Chapter 6

SUMMARY AND CONCLUSIONS

6.1 Summary

Application of rubbers in underwater 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 a 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 Zn 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 viscoelastic properties.
Chapter also reviews underwater 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 outline 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 ingredients, 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. Superposition of dynamic mechanical modulus resulting from the inclusion of carbon black has been conducted. Sound velocity, frequency relationship 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 underwater seals materials. Studies on baffle rubbers include detailed compound optimization studies. The study is directed at achieving constant acoustic velocity 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 underwater 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 viscoelastic 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 underwater aging, influence of wet aging on the kinetics on thermal degradation etc. Chapter also includes a 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.

Her 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 effect 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 relationship 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.