, mechanical (acoustical) and electrical properties. While selecting a material for long term under water service the most important single property to be considered is the interaction between water and the material. Hence in the present study various aspects of water- rubber interaction and associated mechanical, electrical, thermal and acoustical properties have been investigated. Study covers the effect of various compounding ingredients i.e., base polymer, cure system, filler types, filler quantities. Molecular diffusion of water through elastomer is an important consideration in underwater applications. In this study permeability of neoprene rubber has been investigated as functions of composition parameters and temperature. Kinetic parameters of permeation process have been estimated to assess their influence in quantitative terms.

3.1.1 Sample preparation

Following general method has been adopted for preparation of all rubber samples used in this work. Ingredients have been weighed out on the basis of parts (by weight) per 100g rubber (pphr). A laboratory model mixing mill 200x300mm has been used for mixing and incorporation of compounding ingredients. Compound preparation method generally conforms to ASTM D-3182. Roll temperature was maintained at 50°C throughout. Samples have been compression moulded at 105 kg/cm^2. Samples are generally cured at 150°C excepting the specified cases. Cure characteristics have been measured as per ASTM-D-2084 using Monsanto Rheometer R-100, described in Sec.2. Cure time for individual compound has been set at tc90 min. obtained from respective cure curves.

3.2 Neoprene

3.2.1 Water absorption behaviour of neoprene gum vulcanisate

A neoprene rubber sample designated 711 has been compounded with the recipe given in the Table 3.1. Water absorption has been monitored, by gravimetric method as function of soaking time. Diffusion parameters have been calculated using Shen and Springer [1] relation as per the method described by Cassidy et.al [2].

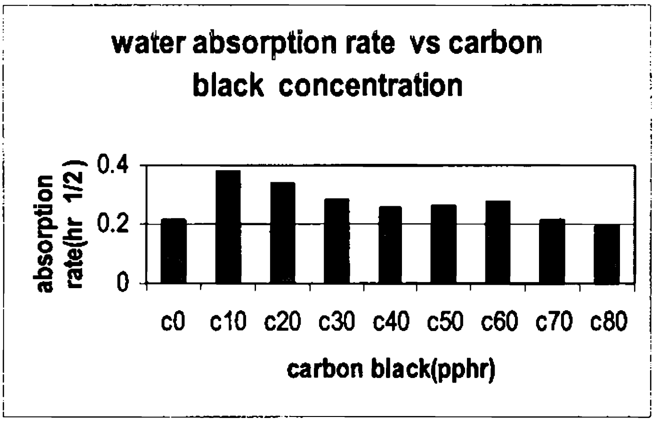

Fig 3.11 water absorption rate with increasing amount of GPF black.

In general in carbon black reinforced compounds absorption rate falls with increasing filler concentration. Water absorption has been plotted as volume fraction of GPF black in Fig.3.12. The data is found to have a declining trend.

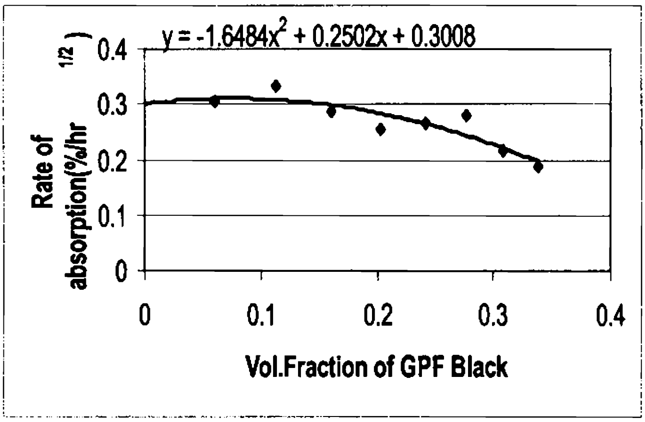

Fig.3.12 Water absorption rate as function of volume fraction of GPF black

Water absorption of compound containing 30 pphr SRF compound has been studied for kinetic parameters. Results are plotted in Fig 3.13 and 3.14

Table3.3 Diffusivity parameters

Filler	D*10^6 cm^2/hr	Slope (%/$hr^{1/2}$)
Blank[711]	1.72	0.089
[711+ FEF]	3.44	0.048
[711+GPF]	5.43	0.052
[711+SRF]	6.25	0.037

Results indicate that diffusivity of SRF filled compound is highest among the types of furnace black studied though the rate of absorption is minimum.

3.2.4 Effect of Salinity

A comparative study of effect of distilled water and salt water (3.5 % sodium chloride) has been carried out. Two formulations designated compositions No.51 and 52 have been used is given in Table 3.4. Water absorption of the two vulcanizates 51 and 52 are plotted in the Fig.3.13.

Table 3.4 Neoprene compositions 51 and 52

Ingradient	Comp. 51 (pphr)	Comp. 52 (pphr)
Neoprene-W	100	100
Stearic acid	0.75	0.75
Magnesium oxide	4	-
Zinc oxide	5	-
Red lead	-	20
Vulcanox 4020	2	2
Naphthenic oil	10	10
Ethylene thiourea	1	1

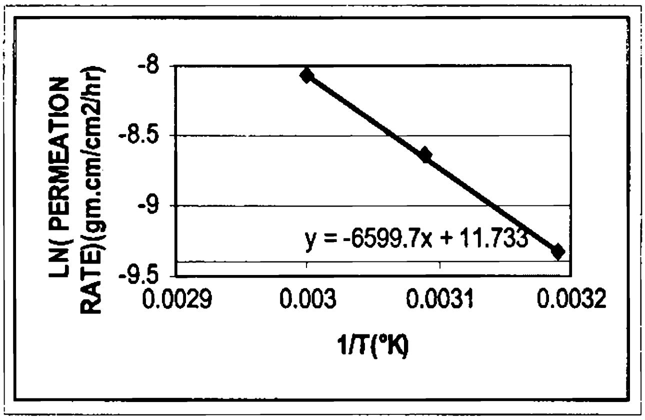

Fig.3.29 Arrhenius plot of permeation rate for Neoprene compound modified with 20FEF black.

The rate at 40 °C is 8.8 $*10^{-5}$. At 50°C the value obtained is 17.5$*10^{-5}$ while the value at 60 °C is 31$*10^{-5}$. Hence there is a doubling of the rate of permeation. However the temperature dependence of the rate has declined as compared to the gum rubber. The activation energy of the permeation process has increased from 41 to about 54 kJ /mole.

3.3 Bromobutyl Rubber

Butyl rubbers are particularly slow to diffusion process. This property has been exploited in design of tire tubes, inflatable balloons. Low permeability is important for encapsulation and potting systems hence it is worthwhile to carry out a comparative study to asses the diffusion characteristics under identical conditions.

3.3.1 Diffusion behaviour of Bromo butyl rubbers

Fig.3.30 presents relative water absorption in four samples namely Bromobutyl and neoprene gum vulcanisate (comp.711) and a modified formulation containing 30 pphr GPF black and 1pphr antioxidant 402. The formulation (comp.1101) studied is BIIR Polysar X2 :100,Stearic acid1.0,Zinc oxide:5, MBTS;1.5,TMTD:1.0.GPF black:30 and Vulcanox 4020:1.0.

3.6 Curing Behaviour of Rubbers

Curing characteristics are important factors determining the suitability of rubbers for most engineering applications. During cure the irreversible reaction takes place leading to a three dimensional molecular network structure. Good knowledge of the process is essential as the final product cannot be realized if it is not properly cured. This is particularly important in underwater electro acoustic transducer applications because optimum cross link density is essential for counter acting the osmotic pressure of imbibed water droplets. Also visco elastic properties are decided by the tightness of the network structure formed. Therefore in the present work an investigation of the cure reactions in neoprene rubber has been included. The rubber formulation comprises of Neoprene -W: 100, Stearic acid:1, Accinox :100 antioxidant: 2, MBTS:1.5, NA-22:0.6 and a varying amount of red lead from 5 pphr to 20 pphr. Study has been carried out on the kinetics of cure reaction. Two rheometric techniques namely Oscillating Disc Rheometer (ODR) and Moving Die Rheometer (MDR) have been used in the study. ODR has been described in chapter 2. In the MDR, a thin sheet of rubber (2mm) is placed between two dies kept at the desired temperature; the lower die oscillates and a reaction torque/pressure transducer is positioned above the rubber die. It has been found [4] that the MDR gives shorter times of cure than the ODR because better heat transfer and higher torque values owing to the die design. MDR analysis is performed at three temperatures to allow evaluation of the kinetic parameters of the cure reaction. Activation energy has been calculated from fractional modulus (torque) time obtained through the rheograph of Neoprene compounds. The modulus was assumed to vary with time following first order kinetics and the rate constant varies with temperature according to the Arrhenius equation [5].

The first part of the study focuses on the amount of red lead on the cure parameters.

The cure parameters shown in Table 3.6 have been generated with Rheometer R-100 of Monsanto, USA. Instrument was run at 3 ° arc, 150° C.

Table 3.6 Cure parameters of Neoprene samples containing varying concentration of red lead

Red lead (pphr)	Scorch Time t_s2 (min)	Cure Time tc90 (min)	Min.Torque ML (lb.in)	Max.Torque MH (lb.in)
5	3.0	38.5	7	37
10	3	37	10	49
12.5	2.5	27	14	59.5
15	2.5	52	10	54
20	3.5	28	10	44

It is found that that cure time reduces initially with increase in red lead from 38.5 minutes to 27 minutes as the red lead concentration is increased from 5 to 12.5 pphr. Minimum torque also increases from 7 to 14 lb.inch and maximum torque increased from 37 to 59.5 lb.in. Beyond 12.5 pphr increase in Red lead concentration does not produce any further increase in cross links. This suggests that the optimum concentration is about 12.5 pphr.

3.6.1 Kinetics of modulus buildup during cure

In the kinetics analysis the following assumptions are made:

(i) The rate of increase in the modulus of the rubber follows a first order equation at the constant temperature [6].

(ii) The internal heat developed by the cure reaction is negligible.

The rate of increase of the modulus E_t is given by the first order equation

$$dE_t/dt = k(E_\infty - E_t) \qquad (3.2)$$

at constant temperature. After integration, this gives

$$E_t/E_\infty = 1 - \exp[-kt] \qquad (3.3)$$

obtained from of their respective cure time -reciprocal temperature plots shown in Fig. 3.37

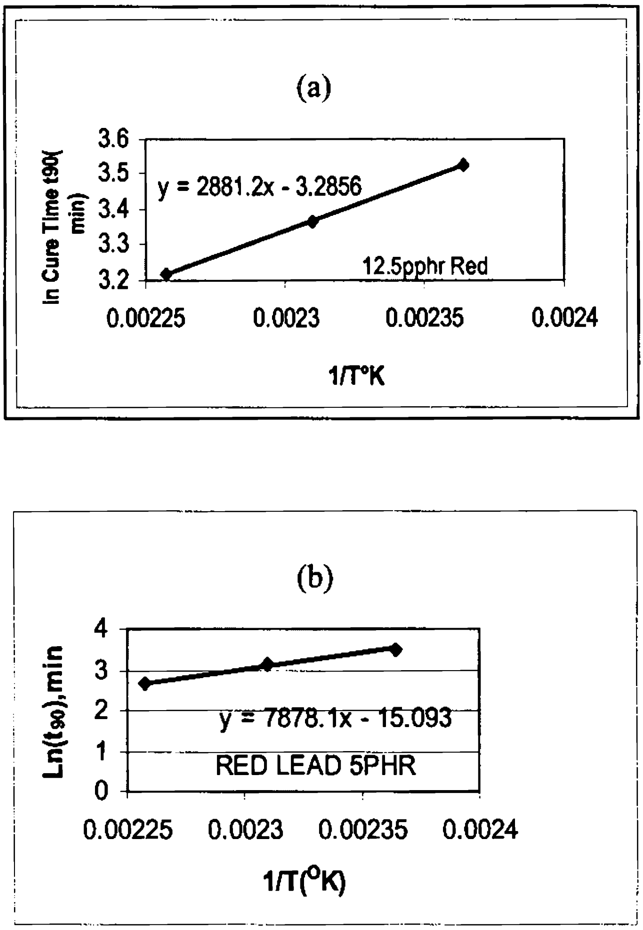

Fig.3.37a,b .Arrhenius cure plots for 12.5 and 5pphr cure systems

It is clear from results that activation energy for cure decreases with increase in red lead concentration. E_a has decreases from 65 to 24kJ/mole when red lead is increase from 5 to 12.5 pphr.

3.6.3 Effect of different types of carbon black on the cure reactions

Influence of different types of carbon black namely FEF, SRF and GPF on the cure reactions have been studied. Details are given in Table3.7

3.6.4 Effects of furnace black on the curing reactions in neoprene rubber with varying quantities of red lead

Samples containing different quantities of red lead have been modified with 30 pphr each of FEF black and cure reactions studied with rheometer R.100 Results are given in Tables 3.8. It is clear that torque levels have increased with incorporation of carbon black. As explained in section 3.6 the deviation in the cure time between MDR and ODR is due to better heat transfer in MDR.

Table 3.8 R-100 Cure parameters of Neoprene containing different red lead concentrations and 30 pphr FEF

Sample details	Scorch time (ts_2) min	Cure time $Tc90$ min	Min.Torque ML(lb.in)	MAX.Torque MH(lb.in)
5Redlead+30FEF	3	35	11	58
10Redlead+30FEF	2	33	13.8	70
12.5Redlead+30FEF	2.5	35	11	62
15Red lead+30FEF	2.5	30	10.5	62
20Redlead+30FEF	2	28.5	10	63

3.6.5 Comparative study on zinc oxide *v* red lead curatives on the physical properties of neoprene rubber

A comparative study on the influence of the zinc oxide v red lead on the physical, mechanical and electrical properties has been undertaken in order to broaden the scope of the present study. The base formulation with zinc oxide/magnesium oxide cure is compound 51 and that with red lead cure is compound 52. Figs. 3.39 to 3.42 show the influence of the cure system on tensile strength, cure safety, Volume resistivity, Cure time respectively of both the cure system.

3.7.1 Structure and properties of Poly ethylene imine

The molecular structure of Polyethyleneimine is that of a branched poly functional amide-imide structure represented as

$$[\text{-HN-CH}_2\text{-CH}_2]_x[\text{-N(CH}_2\text{-CH}_2\text{-NH}_2\text{)CH2CH2-}]_y$$

Mn = 60,000

Mw = 75,000 material is a branched polymer and is used in the form of 50% weight water solution.

3.7.2 Preparation of Samples

Compounding of the rubber was carried as per the standard method as discussed in section 3.1.1 The basic formulations are given in Table 3.9. Volume fraction of the rubber in the vulcanizate was determined by equilibrium swelling method in toluene using standard equation [7]. Vr is related to cross link density by Flory-Rehner equation [8].

Table 3.9. Compounding formulation & vulcanizing systems
Quantities in parts by weight per100 parts of rubber

Ingredients	S1	S2	S3
Neoprene (GRT)[a]	100	100	100
Stearic acid	1	1	1
Accinox B[b]	2	2	2
Red Lead	13	13	13
Poly mine	1.16	1.16	-
DPTU	-	1.16	-
NA22	-	-	0.6
MBTS	-	-	1.5

a- DuPont -Dow Elastomer Product

b- Condensation product of Acetone and Diphenylamine

Three different accelerator systems were incorporated in the master batch. Red lead (Pb_3O_4) was included as the common cross linking reagent. Polymine has been incorporated in sample S1. The sample S2 contained polymine together with an equal amount of Diphenyl thiourea (DPTU). The third Sample S3 contained a conventional accelerator system, comprising NA22 together with MBTS.

3.7.3 Cure Studies using Moving Die Rheometer (MDR 2000)

The Rheometer was operated with an arc of oscillation of ± 0.5. Rubber compounds with different cross link systems, S1, S2 and S3 were analyzed using MDR2000 at temperatures 80, 100, 120, 140, 150, 160 and 170°C. The instrument registered both the elastic (in phase) response S′ and viscous (out of phase) response S″ of the torque as curing proceeded.

3.7.4 Cure Studies Using Modulated Differential Scanning Calorimetry (MDSC)

MDSC [9] separates kinetic information relating to non-reversing and reversing thermal events, based on heat capacity measurements, in addition to providing total heat flow and temperature information. MDSC experiments were conducted using DSC 2910 from TA Instruments, USA to analyze the curing behaviour. Measurement of enthalpy of reactions [10] was carried out from 30 to 250°C at a modulation of 1°C & 80 sec. Underlying heating rates of 3°C/min, 4°C/min and 5°C/min were used to get cure kinetic parameters. Exotherm peak area in J/g of non-reversible heat flow was used to measure heat of vulcanization. Arrhenius activation energy [11] and Bochardt & Daniels (BD) kinetic analysis [12] was carried with thermal analysis software package.

3.7.5 Cure kinetics using DMA

Dynamic mechanical analysis was carried out on rubber compound samples (rubber mix) supported on an inert substrate namely fiber glass material using DMA 983 (TA Instruments, USA) operating in flexural mode. Analysis run was carried out isothermally at temperatures 120,130,140 & 150°C. The strain amplitude was 0.4mm, in resonance. The sample dimensions were maintained approx. at 9x12x2 mm.

Figure 3.44 shows Rheograph obtained for the samples at 80° C. Cure index at 80°C for compounds S1, S2, and S3 are 5.2, 7.29 and 2.33 dNm respectively. Difference between highest and lowest value of S′ was calculated. Temperature- cross-linking index plot is shown in Fig.3.45. It is clear from figure that sample S1 with Polymine and S2 with Polymine-DPTU combination, have higher elastic modulii corresponding to higher cross link density below 120°C.

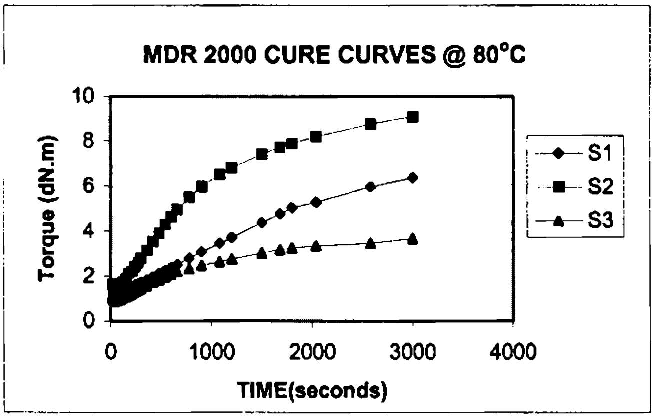

Fig. 3.44. Rheograph of compounds @ 80°C

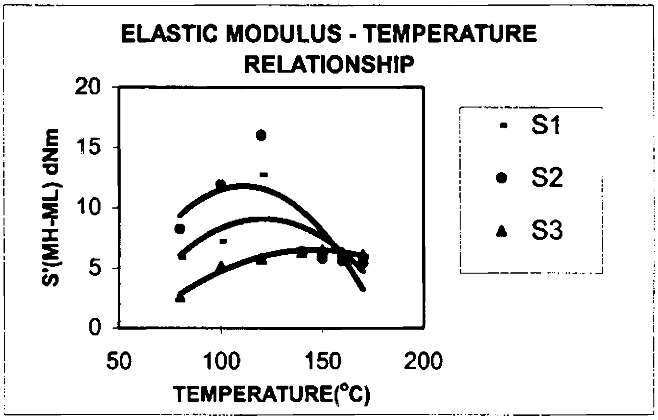

Fig. 3.45. Cross linking index of compounds

Highest torque was registered in S2. Higher cross link density of S2 over S1, is indicative of the synergism of Polymine / DPTU system.

Table 3.10 Curing characteristics and Mechanical properties

Sample	S1	S2	S3
Curing characteristics @ 120°C			
Scorch time (Min)	5.01	1.29	10.95
Cure time (tc90) (Min)	52.06	43	33.88
MH-ML) (dNm)	12.73	15.29	5.77
Volume fraction (Vr)	0.46	0.45	0.44
Mechanical properties (Cured @ 120°C)			
Hardness (Shore A)	60	56	44
Modulus, M_{300}, MPa	4.5	4.1	-
Tensile Strength, MPa	13.78	12.67	17.27
Elongation at	515	630	1250
Break, %	360	368	260
Tear Strength, N/cm T_{gg}°C	-39	-39.46	-38.3
Tensile Strength, MPa (Cured @) (150°C)	-	-	16
Elongation at Break, (%) do.	-	-	1115

Sample S3 with the NA22/MBTS cure system undergoes no significant cross linking below 120°C. Curing characteristics and mechanical properties of the vulcanizates are given in the Table 3.10.V_r of vulcanizate S1 and S2 are higher than those of S3.

Sample S1 has a Shore A hardness 60 and tear strength 360N/cm. For S2 values are 55 Shore A and 368N/cm respectively. Hardness of S3 is 44 Shore A and tear strength 260N/cm. M_{300} values for polymine based vulcanisates are higher (4 MPa) than those of conventional system (2 MPa). These properties point to higher cross link density in samples S1 and S2. Arrhenius plot of MDR cure rate (Fig.3.46) shows that Rate constant (k_1) increases with temperature in all samples. The apparent activation energy (E_a) of sample with Polymine (S1) is found to be 90.0kJ/mole, while that of polymine /DPTU (S2) sample is 84.0 kJ/mole, whereas conventional NA22/MBTS (S3) system gives a value of 94.0 kJ/mole.

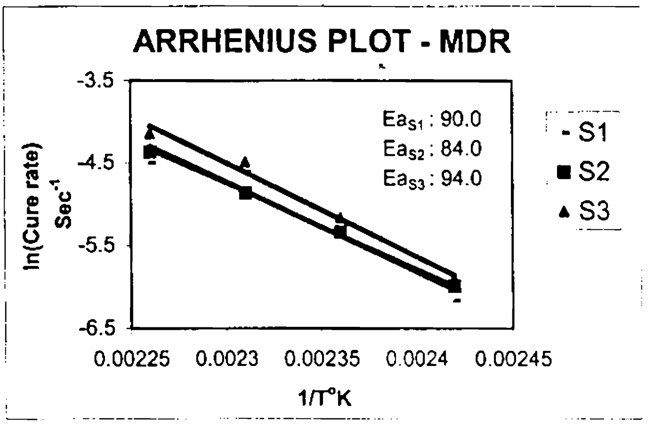

Fig. 3.46 Arrhenius plot from MDR cure data

MDSC measures the total enthalpy of cure as non-reversible heat flow. Fig.3.47 shows cure behaviour of samples for cure rate 3°C/min.

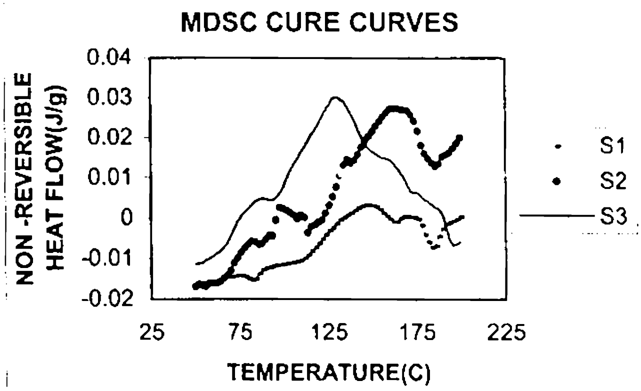

Fig. 3.47 Cure behaviour- MDSC Cure data

MDSC kinetic parameters [13] are given in Table 3.11

Table 3.11. DSC Kinetic parameters

Sample	Heating rate °C/min	ΔH (J/g)	Exotherm (Tp°C)	Arrhenius Ea_{Arrh} (kJ/mol)	B&D ANALYSIS	
					Ea $_{B\&D}$(kJ/mol)	n
S1	3	14.85	145.75	63.71	191.6	3.09
	4	21.49	154. 88			
	5	16.09	159.90			
S2	3	21.09	160.38	108	134.71	2.28
	4	21.65	161.17			
	5	20.92	163.47			
S3	3	54.23	129.74	121	154.7	0.9
	4	62.03	134.08			
	5	64.29	137.29			

Enthalpy of cure for sample S1 is the lowest while that of the conventional system, S3 is the highest. Sample S2 exhibits marginally higher values than S1. Lower cure enthalpy values in Polymine based cure system are indicative of the higher level of pre-vulcanization cure suffered by the material prior to thermal analysis. DSC B&D kinetic analysis [12] of samples show that the order of vulcanization reaction for the samples S_1 and S_2 lie between 2 and 3 & their B&D activation energies lie in the range of 130-190 kJ/mole. Overall reaction order of conventional cure system is found to be first order whereas that of Polymine systems follows a higher order. Progress of curing reaction has been reflected in DMA frequency (storage modulus) V time curves as illustrated in Fig 3.48

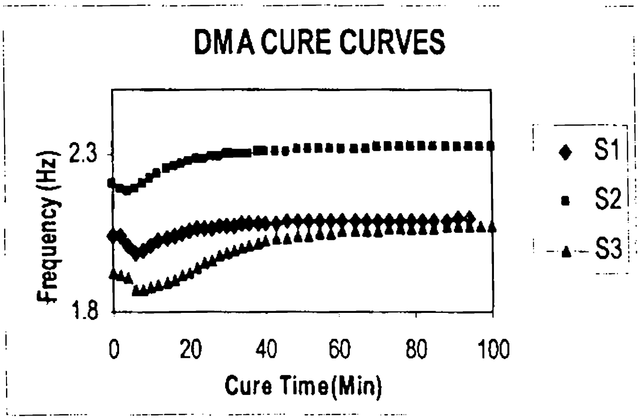

Fig. 3. 48 DMA Cure curves

All curves show two distinct stages in the cure reaction. Stage1 represents softening of the compound as a fall in frequency (modulus) followed by on set of cure with build up of frequency (modulus). Degree of cross linking was calculated using equation.

$$f = (E_t - E_l) / (E_2 - E_l) \qquad (3.5)$$

where, f is the degree of cure, E_t storage modulus at the time t_{c50}, E_l is storage modulus at the onset, and E_2 the final storage modulus. From the results apparent energy of activation (Ea) of cure reaction has been estimated using Arrhenius plots (Fig. 3.49).

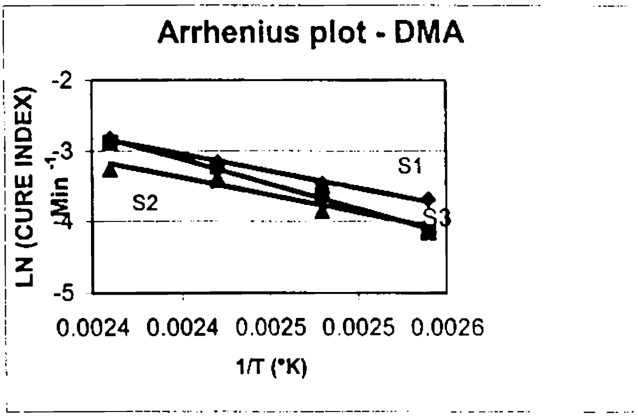

Fig.3.49 Arrhenius plot from DMA cure data

E_a for Polymine based cure systems obtained through DMA is around 40kJ/mole while the same for the conventional cure system is 60kJ/mole. The mismatch in the energy of activation observed between MDR and DMA techniques can be explained on the basis of higher temperature sensitivity of dynamic modulus-temperature relationships.

MDR cure analysis show that Polymine activated rubbers has low cure onset temperature (~80°C) and activation energy of cure. Polymine - DPTU combination has synergism in neoprene rubbers. Physical and mechanical characteristics of neoprene formulations are not adversely affected by these novel cure systems. MDSC results bring out that Polymine based compounds have lower heat of vulanization. Lower heat of vulcanization has been explained on the basis of higher pre vulcanization cure suffered by the compound. Lower activation energies and lower onset temperatures of Polymine based vulcanisates lead to the conclusion that activation threshold of the rubber compounds have been shifted to lower temperatures by the Polymine accelerator.

3.8 Influence of carbon black on Dynamic Mechanical behavior

The viscoelastic nature of rubbers influences performance of rubbers in applications such as encapsulants, acoustic windows, acoustic baffles, transducer mounts etc. In view particular relevance of viscoelastic behavior the present work focuses on dynamic mechanical properties of rubbers. Two significant aspects studied are influence of carbon black filler types and their quantities on the visco elastic behaviour. First part investigates the dynamic mechanical responses on the types of carbon black used The second part considers the effect of varying quantities of carbon black on neoprene as well as Bromobutyl rubbers.

3.8.1 Influence of the type of carbon black

Measurements were made at different frequencies from 0.1 to5 Hz; the temperature range selected for the experiment was from -30 to 30°C. Visco elastic data such as flexural modulil and tan δ in the above ranges of temperature and frequency were made use of in a time-temperature superposition [14] to arrive at properties at frequencies up to 10 kHz. The data obtained have been compared to find the relative efficiencies of the type of carbon black fillers used in Neoprene rubber formulations. From the complex modulus obtained acoustic propagation [15] characteristics viz.sound speed and attenuation coefficient, have been calculated. The elastomer selected for this study was neoprene-W manufactured by M/S Du Pont Co Wilmington, USA. Different compounding formulations studied are given in Table 3.12.

Samples were prepared as per the details presented in Section 3.1.2Curing properties were determined on Monsanto Rheometer 100 (ASTM -D2084). All compositions have plateau cure curves. 90% cure times were 20±3 min. For dynamic analysis, specimens A and B were press moulded and specimens C and D were punched out from precured sheets. Samples A and B were 24mm*5mm*6mm, while C and D were 27mm*3mm*10mm and 30mm*3mm*10mm, respectively. Specimens were preconditioned at room temperature for 48h before testing.

Table 3.12Compounding formulations- in parts per 100 parts of rubber

Ingredients(pphr)	Compound designation			
	A	B	C	D
	(Gum rubber)	(N550)	(N660)	(N770)
Neoprene -W	100	100	100	100
FEF (N550)*	-	25	-	-
GPF (N660)*	-	-	25	-
SRF (N774)*	-	-	-	25
Red lead	20	20	20	20
Naphthenic oil	10	10	10	10
Stearic acid	2.25	2.25	2.25	2.25
NA22[a]	1	1	1	1
Vulcanox 4020[b]	2	2	2	2

a: Ethylene thio urea, b= n-(1-3-dimethyl butyl)-n-p-phynylene diamine, *Carbon black

3.8.1.1 Measurement of dynamic mechanical properties

In order to generate a master curve that can give properties at the ultimate properties of interest time temperature super position technique as described in section 2.5.2.4 was used.

Dynamic mechanical analysis was carried out using Du Pont DMA 983. In this set-up, a rectangular specimen clamped between two parallel arms is deformed in the flexural mode using a sinusoidal exciting force so

Table3.13 Flexural storage modulus- temperature data

Temperature (°C)	Flexural storage Modulus, E′ (MPa)			
	A (Gum Rubber)	B (N550)	C (N660)	D (N774)
-30	9.43	20.16	14.84	-
-20	7.31	17.37	10.49	10.14
-10	5.44	12.95	8.61	9.32
0	4.52	11.16	6.90	8.22
10	3.96	9.77	6.20	7.47
20	3.29	8.60	5.67	6.70
30	2.80	7.59	5.03	6.15

A general increase in storage modulus is observed in the case of all compositions containing carbon black fillers as compared to gum rubber compound. A fall in storage modulus with temperature increase corresponds to an increase in the molecular mobility arising from higher internal energy. Carbon black with finer particle size (N550) produces high reinforcement as could be expected. The steep fall in modulus observed in the temperature region -30 to 0°C suggests that this region succeeds the glass transition in the material. The temperature region 0-30°C represents the rubbery stage.

3.8.1.3 Flexural Loss Modulus

Table 3.14 shows the flexural loss modulus of rubber samples compounded with different filler types measured at various temperatures. The results are presented graphically in Fig.3.51.

formulations. Dynamic response can be modified to a large extent by suitable compounding variations. A good knowledge on the effects of varying quantities of fillers is essential for the design of various material systems.

In this context an investigation on the effects of varying quantities of carbon black on the dynamic mechanical properties of certain rubber vulcanizates has been undertaken.

The rubbers used in this study are Bromobutyl (Polysar-X2) and Neoprene-w. General purpose furnace black (N-660) of varying quantities ranging from 0 to 80 pphr was used in the formulations studied. Tables 3.15 and 3.16 s give the formulations and their viscoelastic properties of BIIR and CR respectively

Table.3.15Details of compositions and viscoelastic properties of bromobutyl rubber

Carbon black	dlogE'/logF (MPa/Hz)	dE''/dT MPa/°C)	dE"/dT (MPa/°C)	sT (kJ/mole)	aT
0	-	-0.004 -	-	-	-
10	-	0.01	-	-	-
20	0.25	-.01	-.0014	3.5	48
30	0.17	-.017	-0.002	-	54
40	0.12	-0.034	-0.003	8.7	79
50	0.10	-.068	-0.005	8.9	89
60	0.10	-0.1	-0.006	-	-
70	0.12	-	-0.0123	9.3	-
80	0.11	-0.13	-0.026	-	116

Composition: (phr)BIIR-100,Stearic acid-1,ZnO-5,MBTS-1.5,TMTD-1,Carbon black as shown

7.06 and 30.08 MPa, respectively. In general, the storage modulus values of N550 carbon black filled samples are higher than those of all other compounds, as could be expected from surface area and particle size considerations. It is observed that the flexural loss modulus values in all the compounds decrease with increase in frequency up to certain values and thereafter increase with increasing frequency. The magnitude of the loss modulus undergoes a 200-300% increase for a frequency change of one decade from 100 to1000 Hz. Increase of modulus with frequency is more significant in the case of lower particle size carbon fillers than higher particle size fillers. The characteristic dips in loss modulus could be better understood by looking at the variation of tanδ with frequency.

Table 3.18 Effect of frequency on flexural loss modulus fillers

Frequency (Hz)	A (gum rubber)(MPa)	B(N550)(MPa)	C (N660)(MPa)	D (N774)(MPa)
0.1	3.06	2.04	2.74	2.33
1	2.95	1.79	2.56	1.49
10	2.74	1.72	2.87	1.26
100	2.73	3.33	4.59	2.37
1000	3.09	9.65	9.65	-
10000	4.14	22.64	-	-

3.8.3.2 Dependence of loss tangent (tanδ) on frequency

The dependence of damping factor (tanδ) on frequency was investigated by superposition technique, taking 20°C as the reference temperature; the results are presented graphically in Fig.3.64

Value $\alpha\lambda$ signifies the attenuation effected per wavelength thickness of material. It is seen that the $\alpha\lambda$ values show a dip with increase in wavelength (λ). A transition is apparent at a wavelength of 10 m. A progressive increase in values is observed at higher wavelengths in all cases studied. Higher values of sound attenuation are observed in gum rubber samples for larger wavelengths, i.e. low frequencies and filled compounds are better attenuators at higher frequencies. The dynamic response of Polychloroprene vulcanizates incorporating different types of carbon black fillers is important, particularly in applications involving wave propagation. Dynamic modulii are seen to increase with incorporation of various carbon black fillers. The trend observed could not be generalized with regard to the type of filler, their particle size or surface area, excepting the inference that the smallest particle carbon black (N550) has the highest reinforcing effect in terms of storage modulus (E'). Carbon black filled compound show a lower damping capacity as compared to unfilled compounds. The damping factors of filled rubbers are not significantly affected by the variation in temperature in the range 0-30°C. However, there is a marked influence at subzero temperatures. In general, the storage modulus E' and loss modulus E" have shown increase with increasing frequency. This increase is more significant in the case of N550carbon black filled compounds. The velocity of sound propagation (longitudinal mode) of different compounds calculated from the values of complex modulus (obtained by time-temperature superposition) is found to increase with frequency in all cases. However, the increase is more pronounced in the case of compounds containing high reinforcing fillers. Where as filled compounds exhibit similar properties in the high frequency zone. The dependence of damping and sound attenuation on factors such as frequency, temperature and filler types brought out by this study may prove helpful in tailoring rubber compounds for specific sound and vibration damping application. However, while designing for such specific applications due considerations will have to be given to the coupling media and interface impedance mismatch problems.

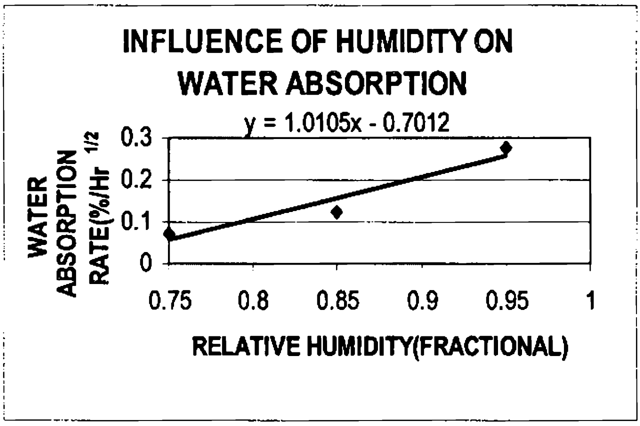

Fig. 3.72 Changes in water absorption rate with relative humidity

From the Figure 3.71 it is found that water absorption rate increases linearly with humidity at under same conditions. Fig 3.72 is the relationship between moisture intake rate and humidity. It is seen that the rate increases linearly with humidity, the slope being close to one. The empirical relationship established from the experimental data will provide a means to estimate water absorption of samples stored in humid sea shore environment.

3.9.4 Influence of inert environment on water absorption

Neoprene and Bromo butyl rubbers have been studied for water absorption behaviour in oxidative (Air) as well as inert (Nitrogen) environment. Water was boiled to expel dissolved oxygen. Samples were soaked in water at temperature of 40°C. Samples contained in deareated water was placed in a pressure vessel. The whole assembly was evacuated and filled with nitrogen. A positive pressure of nitrogen gas was maintained in the pressure vessel. The experiment was repeated with rubber vulcanisate containing 30pphr GPF black and 1 pphr anti oxidant 4020. At periodical intervals samples were taken out and quickly wiped free of water and the weight change noted. The experiment was carried out for a period of over 60 days. Results are given in Table3.21. Water absorption rate has considerably fallen with nitrogen envelope provided in all the rubbers studied.

Table3.21 Water absorption behavior under nitrogen atmosphere

Sample Details	Rate of absorption (%/hr$^{1/2}$)	Maximum absorption (%)	Diffusion coefficient (cm^2/hr)D*10^6
Neoprene gum (Comp.711)	1.07	85	1.03
Neoprene gum+ GPF30+ vulcanox 4020:1	0.40	30.18	1.14
Bromobutyl gum (Comp.1101)	0.16	10.36	1.33
Bromobutyl (comp1101)+ GPF30+ volcanox 4020 :1	0.11	6.56	1.83
Natural Rubber (comp.803) + GPF30+ volcanox 4020:1	0.13	5.38	3.47

Initial slope of absorption-time plot for neoprene gum rubber is 1.07. However the same of Bromo butyl rubber is 0.16. There is a remarkable reduction in the rate (from about 200 % to 85 %) when compared with the same in air atmosphere. In rubber vulcanizates containing carbon black and anti oxidant there is a further reduction in water absorption as shown in the Table 3.21. An interesting observation is that diffusion coefficient is inversely proportional to the absorbed water.

3.9.5 Effect of different quantities of fillers on volume resistivity of different rubbers

Effect of different quantities of carbon black on the volume resistivity has been studied in respect of BIIR.Table3.22 presents composition and results the results. It is found that upto about 40 pphr loading of GPF black along with inorganic fillers volume resistivity remains at about 1* 10 ^{14} to 2*10^{14}ohmcm further incorporation of 10 pphr carbon black lowers resistivity by about 5 orders of magnitude

Table 3.22 Vol. resistivity as function of carbon black Quantity in BIIR

Ingredients(pphr)	Compound numbers				
	240	267	269	273	275
BIIR	100	100	100	100	100
St.acid	1	1	1	1	1
4020	1	1	1	1	1
GPF Carbon balck	50	10	20	30	40
TALC	75	75	75	75	75
CaCO3	35	35	35	35	35
P.WAX	2	2	2	2	2
NAPHTHENIC OIL	10	10	10	10	10
ZINC OXIDE	5	5	5	5	5
TMTD	0.5	0.5	0.5	0.5	0.5
MBTS	0.5	0.5	0.5	0.5	0.5
Physical properties					
ML(Min.Torque)	12	10	10.5	10.5	12
MH(Max Torque)	2.6	21	23	24	26
Ts_2	2.5	3	3	-	3
T_{90}	6	6	6	6	6
Tens. strength(MPa)	-	4.08	4.2	4.2	4.5
EB	-	821	760	462	620
Vol res.1000v,ohm.cm	$3.2*10^{9}$	$1.24*10^{14}$	$1.6*10^{14}$	$2*10^{14}$	$1.5*10^{14}$
Water mg/cm2	-	0.36	0.32	0..325	0.33
Sp.g	-	1.15	-	1.19	1.18

Results show that for 30 to35 pphr carbon black loading, volume resistivity values are very sensitive to changes in filler type and quantity. Inclusion of talc and calcium carbonate brings about an order of magnitude increase in resistivity. Even a minor changes in the carbon black concentration in this region affect the property very significantly. Different vulcanized rubber polymers without fillers have been compared for volume resistivity. It is found that volume resistivity of gum CR vulcanizates give stable values about 10^{10} ohm cm. NR and SBR rubbers remaining about 10^{12} ohm. cm at 1000V.

3.9.5 Acoustic Baffle

Acoustic baffles are used in large transducer arrays for the purpose of isolating ships structure borne noise as well as for improving directivity and sensitivity of the transducer elements. The baffle forms a major passive element contributing to better performance of the system. The materials used for the construction of acoustic baffles are therefore required to posses specific acoustic characteristics and dynamic mechanical properties. As the deployment of baffles is in deep marine environment the material used for the construction should also be compatible with hostile marine conditions such as salinity, hydrostatic pressure, Sub ambient temperature, dynamic loading conditions etc.

The unique combination of stiffness and damping behaviour possessed by rubbers could be exploited for designing acoustic baffle. But a notable limitation to be over come is the enormous variation in the dynamic mechanical properties when subjected to temperature changes. Stiffness of the rubbers increases when cooled. An equivalent change takes place in the stiffness then subjected to cyclic loading. During operation the acoustic baffle encounters a combination of the temperature change and dynamic loading by acoustic waves and vibrational force fields from the mounting structure.

An ideal baffle rubber shall be able to absorb the imposed dynamic load variations and provide a flat acoustic performance over the frequency band of inertest.

Rubbers exhibit in their dynamic modulus- temperatures /frequency response curves a point of inflexion, where the mechanical damping factor goes through a maximum. This region where modulus under goes rapid variation due to temperature/frequency changes is the transition region. Since acoustic properties of rubbers are a direct functions of modulus [15] Thus tailoring of the transition modulus is key to achieving the desirable acoustic response. Desired acoustic response in the case of baffle rubber is constant sound speed over the specific frequency region. Constancy in sound speed in a viscoelastic material is related to low attenuation as per kramers-kroning [18] relations developed by O'Donnel et. al[19].This approximation relates the attenuation coefficient α to the frequency derivative of the phase velocity dc/dω by the relation

$$\alpha(\omega)=\frac{\pi\omega^2}{2c}\left(\frac{dc}{d\omega}\right) \tag{3.6}$$

Where α and c are related to E′ and E″ by Eqs.1.57-1.58.It follows from the Eqn3.7.that a high value of α requires a large dc/dω in the viscoelastic region. Hence it is clear that lower attenuation or mechanical loss factor leads to smaller frequency dependence of acoustic wave velocity. Therefore the study was aimed at developing rubber with low enough damping factor which is constant over the frequency range of 30Hzto 10 kHz.. Styrene butadiene rubber was selected as base material due its low glass transition temperature (-60°C) and the traceable quality. Table 3.24 gives compositions of samples A to D. Dynamic mechanical properties of the compounds A to D are given in Table 3.25. Table 3.26 gives formulation E to H. Composition A contains 70 parts FEF black composition B 50 parts FEF, while compound Contains GPF black 70 phr,. Composition D is a modified composition of C containing additionally 20 pphr precipitated silica. Composition A and B are similar except for the quantity of carbon black. Composition A with 70 pphr FEF has lower tan delta and higher storage and loss modulus. Between C and D there is a significant lower of tan delta and increase in E′. Modulus of this sample shows an increase in the low frequency end and a fall at the high frequency region. Thus there is an overall levelling of the damping curve.

Table 3.24 Acoustic baffle compositions A to D

Ingradients(pphr)	COMP.A	COMP.B	COMP.C	COMP.D
SBR(1502)	100	100	100	100
Stearic acid	1	1	1	1
Zinc oxide	5	5	5	5
Vulcanox4020	2	2	2	2
VulcanoxHS	2	2	2	2
GPF black	-	-	70	70
FEFblack	70	50	-	-
Talc	30	30	-	-
pptd CaCO3	20	20	-	-
Silica	-	-	-	20
BaSO4	-	-	-	-
Naphthenic oil	10	10	10	10
TMTD	1	1	1	1
MBTS	1	1	1	1
Sulphur	0.75	0.75	0.75	0.75

Sound velocity and attenuations of the samples A to D have been calculated from their dynamic mechanical parameters. Results are presented in Tables 3.27and Fig 3.74

Sound velocity in the sample C calculated as longitudinal wave velocity is about 97 m /sec at 30 Hz and which increases to185m/sec at 7 kHz. This amounts to an increase of 90%. In case of sample modified with silica the sound velocity in this region changes from 152 m/sec to196m/sec. This represents an increase of only 28%. This changes have been brought by an increase in the dynamic storage modulus at the lower end of the frequency spectrum without concomitant increase in the loss modulus. Frequency sound velocity plot given in Fig 3.75 shows a that sample containing silica in combination with GPF black has a linear response, while that with GPF black alone is non linear concave upwards.

Table 3.26 Compositions E to H

Ingredients(pphr)	Compo. E	Compo. F	Compo. G	Compo. H
SBR (1502)	100	100	100	70
NR (ISNR-5)	-	-	-	30
Stearic acid	1	1	1	1
ZincOxide	5	5	5	5
Vulcanox4020	2	2	2	2
VulcanoxHS	2	2	2	2
GPF BLACK	40	50	-	70
FEF BLACK	-	-	40	-
TALC	30	30	30	30
PPTD CaCO3	20	20	20	-
Silica	-	-	-	-
BaSO4	-	-	-	20
Naphthenic oil	10	10	10	10
TMTD	1	1	1	1
MBTS	1	1	1	1
Sulphur	0.75	0.75	0.75	0.75

Table 3.27 Sound speed and attenuation of compositions A to D

COMPO.	Freq. (Hz)	Sound speed (m/sec)	Aλ (neper)	A (neper/m)
A	30	167	0.618	0.111
	100	176	0.592	0.335
	1000	196	0.58	2.958
	5000	214	0.618	14.42
	10000	223	0.652	29.134
B	30	141	0.734	0.156
	100	149.6	0.707	0.47
	1000	164.68	0.72	4.37
	5000	177.5	0.795	22.4
	10000	184.4	0.85	46.08
C	30	96.88	1.157	0.358
	100	106.28	1.164	1.095
	500	124.93	1.269	5.08
	1000	136.11	1.367	10.04
	5000	173.87	1.721	49.49
	7000	184.49	184.49	68.73
D	30	152	0.595	0.118
	100	159	0.594	0.3747
	500	170	0.612	1.8
	1000	176	0.631	3.588
	5000	192	0.72	18.7
	7000	196	0.75	26.6

Table 3.28 Dynamic Mechanical parameters of samples E to H

Composition	f (Hz)	E′ (MPa)	E″ (MPa)	Tanδ
E	500	13.5	2.486	0.1934
	1000	14.6	2.985	0.2106
	5000	18.2	5.297	0.3259
F	500	32.7	8.964	0.2761
	1000	35.5	10.73	0.3035
	5000	44.9	18.11	0.4044
G	500	18.4	5.455	0.2991
	1000	19.8	6.407	0.3272
	5000	23.98	10.45	0.4357
H	500	33.4	5.761	0.1744
	1000	34.6	6.369	0.1833
	5000	39.9	8.739	0.2191
	7000	41.20	9.45	0.2294
	10000	42.69	10.034	0.2414

Sample is a co-vulcanized blend of SBR and natural rubber in the proportion of 70:30.The formulation contained 70 GPF as in sample C. The dynamic mechanical properties of the sample show that the co-vulcanizate is lower damping than sample C.

Elastic modulus of the material is lower than the compound D. The sound speed and attenuation of composition E to H have been presented in Table 3.29.As expected stiffer sample F gives higher sound speed. For samples containing equal loading of two different types of carbon black namely GPF and FEF the one with lower particle size gives higher sound speed and attenuation.

Table3.29 Sound speed and attenuation of sample E to H

SAMPLE	f(Hz)	Sound velocity (c)	αλ(Nepers)	α(Neper/m)
E	500	103.47	0.58	2.82
	1000	111.8	-	-
	5000	123.17	0.90	36.52
F	500	157.66	0.85	2.7
	1000	165.4	0.59	5.6
	5000	190.6	0.93	32.06
G	500	122.3	0.92	3.759
	1000	127.48	1.00	7.86
	5000	144.91	1.30	45.19
H	500	157.6	0.544	1.73
	1000	162	0.571	3.53
	5000	174.3	0.68	19.5
	7000	177	0.711	28

Table 3.30 Specific gravity and static mechanical properties

Sample	Sp.g	Hardness (SHR'A)	Tensile strength(MPa)	Elongation at break(%)
A	1.35	80	10.35	301
B	1.34	70	8.76	374
C	1.33	69	11.46	275
D	1.25	76	10.81	240
E	1.27	65	8.3	543
F	1.38	71	8.21	441
G	1.3	70	8.6	465
H	1.36	73	9.47	280

Static mechanical properties as well as specific gravity of the samples studied are given in the Table 3.30. Compound D exhibits lowest specific

Table 3.31 Recipe for seal

Ingredient	Quantity (pphr)
Nitrile Rubber (NBR) ACN-34	100.00
Sulphur	0.50
Stearic Acid	1.0
Zinc Oxide (ZnO)	3.00
Vulcanox 4020	1.50
Vulcanox HS	1.50
Carbon Black (SRF N-770)	45.00
Carbon Black (FEF N-550)	20.00
Tetra Methyl Thiuram Disulphide (TMTD)	1.50
N-Cyclohexyl 2-Benzthiazyl Sulphenamide (Santo Cure CBS)	1.50
Di-Octyl Phthalate (DOP)	10.0

The compound has been tested as per method ASTM-2084 for cure behaviour The cure characteristics are presented in Table 3.32 Sample sheets (15x15x0.2) cm^3 are vulcanised for 30 min at 150 °C by compression moulding method. The material has been tested for various physical and mechanical properties

3.32 Cure Characteristics of Seal rubber

Stock Properties	Values
Scorch Time (ts_2) min	1:05 ± :15
Cure Time (tc_{90})	6 : 0 ± 2:0
Min Torque ML (lb.in)	1.0 ± 0.2
Max torque (MH) (lb.in)	13 ± 1

Properties realized are presented in Table 3.33. The specific gravity is 1.2 and the shore A hardness is 65. Compression set of the sample is only 12%. The material has been further evaluated for its mechanical properties.

The tensile strength is 11.5 MPa and ultimate elongation is 350%.The tear strength of the sample is 435 N/cm thickness is the level envisaged for the material. Sample has been tested for retention of compression set at by keeping the samples compressed condition in the air ovens maintained at three different temperatures.

Table 3.33 Physical and mechanical properties of seal compound

Property	Value	Method
Specific Gravity	1.2+0.1	Wallace balance
Hardness (ShoreA)	65 ± 5	ASTM-D-2240
Compression Set (%)	8.5	ASTM D-395 B
Water Absorption (%)	1.10	ASTM D- 71(40°C, 24hrs3.5% (NaCl Soln.)
Stress at 300% strain (Mpa)	9.5	ASTM D-412
TensileStrength (MPa)	11.5	do.
Elongation at break (%)	350	do.
Tear strength (N/cm)	435	ASTM D-624

The initial compression set was determined at 33°C. Average of ten samples was found to lie at 8.5±0.5. Samples have been tested for compression set as per ASTM method 395 B at temperatures at 40°C, 50°C and 70°C at intervals. Results have been presented in Table 3.34.

Table 3.34.Effect of accelerated aging on compression set.

Duration (Days)	Compression set %		
	40°C	50°C	70°C
13	7.68	8.52	7.02
23	8.50	8.19	7.80
41	8.31	8.23	7.24
62	7.82	7.96	7.06

It is found that there in no noticeable degradation in compression set at 40 and 50 °C even after soaking for over two months. Samples aged at 70° C showed a reduction in set from initial value of 8.5% to7.06%. This indicates the composition has excellent retention of compression set values. Seal rubber samples have been evaluated for the effect of water soaking at three temperatures for 1700hours. Results have been shown in Table3.35. Water absorption for the entire duration does not exceed 1.2%. There has been a leaching effect during the long soaking period. The absorption values presented are the corrected value after making good for leached amount by drying the samples under vacuum at the respective temperatures.

Table 3.35Effect of soaking in water

Duration (Hrs)	Weight increase (%)		
	40°C	50°C	70°C
24	1.00	0.75	1.11
48	1.05	0.92	1.05
96	1.15	0.99	0.96
240	1.10	1.00	-
504	1.08	0.74	0.98
600	1.01	-	-
1032	1.02	0.75	-
1272	0.98	0.87	
1704	0.96	0.86	

Nitrile rubber sanples have been studied for cyclic elastic stress-strain fatigue failure. Wallace-MRPRA flexometer has been used for evaluating the property. The test condition used have been presented in the Table3.36.The fatigue behaviour under cyclic loading has been presented inTable3.37

Table 3.36 Fatigue test parameters

Test parameters	Values
Type of sample	Standard Schopper Ring sample
Specimen Dimensions(mm)	OD : 52.6, ID : 44.6, Thickness : 2
Specimen conditioning	1 hour at test temperature
Test Temperature (°C)	25 ±2
Test Frequency (cpm)	300
Strain Amplitude (%)	265

Table 3.37 Fatigue behaviour of Nitrile rubber

Duration (Hrs) at soaking temp,	Cycle Passed					
	40°C		50°C		70°C	
	Max	Min	Max	Min	Max	Min
24	2500	600	1500	700	1500	700
96	2100	800	2000	600	1600	600
168	1800	1000	1900	800	1200	600
504	2200	500	2900	500	-	-
984	2800	900	1400	600	-	-

Results show no systematic trend on the fatigue behaviour except that with increasing temperature fatigue resistance falls. Sample conditioned at 40°C withstood a maximum of 2800 cycles and minimum500 cycles. Samples conditioned at 50°C the range was from2900 to500 cycles. For samples at 70°C this range was between 1600 and 600. Considering rather high strain amplitude of the test (265%)the value obtained in with the expected limit.

Stress relaxation behaviour of the Nitrile rubber vulcanisate has been studied in the temperature region of 4 to 50 °C. Compressive stress - strain measurements have been carried out with the help of Zwick, German make universal testing machine model: 1476. Test speed was set at 12.5mm/min.

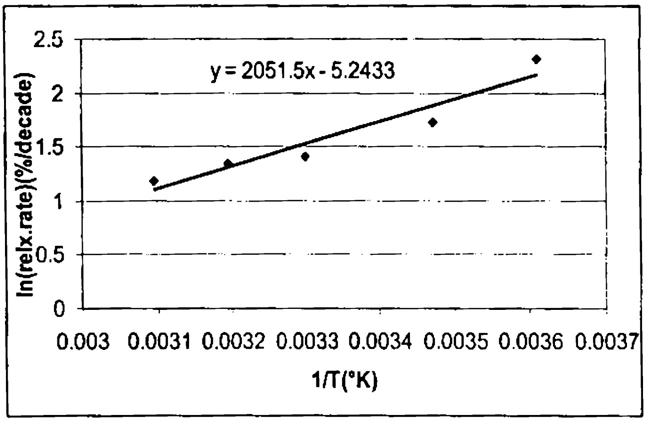

Fig.3.78 Arrhenius plot of compression relaxation processes in nitrile rubber

The glass - rubber transition of medium acrylonitrile nitrile rubber is in the region of -15 °C -25°C. Approach to glass transition temperature region is crucial to many end use situations for rubbers particularly nitrile buradiene copolymer rubber undergoes rapid changes to the tune of three orders of magnitude in mechanical response. Hence it is desirable to study the behavior of nitrile rubber for temperature induced changes in this region. Tensile stress-strain behavior of rubber there fore been studied for the interval between -16 °C to +50°C.The tensile test is done employing Zwick Universal Machine model:1476 provided with a *in situ* temperature chamber. ASTM D-412 test method at 500mm/min speed was has been followed for the test. Results are given in Table 3.39

It is observed that modulus at 100 % strain (M_{100}) increases from 4.4 to 13.1MPa when temperature is lowered from+27 to -16°C while the modulus at 200 % elongation increases from around 10 MPa to20 MPa. Tensile strength (TS) however does not undergo same level of change for this temperature region. It has increased only by 5 from 15 to 20 MPa. Ultimate elongation (EB) shows a plateau (290%) in the mid ambient region of +4°C to+27°C. EB however fall to ~ 200% levels at both the extremes

Table 3.39 Temperature dependence of static mechanical properties

Test temp. °C	Modulus at 100 % strain (MPa)	Modulus at 200 % strain (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
50	4.13	9.0	9.85	223
27	4.4	9.7	14.47	290
15	5.1	11.13	16.03	283
4	6.05	12.95	18.68	297
-8	8.15	16.85	19.28	235
-16	13.1	20.0	20.0	200

Fig.3.79 Shows the variation in TS values with temperature. It is observed that TS temperature relation ship is a plateau at subzero temperature and has a point of inflexion around 0°C and a linear decrease a as the temperature increase to 50 °C.

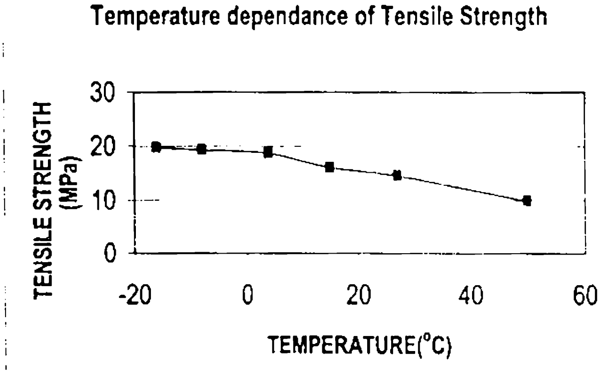

Fig.3.79 Temperature dependence of tensile strength

The useful sealing life of an O-ring or seal depends on two viscoelastic material properties: compression set, the residual deformation of a material after the load is removed; and stress relaxation, the decrease in stress after a given time at a constant strain. These properties reduce the resiliency of the seal material and must be taken into account in the design

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Chapter 4

AGING STUDIES

This chapter gives a brief account of th theoretical and experimental studies conducted on aging associated degradation phenomena in rubbers with particular reference to functional properties of interest such as water absorption, water permeation, static mechanical properties dynamic mechanical properties and electrical properties

4.1 Aging phenomena

Properties of polymeric materials change with time. Polymeric materials age under the action of heat, atmospheric oxygen, light, mechanical stresses and other environmental factors. Processes occur in them, which are accompanied by changes in their chemical and physical structures leading to deterioration in their properties. Practical use of polymeric materials requires the knowledge of their long behavior under service environment. In order to acquire such knowledge it is necessary has to investigate the accelerated aging of the materials by following the change in their properties due to thermal, thermo oxidative or other processes.

By extrapolation of the experimental results obtained from accelerated aging to the operating environment serviceable life time has been estimated[1-2].The creation of polymer composites with increased aging resistance is of great practical importance. It is necessary to ensure long- term durability and serviceability of polymeric materials in actual service conditions under the combined action of external factors. Prediction of useful life of a polymeric material is a complex, multifactor, multivariable problem involving several unknowns. The essence of such a prediction resides in the extrapolation of the results of testing the finished article under accelerated conditions. Prediction of service life should take into account the possible variability of aging processes over the extrapolation interval and develop methods for extrapolation of results of accelerated tests to continuously varying real operating environment. Prediction of service life is in effect prediction of the rates of change of properties to adequate performance.

Double bond in the molecule while facilitating sulphur vulcanization of rubber makes them vulnerable to oxidative degradation. Rubbers containing high amounts of unsaturation such as NR, SBR are more prone to oxidative degradation or ozone attack than those rubbers containing low amounts of unsaturation such as butyl rubber and EPDM.

The basic mechanism of the oxidative degradation of rubbers is now well understood. Based on model substance studies it has been established that attack begins at a methylenic carbon atom in the chain. A hydrogen atom is abstracted and an oxidative reaction chain is initiated (in presence of oxygen) which propagates if unchecked:

1. $RH \rightarrow R^{*}+H$
2. $R^{*}+O_2 \rightarrow ROO^{*}$
3. $ROO^{*}+RH \rightarrow ROOH+R^{*}$
4. $ROOH \rightarrow RO^{*}+OH^{*}$
5. $RO^{*}+RH \rightarrow ROH+R^{*}$
6. $OH^{*}+RH\cdot \rightarrow R^{*}+H_2O$

The original free radical has gone through a single reaction cycle giving a degraded rubber (ROH) and three new free radicals (R*). The cross linking reaction can be represented by

$2R^* \rightarrow R.R$

$ROO^* + R^* \rightarrow ROOR$

In order to prevent the auto catalytic development of the reaction either the free radical formed must be captured and/or the peroxides formed produced decompose into harmless products. Possible inhibition reaction where AH is an inhibitor are

1. $R^* + AH \rightarrow RH + A^*$
2. $ROO^* + AH \rightarrow ROOH + A^*$
3. $ROOH + AH \rightarrow$ Harmless fragments

Theoretical considerations assume that there is sufficient antioxidant present and to reach the points of attack. In this context water extraction of anti degradents is a problem in such articles as under water transducers.

4.1.1 Controlling Parameters

Different properties vary at different rates during aging, and estimate of life depends on which properties are selected. Controlling parameters must be sensitive to aging process. The controlling properties should vary monotonously with time. Customary approach to life estimation based on any one of the determining properties, is inadequate for multi functional components. In practical situations

A combination of different properties decide the service performance. Hence service life prediction techniques should take into account all such properties.

In the context of the present work, reliable service life prediction is a topic considerable practical interest. Failure of naval transducers for example will be catastrophic both in terms of fleet readiness and cost of repair. The major parameters controlling the service life of a transducer have been identified as water intake characteristics, static mechanical properties, dynamic mechanical properties and electrical properties. Investigation will focus on the most sensitive characteristics out of the above parameters.

4.1.2 Accelerated Aging

Estimates of life are considered most confident, if they are obtained by exposing specimen to natural conditions representative of service environment. However this is too long a time to be practicable. Practice is therefore to use accelerated test procedures which permit the deduction of the manner in which the material will perform under service conditions from the short-term aging behavior.

Accelerated aging tests are viewed as the only conceivable way of predicting long-term behavior of the materials. Test conditions are selected from the knowledge of the dynamics of the critical property variation.

Thermal aging tests are conducted by keeping the sample in a hot chamber at fixed predetermined temperature, T, for an equivalent time, t_a. Acceleration factor thermal degradation must be obtained in such a way that the degradation mechanism is identical with that at the operating condition. General method of choosing t_a is based on determining the rates of variation of a particular material characteristics during aging so as to enable plotting the prediction curve, $y_j(t)$, under given service condition and the curve, $y_{j(ta)}$ under boosted test condition(T=Ta).From the prediction curve the variation of Y_j and the time t_a at which this variation is attained can be determined.

The properties of a rubber will generally change after prolonged exposure to high temperature. NR will become soft and gummy whilst neoprene will harden slowly under the same condition. The extent to which either softening or hardening is undesirable will depend upon the particular service required. The rate at which the properties of an elastomer change, increases logarithmically with temperature. Relatively small change in temperature may therefore cause large difference in the degree of deterioration

Tests for heat aging are carried out for two purposes, firstly to establish the changes in physical properties at elevated temperature. Secondly, there are accelerated aging tests at high temperatures which attempt to predict the long -term performance at lower temperatures. The international standard for both is ISO188. The test consists of aging test piece for a given period at a given temperature and then measuring the physical properties that are considered important.

In the oven method the test piece are exposed to air at atmospheric pressure in either the usual single chamber oven or a multi cell oven. The air flow in both the type of oven must be at a rate that provides between 3 and 10 complete changes of air per hour. Accelerated aging tests have been used for prediction of service life. Method used is to measure deterioration of a controlling property such as elongation at break and plotting the logarithm of time to reach a specific level say 100% EB, against reciprocal of absolute temperature.

4.1.3 Aging models

The most commonly used model [3-4)] is based on first order reaction and is of the form

$$P=P_0\,(1-e^{(-kt)}) \tag{4.1}$$

Where P is the property at any time, t. P_0 is the initial property. An exponential relationship between the extent of degradation and accelerated aging time is of the form

$$Y=A\ \exp\ [B\,(t-C) \tag{4.2}$$

Where A, B, C are constants and may be estimated from laboratory studies. A widely used extrapolation technique is based on Arrhenius equation [1.2]. It has been known since time that many reactions approximately double or treble their rates with 10° C rise in temperature. The prudent starting point for developing a theory of reaction rate is the Arrhenius relationships [5] which has been thoroughly confirmed by experimental data.

Arrhenius equation is based upon the variation of the equilibrium constant D with temperature i.e., the van't Hoff equation,

$$\frac{d\ln K}{dT}=\frac{\Delta H}{RT^2} \tag{4.3}$$

Since the equilibrium constant is equal to the ratio of k and k', the forward and reverse rate constants,Eq.4.3 may be written

$$\frac{d\ln k}{dT}=\frac{d\ \ln\ k'}{dT}=\frac{\Delta H}{RT^2} \tag{4.4}$$

The right hand side of the Eq.4.4 also could be divided into two parts provided the over-all heat of reaction is broken up into an energy change for each direction, as follows

$$\Delta H=\Delta H-\Delta H'=E-E' \tag{4.5}$$

Equation 4.5 then takes the form

$$\frac{d\ln k}{dT}-\frac{d\ln k'}{dT}=\frac{E}{RT^2}-\frac{E'}{RT^2} \tag{4.6}$$

The two separate expressions, one for the forward and one for the reverse reaction, having a difference in agreement with the equilibrium requirement are

$$\frac{d\ln'k}{dT}=\frac{E}{RT^2} \tag{4.7}$$

$$\frac{d\ln k'}{dT}=\frac{E'}{RT^2} \tag{4.8}$$

Integration of Eqn.(4.8) yields the Arrhenius equation,

$$k = Ae^{-E/RT}$$

or

$$\ln k = \ln A - \frac{E}{RT} \tag{4.9}$$

According to this equation a plot of ln k vs 1/T should give a straight line with a slope-E/R and an intercept of ln A.

Activation energy E was interpreted by Arrhenius as the excess over the average energy that the reactants must posses in order for reaction to occur. The only limitation on E is that the difference E-E′ must be equal to the overall heat of reaction, i.e., the average energy difference between the products and reactants. This suggests the existence of an intermediate state of activated reactants. Although Arrhenius developed his concept in 1889[6] modern kinetic data agree with it remarkably well. In fact when measured rates don't agree with the theory i.e., ln k vs 1/T does not indicate a straight line, it has been found that unknown complexities such as side reaction. Thus whether the changes in the material are due to chemical reaction, diffusion or volatilization we can expect a linear relationship between logarithm of life (time to failure) and reciprocal of absolute temperature. For the thermal degradation of large number of polymers, the temperature dependence follows Arrhenius model(7-10). Budrugeac [11] has carried out accelerated thermal degradation studies on nitrile rubber, ethylene propylene rubber (EPR)and low density polyethylene(LDPE) in air at ambient pressure and also in air and oxygen at higher pressures and temperature. He derived a kinetic equation (5,12) of thermal degradation of the investigated property.

$$\varepsilon(P,T,t)=\alpha\varepsilon_0 \exp[-AP^{n'} \exp(-\frac{E}{RT})] \qquad (4.10)$$

Where ε is retention of ultimate elongation, P,T and t are pressure temperature and time respectively. α a characteristic constant of the material. It is the ratio of the property at two pressures. A_0 is the Pre exponential factor ambient pressure. n′ is the pressure index. Tual et.al [13] studied the effects thermal aging on the mechanical properties of CR,NBR, and SBR by storing rubber components at elevated temperatures and analyzing the results using Arrhenius equation. Based on the limiting value time for EB to reach 150% the authors came to the conclusion that the shelf life of a properly compounded rubber to be15.5 years. Their study also showed that the over a 10 year period loss in EB was about 30% as compared to 17% in storage. Shmakov and Bogdanov[14] studied the aging resistance of rubbers by subjecting to different climatic condition involving exposure to water, air, sunlight, temperature. The service life of the rubbers was determined by projecting the dependencies obtained from the tests. Petrukhnenko et al[15] investigated influence of thermal, heat and moisture aging on the electrical properties of polymeric materials such as poly amide(PA), poly propylene(PP), poly oxy methylene (POM). They found that an increase in humidity from 80 to 96% leads to a greater degree of deterioration in the dielectric properties than an increase in temperature from 40 to 60°C.The was no degradation in properties in PP and POM

In general aging of a polymer can be described by series of chemical reactions each assumed to have Arrhenius behavior. Kinetic analysis of these reactions result in a steady state expression. If this series of reactions remain unchanged throughout the temperature under analysis, a linear relationship will exist between the logarithm of time to the extent of material property change and 1/T. The value of Ea is obtained from the slope of time- temperature plot. If on the other hand the set of reactions change with change in temperature, the effective Ea is expected to change and this would lead to a non-lineority in the Arrhenius plot. Major problems to be over come in dealing with Arrhenius extrapolation are confirming the assumption that the value of E remains constant at lower temperature and also distinguishing heterogeneous oxidation [16]from diffusion limited oxidation.

Several workers have addressed the above limitations in Arrhenius extrapolation, and several refinements have been proposed. One interesting model is an integral equation [17] of the kinetics of aging is in the form of Avrami equation:

$$X= X_0 \exp[-At^n \exp(-En/RT)] \quad (4.11)$$

This equation satisfactorily describes the kinetics of heat aging of plastics films such as polyimides, for which ultimate elongation or tensile strength has been taken as the criterion of retention. Further for predicting heat aging several successful models employ time temperature analogy[18] (TTA). Accordingly the isotherm of aging can be obtained by multiplying function, $G(\tau)$, known for one temperature T_1 by the ratio $K(T_1)/K(T_2)$:

$$G(\tau_2)_{T2}=\{K(T_1)/K(T_2)] \times G(\tau)_{T1} \quad (4.12)$$

The coefficient of shift, αT, is expressed by the equation:

$$\alpha T=E/R\times \exp\ (1/T_R-/1/T) \quad (4.13)$$

The technique facilitates generation of master curves, which satisfactorily estimate the lifetime from the kinetics of aging processes

4.1.4 Thermogravimetric degradation and kinetics

Thermogravimetric [TG]studies on polymers were started early by Murphy[18] and Coats and Redfern[19], and Maurer[20]. The thermogravimetry depends on following changes in mass in relation to temperature. The measurements are carried out under given rates of temperature rise (dynamic method) or at constant temperature with time (isothermal). The factors affecting the measurements are the atmosphere (air, inert gas), rate of heating, sample size and degree of packing etc.

Thermogravimetric analysis can be used in understanding various processes taking place with changes in mass of polymers e.g. Degradation, decomposition, pyrolysis.

In the studies of elastomers the monitoring of the processes of degradation and thermal decomposition parameters are especially important. Interesting work relating to the assessment of hydrocarbon elastomers based on the analysis of DTG, TGA, DTA curves has been reported by Skusarski[21]. Polychloroprene (CR) exhibits a higher thermal stability compared with PVC. In the main decomposition about 90% of the theoretical chlorine is released, whereas the total mass loss is around 45% as shown by Gardner and McNeill[22]. Brazier [23] analyzing the problem of carbon residue of polychloroprene, suggests the elimination of errors by subtracting from the total mass of carbon, residue of the polymer after pyrolysis in nitrogen

Thermal analysis techniques[24]Thermo gravimetric analysis or differential scanning calorimetric analysis, provide a very rapid and accurate way for life prediction, provided the correlation between thermal degradation and long term life testing can be established.

The method involves measuring decomposition profiles of test materials at several heating rates between 1 and 20^0/min. The temperature for a selected value of conversion is noted from TG curve of heating rate versus 1/T. The Activation energy for decomposition process is derived by plotting the log of heating rate against 1000/T for a constant decomposition percentage. Life estimation through TGA decomposition kinetics are performed based on Flynn and wall[25]Eqn.2.8. described in chapter2 The life of a polymer is estimated by the Toop's[26] Eqn.2.9.

Equation 2. 9 may be used to create a plot in which the logarithm of estimated life time is plotted versus reciprocal of the failure temperature. In the present work a neoprene sample aged humid environment has been studied for TGA kinetics. For comparison results of a control sample is also analyzed under identical conditions. An oven aged BIIR sample along with its control is are also analyzed. Degradation kinetic parameters obtained with TGA Decomposition kinetics programme(27) is presented in the Table.4.1

Table 4.1 Degradation kinetics parameters

Sample Details Ingredients in parts per 100 rubber	Kinetic Parameters at 5% Conversion.°C			Rate constants and1/2life at 100°C		Estimated Life time at 100°C
	Eact. (kJ.mole)	log (z) 60 min^{-1}	1/2 lifeTemp 1/min	Rate constant (min)$^{-1}$	Half-Life (min)	Hours
CR711 CB30, vulcanox 4020A/O); 1.5, unaged	120.1	9.16	292	2.24*10^{-8}	3.0910^{7}	2.4*10^{6}
711CB:30; a/o:1.5, [95 RH, 60°.C, 60days]	25.4	1.05	171.6	0.00308	224.6	0.26
BIIR + CB30, A/01.5, Unaged]	155.1	12.11	303	2.5*10^{-10}	2.7*10^{9}	-
BIIR {1101-CB30, A/O:1.5} OVENAGED70°C, 60AYS	173.9	13.51	311.1	1.9*10^{-11}	3.5*10^{10}	4*10^{7}

Results show that activation energy for the control CR is 120kJ/mole, this has fallen to 25kJ/mole due to accelerated aging in hygrothermal aging for two months. In case of BIIR the activation has increased due to oven aging. The observed behavior can be explained on the basis excessive swelling and degradation suffered by neoprene and densification of BIIR due to oven aging.

From the plot of this nature dramatic increase in estimated life time for a small decrease in temperature can be easily visualize

4.1.5water absorption and permeation

In the context of underwater elastomers the question of permanence of properties is linked to the water -rubber interaction besides thermal and oxidative degradation. The action of liquids in general depend on the net effect arising from physical swelling of the polymer, degradation of the polymer and fillers and the leaching of or attack on plasticizing agents. The presence of water soluble salts in the vulcanisate is detrimental as they facilitate the ingress of water. Up take of water through diffusion and permeation process are relevant issue to be considered.

All polymers absorb water. Extent of water absorption vary considerably with the chemistry of the polymer and it component materials. Large absorption is detrimental for service in underwater devices. Hence estimation of water intake by rubber through diffusion and permeation is crucial in life estimation studies

For rubber exposed to the effects of water on a long term basis, the kinetics of sorption assumes critical importance. Many a sensitive age determining characteristics like electrical properties and, dynamic mechanical properties are affected by the intake of water. Hence construction of any model to predict service life should take into consideration the total fluid taken up during the design life of the device and asses the long term effects using appropriate accelerated tests. Estimate of moisture intake has been successfully modeled by several workers employing Ficks laws[28] of diffusion. Shen and Springer[29]expression for water diffusivity in polymers has been extensively used for estimating diffusion coefficient. Diffusion coefficient obeys Arrhenius type relationship (Eqn.4.16)

$$D = D_0 \, EXP\left[-\frac{E_D}{RT}\right] \tag{4.14}$$

This relationship permits extrapolation of water intake by accelerated testing. Penetration rate P of water into polymer is given by the equation

$$P=(4D/\pi)^{1/2} \tag{4.15}$$

from which the depth of penetration for given thickness can be calculated. The unit of P is cm*sec$^{-1/2}$. Time taken for moisture to penetrate a given thickness can be calculated using the above equation. The service life of under water transducers are critically dependent the kinetics of water absorption and permeation through the encapsulating material. Therefore the present work includes an investigation on quantitative water intake through diffusion and permeation.

Detailed experimental studies were conducted during the course of the present study samples of rubber (25*25*2mm) were cut out from standard sheets made with composition given in Table 3.8. Samples are dried to constant weight. Samples were immersed in (3.5% NaCl) salt water solution contained in glass bottles as per ASTM-D-471 method. The assembly was placed in ovens maintaining constant temperatures40°C, 50°C, 70° C respectively. The weight gain of the sample was monitored gravimetrically. The water absorption isotherm is generated from the weight gain data (Fig.4.2)

Table4.2 Water absorption and diffusion parameters as function of temperature and period of soaking

<table>
<tr><td colspan="3" rowspan="2">Period (hour)$^{1/2}$</td><td colspan="3">Water absorption (%)</td></tr>
<tr><td>40°C</td><td>50°C</td><td>70°C</td></tr>
<tr><td colspan="3">0</td><td>0</td><td>0</td><td>0</td></tr>
<tr><td colspan="3">4.9</td><td>0.56</td><td>0.81</td><td>1.41</td></tr>
<tr><td colspan="3">10.95</td><td>1.05</td><td>1.38</td><td>1.92</td></tr>
<tr><td colspan="3">12</td><td>1.3</td><td>1.42</td><td>2.05</td></tr>
<tr><td colspan="3">13.86</td><td>1.33</td><td>1.52</td><td>2.1</td></tr>
<tr><td colspan="3">14.7</td><td>1.34</td><td>1.56</td><td>2.13</td></tr>
<tr><td colspan="3">16.97</td><td>1.48</td><td></td><td>2.4</td></tr>
<tr><td colspan="3">18.33</td><td>1.6</td><td>1.59</td><td>2.65</td></tr>
<tr><td colspan="3">Rate of absorption (%/hr$^{1/2}$)</td><td colspan="3">Diffusion coefficient. D *10^{6} cm^{2}/hr</td></tr>
<tr><td>40°C</td><td>50°C</td><td>70C°</td><td>40°C</td><td>50°C</td><td>70°C</td></tr>
<tr><td>0.86</td><td>0.089</td><td>0.127</td><td>8.19</td><td>8.91</td><td>16.9</td></tr>
</table>

From the knowledge of the diffusion coefficient at the service temperature, the time taken by the diffusing water front to advance into any known depth of the rubber encapsulation can be calculated. Thus in the case of compound presented in Table 3.8 the time taken for the diffusing water front to reach the depth of 1mm takes around 15 years at a reference temperature of 27^0 C

Permeability is a measure of the ease with which a liquid/vapour or gas can pass through an elastomer or laminate. The process is one of absorption and diffusion. The fluid will dissolve into the elastomer and the dissolved material diffuse through the film to the opposite side, where evaporation takes place. The definition of permeability is the rate of flow of the fluid, under steady state condition, between opposite faces of a unit cube of the elastomer, when subjected to unit pressure difference and controlled temperature.

Permeation is an important aspect of water intake by polymers. Quantitative estimation of permeation characteristics is an important in the context of under water transducers. meability is an important consideration in much application for elastomers such as packaging applications. lining materials. inner tubes, inflatable boats and is of critical importance for underwater electro acoustic transducer applications.

The most usual method of measuring the rate of water vapour transmission is the dish method described in ISO2528. The method consists of using a thin disk of the material under test to seal a circular disk containing anhydrous calcium chloride Edges of the disc are sealed with a wax mixture. The dish assembly is placed in a cabinet at a controlled temperature and humidity and it is weighed at interval to measure the amount of water vapour transmitted through the test piece. Using the equation [4.16]

$$\frac{q}{t} = \frac{P(P_1 - P_2)A}{h} \tag{4.16}$$

Table 4.3 Water permeation data

Period hours	Wt.loss % At 40°C	Wt.loss (%) at 50°C	Wt.loss (%) at 60°C
24	0.0464	0.029	0.0427
48	0.0606		0.084
72	0.0769		
96	0.1323	0.0135	
120		0.0573	
144		0.0762	
168		0.1006	0.2641
192	0.151	0.1262	0.3001
216	0.1579		0.35
240	0.1657		0.3847
264		0.1925	
288		0.2086	
312		0.2378	
336		0.2552	
360	0.2125	0.2793	
384	0.2232		
408	0.2396		
432	0.2477	0.359	
528		0.4105	
600		0.4766	
648			0.9449
696		0.5548	0.9877
720			1.0392
744			1.0392
768		0.5329	
792		0.5734	
816			1.1221
840	0.4323	0.6034	1.1672
888	0.4496		1.2424
912	0.4706		
936	0.4706	0.6952	
984			1.4016
1008	0.5086		
1032	0.5137	0.7823	
1056			1.508
1080	0.5425		
1104		0.856	

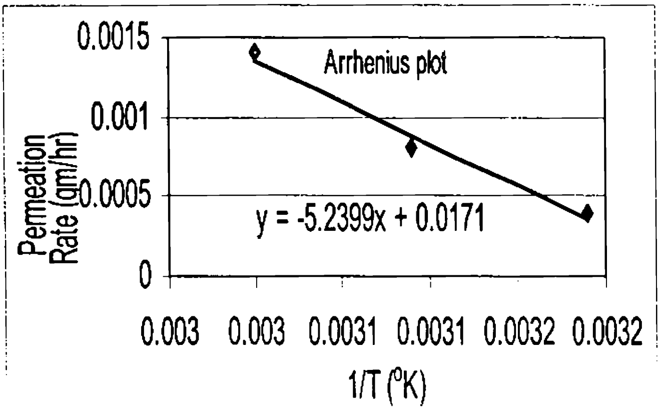


Fig.4.4 Arrhenius plot on water permeation through neoprene rubber

The weight loss corresponding to water permeated is measured and plotted as functions of time for different temperatures in Fig. 4.3. Permeation rate is calculated from the slope of the curve (Fig4.4) using the Eqn.1.21.Ep value for the rubber in the present case is found to be 43.56kJ/mole. An estimate of water transported across the sheet can be the made from the knowledge of the thick ness and the covered area of the sample

4.2 Effects of aging on properties and Life prediction

4.2.1 Ultimate elongation

Time -temperature super position technique has been applied in this case for predicting the service life. The property selected was ultimate tensile elongation. The choice of this characteristic is based on the sensitivity of this property on the aging processes.

Sample studied is same as in the previous section is given in Table 3.8. Five samples each of the vulcanisate materials are exposed to salt water (3.5%Nacl solution) by total immersion. Samples are placed in thermo static ovens maintained within ± 1° C of following temperatures : 23°C, 40°C, 52°C, 70°C. Samples were tested for tensile strength and ultimate line of the material at 23° C. The best fit model of the master curve predicts the life of the material. In this particular case the estimate of life for the material for 80% retention of tensile elongation is ~15 years. It is to be noted that the life predicted will be different if the retention of initial property is changed.

Table 4.6 Estimated time and retention obtained by shifting data to 23°C

Period of aging Ln(hours)	Retention at 23°C	Period at 40°C Ln (hours)	Retention at 40°C	Period 50°C Ln (hours)	Retention at 50°C	Period at 70 °C Ln(hours)	Retention at 70C
3.135	1	4.888	1	6.015	1	7.557	1
6.463	0.954	7.313	0.988	8.44	0.983	9.982	0.897
7.997	0.897	8.216	0.953	8.941	0.949	10.483	0.851
8.252	0.886	9.749	0.835	9.342	0.909	10.884	0.828
8.514	0.874	10.266	0.782	10.876	0.766	12.418	0.684
-	-	-	-	11.131	0.743	12.674	0.655
-	-	-	-	11.393	0.709	12.935	0.563

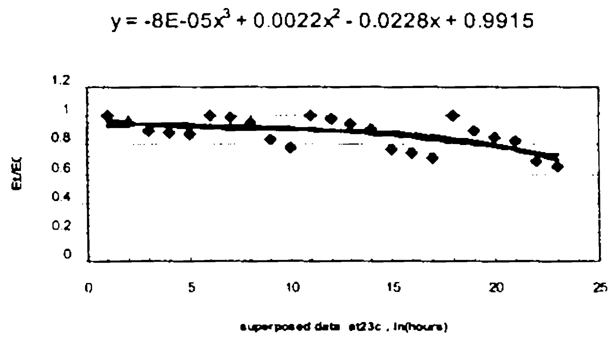


Fig.4.7 Master curve retention of ultimate elongation and the response equation

4.2.2 Compression stress relaxation

Compression stress relaxation technique is an emerging area [30]in life prediction methodology of rubbers. The technique is particularly relevant to seals and gaskets, besides in anti shock and vibration mount materials. The technique is important, as there is a direct correlation between operating conditions in the device and property measured. The relaxation of mechanical stress in a sample held under restraint is a test, which provides a valuable insight into the physical and chemical changes occurring. Cross linking caused by Oxidation leads to increase in modulus and hardening of rubber reducing its ability to function as a seal. In the case elastomeric seals used in deep water, material is subjected to extremes of temperatures and, hydrostatic pressure variations. Rubbers undergo considerable relaxation of mechanical stresses in such situations. Residual stresses at the interface between the elastomer and rigid surface is important for efficient sealing. The relaxation spectrum is a function of modulus of the elastomer and the strain applied. Compression stress relaxation detects and measures changes in modulus with time, temperature and environment. Estimation of long term compressive stress in seal is important for ensuring the Sealing efficiency.

Compression stress relaxation behavior has been selected as the age controlling parameter to estimate life of elastomeric seals. The technique is implemented in nitrile rubber vulcanizate discussed in section 3.9.6.

Sealing force has been determined at 40°C, 70°C and 100°C. relative sealing force as a function of temperature and time is given in Table 4.7. Sealing force is measured as per MethodISO3384. In Fig.4.8 normalized sealing force has been plotted as a function of aging period. The time required for 80% retention of sealing force is estimated from the above plot and Logarithm of time is plotted against reciprocal of absolute temperatures as shown in Fig.4.8

The volume resistivity values showed too wide a scattering to justify drawing of trend lines. Values still remained within an order of magnitude 10^{10} ohm cm for entire soaking period of 170 days in salt water.

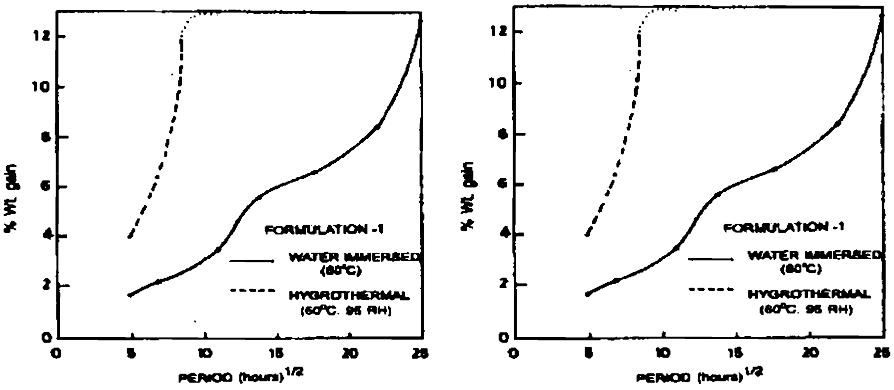
4.3 Influence of water exposure on aging

4.3.1 The Influence water immersion and humidity

The question of storage of underwater electro acoustic transducers while not in operation has been a topic of practical interest. Tropical humid environment has been considered to be as aggressive as marine water for polymer materials. The present investigation also addresses the issue of storage environment on the life of neoprene rubber formulations with respect to and reports the namely quantum of water absorption, electrical resistivity and dynamic mechanical properties.

Rubber chosen for investigation was Polychloroprene(Dupont Neoprene-W). Two simple formulations were selected for the study. The formulation 1 contained zinc oxide/magnesium oxide cure system (Formulation:711)whereas formulation 2 contained red lead cure system (formulation:712). Cure times were 27 and 25 minutes respectively for formulation 1 and 2. Water absorption (WI) study was carried out on specimen of size 2.5*2.5*0.2 cm^3. Samples were dried to constant weight over calcium sulphate desiccant and immersed in distilled water taken in bottles with stoppers. The bottles containing immersed samples were kept in a thermostatic oven. The temperature of the oven was 60±1.0°C. The increase in weight of the samples was monitored at regular intervals. Percentage water absorbed was calculated as per ASTM-D-471.

Water vapor absorption (HGT) study was carried out by suspending the samples freely in a Blue star-Tenny humidity temperature chamber. The sample size was 2.5* 2.5*0.2cm^3. The chamber was set to 95±3% RH and 60±1°C. The weight increase was monitored gravimetrically at regular intervals as in the case on liquid water absorption. The weight gained by the samples due to the ingress of moisture from the respective environment is presented in Figure 4.12(a-b) as a function of square root of time.



(a) (b)

Fig. 4.12. a-b Water absorption behavior as function of soaking environment

It is seen that in respect of formulation 1 initial water absorption of hygrothermally aged sample (in 2 days) is about 6.39%as against 2.19% of water immersed sample. For the formulation 2 corresponding figures are 3.04% and 0.57% respectively. The substantially higher water absorption in the hygrothermally aged sample as compared to water immersed sample can be explained if we consider that neoprene rubber vulcanizates contain large number of hydrophilic impurity sites dispersed in the rubber phase and water ingress into these sites by osmotic effects. Hydrophilic impurities like emulsifying agents used in the polymerization process and water soluble chlorides of magnesium, zinc and lead formed during vulcanization can act as water sinks. Water diffuses through the rubber phase and collects around the hydrophilic impurities forming droplet solutions[31,32]. The droplet solution will exert osmotic pressure on the rubber which acts as a semi permeable membrane. The droplet continues to grow till the osmotic pressure differential is balanced by the elastic stress in the rubber. The process is diffusion controlled and hence, the droplets nearer to the exposed surface can be expected to be larger in size than those

120mm dia., 3mm thick. Graphite paint was applied on both the surfaces for ensuring better electrical contact. Volume and surface resistivity apparatus [33] of M/s Davenport, UK was used for the measurement. Applied voltage was 500V and the time of application was 1 minute. Dependence of volume resistivity on the period in the storage in the two environments is shown in Figure 4.14. A marginal increase in resistivity occur in both the cases[34]

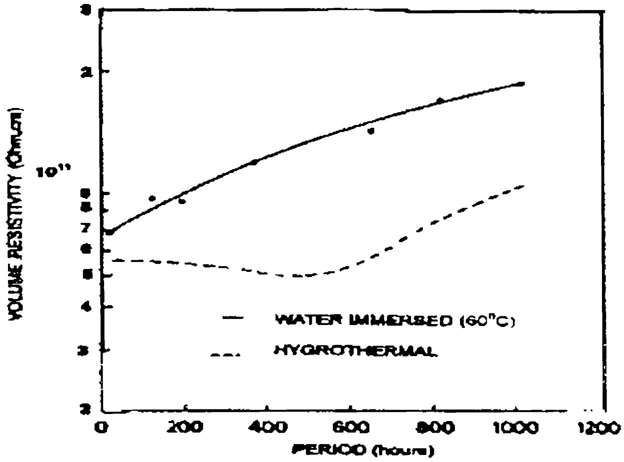


Fig.4.14 Dependence of volume resistivity on aging environment

4.3.3 Dynamic Mechanical Properties

Dynamic mechanical properties of formulation 2 were determined using Dupont DMA-983[35]. Rectangular samples were cut from vulcanized sheets. The samples were immersed in distilled water and humid environment maintained at 60°C. Oscillation amplitude was 0.2mm and measurement was done in the flexural mode. Temperature range studied was from -60°C to +40°C.

4.3.3.1 Storage Modulus (E')

Figure 4.15 shows storage modulus as a function of storage environment and temperature. It is seen that storage modulus undergoes substantial increase under the influence of accelerated aging in storage modulus is due increase in the cross linking in the materials. Process both in underwater and humid environment. Increase

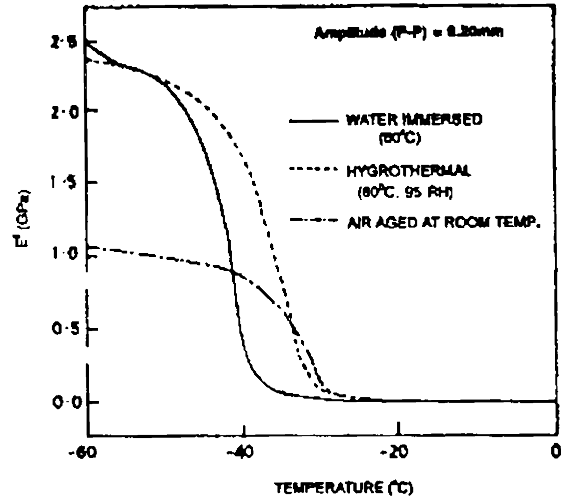


Fig 4.15 Storage modulus as a function of storage environment

The glassy modulus at 60^0 C is of the order of 2.44 GPa in both the cases as compared to 1.1 GPa in shelf aged sample. It is observed that temperature dependence of storage modulus is significantly influenced by absorbed water. Temperature dependent relaxation transition in the shelf aged sample was - 35.8 to -27.6^0C. This was undergone a shift to -45.61 to 38. 1^0C in water immersed sample, whereas in case of hygrothermally aged sample the same range lies between -45.67 to -30.15^0 C. This implies that there has been an increase time due to hygrothermal aging. In the case of hygrothermally aged sample the relaxation temperature range is nearly the same as that of the shelf aged sample.

4.3.3.2 *Loss Modulus (E")*

Dependence of flexural loss modulus on the storage environment is presented in Figure 4.16. It is observed that glass transition as represented by loss modulus maximum, has shifted from -31.55 to -40.82^0 C in case of water immersed sample while in hygrothermally aged sample is shifted only up to - 34.6°C. This implies that greater level of plasticization is occurring in water immersed sample, which in turn can be attributed to the introduction of additional free volume of water in clustered form. This suggests that it is the geometry of the water molecules that affects the glass transition rather that the amount of water. Energy dissipation maximum is also higher in WI sample than in HGT sample. Each rubber chain has in its vicinity water molecules as well as other molecular segments, the former can be displaced in translatory motion much more easily, effectively lowering local viscosity. This accounts for higher depression in the glass transition in water immersed sample.

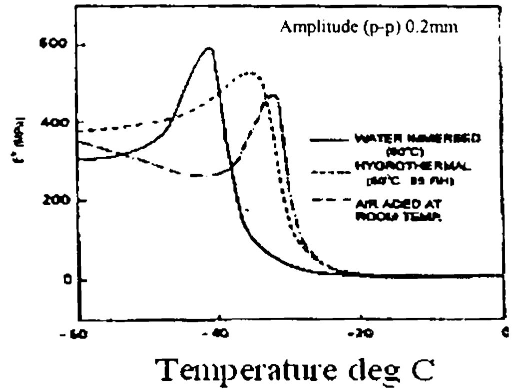


Fig 4.16.Dependence of flexural loss modulus on storage environment

4.3.3.3 *Dynamic Loss Factor (tan δ)*

Relative contribution of storage and loss modules in viscoelastic damping is presented in the form of a plot of tan δ vs temperature in Figure 4.17

It is seen that the loss factor, has been reduced marginally when exposed to accelerated water/ humid environments. Damping maximum has shifted to the lower temperature in both the cases. A fall in tanδ_{max} from 2.26 to about 1.8 is seen in both the cases.

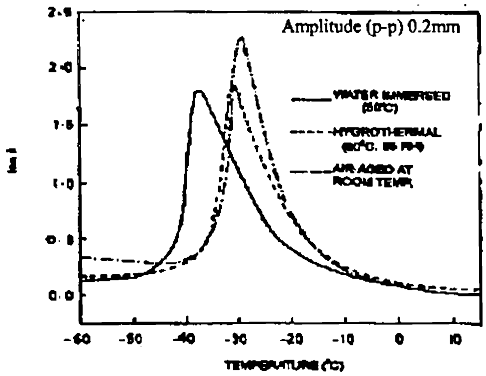


Fig. 4.17 Tanδ versus temperature plot

The decline in damping is clearly due to relative increase in storage modulus rather than decrease in loss modulus. A lowering of mechanical damping is the net effect of cross linking reactions and the plasticization effect of water.

4.3.4 Influence of hot humid aging on the transient response

Behaviour of rubber under dynamic stress- strain and temperature conditions has significant influence on the performance as passive acoustic materials in sonar transducer technology. Changes in transient response under the influence of heat and humidity are topics of special interest [36]. Hence an investigation on the dynamic response of a neoprene vulcanisate subjected to hot humid conditions has been under taken in the present context. Influence of aging under humid heat at 50°C and 95% RH on stress relaxation, recovery and dynamic modulus have been studied. Long time behaviour under hot humid environment has been estimated by time temperature superposition technique (37).

Sample selected was neoprene vulcanisate 711 modified with 1 pphr paraphynelene diamine and 30 pphr carbon black (GPF). Samples have been compression moulded. Cure time was 27 minutes. Hot humid environment was simulated in a Bluestar- Tenney humidity temperature chamber.

Viscoelastic properties were determined using Dupont DMA- 983 (35). Rectangular samples were cut out from vulcanised sheets and aged under humid heat. Oscillation amplitude for resonance mode measurement was 0.2 mm and displacement for stress relaxation measurement was 0.2mm.

4.3.4.1 Short time stress relaxation and recovery

Changes in the stress relation behaviour in rubber subjected to short time hygrothermal (humid heat) aging is shown in Table 4.9

Table 4.9 Stress relaxation parameters

Properties	Short time behavior				Long time behavior		
Period days	0	18	32	36	0	32	36
Relaxation rate	8.6	8.2	14	22	0.029	0.031	0.037
Recovery rate	4.9	-	6.5	4	-	-	-
Activation energy(kJ/mole)	8	32	41	72	289	223	111
WLF Constants : C1	-	-	-	-	49.8	38.4	19.1
C2	-	-	-	-	303	303	303
α_f at 30°C	-	-	-	-	0.009	0.015	0.023
α_c*10^5 (per°/C	-	-	-	-	2.9	3.7	7.5

unit for short time behavior : percent/ decade, long time behavior: per second

No significant change is observed in the relaxation rate up to about 3 weeks of aging however beyond this period relaxation rate is increased. By the fifth week of continuous exposure the stress relation rates increased by about 140% when measured at 30°C. Fig.4.18 shows a fall in relaxation rate with increase in temperature

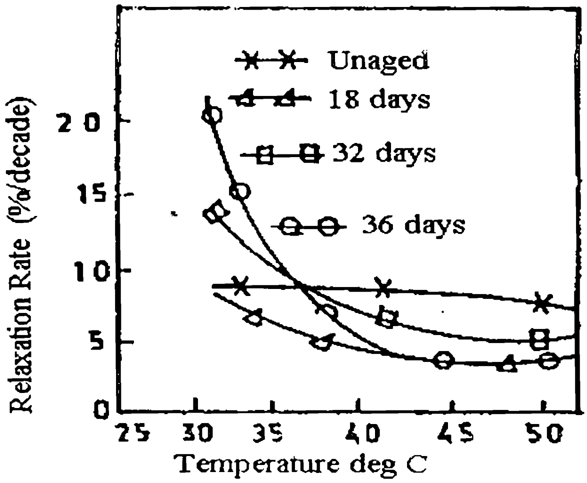


Fig.4. 18 Relaxation behavior as functions of temperature and hygrothermal aging

This can be explained on the basis of (1) negative slope in the stress temperature relationship of rubber at low strains and (2) increased rate of desorption of water as the temperature rises. Estimated Arrhenius activation energy (Ea) increases with period of hygrothermal aging. Unaged material has an Ea of 8 KJ/mole. One month exposure causes Ea to increase 8-9 times Increase in Ea suggests increased resistance to segmental mobility with progressive aging.

Recovery behaviour presented in Table-4.9 shows that recovery rates are slower than corresponding relaxation rates. Also recovery rates are not significantly affected by aging. On an average recovery rate remains at 4% per decade for the period studied.

4.3.4.2 Long time stress relaxation behaviour

Table 4.9 shows long time stress relaxation parameters obtained from the time-temperature superposition of relaxation data [37]. It is seen that overall relaxation rate increases with aging. The master curve in Fig.4.19 shows two linear portions.

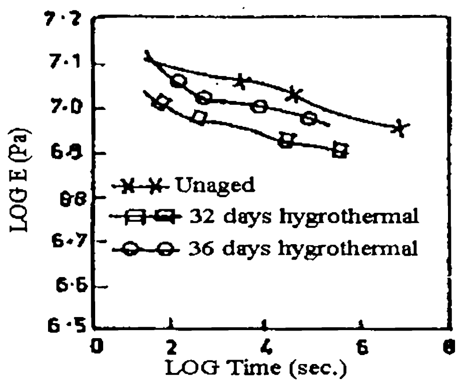
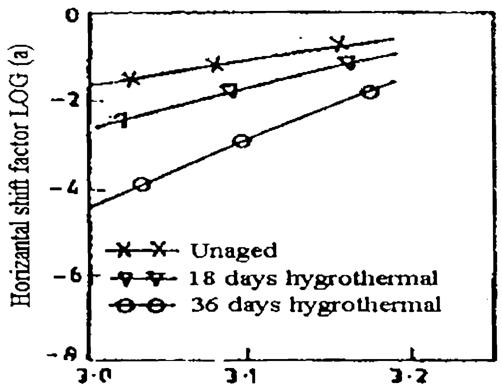


Fig. 4.19 Stress relaxation master curve

The first portion is steeper and reflects the increased viscoelastic response due to humid heat aging while the second could be due to changes in the molecular network structure. Shift factors vary linearly with reciprocal temperature as shown in Fig.4.20



1000/ T (°K)

Fig.4.20 Horizontal shift factor versus temperature

The Arrhenius activation energy of un aged rubber is estimated to be about 289 KJ/mole. The Ea falls to about 111KJ/mole on aging for 36 days. Free volume fractions calculated from WLF constants [38] increased with aging. This leads to the conclusion that aging causes free volume to increase. This observation has been confirmed from the shift of glass transition to lower temperature as seen in Fig.4.21

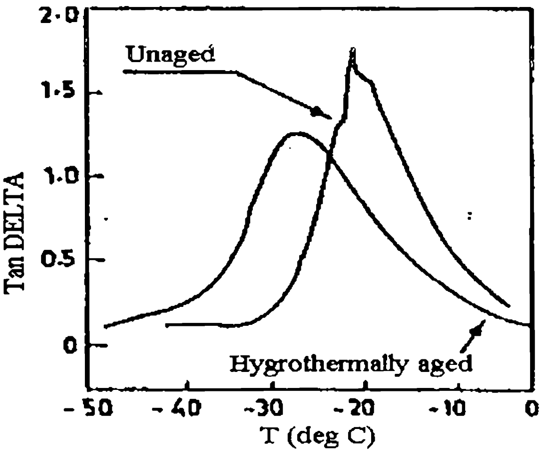


Fig. 4.21 Effect of damping behavior (tanδ) with aging

4.3.4.3 *Dynamic modulus*

Changes in the elastic modulus has been studied as a function of aging period. Figure-4.22 shows variation of modulus retention Et/$E_0$with period of aging.

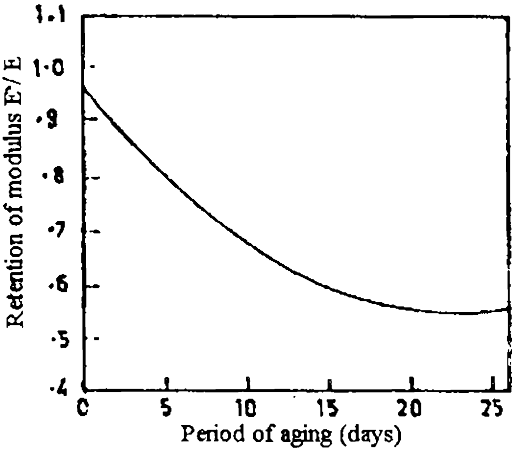


Fig.4.22 Variation of modulus retention with aging

It is observed that modulus reduces by 30% in 4 days and continues to decline rapidly for 20 days and remains at 55% of the original thereafter. Decline in storage modulus follows a quadratic law. Temperature dependence of modulus with temperature can be seen in Fig.4.23.

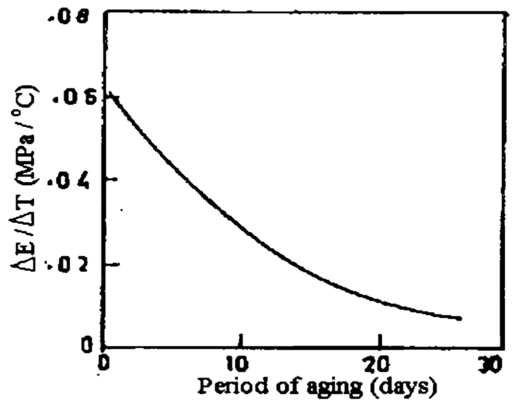


Fig.4.23 Variation of temperature response of elastic modulus with aging

It is found that modulus-temperature slope decreases with period of aging. The slope in unaged material is 0.06 Mpa/°C which declines to about 0.01 in 26 days of hygrothermal aging.

4.3.4.4 Effects of long term salt water aging on dynamic mechanical properties

Importance of dynamic mechanical properties on the performance of passive acoustic rubbers, have been discussed in detail in the earlier sections. Effect of long term exposure of rubber on the dynamic mechanical response is a topic practical interest. Present investigations considers this aspects in some detail. The rubbers studied mainly are Bromo butyl rubbers and neoprene rubbers.

Neoprene rubber vulcanisate based on composition 711 discussed in section modified with 30pphr carbon black and 2pphr anti oxidant vulcanox 4020 has been studied for influence of aging on the dynamic mechanical properties.

In order to study the influence of aging on the dynamic mechanical response samples of neoprene vulcanizate has been immersed in 3.5% NaCl solution maintained at 40°C,70°C and 80°C respectively and a control sample at room temperature in air. Dynamic mechanical properties were

The above study leads to the conclusion that aging in water medium at elevated temperature causes loss modulus\tandelta peak to shift to higher temperatures and the peak height undergo sharp fall associated with a reduction in the area under the curve. Aging in water under accelerated condition causes neoprene rubber to become less damping and causes glassy modulus to fall to one third of its original value.

4.3.4.5 Effect of aging on frequency response

Neoprene vulcanizates based on composition 711 modified as in 4.3.4.4 has been used in the this study also. Sample has been conditioned in salt water and aged in a thermostatic oven at 70 °C. Viscoelastic parameter storage modulus and loss modulus have been studied by TTS. Data is given in Table 4.11

Table 4.11 TTS data from master curve

E' DATA		E" DATA	
Frequency(Hz)	E'(Pa)	Frequency(Hz)	E''(Pa)
$1*10^{-6}$	$3.628*10^{6}$	$3.162 * 10^{-8}$	$1.187*10^{7}$
$1*10^{-6}$	$4.723*10^{6}$	$1 * 10^{-5}$	$1.142*10^{7}$
$1*10^{-5}$	$6.408*10^{6}$	$3.371*10^{-4}$	$1.25*10^{7}$
0.001	8.688*106	0.00484	$1.664*10^{7}$
0.01	$1.17*10^{7}$	0.0696	$2.94*10^{7}$
0.09085	$1.771*10^{7}$	1	$6.254*10^{7}$
1	$4.289*10^{7}$	15.98	$1.332*10^{8}$
3.162	$8.496*10^{7}$	284.3	$2.247*10^{8}$
9.085	$1.753*10^{8}$	3671	$2.775*10^{8}$
90.85	$7.516*10^{8}$	89890	$2.825*10^{8}$
1334	$1.66*10^{9}$	$4.682*10^{8}$	$2.323*10^{8}$
9085	$1.932*10^{9}$	-	-
90850	$2.039*10^{9}$	-	-

Results are shown in Fig.4.30. The data fits the WLF model Log(aT)=C1(T-T$_0$)/C2+(T-T$_0$)C1=21.25,C2=106.9, T$_0$=-19.1°C

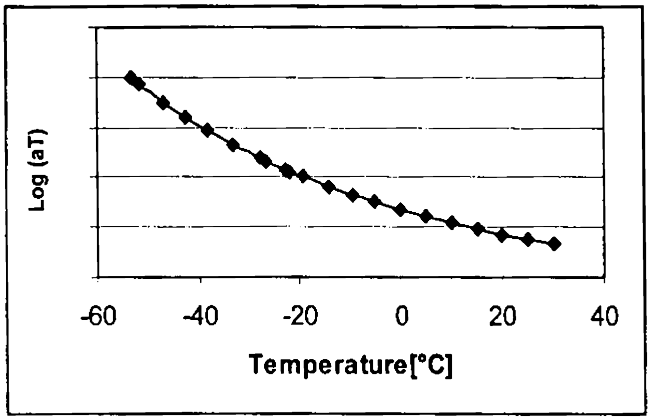


Fig. 4.29 E′ Shift function versus temperature plot on neoprene aged in water at 70 °C for 300 days.

The master curve generated with WLF model foe E′ is presented in Fig.4.30.

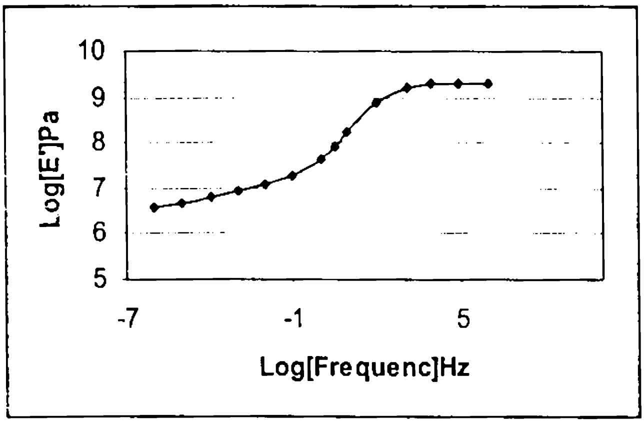


Fig.4.30 Frequency- E′ Master curve [Ref temp:-19.1] of neoprene rubber aged in sea water at 70°C for 300days

The curve shows transition in the frequency band of 0.1Hz to 90 kHz. Fig. 4.31. Shows master curve on the flexural loss modulus. The curve shows E″s peaks at 90kHz. At still higher frequencies loss modulus falls with increase in frequency. Loss modulus master curve is also found to fit a WLF Equation Log(aT)=C1(T-T$_0$)/C2+(T-T$_0$)C1=16.31,C2=48.01 To=-19.1°C.

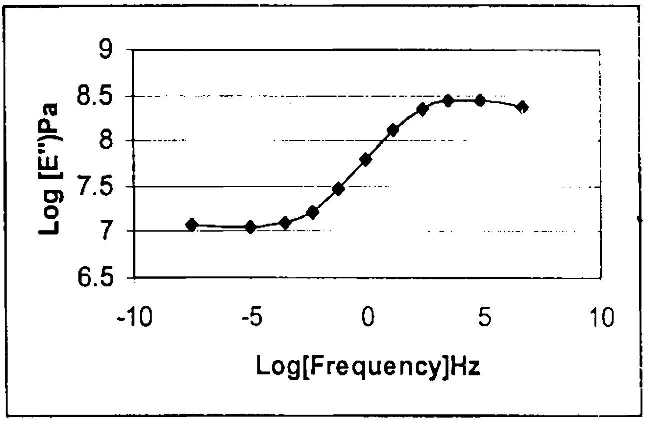


Fig. 4.31 Loss modulus master curve for neoprene aged on salt water for 300 days

4.3.5 Influence of wet aging on the kinetics of thermal degradation

Heat and moisture are two major contributing factors in the degradation process of rubbers. A knowledge of the mechanism and kinetics of thermal degradation is necessary for understanding of aging processes which are influenced by thermal\hygrothermal stresses. An investigation has been carried out on how the kinetics of thermal degradation is influenced by environmental stresses. The study also examines the mechanisms responsible the change in thermal activation energy with aging.

4.3.5.1 Experimental procedure

Rubber samples were prepared from Dupont USA Neoprene W. Formulation B given in Table 4.12 represents a practical underwater elastomer while Formulation A is a gum vulcanisate. For preparation of sample Standard procedures were followed[39,40]. Cure times were 30 min. each.

Table 4.12 Compositions of the sample rubber

Ingredients	Compound Design	
	A	B
Neoprene	100	100
Stearic acid	1	1
Vulcanox 4020	1	1
Zinc Oxide	5	5
Magnesium oxide	4	4
Carbon Black GPF	-	30
MBTS	1.5	1.5
NA 22	1	1

Thermal analysis of samples were carried out using a TA Instruments, USA, Thermogravimetric Analyzer (TGA 951) and modulated DSC under nitrogen flow @ 50 ml/min and 100 ml/min respectively. Both isothermal and dynamic TGA runs were carried out. MDSC measurement was done at a heating rate of 5°/min. in dynamic mode. Dupont TGA decomposition kinetic software [41] based on Flynn and Wall method was used for calculation of decomposition kinetic parameters. Avrami analysis was [42]) performed to estimate nucleation parameter 'n'. Gum rubber samples (25 dia * 13 mm thick) were exposed to 3.5% salt solution at 70°C and aged for 3 months.

4.3.5.2 Influence of aging environment

Sample TGA thermograms showing degradation profiles of humid heat (HgT) and dry aged (DA) samples and for reference un aged neoprene vulcanisate, are,presented in Fig. 4.32.

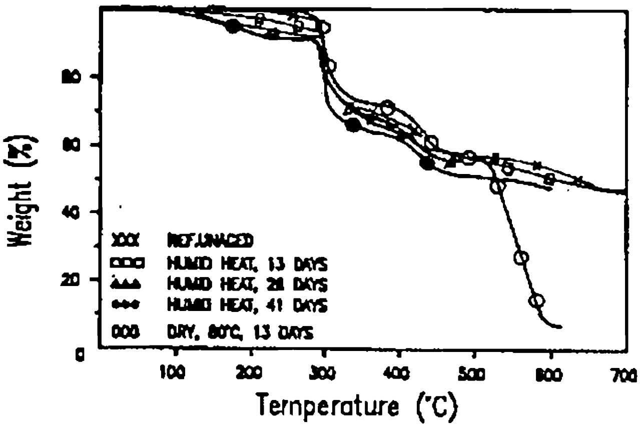


Fig.4.32 TGA Thermograms of humid aged, dry aged and control samples

Three major stages in degradation process besides a pre-stage can be seen in hygrothermally aged samples. The pre-stage in these curves represents desorption of water. The amount of volatiles escaping has been found to agree with the quantum of absorbed water during soaking. The second stage is major polymer degradation and the same corresponds to the breakdown to polymer backbone.

The second and third stages also could be representing the formation and pyrolysis of graphitic carbon. Thermograms of HgT samples (2-4 weeks) show an upward shift in the initial temperature indicating an apparent increase in stability. However on continued aging, initial temperature falls below that of the unaged reference sample, thereby offsetting the apparent stability. Dry aged material shows negligible pre-stage as can be expected. First and second stages of the decomposition show marginal increase due to thermal activation. Table 4.13 shows kinetic parameters of the decomposition reactions of aged and unaged samples. Table 4.14 gives kinetic parameters at 5% conversion

Table 4.13 TGA Kinetics parameters

Aging period Days	Unaged	Hygrothermal (RH: 95, TEMP: 50)°C			Dryheat 80°C
		13	26	41	13
Degradation Range (Temp°C)	282-357	280-357	291-366	277-352	277-353
Peak Temp (°C)	301	298	308	299	300
Fraction reacted %	27.11	26.62	25.32	26.0	26.6

Table 4.14 Kinetic parameters at 5% conversion

Aging period Days	Unaged	Hygro.(95%,50°C)		
		13	26	13
Energy of activation kJ/mole	191	204	120	107.9
Log(pre-exponential factor) 1/min.	15.85	17.1	8.99	8.05
60min. ½ life temp °C	287.70	286.0	290.6	291.40

4.3.5.3 *Changes in the activation energy*

Changes in the activation energy of decomposition (Ea) as functions of conversion percentage and aging period are shown in Fig.4.33

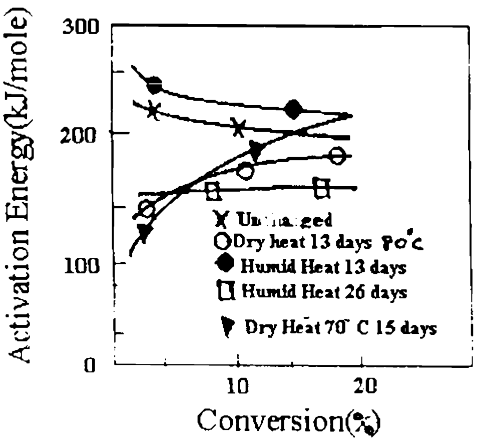


Fig.4.33 Changes in activation energy as function of aging and degree of conversion

Ea has progressively declined with increase in conversion level in unaged reference sample. Ea at 1% conversion is 204kJ/mole which reduces to 173kJ/mole at 20% conversion. Sample aged in HgT environment for 13 days shows a similar behavior. As period of exposure id increased to 26 days a reversal in the declining trend is observed. The behavior is reflected in the case of dry aged sample. It is suggested that the reversal in Ea could reflect a change in the mechanism of thermal degradation. Thermal decomposition can be visualized as taking place from the outer surface to the inner. During aging oxidative degradation gets initiated at the exposed surface, which then progresses inwards through a diffusion process. The interior of the rubber samples remains unaffected even as extensive degradation takes place at the surface. This results in lower Ea at the start of the thermal degradation which goes on increasing as the degradation proceeds inwards.

4.3.5.4 *Avrami analysis*

The reversal in Ea has been examined further on the Avrami model [42]

$$1\text{-}\alpha = \text{Exp}\ (-kt^{n}) \qquad (4.18)$$

where a is the fractional conversion at time t, k, specific reaction rate and n the Avrami exponent n = r + h in which r is the number of steps involved in nucleus formation, h, the number of dimensions in which nuclei grow.

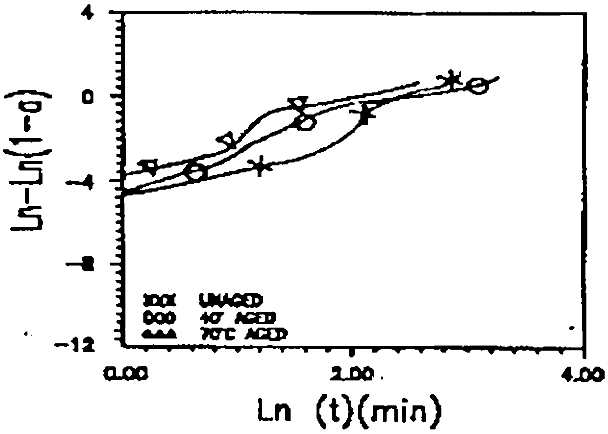


Fig.4.34. Plot of ln(ln(1-α))versus ln t for estimation of Avrami exponent

A plot of ln(-ln(1-α)) vs ln t (Fig. 4.34) yields the value n, values obtained for unaged rubber is 2.3 and that for sample aged at 70°C for 3 months is 0.7. The change in values implies a change in reaction mechanism from that of random nucleation to diffusion controlled process (42, 43).

4.3.5.5 *Influence of salt water*

A neoprene gum rubber, formulation (A), has been studied for relative degradation behavior. A circular disc of appox. 2mm thick has been sliced from across the middle portion of the cylindrical sample and a specimen has been cut from its central core (specimen 'X'). Another specimen has been taken out from a position 1mm below the exposed surface (specimen 'Y'). The thermal degradation behavior of the specimen has been studied using TGA and MDSC techniques. The thermograms obtained (Fig. 4.35 and 4.36) for specimen show significant difference in their thermal degradation behavior.

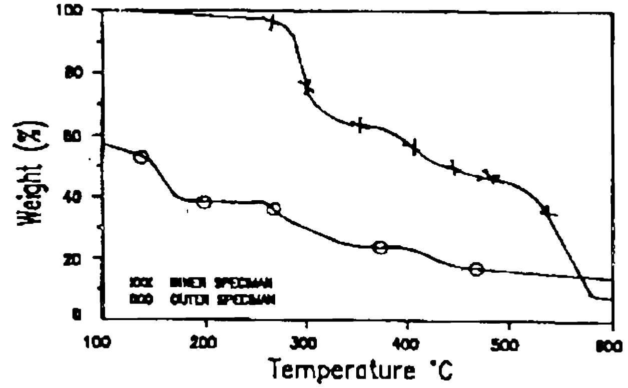


Fig 4.35 TGA thermograms of outer /inner materials from the sample

The inner specimen 'X' has been found to thermally degrade at around 300°C in TGA. The oxidized outer portion (specimen 'Y') degraded at around 150°C. MDSC has shown as exotherm at 300°C for specimen 'X' while oxidatively degraded specimen 'Y' decomposed at about 150°C.

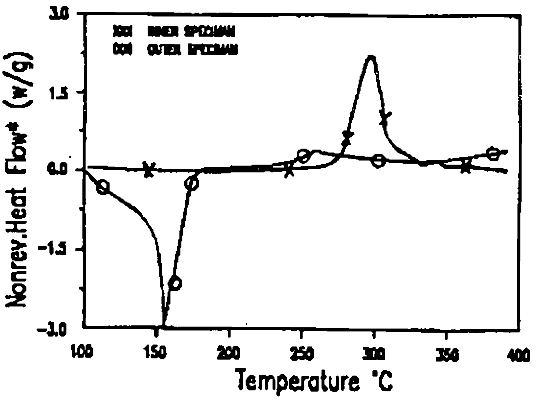


Fig. 4.36 MDSC thermograms of outer /inner materials from the sample

The small exotherm appearing at 280°C could be an indication of some trace of un decomposed material remaining in the outer layer.

4.3.6 Analysis of glass transition and clustered water

The amount water absorbed by the rubber during exposure is an important indicator on the service life a rubber component. All the known techniques for the analysis of water in polymers give the information only of the total water present in a polymer [44,45]. But the form in which water exists in a rubber matrix is very important. Clustered form of water is responsible for the loss in the dielectric properties of rubbers. Estimation of the amount of water trapped in the rubber matrix is an indication of the period of exposure. In a practical situation this information will enable the prediction of the remnant service life. In the course of present work a study was carried out on the amount of clustered water in neoprene rubber. Rubber samples are prepared with the formulation 711. The composition additionally contained 30 pphr GPF carbon black. MDSC technique has been investigated for the analysis. This technique as has been discussed in chapter 2, resolves the total heat flow associated with a thermal event to heat capacity dependent component (reversible heat flow) and kinetic component (non reversible component). Reversible heat flow signal has a melting endotherm as the clustered form only will show the melting cluster increases but the melting event is complete in all cases sharply at 0 °C. A red lead cured sample soaked in salt water for 4 years in salt water(3.5%Nacl) at ambient condition has been studied. Results are plotted in Fig.4.39

The total water absorbed over the period is only 2.69 % and the clustered water in this is only 1.79%. The position of glass transition range after the long exposure time is found to be -45.34 to -40.32°C. This represents a shift in the Tg by about 4 degrees Celsius in the Tg onset, indicating a plasticization effect. Thus long term exposure of rubber in salt water lead to lowering in Tg. This observation is contrary to the effect observed in thermally accelerated soaking, wherein Tg shifts to higher temperature. The effect can be explained in view of the fact that in hot environment stiffening of the rubber dominate over plasticization. This observation demonstrates the advantages of red lead curing. This investigation opens up a method for assessing the service life of a rubber encapsulated device exposed to underwater environment.

Reference

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Chapter 5

RESULTS AND DISCUSSION

In this chapter results of experimental studies carried out on compounding techniques, underwater aging phenomena of rubber vulcanisates and life prediction techniques are consolidated and presented. Trends are discussed and conclusions are arrived at presenting guide lines for compound design.

5.1 Compounding considerations

From an understanding of the published work of several researchers and the experimental findings of the author himself, Neoprene has been identified as one of the best suited base polymers for detailed investigations as an ideal underwater engineering polymer. Major advantages are its greater sea water compatibility, bonding with metals, scope for tailor making of mechanical properties and above all the very good weathering resistance and oxidation resistance. Despite these advantages, the major drawback of neoprene is its rather high water absorption. The major objective of the present study was to develop appropriate compounding techniques which will reduce water absorption of rubbers, neoprene in particular and to achieve optimal property levels for use in underwater electro acoustic transducers. Design inputs have been generated on following parameters relating to sonar passive materials in general and encapsulation material in particular:- 1. Diffusion, 2. Permeation of water, 3. Curing processes and cure acceleration and 4. Viscoelastic behavior. Specific applications like encapsulation, acoustic baffles and underwater seals have been focused on for the study. Studies on aging processes, the mechanisms and kinetics have been another area for specialized investigations. The understanding a control has been useful in aiming at realistic life prediction approach for rubber components under the stringent underwater environment.

5.2 Water intake by rubbers

The study was initiated on a gum neoprene vulcanisate without age resistors and fillers. The sample absorbed more than 200% of water at 60°C over a period of 20 days. The temperature dependence of the absorption curve followed Arrhenius pattern. The activation energy of this absorption process is estimated to be 4.2 kJ/mol. When the sample was modified with suitable red lead cure system water absorption dropped to 60%. Gum rubber composition when modified with anti degradent and carbon black the absorption value got reduced to about 20%. Thus an order of magnitude reduction in the water absorption could be achieved with compound modification involving cure system, fillers and anti oxidants.

The influence of soaking rubbers in humid and underwater environment on water absorption has been investigated. Underwater transducers are often exposed to moisture laden tropical environment with relative humidity close saturation levels and temperature as high as 40°C. The lower absorption by red lead cured rubber is a result of lower levels of water soluble products formed during vulcanization. Effect of increasing the concentration of carbon black from 10-80 pphr is a sharp decrease in water absorption. With reference to Fig.3.12. the relationship between absorption rate and volume fraction of carbon black is found to fit a polynomial response equation, $y=(-)1.648f^2 + 0.25f+0.3008$. 'f' is The response represents a declining trend beyond 50 pphr carbon black., f is the volume fraction of carbon black and y′ the absorption rate. When carbon black is added to the rubber the energy of activation increases. In the case of GPF black (30pphr) this increase is as much as 100% from that of the blank rubber.

Diffusion process studied as a function of type of carbon black reveals that the absorption is lower in rubbers compounded with lower particle size carbon black. Thus diffusivity of SRF black filled vulcanisate is higher than that with FEF black. This could be explained on the basis of the higher packing density of filler associated with a lower particle size carbon black.

Investigation on the effect of salinity on the water absorption behavior shows that absorption of distilled water is higher than salt water in all cases studied. This is in agreement with the finding of Cassidy et.al. [refer 3.2] and Muniandy and Thomas[refer1.21]. The higher absorption from distilled water can be explained on the basis of the increased amount of water needed to balance the elastic pressure surrounding the impurity droplets. Red lead cured sample also showed higher water absorption of distilled water. Absorption of distilled water is about 3% as against 1% of salt water. Varying the type of carbon black did not produce any noticeable change in the absorption of distilled water.

Influence of different types of inorganic fillers (like calcium carbonate, talc and clay) individually incorporated, has been investigated. Talc controls water absorption behavior in neoprene gum rubbers moderately and results in a marginal reduction in water absorption over that of calcium carbonate filler. As can be seen from Table.3.2 the diffusion coefficient is found to fall with increase in concentration of the carbon black. Diffusion coefficient at 20 °C is in the range of $7.4 * 10^{-8}$ to $3.5 * 10^{-8}$ cm²/hr. At 40°C the value ranged from $2.25*10^{-7}$ to$1.46 * 10^{-7}$ cm²/hr. At 50°C, the corresponding range is from $4.39*10^{-7}$ to $2.87 *10^{-7}$ cm²/hr. Activation energy of diffusion processes is found to increase with increase in fillers i.e. E_a increased from 11.6-14.03 kJ/mol.

Comparative study of water absorption in different basic rubbers showed that neoprene absorbs maximum water while nitrile rubber absorbs the least under the same conditions. However considering the totality of the properties like sea water compatitability, bondability to metals, environmental resistance etc., required for the end use, it considered that Neoprene is the optimal material in comparison with the other rubbers. Water absorption behavior on neoprene could be tailored by judicious compounding so that absorption can be limited to a minimum. Hence the study was concentrated mainly on Neoprene. Study of rate of moisture intake by a rubber soaked in a known humid environment has yielded a linear response equation, $m_r = 1.007H - 0.7$. Where m_r stands for moisture intake rate and H fractional humidity. Springer[1] has derived a power law relation for moisture absorption in composite materials. The model provides a means to estimate the water absorption in a sample stored at high relative humidity. Practical significance of such a relation ship is that this gives an estimate of possible moisture absorption of rubber components during shelf storage in dockyard environment.

Effect of oxygenated environment as against inert environment on the water absorption rate has been studied. This study showed that the rate of absorption as well as the maximum absorption at a given temperature is lower in oxygen free environment. Oxidative degradation enhances water absorption. Neoprene blank showed a lowering of water absorption of over 100% in nitrogen environment. Vulcanizate containing carbon black as well as anti oxidants showed further lowering of absorption (Table.3.21). Thus absorption by neoprene gum rubber has reduced to 0.4% from the original value of 1.07%. Maximum absorption has reduced in this case from about 85% to 30% and the diffusion coefficient underwent a change from $1.03*10^{-5}$ to$1.14*10^{-5}$ cm^2/hr. The study further revealed that diffusion coefficient actually falls when the maximum absorption is high. Explanation is implicit in the diffusion equation (3.1) wherein $D=\frac{\pi\theta^2h^2}{16M_S}$, hence diffusivity D is inversely proportional to M_s, the maximum absorption. In practical situations diffusivity signifies the speed of absorption not the quantum. In comparison with neoprene rubber rate of water absorption of BIIR is only 1/5th. Maximum absorption is 1/8th. But Diffusion coefficient in BIIR is 30% higher. In the filled (carbon black) BIIR water absorption rate is 1/4th and maximum water absorption is 1/5th of the corresponding neoprene sample. Between both the gum vulcanizates lower water absorption in BIIR follows from the chemistry of structure of the respective rubbers. Rather bulky and spread out isobutylene structure is expected to shield or obstruct movement of foreign molecules more effectively than chloroprene. Between the corresponding filled vulcanizates the difference in the absorption is narrowed down. Conclusion is that additives are more effective in neoprene rubber. Diffusion coefficient of carbon black filled BIIR is 50% more than corresponding neoprene sample. Reason for higher diffusion coefficient value despite lower amount of water diffused in, is implied in the equation already out lined. Study leads to the conclusion that as more water gets in tendency (diffusion flux) for further absorption reduces in other words diffusion becomes concentration dependent. Another finding is that water absorption of natural rubber is only marginally higher than bromobutyl rubber and in specific compositions with lower total water intake can be realized.

A study on the water absorption behavior of natural rubber shows that the absorption rate range between 0.03 to 0.05%/hr$^{1/2}$. E_d of water absorption is about 5.55kJ/mole. This value is close to that of neoprene gum rubber. Influence of varying amount of anti oxidants in the water absorption behavior of natural rubber has been studied. It is observed that maximum rate of absorption occurs in samples containing up to 1pphr antioxidants (Para phenylene diamine). Higher amount of antioxidant does not have a significant effect on water absorption rate.

Comparative study on the influence of water absorption from distilled water and salt water on Neoprene based on zinc oxide and red lead curing systems indicates higher water absorption in distilled water than in salt water. Salt-water absorption reaches equilibrium values in about 6 months of soaking while distilled water absorption continues to increase. This is explained on the basis of higher distilled water requirement to balance the osmotic pressure between the medium and the water sink formed inside the vulcanisate at the impurity sites. The present study supports the findings of Muniandy and Thomas. Between the two curing systems red lead cured sample is found to absorb much less water i.e. distilled water absorption is 3% in the case of red lead where as it is 15% for zinc oxide.

Three types of carbon blacks are studied for distilled water absorption. However no significant difference is found in the water absorption but a significant lowering of absorption is observed in general with the filler incorporation carried out by soaking in distilled as well as in salt water. There is a further reduction of water absorption in salt water. Effect of inorganic fillers namely precipitated calcium carbonate, talc and clay has been studied. Results indicate that there is no significant influence on the quantum of absorption. However the plot tends to reach a plateau after about 5 months of soaking in distilled water. Ultimate absorption is about 30% for calcium carbonate and clay filled samples. Talc is found to contain absorption at a level of 27%. A conclusion drawn from the study is that red lead is globally effective curing system in controlling water absorption of neoprene rubber, as against the most widely used ZnO-MgO curing system.

Permeability of water through rubber is crucially significant for the performance of devices wherein rubber serves as the protective lining.

Neoprene gum vulcanizates studied give permeation rates $4.43*10^{-5}$, $11.11*10^{-5}$,, $22.22 *10^{-5}$ gmcm/cm^2/hr respectively at temperatures 20°, 40° and 50°C. Activation energy of the process is found to be 41.kJ/mole. Higher concentration of antioxidant is expected to result in lower permeation by increased protection however Permeation behavior of neoprene (30 pphr GPF black) with varying quantities of anti oxidants indicate that the permeation rate remains unchanged with concentration of anti oxidant. However the over all sensitivity of the permeation process has been affected as reflected from energy of the activation. Activation energy is estimated to be 62±1kJ/mole. Effect of FEF carbon black one permeability is that rates are systematically higher than the corresponding values for GPF filled samples. The permeation rates doubled with every 10°C rise in temperature in both cases. Present study has established permeability and activation parameters of neoprene and other rubber formulations and found agreement with the values published by Cassidy et.al [refer 3.35].

5.3 Electrical resistivity considerations

Electrical resistivity of neoprene samples subjected to long time soaking in water resulted in a decline in volume resistivity. As can be seen from Fig.4.10. the change is from $5.5*10^{10}$ ohm.cm to $3.5*10^{10}$ ohm.cm. During this period 8% water has been absorbed by the sample. Both the rate of absorption and fall in resistivity satisfy a quadratic fit. $y= -0.05t^2+1.3t+0.127$ for water absorption and $y=0.002t^2 -0.05t +10.7$ for resistivity changes. t stands for the period of soaking(hrs). In the case of red lead cured rubber both water absorption and resistivity change show no systematic trend. There is negligible variation in resistivity. There was no noticeable water absorption by the sample as well. A general observation from this study is that soaking in water does not cause any appreciable change in the volume resistivity of low water absorbing rubbers. Since there is no significant variation due to aging, this parameter has been excluded from life assessment studies. However by virtue of being a crucial property in the underwater transducer performance, particularly for acoustic projectors handling high power, compounding studies have been carried out to optimise parameters accordingly. Study has been carried out on level of electrical properties achievable by different in basic rubbers. Results showed that volume resistivity better than 10^{10} ohm.cm is achievable with neoprene and above 10^{12} ohm.cm could be achieved with BIIR and SBR rubbers. Studies further showed that resistivity of rubber compounds are very sensitive to the variation of carbon black loading beyond 30 pphr in neoprene and beyond 50 pphr in BIIR and SBR rubbers. Conclusion of the study in respect resistivity provide useful design input for compound development.

5.4.Transducer Encapsulations

Based on the parametric variation studies conducted on a number of rubber compounds relating to water absorption, a typical transducer encapsulation rubber has been designed and its water absorption investigated. Result shows that equilibrium absorption at 40°C is 1.5%, at 50°C it is 2.6% and at 70°C value is 2.5% and rate of absorption was 0.091, 0.104 and $0.1366\%/hr^{1/2}$ at the respective temperatures. The time to reach equilibrium absorption reduces with the increase in soaking temperature. Diffusion coefficient was found to be between $8*10^{-6}$ and $16*10^{-6} cm^2/$ hr and the activation energy of the process is 21.87kJ/mole.The study has further led to the development of a highly water resistant encapsulation material, with stable electrical properties and optimal combination of other properties. Typical properties realized are reproduced in Table 5.1. Fig 5.1 shows a comparison of water absorption behavior of the compound in comparison with conventional encapsulation rubber(CR)

Table 5.1 Typical properties of encapsulation rubber

Water absorption (%)	Water permeation (gm.cm/cm^2 hr	Vol. Resistivity Ohm.cm, 1000v	Static.mech TS,Tear (MPa)strength N/cm	Dyn.mech. E′(MPa) E″(MPa) (5000Hz)
0.58	`10^{-6}	`10^{11}	10 355	E′ E″ Tanδ 22 4.6 0.21

The formulation has been subjected to aging studies and has an estimated life of 10 years. Fig.5.2 shows the echo reduction of encapsulation rubber. It is seen that the material is a very good acoustic window material.

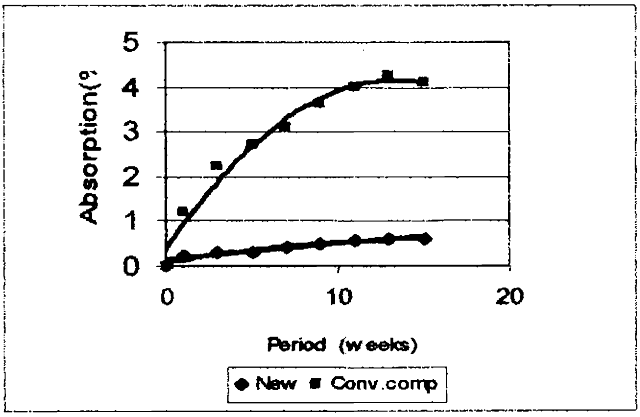

Fig.5.1 Comparison of water absorption of neoprene encapsulations: new based on present studies and conventional cured with ZnO/MgO

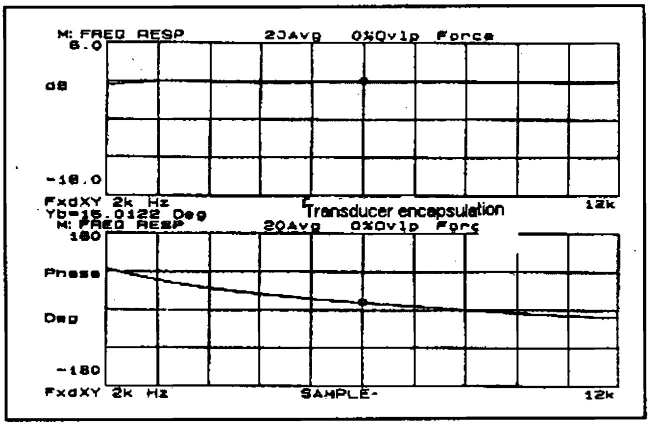

Fig.5.2Echo reduction

5.5 Curing Process and Accelerators

Having identified Red lead cured CR as an outstanding formulation for underwater applications. Curing behavior of Neoprene rubber with varying quantities of Red lead has been studied in great detail. Rheometers MDR2000 and R100 have been utilized to follow the curing reactions. Fall in cure time as well as increase in the minimum and maximum torque occur as the concentration of Red lead is increased from 5 to 12.5 pphr. Beyond 12.5 pphr there is no corresponding increase in torque. This suggests that the optimum concentration of red lead is around 12.5pphr. The kinetics of the curing process has been investigated. The study showed that the reaction is faster with the red lead system. The cure time is 20 minutes for 12.5 Red lead as against 40 minutes for Zinc oxide (5pphr). The activation energy of the cure reaction shows that 5 pphr Red lead has as E_a 65kJ/mole as against 24 k/mole for 12.5pphr Red lead. This shows that activation energy decrease with increase in Red lead concentration.

Equal quantities (30 pphr) of 3 different carbon blacks were studied for the cure acceleration in combination with 12.5 pphr Red lead. The finding shows that FEF black enhances the specific reaction rate more than the other two types of carbon blacks GPF and SRF. The values obtained are 0.14min^{-1} in FEF and 0.714 min $^{-1}$for SRF. GPF remained at 0.87min^{-1}. FEF black (30 pphr) is studied with different quantities of Red lead and the cure reactions show that the maximum torque is registered with 10pphr Red lead. With 12.5 pphr the maximum torque was 62 lb.inch. The cure time for 5 and12.5 pphr was around 33min.

A comparative study of two cure systems, zinc oxide and red lead on the mechanical properties of Neoprene vulcanisate has been carried out. The result shows that zinc oxide is more active in raising the tensile strength. The scorch safety of Zinc oxide cured sample is higher. The volume resistivity of all Zinc oxide cured vulcanizates is higher than that of Red lead cured vulcanizates. The maximum torque is achieved with red lead system. Faster cures, higher torque values and lower activation energy of cure lead to the conclusion that a concentration in the region between10 and 15 pphr loading is optimum quantity of red lead for neoprene W cure. Between 5pphr ZnO and 12.5 pphr red lead. It is found that the latter gives faster cure.

5.6 Low Temperature Vulcanisation

Conventional neoprene vulcanisates cure around 150°C. A temperature of this range is detrimental for the thermal aging of piezoceramic and PVDF sensor materials used for fabricating sonar transducers. During the course of the present study a new material namely Poly ethylene imine (polymine) has been identified as an accelerator for neoprene rubber which can cure the rubber at temperatures as low as 60°C. An investigation into the kinetics of the curing process of neoprene incorporating this accelerator and a conventional accelerator system has been under taken[1]. Different thermo analytical methods have been used to study the process. Rheometric studies show that maximum torque is developed with new accelerator (polymine). A combination of polymine and Diphenyl thiourea (DPTU) (S2) gives maximum crosslink density indicating synergism. Conventional cure system comprising of neoprene accelerator NA22/MBTS(S3) imparts no significant cross linking below 120°C. Curing characteristics and the mechanical properties(Table5.2a) show that sample with polymine (S1) alone has a curing time of 52 minutes whereas polymine/ DPTU has a cure time of 43 minutes. Data on cure parameters and mechanical properties are reproduced in Table 5.2a and 52b respectively

Table 5.2a Curing characteristics @ 120°C

Sample	S1	S2	S3
Scorch time (Min)	5.01	1.29	10.95
Cure time (tc90) (Min)	52.06	43	33.88*
MH-ML (dNm)	12.73	15.29	5.77
Volume fraction (Vr)	0.46	0.45	0.44

*Leveling at a low torque

Table 5.2b Mechanical Properties @ 120°C

Sample	S1	S2	S3
Hardness (Shore A)	60	56	44
Modulus, M_{300}, MPa	4.5	4.1	-
Tensile Strength, MPa	13.78	12.67	17.27
Elongation at Break, %	515	630	1250
Tear Strength, N/cm	360	368	260
T_g°C	-39	-39.46	-38.3
Tensile Strength, MPa (Cured @ 150°C)	-	-	16
Elongation at Break, (%) (Cured @ 150°C)	-	-	1115

The cure index for the former is 12.7dNm and the latter is 15.29dNm. Conventional system has a cure index of 5.7. The cross linked density represented by the volume fraction Vr of rubber in a swollen network shows that the Vr of polymine cured rubber is 0.46 as compared to the conventional rubber with 0.44. The mechanical properties of polymine cured rubber compares favorably with vulcanisates cured at 150°C (with the conventional curing system). Tear strength of polymine cured systems shows 360N/cm whereas in the case of conventional is around 260N/cm. Shore hardness of polymine cured system is 60 as against 44 of conventional system. Modulus at 300% elongation (M_{300}) is 4MPa and that of conventional sample is 2MPa. The apparent activation energy of cure reaction estimated from rheometric study showed that polymine has an activation energy of 90KJ/mol while polymine DPTU is 84KJ/mol whereas conventional system has 94 KJ/mol. MDSC kinetics parameters from the study shows that enthalpy of the reaction of polymine system is around 40-20J/g while for conventional system it is around 60J/g. Dynamic mechanical analysis has been carried out to investigate the cure reactions The results show that the cure activation energy in DMA is 40kJ/mol for polymine system. Conventional systems on the other hand needs 60kJ/mol. Apparent mismatch in Ea in DMA and MDR analysis can be explained on the basis of higher temperature sensitivity of DMA. Thus the study shows that polymine can bring down the vulcanization reaction temperature. Lower heat of vulcanization of this system is due to higher prevulcanisation cure under gone by the samples. Lower activation energy and lower onset temperature of polymine cured vulcanisate lead to the conclusion that the activation threshold of cure has been shifted to lower temperature by the new accelerator. Introduction of a polymine as new accelerator and generation of kinetics of curing neoprene at low temperature has been a major highlight of the present study.

5.7 Viscoelastic Behavior

It has been established that viscoelastic properties of rubbers confer several unique advantages for rubbers to function as an engineering material. In the field of passive acoustic rubbers also these viscoelastic response has been exploited in diverse ways. Carbon black is the dominant reinforcing filler used in rubbers for tailoring dynamic mechanical properties. The present investigation considers two vital aspects on the interaction between rubbers with carbon black one is the effect of the concentration of carbon black and the other is the types of carbon black. Investigation on the influence of carbon black concentration showed that carbon black contributes significantly to the dynamic modulus of neoprene and bromo butyl rubbers. The increasing slope for the modulus plots with increasing carbon black implies that temperature response of dynamic mechanical properties of carbon black filled rubber vulcanisate are more sensitive than unfilled rubbers. Results also revealed that neoprene is more temperature sensitive than Bromo butyl rubber in the rubbery zone. The reason for this behaviour can be traced to the fact that glass transition in brome butyl is lower than that in Polychloroprene. The storage modulus frequency relationship is linear in both the rubbers. The frequency dependence of modulus decreases with increasing filler content. The trend is same in both the rubbers. Frequency dependence is more in case of BIIR than in CR for the same loading of filler. In both the rubbers, reinforcement factor E_f/E_0 varies exponentially with volume fraction of carbon black. Temperature change does not significantly affect the relationship in the case of CR. In Bromo butyl rubber however, the relationship shows higher dispersion with temperature at high concentrations. The strain amplitude dependence of storage modulus shows that with increasing strain amplitude, storage modulus decreases. This observation suggests that carbon black structure is amplitude sensitive. Tan δ starts with a low value at small amplitude in highly filled samples indicating that carbon black deforms elastically in this region. This results in higher damping at intermediate amplitudes. Regarding the activation energy of the relaxation processes it is seen that activation energy increases with filler loading. This implies a fall in the relaxation rate with increase in the filler concentration. This is expected since in the rubbery zone, the temperature changes are dominated by modulus magnitude than relaxation rates. Shift factor corresponds to temperature dependence of molecular relaxation time. This observation together with the decrease in the modulus with increase in strain amplitude suggest that breakdown of carbon black structure contributes significantly to the energy dissipation process and hence to the viscoelastic behaviour in the rubbery zone

Loss modulus is more sensitive to temperature variation than elastic modulus. Superposition of viscoelastic functions reveals that in the rubbery zone changes in the modulus magnitude dominate over relaxation transitions. Apparent activation energy of the shift functions increase linearly with filler loading. The temperature dependence of the modulus decrease with increase in strain amplitudes. Increase in the energy of activation of shift functions suggests that the visco-elastic properties of carbon black filled vulcanizates in the rubbery zone result from reversible dissociation of carbon black network junctions.

Energy storage capacity expressed as modulus difference from low and high strain amplitudes, increase with increase in fillers. The effect is more pronounced in neoprene rubber than in bromo butyl rubber. This is attributable to strain induced crystallinity in neoprene rubbers. The transition from linear to nonlinear viscoelastic behavior occurs at lower strains as the concentration of carbon black increases. Present study gives a comprehensive coverage of the effects of carbon blacks concentration on the visco elasticity of rubbers. Reversible dissociation of carbon black network junctions is responsible for dynamic responses of rubbers in the post transition region.

Effect of different carbon black filler types on dynamic mechanical properties of rubbers is relevant to several applications. In the present study a general increase in the storage modulus is observed in all compositions containing carbon black. A fall in storage modulus corresponds to increase in the molecular Mobility arising from higher internal energy. Higher modulus value is expected where finer carbon black is used. Steep fall in the modulus in the temperature region of -32°C to 0°C suggests that this region succeeds the glass transition in the material. 0°C to 30°C is the rubbery stage. The dynamic response of polychloroprene vulcanizates incorporating different types of carbon black fillers is important, particularly in applications involving wave propagation. Dynamic moduli increase with incorporation of various carbon black fillers. The trend observed could not be generalized with regard to the type of filler, their particle size or surface area, excepting the inference that the smallest particle carbon black (N550) has the highest reinforcing effect in terms of storage modulus (E′). Carbon black filled compound show a lower damping capacity as compared to unfilled compounds. The damping factors of filled rubbers are not significantly affected by the variation in temperature in the range 0-30°C. However, there is a marked influence at subzero temperatures. In general, the storage modulus E′ and loss modulus E″ have shown increase with increasing frequency. This increase is more significant in the case of N550 carbon black filled compounds. The velocity of sound propagation (longitudinal mode) of different compounds calculated from the values of complex modulus obtained by time-temperature superposition are found to increase with frequency in all cases. However, the increase is more pronounced in the case of compounds containing high reinforcing fillers. The estimated sound attenuation values (per wavelength thickness of the material) reveal that unfilled neoprene rubbers cause a larger attenuation of low frequency sound, whereas filled compounds exhibit similar properties in the high frequency zone. The dependence of damping and sound attenuation on factors such as frequency, temperature and filler types brought out by this study may prove helpful in tailoring rubber compounds for specific sound and vibration damping application. However, while designing compounds for such specific applications due considerations will have to be given to the coupling media and interface impedance mismatch problems. Conclusions that can be drawn on the effects of carbon black type on the viscoelastic behavior of neoprene rubber are that gum rubbers attenuates at low frequencies while highly filled rubbers exhibits damping at high frequencies No generalization is possible with regard to the type of carbon black particle size, or surface area on the viscoelastic parameters. Results serve as valuable design input for acoustic material design.

5.8 Acoustic Baffles

Acoustic baffles are used in large transducer arrays for the purpose of isolating ships noise as well as for improving directivity and sensitivity of the transducer elements. The baffle forms a major passive element contributing for better performance of the system. The materials used for the construction of acoustic baffles are therefore required to possess specific acoustic and dynamic mechanical properties. As the application of baffles is in deep marine environment the material used for the construction should also be compatible with hostile marine conditions such as salinity, hydrostatic pressure, sub ambient temperature, dynamic loading conditions etc. Rubbers exhibit in their dynamic modulus- temperatures /frequency response curves a point of inflexion., where the mechanical damping factor goes through a maximum. This region where moduli under go rapid variation due to temperature/frequency changes is the transition region. Since acoustic properties of rubbers is a direct functions of modulus [1.37] Tailoring of the transition modulus is key to achieving the desirable acoustic response. Desired acoustic response in the case of baffle rubber is constant sound speed over the specific frequency region. Constancy in sound speed in a viscoelastic material is related to low attenuation as per kramers-kroning [3.18] relations developed by O'Donnel et. al [3.19]. Accordingly a high value of α requires a large $dc/d\omega$ in the viscoelastic region. Hence it is clear that lower attenuation or mechanical loss factor leads to smaller frequency dependence of acoustic wave velocity. Therefore the study was aimed at developing rubber with low enough damping factor which is constant over the frequency Band of a few Hz to 10kHz. Styrene butadiene rubber was selected as base material due its low glass transition temperature(-60°C). Availability of the material meeting stipulated specification and the traceable quality as compared to NR which is subject to changes from clone variations. Detailed investigations on the effects of different fillers on damping behavior revealed that incorporation of about 20 pphr silica in a formulation containing carbon black is effective in wideband damping factor. Dynamic mechanical properties of the material proved that glass transition has shifted to higher frequency region due to the effect of silica. There has been an increase in elastic modulus without concomitant increase in loss modulus. With the result that a flat sound velocity - frequency band has been realized. Tan δ values remain at an average value of 0.2 in the frequency band of 30 Hz to 10 kHz. Sound velocity in the region is 175 ± 20m/sec. Sound attenuation ($\alpha\lambda$) is about 0.6-0.7 Neper. Some very interesting conclusions emerge from the studies on baffle material. Silica is effective in increasing elastic modulus of rubbers without concomitant increase in loss modulus. This effectively shifts the frequency dependent transition region to high frequency end(Fig.3.76)with the result that a low damping plateau is produced in the tandelta-frequency spectrum. Associated with low damping frequency band is the constant sound velocity- frequency band.

5.9 Underwater seals

The present investigations includes a systematic study on the Elastomeric seal material based on nitrile rubber. Major highlights of the studies is realising flat compression set value which remains at an average value of 8 ±0.5%. Accelerated thermal aging shows excellent retention (7%)even at 70 °C over 2 months of soaking. Water absorption study shows that absorption does not exceed 1.2 % over a period of 3 month when soaked in water at temperatures from 40°C to 70° C. Variation in compression stress relaxation of the material as a function of temperature indicates that maximum variation occurs at sub ambient temperatures. Thus at temperature between 4 and15 °C value is only 5%/ decade, between 15 and 30 it is 1.5% while the value between 30°C and 50°C is 1%. Activation energy of the stress relaxation process has been found to be 17 kJ/mole. A study on temperature dependent changes in the tensile stress strain behavior when temperature is lowered from+27° to -16°C shows that M100 increased from about 4 MPa to13 MPa. Tensile strength changed only by 5 Mpa in the interval. Elongation at break remained at a plateau of 290% in mid temperature region of 4 and 27°C. Tensile strength decreases linearly with temperature in temperature above 0°C. At subzero temperature the response is flat. Sealing force is a sensitive indicator of the sealing efficiency. Study of this parameter shows that rate of fall in sealing force is faster in water soaked samples. The rate increases with service temperature. Realization of an elastomeric seal material suitable for deep water application with stable property for an estimated service life of 10 years is the out come this study.

5.10 Aging and Life Prediction

Life prediction of polymers is a complex, multivariable, multifactor problem involving several unknowns. Conventional technological tests on life predictions generally consider tensile strength alone as the controlling parameter. This approach is inadequate in the context of present day high performance polymers, particularly those used in underwater electro acoustic transducers. Controlling properties vary according to the end use situations. In many cases a combination of life determining properties rather than any single property is important. Studies on ultimate tensile elongation, water diffusivity, compression stress relaxations have indicated that compression stress relaxation transitions are more sensitive to aging processes than ultimate elongation and diffusivity. Present study covers a life estimation methodology involving, diffusion, permeation, static mechanical/dynamic mechanical properties, compression stress relaxation and clustered water estimation. In the diffusion method, diffusion coefficient is estimated from accelerated water absorption experiments. From the Arrhenius plots of diffusion coefficient, the value at the temperature of interest can be obtained. Life of the device, for example, an underwater transducer element equals the time for water to advance to the thickness of the encapsulation. Life estimation based on permeability has been carried out in similar lines as that of diffusion. Here the time needed for the permeant to reach the sensor element and saturate the available free volume decides the life. The third approach takes into account the degradation in mechanical properties such as ultimate elongation or Dynamic modulus.

The method is designed to follow the time dependent degradation at a series of temperatures in service medium, generate best fit regression models of the property change, estimate the time for specific degradation levels and construct Arrhenius plots. In case of linear plots the Arrhenius extrapolation is valid. A set of shift functions can be generated for different accelerated test temperatures using the relation 4.13. By multiplication of raw data obtained for service temperature with the respective shift function the data needed for generation of a master curve is obtained. Life of the device can be estimated from the master curve.

Estimation of life of a seal material envisages the use of sealing force retention. 80 % retention of sealing force has been taken as the index of failure, from field experience. Time for 80% retention of original sealing force has been determined by testing the sample materials in a compression stress relaxometer after aging them in simulated service environments at different temperature conditions. An Arrhenius plot has been generated with the time and temperature parameters. The selected example of the case has shown a life of 11 years at 30°C, which enables estimation at the required temperature. Estimate of life based on diffusivity, permeability, retention of EB etc of a typical encapsulation rubber has been found to be 15-years. A life estimation technique based on water intake kinetics, static mechanic properties, dynamic mechanic properties, and clustered water estimation has been implemented. Using the technique service life of an underwater elastomer has been estimated to be 10 years.

Effects on long time aging of rubbers on their dynamic mechanical properties have been investigated during the course of the present study. Results show that that heat aging in water causes a shift in glass transition to higher temperature. Explanation for the shift and lowering of tanδ (damping) is that the dominating influence is thermally accelerated stiffening. Frequency response at glass rubber transition region in water aged neoprene shows that transition region in both E'and E'' spans 6 decades from10^{-2} to 10^{4} Hz E'', peaking occurs at 90 kHz. E'' value starts to decrease beyond 90kHz indicating that material is unable to respond to still higher frequencies. In other words this represents a mechanical glass transition. Master curve has characteristic WLF response even in water soaked neoprene rubber. WLF constants are also close to universal values.

In conclusion hot water aging causes neoprene rubber to stiffen and glass transition temperature region to shift to higher temperature. Very high frequency leads to mechanical glass transition.

Influence of hygrothermal environment and water immersion conditions on the water absorption behavior of neoprene rubber formulations show that water uptake from hot humid environment is higher than that from hot water. Swelling and degradation are also higher in hygrothermally aged samples.Fig.5.3 shows a surface scan of neoprene gum vulcanisate aged at 95RH and 60°C for 100days and Fig.5.4 is the surface scan of water immersed sample at 60°C for 100days. The Figures show the relative effect of the two environments.

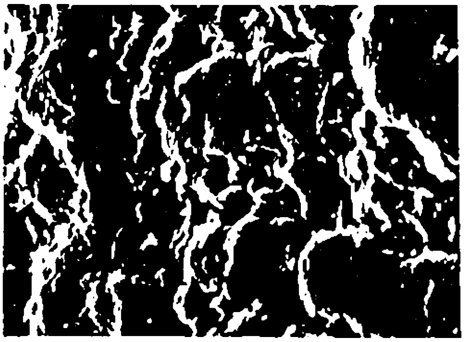

Fig 5.3 SEM micrograph X3000 of hygrothemally aged neoprene rubber

Fig.5.4 SCM Micrograrгh X3000 of water aged sample

In hygrothermal environment water molecules form a uniform dispersion in rubber phase and this has been suggested as the reason for the initial decline in volume resistivity. Net rise in electrical resistivity can be concluded to have been caused by the following factors, i)increase in electrical resistivity due to the progress of cross linking during thermal aging ii)increase in resistivity due to enhanced swelling process. iii) Marginal fall in resistivity due to intake of water into the specimen.

The above cross linking process also manifests in increase of storage modulus without any corresponding increase in loss modulus resulting in fall in tanδ. Aging in accelerated moist environments also enhances the elastic response of the materials by restricting molecular movement. Glass transition temperature in the material is lowered by about 10°C by water immersion for about 4 months. Plasticization is more in the case of the total immersion than by storage in humid environment. Value of loss factor has also got reduced for the same reasons. In hygrothermally aged sample plasticisation and degradation dominate. Results of the present study leads to the conclusion that storage in hot humid environment is more detrimental to the performance of transducer elastomers[3] as compared to long term underwater deployment as far as water absorption and electrical resistivity are concerned. In terms of viscoelastic parameters, hygrothermal aging causes the glass rubber transition zone to widen and damping maximum shift to lower temperatures.

Large decline in activation energy takes place in neoprene vulcanizates aged under hot aqueous environment. Activation energy for decomposition decreases with increase in percentage conversion in unaged rubber. In aged rubber, activation energy decreases with increase in conversion. A change in mechanism of thermal degradation has been suggested to explain the behavior[4]. Decrease in Avrami exponent from 2.3 to 0.7 due to aging supports the observation. Thermo oxidative degradation is initiated at the outer surface and proceeds inwards as time advances. Both TGA and MDSC analysis confirm this finding.

Stress relaxation rate in neoprene rubber increases with hygrothermal aging. Though the increase is negligible during the first 15-20 days, an increase up to about 140% occurs in a little over 5 weeks. Relaxation rate falls with increase in temperatures between 30 and 60°C. This apparent contradiction follows from the negative coefficient of thermal expansion in rubbers. Activation energy of the relaxation process increases with hygrothermal aging. In conclusion two opposite processes take place in hot humid environment. Relaxation increase with time, but decreases with temperature. Mechanism is explained in light of the theory of rubber elasticity. Recovery rates are generally lower than corresponding relaxation rates. Observed increase in the spontaneity of relaxation process is expected in rubbers containing large amount of absorbed water. Hygrothermal aging causes significant increase in relaxation rates [5] while its influence on recovery rate is only marginal. Long term relaxation rate also increases with aging. Long time hygrothermal aging cause fractional free volume and coefficient of expansion to increase. The fall in glass transition temperature with aging confirms this observation.

Nature of water absorbed within the rubber matrix has been studied. Reversible signal of the MDSC plot shows two distinct thermal events. A step change in the base line (Fig.4.37) seen at the lower temperature end of the plot is the glass transition in the material. A prominent endotherm with onset at -15°C is the melting transition of water. Endotherm appearing in the reverse heat flow signal is obviously due to clustered form of water as the same can only appear in reversible endotherm signal. Besides, freely absorbed water is expected to be bound to the surface of the rubber molecules as a single layer through hydrogen bonding. These water molecules are not free to freeze while clustered form of water can freeze, if temperature is lowered sufficiently.

An interesting out come of this finding is that it opens up a method for estimating water absorbed by a polymer exposed to underwater environment. This information in turn enables the estimation of total period of exposure if the material is calibrated for water intake. Experiments have been reported in the present study in which samples exposed to water for different periods (3 days at 40°C, 12 days at 40°C and shelf aged for 4 years at room temperature.) have been studied for clustered water analysis. Amount of water absorbed has been correlated with direct gravimetric method. Typically results of clustered water analysis give 0.82% for 3 days immersion at 40°C when direct weighing method gives a value 0.78 %. Water absorbed by an encapsulation rubber sample soaked at room temperature over a period of 4 years give a value 2.69%. This study opens up a method of analysis for clustered water in rubbers which enables a quick estimate of service life of underwater polymers.

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Chapter 6

SUMMARY AND CONCLUSIONS

6.1 Summary

Application of rubbers in under water electro acoustic transducers ranks among the most sophisticated end uses. Functional requirements are complex combinations of physical properties, mechanical properties, acoustic properties, electrical properties, besides environmental resistance. Reliability of the system itself is dependent on performance of certain rubber components. A range of passive materials, besides the active sensing material go into the construction of underwater electro acoustic transducers. Reliability of the transducer is critically dependent on these passive materials. Rubbers are a major class of passive materials. Present work concentrates on these materials. Of the common engineering rubbers, Neoprene is optimally suited for the applications. Conventional rubbers are inadequate to meet many of stringent function specific requirements. There exists large gap of information in the rubber technology of underwater rubbers, particularly relating to underwater electro acoustic transducers. Present study is towards filling up the gaps of information in this crucial area. Water intake into rubber is considered as the single most important issue for the long term performance of rubbers, especially Neoprene. In the present study, the cause and effects of a range of parameters affecting the water absorption by diffusion and permeation have been investigated.

Kinetics of the diffusion process, have been studied. Curing process and curing acceleration are important issues in Neoprene vulcanization. Conventional neoprene absorb large amount of water(>200%). Major cause of very high water absorption in Neoprene has been traced to Znc oxide-Magnesium oxide curing system. Alternate curing system, based on Red lead, is known to be difficult in processing. It will lead to pre-cure vulcanisation and low electrical insulations etc., In present study much attention was paid to the issue and a viable formulation has been arrived at.

In transducer fabrication, use of high processing temperature is detrimental because of the possibility of accelerated degradation. There is also requirement for low temperature splicing of neoprene sheathed cables, with thermoplastic materials. Present study has resulted in identifying low temperature curing systems. Viscoelastic behavior is an important consideration for under water electro acoustic transducer technology. Nature of base rubbers, as well as type and quantity of carbon black decide the viscoelastic response. Influence of type and quantity of the carbon black on dynamic mechanical properties have been studied with a view to optimizing the compounding formulation. Rubber used in underwater and above water surface come under the influence of total immersion and hygrothermal environment. The relative effects are important in the context of underwater transducers, particularly because of the shelf storage requirements in dockyards. Present study covers investigations in both the environments and conclusions drawn on the effects of storage environment on the diverse characteristics affecting the transducer passive rubbers. The properties studied include, electrical, interaction with water, viscoelastic behavior as well as thermal stability. Parameters critical to certain functional properties for some of the important applications such as encapsulation materials, acoustic baffles, seals etc., have also been studied.

Prediction of service life is an important aspect of any engineering device. The question is more relevant to the naval transducers as the failure of a transducer may lead to total failure of the sonar system. In the present study an aging methodology has been implemented. The approach involves study of a number of key rate controlling properties such as water intake through diffusion and permeation, ultimate elongation, clustered, water analysis, compression stress relaxation etc. Further life prediction approaches have been developed based on the studies. The thesis comprise of six chapters expounding introduction, theoretical studies on compounding, experimental investigation on compounding, theoretical as well as experimental studies on aging and degradation, discussion and consolidation of results, summary and conclusions.

Chapter I discusses the role of rubbers in underwater engineering, their mechanical properties, electrical properties, and vicoelastic properties. Chapter also reviews under water properties of rubber, diffusion and permeation of water, mathematical considerations of diffusion, sealing properties, acoustic behavior dealing with wave propagation through elastic medium, various acoustic parameters, relationship between dynamic mechanical properties and acoustic properties etc. This introductory chapter also gives a brief out line on acoustic acoustic transduction and active, passive transducer materials leading to the subject matter of the work namely rubber as a passive acoustic material.

Chapter 2 deals with theoretical aspects of rubber compounding, compounding ingradients, base rubbers, curatives, accelerators fillers, antidegradents etc. This chapter also discusses the principles of compounding, compounding for specific properties, such as hardness, modulus, viscoelastic properties, resistance to abrasion and tear,resistance to cyclic stress, flex cracking, resistance to fluids, rheology, mooney viscosity. A discussion on the engineering properties of the rubber vulcanisates, static mechanical properties, tensile stress strain tests, compressive stress strain tests, dynamic mechanical analysis etc. have been presented. This chapter also includes techniques and application of instruments like DMA, use of time -temperature superposition, environmental properties, effects of fluids, acoustic properties, thermal analysis of rubber including thermogravimetric analysis, DSC, their principles of working etc.

Chapter 3 discusses the exploratory study of different rubbers like Neoprene, Bromobutyl, Styrene Butadiene, Natural rubber and Nitrile rubber. Effects of various functional parameters on the water absorption behaviour of rubbers, particularly Neoprene have been studied. The specific studies conducted include the effects of cure systems, nature and kinetics of water absorption, effects of concentration and type of carbon black on water absorption, kinetics of diffusion process as functions of these parameters. Study also covers effects of salinity, effects of inorganic filler, permeability of water into rubber, effects of anti oxidants and quantities of carbon black on water permeability. Besides Neoprene diffusion characteristics of Bromobutyl, Natural rubber have also been studied. Another aspect coming under the study is curing behaviour of rubbers: Cure kinetics involving red lead, kinetics of modulus build up, effects of added carbon black on cure kinetics etc have also been covered. A comparative study on the effects on the cure systems on mechanical properties and cure kinetic parameters have been studied. Low temperature vulcanisation of Transducer rubbers have been investigated. Polyethyleneimine as a cure accelerator has been investigated. Comparative study of this accelerator along with conventional cure system has been carried out the efficiency of curing. Influence of carbon black on the dynamic mechanical behaviour comprising the influences of carbon black type on the flexural modulus characteristics, loss modulus characteristics and tanδ have been studied. Effects of concentration of carbon black on Neoprene and Bromobutyl rubber have been investigated. Frequency response and temperature response as functions of carbon black concentration have been studied. Changes in the reinforcing factor with temperature and volume fraction of carbon black have been studied.

Amplitude dependence of viscoelastic parameters has been covered. Super positioning of dynamic mechanical modulus resulting from the inclusion of carbon black has been conducted. Sound velocity, frequency relation ship has been studied. Dependence of carbon black type on the sound attenuation has also been explored. Application specific studies on following specific aspects have been included in this study. Water absorption behaviour of encapsulation rubber, comparison of water absorption by different rubbers, absorption of moisture from humid environment, influence of inert environment on different rubbers. Specific materials studied are acoustic baffle materials and under water seals materials. Studies on baffle rubbers include detailed compound optimization studies. The study is directed at achieving constant acoustic velocitv over a wide frequency band of interest. Study included a section on rubber seal material for deep sea application.

Chapter 4 starts with a discussion on aging phenomena in rubbers, controlling parameters, aging models, thermogravimetric degradation and kinetics. This chapter gives different life prediction approaches developed for under water rubbers during the course of this study. Separate sections on different controlling properties i.e. water absorption kinetic method, permeability method, ultimate elongation, compression stress relaxation etc., have been included. Other aspects included in this chapter are the influence of long term water exposure of rubbers on visco elastic properties, hygrothermal aging, changes in the electrical resistivity due to water exposure. Change in transient response of the rubbers exposed to hot humid environment. Effects of long term aging on dynamic mechanical properties, changes in the frequency response due to under water aging, influence of wet aging on the kinetics on thermal degradation etc. Chapter also includes section on clustered water analysis as a means of assessing the underwater service rendered by a rubber component.

Chapter 5 consolidates the results of various studies covered under Chapter 3 and 4. This also includes the conclusions drawn from the studies. Chapter 6 gives a brief summary of the work.

6.2 Conclusions

The following major conclusions are drawn from this work.

- By application of judicious compounding techniques, it is possible to realize highly water resistant encapsulation materials based on Neoprene rubber for underwater transducer applications[Indian patent No.185889 March (2002)]
- During the process of the investigations polymine has been identified as a special Neoprene cure accelerator. It has been established that by using this accelerator low temperature vulcanization of Neoprene rubber is practically feasible[refer 5.2].
- Even though dynamic mechanical properties of rubber are strongly frequency dependent, it is possible to achieve rubber compounds with nearly invariant sound speed or wide frequency bands so as to make them suitable for acoustic baffles.[Patent Pending]
- By recognizing cardinal properties and understanding the degradation mechanisms it is possible to develop rubber based seal materials that facilitate deep water elastomeric seals having life expectancy of 10 years or beyond.

Other important conclusions include

- Hot humid environment is more detrimental for the degradation of Neoprene rubber as compared to total water immersion. [refer 5.3]
- Differential scanning calorimetry can be effectively utilized for estimating clustered water intake in polymeric materials, opening up a means to assess the elapsed term of under water exposure.

- Kinetics of diffusion process has been studied in detail and effects of carbon black types and quantity have been established.
- Curing process of rubber compounds can be tracked through several techniques including DMA, as has been demonstrated in the study.
- A definite relation ship has been established between humidity and shelf storage life. This profile helps in estimating the storage life of a rubber encapsulated device in dockyard situation.
- Orders of magnitude reduction in the water absorption can be achieved by changes in curing agents, fillers and antioxidants.
- Filler addition increases Energy of activation of diffusion.
- Under dynamic loading Carbon black structure is amplitude sensitive. Rubbery zone modulus is dominated by temperature changes rather than frequency changes.
- Break down in carbon black structure contributes to energy dissipation processes and viscoelastic behaviour.
- Unfilled rubbers attenuates sound in the low frequency region more than the filled rubbers. Filled rubbers are more effective for damping at high frequencies.
- Silica is an effective acoustic modifier for SBR rubbers. Silica increases stiffness(modulus) without concomitant increase in loss modulus(damping).
- Absorbed water enhances compression stress relaxation rate of seal materials.
- Life prediction approach with a combination of critical properties of rubbers has been demonstrated.
- Long term under water aging in hot environment shift glass transition to higher temperature.

- Viscoelastic functions generated from seawater aged samples are amenable to time temperature superposition. WLF constants in such cases are close to universal values.
- Hygrothermal aging can cause run away absorption, plasticisation and degradation in gum rubbers. [refer5.3]
- Thermal degradation process accompanies a change in mechanism due to aging .This causes a decrease in Avrami exponent.[refer5.4]
- Stress relaxation rate increases with hygrothermal aging[refer5.5]
- In humid environment relaxation rate increases with time ,decreases with temperature.
- Recovery is slower than relaxation in water aged rubbers.
- Spontaneity of the relaxation process increases with higher water absorption.

Scope For Further Work

The present thesis covers transducer encapsulation materials based on single rubber polymer. These materials serve as acoustic window material for transferring acoustic energy across with minimum losses. One limitation is that these are effective for a narrow frequency band, depending on their mechanical glass transition. As a logical extension, there is scope for further work to achieve wide band acoustic window material. We have found that fillers like silica act as acoustic modifier in selected frequency range. In the similar lines combination of fillers or blending of polymers can be a starting point for the work.

In most sounds absorber materials, the energy dissipating mechanism is viscoelastic damping. Viscoelastic damping is generally effective, in high frequency regions. An attractive way to enhance damping in the low frequency would be to investigate an active - passive combination. A composite of piezoelectric materials and rubber polymer could be designed, which converts mechanical energy of propagating wave into heat which could be carried away or dissipated from within. Rubber will additionally dissipate energy from visco elastic mechanism.

Functionally graded rubber matrix composite materials have immense scope to be tailored for diverse acoustic functions. Gradual change of mechanical properties avoid sharp discontinuity will enable mode conversion. Such an approach in the design of passive acoustic rubbers will enable materials which can direct sound propagation as desired.

List of Abbreviations Symbols

$\frac{\partial c}{\partial t}$ - rate of change in concentration

$\frac{\partial c}{\partial x}, \frac{\partial c}{\partial y}, \frac{\partial c}{\partial z}$ - change of concentration along x,y,z planes

C - concentration at the surface (chapter1)

Co - initial concentration

D - diffusion coefficient

h - thickness

x - position(chapter1)

Mt - mass absorbed at time t

M - equilibrium value absorbed

Ms, M_x - maximum absorption

n - an integer

Px - rate of advancing of boundary

C - concentration water

R - universal gas constant,8.314J/mole

T - Temperature degree kelvin

E - Youngs modulus

Λ - extention ratio(chapter1)

p - elastic pressure

πo - osmotic pressure external

π_1 - osmotic pressure of the droplet

W - weight of membrane

Wd - dry wieght

θ - slope of water absorption plot

D - Diffusion coefficient in any plane

D_x, D_y, D_z - Diffusion coefficient ,x,y,z,planes

Q - amount of substance permeated

S - solubility

p_1,p_2 - water vapour pressure inside and outside respectively

A - area of permeation

L - thickness of to be film to be permeated

P - permeability coefficient of water

F - force

K - spring constant

σ - stress

ε - strain

ηe - Newtonian viscosity

$\partial\varepsilon$ - incremental strain

dt - time increment

εo - initial strain

i - $(-1)^{1/2}$

η - viscous component of stress

E_1, - real part of wave number

E_2 - imaginary part of the wave number

oo - stress amplitude

δ - phase angle

E'' - loss modulus

E' - storage modulus

E^* - complex dynamic modulus

P_0 - initial phase

Φ_0 - total phase

f - frequency

z_1 - acoustic impedance of medium1

z_2 - acoustic impedance of medium2
ρ_1 - density of medium1
ρ_2 - density of medium2
c_1 - acoustic wave velocity of medium1
c_2 - acoustic wave velocity of medium2
R - intensity of reflection
ω - angular frequency
r - $\alpha c/\omega$
c - acoustic velocity
α - attenuation
Rp - Acoustic pressure reflectioncoefficient
Tp - acoustic pressure transmission coefficient
PD - acoustic power dissipation
Pt - Transmitted pressure
Pi - Incident pressure
ER - Echo reduction
TL - transmission loss
ΔG - free energy change
ΔH - enthalpy change
T - temperature
ΔS - entropy change
ψ - solubility parameter(chapter2)
A - area of diffusion
dm - change of mass (mass diffusing)
dc/dt - rate of change of concentration
dt - time increment
dc - change of concentration
t - time
x - distance

h - thickness
D_{av} - Average diffussion coefficient
t_{av} - Average time
q - quantity permeated
dQ - quantity of heat
Cp - heating capacity
F_R - rate dependent function
F_A - temperature dependent function
dT - temperature change
b - constant0.457
Θ - heating rate(chapter 2)
E - energy of activation (chapter 2)
P(Xf) - a function whose value depends on energy of activation
Tf - failure temperature
H - heat of transition
M - mass
K - calibration constant
Tg - glass trasition temperature
E_D - activation energy of diffusion
Ep - activation energy of permeation
dEt - modulus(torque) change
k - rate constant of cure reaction
Et - modulus at time t
Eo - modulus at zero time
ko - rate constant at zeroconversion
MH - maximum torque
Mpa - Mega pascal
E_1 - storage modulus (chapter 3)

E_2 - loss modulus (chapter3)

f - frequency cycles per sec

$\alpha(\omega)$ - attenuation at ω

dc - change in sound speed

$d\omega$ - change in frequency

c - sound speed(chapter3)

P - property (chapter 4)

Po - initial property

Et/Eo - ratio of property retention(e.g.ultimate elongation)

k - rate constant ;exponent(=E/R)(chapter 4)
Y - value of property

A, B, C - constants

K - van't Hoff rate constant

ΔH - change in heat content

$\Delta H'$ - heat content change in the reverse reaction

E - energy of forward raction

E′ - energy of reverse reaction

k′ - reverse rate constant

$\varepsilon(P,T,t)$ - property as functions of pressure, temperature and time

α - a constant characteristic of material; fractional conversion(chapter 4)

n - avrami exponent(chapter4)

εo - pre exponential factor

T_R - Reference temperature

$G(\iota)$ - a function of property

T1, T2 - temperature at two reacting system

X, Xo - property at any time tan δ and initial property

D_O - diffusivity at initial temperature

List of Compounding Ingredients Used

Sl.No	Ingredient		Chemical Name	Source
	Name	Symbol		
1.	Natural Rubber	NR	*cis*-1,4 Polyisoprene	RRII Kottayam
2.	Nitrile Rubber KNB 35L	NBR	Acrylonitrile Butadiene Rubber	M/s Korean Synthetic Rubber Co., Korea
3.	Butyl Rubber	IIR	Isoprene isobutylene Rubber	Polysar Ltd, Canada
4.	Bromobutyl Rubber	BIIR	Brominated Isoprene isobutylene Rubber	Polysar Ltd, Canada
5.	Kosyn-1502	SBR	Styrene Butadiene Rubber	M/s Korean Synthetic Rubber Co.
6.	Neoprene Rubber (W)	CR(W)	Polychloroprene Rubber	M/s Du Pont, USA
7.	Neoprene Rubber(GRT)	CR(GRT)	Polychloroprene Rubber	M/s Du Pont, USA
8.	Vulcanox - HS	HS	Polymerised (1,2,Dihydro 2,2,4 trimethyl quinoline)	M/s Bayer India, Mumbai
9.	Vulcanox - 4020	4020	N-(1,3 dimethyl butyl) N-Phenyl-P-Phenylenediamine	M/s Bayer India, Mumbai
10.	Diphenyl thiourea	DPTU		M/s Goldie Lab Chem, Mumbai
11.	Naphthenic Oil	Elasto 541		M/s Hindusthan Petroleum Ltd., Ernakulam
12.	Pptd,Calcium Carbonate	$CaCO_3$		M/s Rubosynth Impex Pvt. Ltd ,Mumbai
13.	Silica (Hisil 500)	SiO_2	Silicone dioxide	M/s PPG Ind.inc., USA
14.	Magnesium Oxide	MgO		M/s Rubosynth Impex Pvt. Ltd ,Mumbai
15.	Zinc Oxide	ZnO		M/s Rubosynth Impex Pvt. Ltd ,Mumbai
16.	Santocure CBS	CBS	N-cyclohexyl2Bebz.thyazyl sulphanamide	M/s Goldie Lab,Mumbai
17.	Dicumyl peroxide	DCP-KE	-	Vanderbuilt,USA
18.	Vulcacit thiuram /c	TMTD	Tetra methyl thiuram disulphide	M/s Bayer India Ltd. Mumbai
19.	Vulcacit - dm/c	MBTS	Benzothiazyl disulphide	M/s Bayer India Ltd. Mumbai
20.	Ethylene thiourea	NA22	2 Mercaptoimidazoline	M/s Du pont, USA
21.	GMF	GMF	Di benzo quinone dioxime	M/s Goldie Lab,Mumbai
22.	Carbon Black, HAF	N 330		M/s Phillips Carbon Black LtdLt Ltd., Kochi.
23.	Carbon Black, FEF	N 550		"
24.	Carbon Black, GPF	N 660		"
25.	Carbon Black, SRF	N 770		"
26.	Carbon Black, MT	N 990		M/s Cabot Corporation,USA
27.	Polymine		Poly ethylene imine	M/s The Chemical Centre. Mumbai-2

List of Publications and Patents emerging from the work

A. PATENTS

1. An improved process of preparation of a rubber Vulcanizate
   Inventors VB Pillai & Narayana Das, J
   Indian Patent No.185889 March 2002
2. A process for Preparation of Rubber Based Passive Acoustic Material
   Inventors:- VB Pillai & Narayana Das. J
   Indian Patent(Pending)
3. An Improved Polychloroprene Vulcanisate and Process for preparation thereof.
   Inventors: VB Pillai & Mohana das P.N
   Indian Patent (Pending)

B. PUBLICATIONS

1. Pillai. V.B., Narayana Das. J, Francis.D.J, Influence of Wet Aging on the Kinetics of Thermal Degradation of Certain Rubber Vulcanizates, Proc. of the International Conference on Rubbers, Vol.II p-p Calcutta, Dec'12-14, (1997)
2. Pillai. V.B., Narayana Das. J, Francis. D. J. Influence of Hot Humid Aging on the Dynamic Mechanical Response of Neoprene Rubber Vulcanizate,Vol.III,pp,Calcutta,Dec'12-14,(1997).
3. Pillai. V.B., Narayana Das. J, Francis.D.J Studies on the influence of storage environment on aging of underwater elastomer Materials for Marine applications, Editor :Ramji Lal, Naval Materials Research Laboratory, Bombay (1996).
4. Pillai. V.B., Narayana Das. J, Francis.D.J "Studies on carbon black on the viscoelastic behaviour of certain Bromobutyl and Polychloroprene rubber vulcanizates in rubbery zone" Proc.of the

National Seminar on the Advances in Polymer Technology, Kochi(1996)

5. Pillai, V. B. and Narayana Das, J., Influence of carbon black filler types on dynamic mechanical properties of certain underwater poly chloroprene rubber vulcanizates, *Plastics, rubber and composites; processing and applications*, 18, 155-160(1992)
6. Vasudevan. S, Pillai, V. B., Evaluation of metal powder embedded Passive acoustic Materials using improvised impulse measurement technique, Vol.25, Pt.1,Proceedngs of Institute of Acoustics, London (2003)
7. Pillai V. B. and Mohana Das.P.N, Thermo-analytical studies on the curing behavior of certain neoprene rubber accelerators used in sonar transducer passive materials, *Proceedings of the international conference on sonar-sensors & systems* (icons-2002) vol.2,693,(2002)