STUDIES ON PERMEATION RESISTANT ELASTOMERS

by

VINITA DUBEY

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DEDICATED

TO

MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled, " **Studies On Permeation Res Elastomers,**" being submitted by **Ms. Vinita Dubey** to the **Indian Instit Technology, Delhi**, for the award of the degree of **Doctor of Philosophy** record of bonafide research work carried out by her. Ms. Dubey has worked our guidance and supervision, and has fulfilled the requirement for the subm of this thesis, which to our knowledge , has reached the requisite standard.

The results contained in this thesis have not been submitted, in part c to any other University or Institute for the award of any degree or-diploma.

(Dr. S.N. MAITI)
Research Supervisor,
Professor,
Centre for Polymer Sci. & Eng.,
Indian Institute of Technology,
Hauz Khas, New Delhi-16 (India)

(Dr. A.K. GUPTA)
Research Supervisor,
Professor & Head,
Centre for Polymer Sci. &
Indian Institute of Technol
Hauz Khas, New Delhi-16

(Dr. N.B.S.N. RAO)
Research Supervisor,
Scientist"F" & Joint Director,
Defence Research & Development Establishment,
Ministry of Defence,
Jhansi Road, Gwalior (M.P) -474002 (India)

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Vinita Dubey

(VINITA DUBEY)

ABSTRACT

Over the last few years, attempts were made world wide to develop synthetic rubber compositions with an over-riding requirement of permeation resistance to hazardous chemicals, especially those chemicals which may be used in warfare or perpetrating illegal activities. One such hazardous chemical is blister agent, **bis(2-chloroethyl)sulphide** (abbreviated as SM), which alkylates body cells even on short term exposure and penetrates most materials. Very little information has been available in open literature on permeation of SM through elastomeric barriers. The inherent resistance to permeability of elastomers like poly(isobutylene-co-isoprene), poly(butadiene-co-acrylonitrile), poly(2-chloro-1,3-butadiene) and flouroelastomers was exploited in the development of gas masks, gloves and overshoes. However, most of the reported rubber and blend compositions have been patented and there appeared to be no reports on systematic studies on permeation of toxic warfare agents through these materials. A detailed investigation of the permeation of SM and its model compound **bis(2-chloroethyl) ether**, designated as **OA**, was therefore planned in order to understand the basis for the use of barriers materials for protective purposes. OA is structurally similar to SM in molecular dimensions with no perceptible blistering effect. The permeating media were solution cast (10% w/v in toluene) membranes of elastomers such as, polyisobutylene (**PIB**), natural rubber (**PI**), butyl rubber (**IIR**), polybutadiene (**PB**) rubber, styrene-butadiene rubber (**SBR**), nitrile rubber (**NBR**) and ethylene-propylene diene methylene (**EPDM**) rubber.

The work involved formulating and compounding of elastomer membranes, designing suitable methods for evaluation of their permeation resistance and quantifying the permeation parameters. Dependence of these parameters on the variables (pertaining to the permeant, permeating medium and the test conditions) influencing the permeation process were also studied. The data was analysed on the basis of appropriate models of sorption theory and

theoretical models. These studies and their results are incorporated into the thesis which is divided into seven chapters.

CHAPTER 1: Fundamental aspects including **introduction and literature survey** were dealt in this chapter with a view to provide an insight into the work done on various aspects of permeation, especially with respect to isobutylene based elastomers. Since the present research work has been based on studies on permeation of chemical warfare (CW) agents through elastomers, an introduction to various aspects (pre-requisites, classification and use) of these agents was also included. An overview of the methods reported for evaluation of permeation resistance as well as mechanistic aspect of permeation was also provided.

CHAPTER 2: This chapter describes the **materials and methods** used to study the permeation resistance of elastomers. Details regarding the preparation and characterization of membranes, permeation measurements and experimental protocol have been elucidated. Suitable permeation cells in glass and Teflon were designed and methods such as spot disc breakthrough time **(SD BTT)** test, change in weight, and gas chromatography **(GC)** were devised for evaluation of diffusivity of the toxic chemicals in the membranes.

CHAPTER 3: The **sorption plots and permeation parameters** were discussed in this chapter. The permeation was quantified in terms of breakthrough time **(BTT)**, and coefficients of diffusion **(D)**, sorption (S) and permeability **(P)**, which were determined from the sorption kinetics (log Q_t Vs $\sqrt{t}$, where Q_t is the mole% sorption and t is the time) for elastomer-mustard system.

For equivalently cross-linked elastomers with the same order of molecular weight (10^5), the permeation resistance to SM varied in the order of PB<PI<SBR<EPDM<NBR<IIR<PIB, the SM BTT of PB was only one minute as against 8 hours for IIR membrane of the same thickness. The permeability coefficient (**P=D**xS) of OA ranged from 10^{-15} to 10^{-8} moles. $m^{-1}.s^{-1}$ Pa^{-1} in these elastomers. It was also observed that OA permeated faster than SM as manifest

by shorter BTT and larger D values of OA. The permeation trends were attributed to a combination of factors such as chemical structure of the polymers, chain flexibility, intermolecular interaction and macromolecular packing density.

CHAPTER 4: The **effect of different variables on permeation** was described in this chapter. Besides the nature of elastomer, membrane thickness also influenced the resistance to permeation, as inferred from the higher BTT values of thicker membranes for a given elastomer. Permeation was also found to depend on the nature and physical state of the permeant. The permeation was faster when the chemical was in the liquid state than in the vapour state, as evident in the shorter BTT and higher diffusion coefficients for liquid permeation. BTT was however observed to be independent of concentration of the permeant.

Permeation was also studied as a function of the nature and amount of fillers in butyl rubber membranes, filled with carbon black (GPF N660) and inorganic fillers (talc, clay and precipitated $CaCO_3$). The volume fractions of the fillers were varied from 5 to 50% and their content was optimised in terms of SM BTT value. The carbon black content of 20 phr was found optimum for a high BTT (38 h). At any fixed filler level, the order in SM BTT was Carbon > $CaCO_3$ > Clay > Talc. The BTT was also found to decrease with an increase in temperature, which was described in terms of Arrhenius equation; the activation energy was calculated to be 80 kJ/mole for butyl rubber and 71 kJ/mol for nitrile rubber. Furthermore, BTT increased in nitrile rubber with increase in relative humidity **(RH)**, while it was unaffected in butyl rubber.

CHAPTER 5: The **analysis of results and theoretical models of permeation** were described in this chapter. Diffusion mechanism of SM in butyl and nitrile rubbers was interpreted on the basis of dynamic adsorption theory and Arrhenius relation. Solubility parameters (δ) and cohesive energy densities of polymers and permeants were calculated from the group contribution methods and were used to analyse the experimental results. Further analysis was also attempted using the free volume models and molecular theories of diffusion.

CHAPTER 6 : **Post characterisation of membranes exposed to the chemicals** in order to investigate the permeation induced changes in the structural and surface relief features, mechanical properties and residual protection potential of the membranes was described in this chapter.

The leaching of rubber ingredients by OA was confirmed in natural rubber by GC. The SM contaminated membranes also showed a deterioration in their protective potentials as evidenced by a significant drop in their BTT values. It was found that about 15-20% of SM remained entrapped in rubber matrix preventing its complete desorption; therefore, only partial decontamination was possible in rubber samples.

CHAPTER 7 : **Summary and conclusion** highlighting the salient features of the work were incorporated in this chapter. A related study on thermal degradation of butyl rubber was incorporated in appendix 1.

The present work established the protection potential of isobutylene based elastomers for Defence applications. Carbon loading of the membranes further enhanced the protection provided against toxic chemicals. New and safer methods were designed for evaluating the protective performance of the membranes. A suitable model compound (OA) for the blistering agent (SM) was identified for permeation studies. The experimental results analysed by various theoretical models showed a good consistency.

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