

Defence Science Journal, Vol. 59, No. 5, September 2009, pp. 505-511
© 2009, DESIDOC

Bromo-butyl Rubber for Face Piece of a Respiratory Mask

G.K. Kannan*, Upendra Simha*, Leeladhar Gaikwad**, Nirmala L**, and N.S. Kumar**

*Defence Bioengineering and Electromedical Laboratory, C.V. Raman Nagar, Bangalore-560 093

**High Energy Materials Research Laboratory, Pune-411 021

ABSTRACT

Respiratory mask contains a number of components made of materials like rubber, plastics, and metals. Out of all the components, face piece is the main component exposed to the external environment. This study aims to evaluate degradation of bromo-butyl rubber. The experiments were carried out for thermal exposure, swelling study, saline exposure, etc. It is observed that the elongation at break was increased by 10 per cent when these were exposed to 100 °C. However, the tensile strength has been observed to decrease by 50 per cent when exposed to 55 °C. It is decreased to around 63 per cent when exposed to 80 °C and 100 °C. The morphological appearance of unaged sample was intact. Only samples at 120 °C aged for 48 h appeared to have developed minor cracks of <0.01 µm. There were no significant changes observed when the samples were exposed to saline (3 % NaCl) and artificial sweat solution.

Keywords: Respiratory mask, degradation, bromo-butyl, thermal oxidation, saline exposure

1. INTRODUCTION

Personal protection is essentially required in a hostile environment. Rubber is extensively used for the development of nuclear biological chemical (NBC) personal protective equipment such as respiratory mask, resuscitator, gloves, boots, etc. Respiratory protection is taken care by a mask. The mask comprises a canister which filters the toxic gases and allows breathable air [1]. In addition to canister, the mask comprises rubber and plastic components. The per cent usage of various types of rubber in the equipment varies depending upon the functional requirement. The material composition of mask on weight basis is bromo-butyl rubber (65 per cent), plastic (19 per cent), neoprene-natural rubber blend (8 per cent), silicon rubber (1 per cent), and metal (7 per cent) [2,3]. The Indian NBC respiratory mask contains 49 components. Face piece is the only component made from bromo-butyl rubber. However, the face piece covers major portion of the mask [4]. All the components have to be intact without any degradation during the shelf life period. The reported degradation of polymer components mainly occur due to thermal [5-7] oxidants such as ozone [8], ultraviolet radiation [6,8], photo oxidation [6,9], thermal oxidation and hydrolysis leading to chain scission or cross linking [10,7], swelling and hydrolysis [11]. A number of techniques used are

- FTIR to investigate scission in the backbone [12]
- Change of tensile properties [13-14]
- Thermo-gravimetric and differential scanning calorimetry to evaluate thermal stability and glass transition (T_g) behaviour.

The NBC respiratory mask protecting the wearer in

the highly toxic environment, needs to be completely leak-proof. Failure of any one of these components leads to the risk of the personnel who wears the mask. Out of all the components, face piece (having 65 % of the total weight and approximately 80 % of exposed surface area coverage of the mask) is the main component exposed to the external environment compared to other components, which are placed relatively inside the face piece [3]. The study aims to

- Evaluate the degradation of bromo-butyl rubber used in the face piece of NBC respiratory mask,
- Study morphological changes of the bromo-butyl rubber using thermal ageing, and
- Evaluate the degradation of the bromo-butyl rubber through FTIR evaluation, hydrolysis, and solvent swelling.

2. EXPERIMENTAL

2.1 Rubber Materials

Based on the functional requirements, a suitable bromo-butyl rubber formulation had been formulated with compression moulding for 2 min at 190 °C and 20 bar pressure and used in the development of NBC respiratory mask. The major ingredients of the formulation are bromo-butyl rubber (100 PHR), carbon black (30 PHR), zinc oxide (5 PHR), stearic acid (2 PHR), accinox (1 PHR), paraffinic oil (12.5 PHR), and sulphur (1.5 PHR). The same bromo-butyl rubber formulation was moulded into sheet (2 mm thickness). The bromo-butyl rubber sheet was cut into the required shape as per the ASTM standard D-412 [15] and used for various experiments. The physical properties of bromo-butyl rubber used for the NBC mask development are given in Table 1.

Received 20 May 2009

Table 1. Physical properties of bromo-butyl rubber

Parameter	Bromobutyl
Vulcanisate structure $m = 2$ $n = 98$	
Density, g/cc	1.06
Hardness (Shore – A)	40-50
Tensile strength, kg/cm ²	115
Elongation, %	575
Ash content, %	6
Angle tear strength, kg/mm	2-3.5

2.2 Thermal Degradation Experiment

The degradation study of bromo-butyl rubber was carried out for air oxidation. The representative numbers of cut samples were exposed at 35 °C, 50 °C, 80 °C, 100 °C, 120 °C continuously in a hot air oven thermostatically controlled at ± 1 °C. The exposure period was 48 h. Similarly, the rubber samples were also exposed to low temperatures such as -10 °C, -50 °C, and -65 °C using CMEIPL environmental chamber. The samples were periodically taken out, conditioned at room temperature. The samples were analysed using various instrumental techniques.

2.3 Swelling Studies

Representative bromo-butyl rubber samples earlier exposed at -65 °C (cold temperature), 35 °C (room temperature) 120 °C (hot temperature) temperatures, were immersed in 2,4-dioxin to study the swelling trend after exposure. Saline exposure study was also carried out to ascertain the degradation during the actual usage of NBC mask in the Navy related activities, where the mask is exposed to saline medium. Cut samples were exposed to various concentrations of sodium chloride solution, viz., 0 per cent, 1 per cent, 3 per cent, 5 per cent, and 10 per cent. Artificial sweat was also prepared as described in ISO (3160/2) standard.[16] Accordingly, 20 g/l NaCl, 17.5g/l NH₄Cl, 5g/l acetic acid, 15g/l d, 1 lactic acid with pH adjusted to 4.7 by NaOH. At various intervals the specimens were removed, gently wiped to clean the surface solvent and weighed. The degree of swelling was calculated using the reported equation.[11] Exposed bromo-butyl rubber samples were also evaluated for the change of mechanical properties.

2.4 Instrumental Analysis

The elongation at break and tensile strength of the unexposed and exposed specimens was determined within ± 1 per cent by using a hounsfield universal testing machine (Model H10KS). The load cell of 2 ton capacity, at the speed of 1 mm/s was used. The morphological changes on the surface of the bromo-butyl rubber were visualised through scanning electron microscopy (SEM) with JSM-

840 JEOL microscope of JEOL Techniques Ltd, Japan, at 1000x magnification with gold sputtering. A set of exposed samples were conditioned at room temperature and analysed in Perkin Elmer FTIR spectrophotometer. The attenuated total reflection (ATR) with Zn-Selenide crystal was used. The scanning was done for the entire range of wave numbers from 700–4000 cm⁻¹. The spectra were analysed using the spectrum-1 software of the instrument.

3. RESULTS AND DISCUSSION

3.1 Thermal Degradation Study

The changes in mechanical properties of bromo-butyl rubber exposed to wide range of temperatures is shown in the Fig. 1.

The degradation appeared to be very fast and the tensile strength decrease by 60 per cent at 80 °C and 100 °C exposure. At low temperature (-65 °C for 48 h exposure) also the decrease has been observed to be 50 per cent. However, the elongation observed to have slightly increased by 10 per cent compared to the unexposed one. This is the general behaviour of bromo-butyl rubber to increase in elongation when the tensile strength is reduced [12].

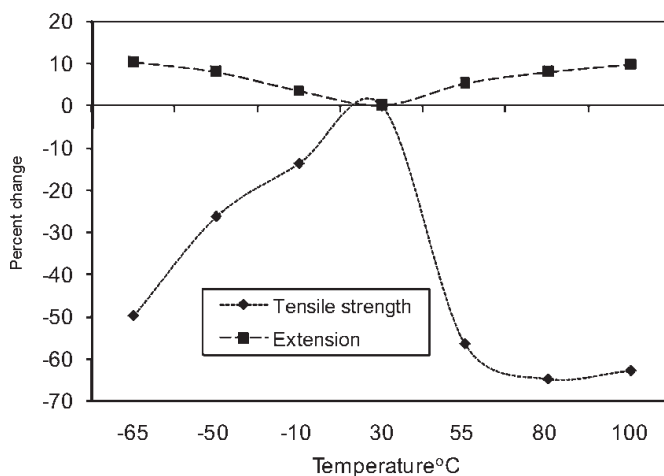


Figure 1. Changes of extension and tensile strength of bromo-butyl rubber exposed to wide range of temperatures.

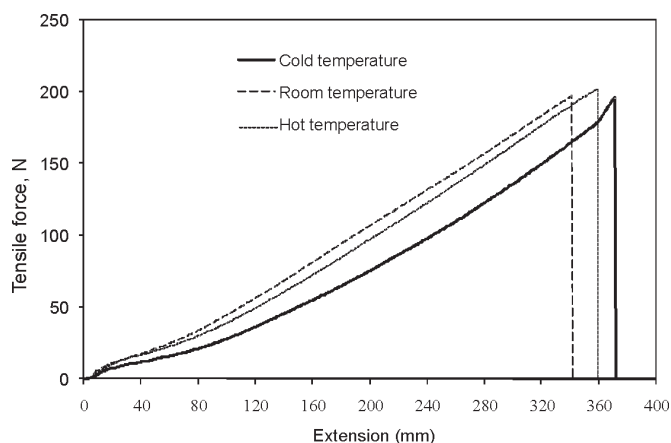


Figure 2. Tensile force and elongation of bromo-butyl rubber exposed to various temperatures.

Stress-strain curve of bromo-butyl rubber exposed to various temperatures is shown in Fig. 2.

The bromo-butyl rubber samples exposed to hot temperature were found to have more increase in elongation. However, the elongation was to be less in case of samples exposed to cold temperature.

3.2 Swelling Study

Liquid absorption of rubber material will be a good indication to correlate the degradation of rubber material. The swelling expressed in terms of per cent increase of material over a time period until the saturation. Swelling studies of bromo-butyl rubber in 2,4-dioxin after exposure to various temperatures is shown in Fig. 3.

Fresh and old bromo-butyl rubbers were found to have increased their mass loading. The saturated mass loading achieved at various time lapse. It was observed that reference rubber has saturated mass loading of 15 per cent after 60 h of exposure in 2,4-dioxin. However, the hot temperature (120 °C)-exposed bromo-butyl rubbers had saturated mass loading of 25 per cent after 64 h. Similarly the samples exposed to cold temperature

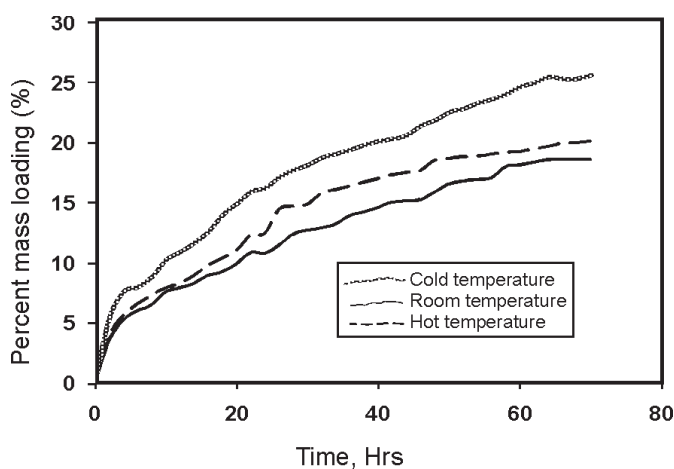


Figure 3. Swelling studies of bromo-butyl rubber in 2,4-dioxin after exposure to various temperatures.

(-65 °C) had mass loading of 18 per cent much before 48 h. It is seen from the Fig. 3 shows a linear dependence in all the old and fresh samples. The increased mass loading indicates more swelling of the bromo-butyl rubber when exposed to extreme by low as well as high temperature. Since the tensile property tends to decrease in the samples exposed to this extreme temperature, indicating the weakening of the bonds, and hence swelling occurred. Similar observations have been reported for swelling study in the literature [10].

3.3 Saline Exposure Study

The NBC mask meant for naval applications is bound to be exposed to saline environmental conditions. Also, the sweat from the face and the neck of the personnel, who puts on the mask, is likely to come in contact with the NBC mask. Hence, bromo-butyl rubber was evaluated for degradation due to various saline concentrations. The result of the permeation studies of bromo-butyl rubber to various saline concentrations are shown in Fig. 4. Water permeation was more in 0 per cent (9.45 $\mu\text{g}/\text{mm}^2$) and 1 per cent (6.9 $\mu\text{g}/\text{mm}^2$) saline solution compared to higher saline concentrations. The observed values were 0.8-2.0 $\mu\text{g}/\text{mm}^2$ in the higher saline concentration. The saturation of mass loading occurred between 20-25 h. The mass loading of bromo-butyl rubber in the artificial sweat composition was observed to be 2.2 $\mu\text{g}/\text{mm}^2$

The changes in mechanical properties such as tensile strength and elongation at break of bromo-butyl rubber exposed to various concentrations of saline solution and artificial sweat composition are shown in Fig. 5. The elongation change increased by 5 per cent and tensile strength decreased by 18 per cent in 0 per cent saline solution. In the saline solution the behaviours observed were:

- More elongation change (+13 per cent) and less tensile change (-5 to -9 per cent) in the lower saline concentration (1-3 per cent).
- Reverse trend of the first in the higher saline concentration (5-10 per cent), i.e., less change in elongation (+7 to

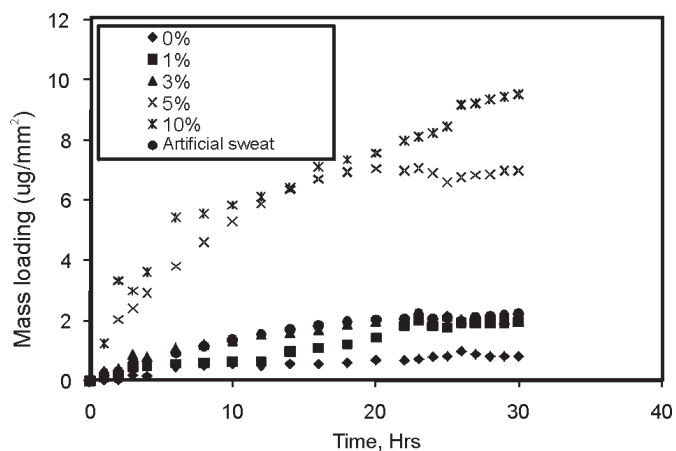


Figure 4. Permeation studies of bromo-butyl rubber in various concentrations of saline and artificial sweat composition.

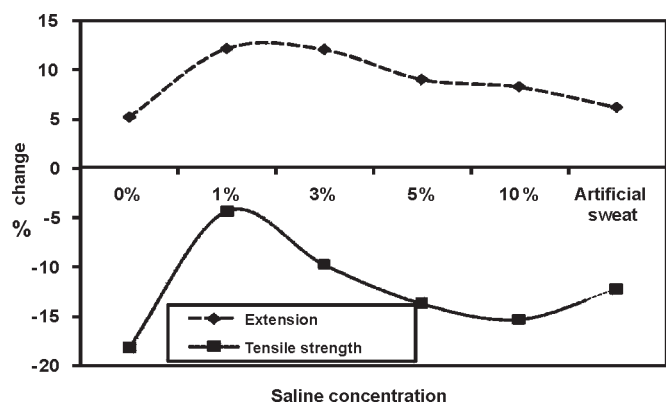


Figure 5. Change of mechanical properties of bromo-butyl rubber exposed to various concentration of saline solution.

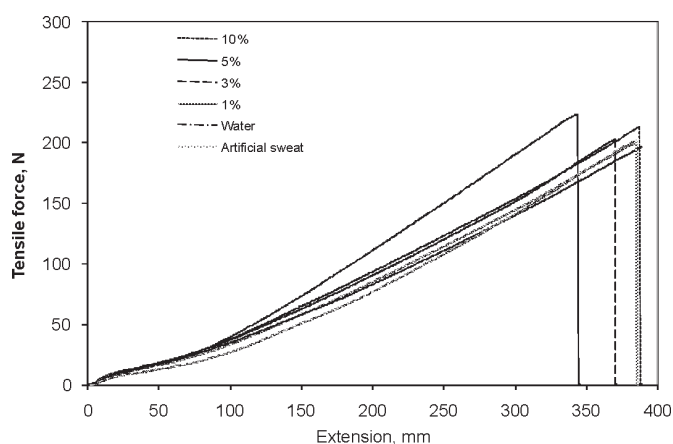


Figure 6. Stress strain curve of bromo-butyl rubber exposed to various concentrations of saline solutions.

+9 per cent) and more changes in tensile (-12 to -14 per cent).

However, in the actual usage, only the lower saline concentration is prevailing in the environment.

Stress strain curve of bromo-butyl rubber exposed to various concentrations of saline solutions is shown in Fig. 6. The artificial sweat exposure study was comparable to the exposure study of 5 per cent saline solution. The changes in the elongation and tensile strength are at par with the 5 per cent saline solution. However, the salinity of the artificial sweat composition is around 3 per cent.

3.4 FTIR Analysis

The FTIR spectral changes obtained by attenuated total reflection (ATR) method for the rubber samples exposed to various experimental conditions have been shown in Fig. 7 (4 days exposure) and Fig. 8 (12 days environmental exposure). For four days exposure there was no observable changes.

However, 12 days exposure showed increased absorption at wave number 2917 cm^{-1} indicating more methylenic group decreased absorption at 2849 cm^{-1} showing less alkyl group. In case of *C-Br* bond at wave number 810 cm^{-1} , the thermally oxidised samples showed decrease in absorption representing dehydrohalogenation in the process. Whereas, it almost vanished in saline-treated sample, representing more dehydrohalogenation. Saline-treated samples showed diminishing *C-S* bond at 1020 cm^{-1} indicating devulcanising, whereas in thermal exposure samples, it is exhaustive and no absorption in this region.

3.5 Morphological Study

The SEM images taken at 1000x for unexposed and exposed samples are shown in Figs 9 (a) and 9(b) exposed samples of bromo-butyl rubber. The unexposed samples were observed to be intact in the morphological appearance. However, the samples exposed at temperature ($120\text{ }^{\circ}\text{C}$, 36 h) showed major networks of submicron cracks. In other studies also, ageing has reported to have caused surface and cross section area of about $100\text{ }\mu\text{m}$ for cross-linked silicone rubber [17].

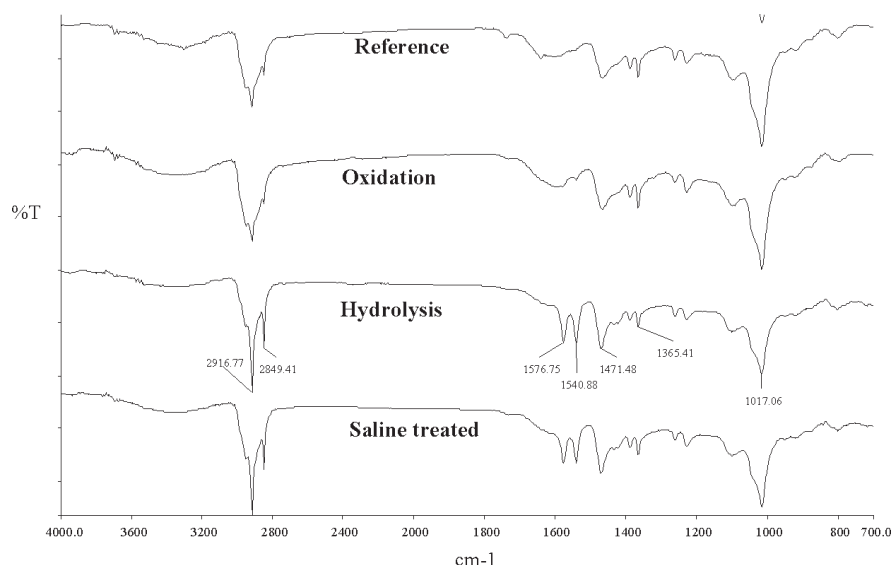


Figure 7. FTIR spectral changes for bromo-butyl after 4-day environmental exposure.

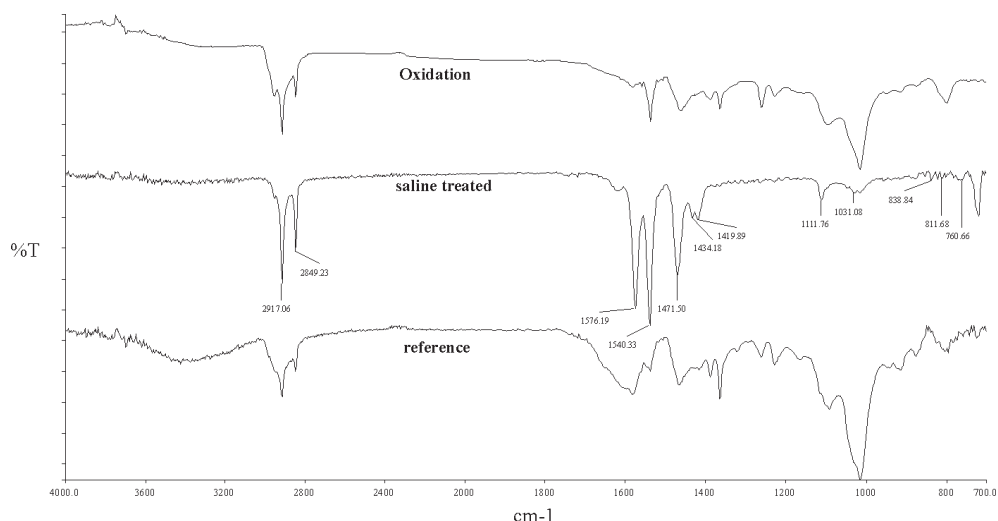
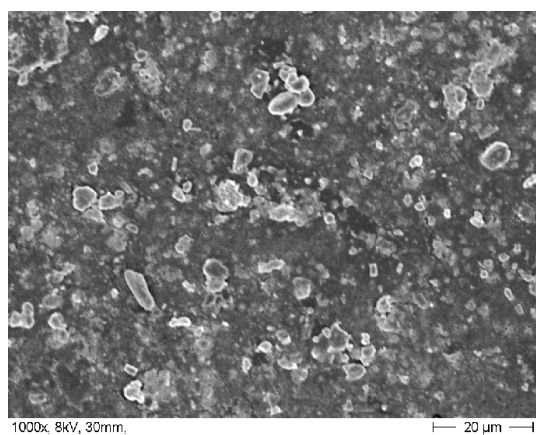
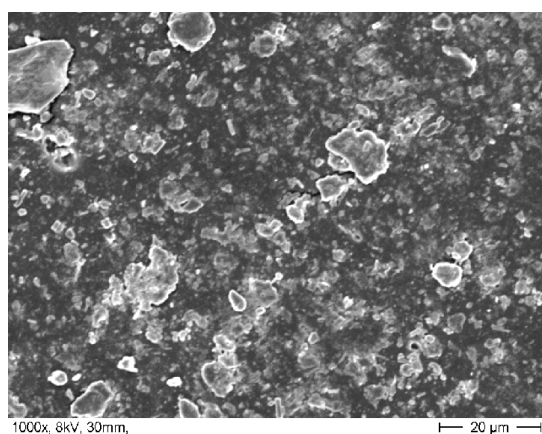


Figure 8. FTIR spectral changes for bromo-butyl rubber after 12-day environmental exposure.



(a)



(b)

Figure 9. SEM images of: (a) reference and (b) temperature (120°C) -exposed for 36 h sample of bromo-butyl rubber.

3.6 Probable Degradation Mechanism

The effective service life of a rubber article depends on its ability to withstand the conditions under which it has to operate without suffering permanent changes [18]. The rate of change of stiffness, resilience, tensile strength,

the surface cracking and the separation of bonds are the most important phenomena associated with aging. The chemical unsaturation of rubber, which makes possible the changes brought about by vulcanization, also makes it susceptible to deterioration by oxidation. The synthetic rubbers are generally superior to natural rubber in their resistance to oxidation. Bromo-butyl rubber polymers normally degrade in many ways. One of the common observed phenomenon is that the backbone of the polymer may degrade at random position, leads to notable reduction in mechanical properties, but specified changes in the molecular structures may be noted. In this study also the samples exposed to saline as well as different temperature ranges showed significant changes in the mechanical properties. The probable degradation mechanism for thermal oxidation and saline reaction is shown in Figs 10 (a) and 10 (b). In the thermal degradation, initially the uncured sulphur gets cured and increases the tensile strength. However, in the continuous prolonged exposure is likely to degrade C-H bond and also C-Br bond. The resultant is expected to be HBr. In case of saline exposure, most likely occurrence is the breakage of C-S bonds and formation of Na_2S . This will weaken the backbone of the bromo-butyl rubber and trigger the succession of degradation.

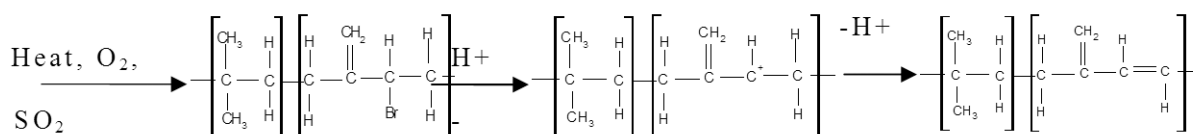
In addition to the above types, degradation at vulcanization points was also noted for many polymers. This leads to reduction in tensile strength and increase in percentage elongation[19] which has been observed in the study.

4. CONCLUSIONS

Since the rubber vulcanisation is meant for manufacturing of life saving equipment, the degradation of the formulations becomes very significant.

- (i) At high temperature (120 °C) the degradation appeared to be very fast and the decrease in tensile strength is around 60 per cent. In the lower cold temperature (-65 °C) the tensile change observed were -50 per cent.

(a) Thermal oxidation



(b) Saline treated

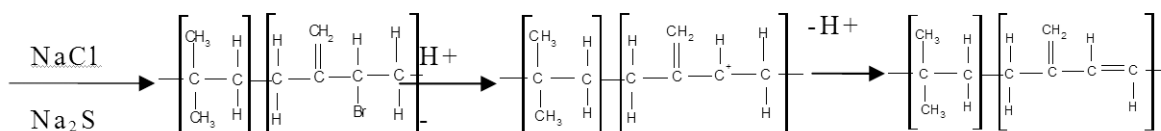


Figure 10. Probable degradation mechanisms of vulcanised bromo-butyl rubber.

- (ii) The unexposed samples appeared to be intact in the morphological structure shown in the SEM images. Sample exposed at 120 °C (48h exposed) showed mesh of submicron cracks in one or two places.
- (iii) The FTIR saline exposure study showed diminishing of C-S bond at 1020 cm⁻¹ indicating devulcanising. The saline study also showed that there is a minor change in the mechanical properties of the samples exposed to saline and artificial sweat solution.
- (iv) Thermal exposure samples showed decrease in absorption at wave number 810 cm⁻¹ representing dehydrohalogenation of C-Br bond in the process.
- (v) Since these studies carried out with the samples exposed at accelerated thermal oxidation, and in the normal ambient temperature (30 °C to 50 °C for Indian conditions) usage of the formulations is likely to be unaffected. The mechanical and chemical properties are unlikely to get degraded. In the normal usage, the shelf-life of the rubber formulation is expected to be better.

ACKNOWLEDGEMENTS

The authors express their gratitude to Dr V.C. Padaki, Director, and Dr A.S.K. Prasad, Associate Director, Defence Bioengineering and Electromedical Laboratory, Bangalore, for their support and permission to publish this paper.

REFERENCES

1. Prasad, G.K.; Singh, B. & Vijayarghavan R. Respiratory protection against chemical and biological warfare agents. *Def. Sci. J.*, 2008, **58**(5), 686-97.
2. Rubber review, 2003-2004. *Rubber India*, 2005, **57**(1), 35-7.
3. Project closure appreciation on development of small and large size NBC respirator. DEBEL, Ministry of Defence, July 2001. Report No. SL-P1-98/DEB-89.
4. Specification for NBC respiratory mask. DEBEL, Ministry of Defence, June 2000. Report No. DEBEL/NBC/07.
5. Gueguen, V.; Audouin, L.; Pinel, B. & Verdu, J. Thermal oxidation of EPDM terpolymer and vulcanisate. *Poly. Deg. Stab.*, 1994, **43**, 217-23.
6. Delor-Jestin, F.; Drouin, D.; Cheval, P-Y & Lacoste, J. Thermal and photochemical ageing of epoxy-resin-influence of curing agents. *Poly. Deg. Stab.*, 2006, **91**, 1247-255.
7. Rodriguez-vazquez, Miguel.; Liauw, Christopher Mark; Allen, Norman Sidney; Edge, Michele & Fontan, Eusebio. Degradation and stabilization of poly (ethylene-stat-vinyl acetate):1-spectroscopic and rheological examination of thermal and thermo-oxidative degradation mechanisms. *Poly. Deg. Stab.*, 2006, **91**, 154-64.
8. Mendelsohn, M.A.; Luck, R.M. & Yeoman, F.A. Fall meeting proceedings of the ACS Division of Rubber, 1980, Detroit, Mich. USA. 8, 27.
9. Rabek, J.F. Photostabilisation of polymers. Elsevier Applied Science, London, New York, 1990.
10. Bernstein, Robert; Derzon, Dora K. & Gillen, Kenneth T. Nylon 6.6 accelerated aging studies: Thermal oxidative degradation and its interaction with hydrolysis. *Poly. Deg. Stab.*, 2005, **88**, 80-488.
11. Proikakis, C.S.; Mamouzelo, N.J.; Tarantili, P.A. & Andropoulos, A.G. Swelling and hydrolytic degradation of poly (D,L-Lactic acid) in aqueous solution. *Poly. Deg. Stab.*, 2006, **91**, 614-19.
12. Liu, Mingzhu; Bian, Fengling & Sheng, Fenling. FTIR study on molecular structure of poly (N-isopropylacrylamide) in mixed solvent of methanol and water. *Eur. Poly. J.*, 2005, **41**, 283-91.
13. Gillen, Kenneth T.; Bernstein, Robert & Derzon, Dora K. Evidence of non-arrhenius behaviour from laboratory aging and 24-year field aging of polychloroprene rubber materials. *Poly. Deg. Stab.*, 2005, **87**, 57-67.
14. Zhihur, Yin; Yajie, Zhang; Xiaomin, Zhang & Jinghua, Yin. Effects of the compatibililiser PP-g-GMA on morphology and mechanical properties of PP/PC blend. *Polymer*, 1998, **39**(3), 547-51.
15. Standard test methods for rubber properties in tension, 1987. Standard No. ASTM D-412-87.
16. Standard procedure for artificial sweat composition, 1987. Standard No. ISO (3160/2).
17. Ghanbari-siahkali, Afshin; Mitra, Susanta; Kingshott, Peter; Almdal, Kristoffer; Bloch, Carsten & Rehmeier,

Helle Kem. Investigation of the hydrothermal stability of cross-linked liquid silicone rubber (LSR). *Poly. Deg. Stab.*, 2005, **90**, 471-80.

18. Budrugaec, P. Accelerated thermal ageing of nitirle-butadiene rubber under air pressure. *Poly. Deg. Stab.*, 1995, **47**, 129-32.
19. Rodriguez, Ferdinand. Principles of polymer systems, Ed. 4. Taylor & Francis, Washington DC, 1996.

Contributors



Dr G.K. Kannan has obtained PhD in Environmental sciences, and is currently working in Defence Bioengineering and Electromedical Laboratory (DEBEL) as Scientist 'D'. He has been working in the area of air quality and emission monitoring, and environmental impact assessment and development of explosive vapour detection.

His current research includes filter development and evaluation. He has published a number of research papers in the area of air pollution in various reputed journals. Also he has presented his research findings in national and international conferences.



Mr Upendra Simha obtained his MSc (Chemistry) from Mysore University. He was working as Research Fellow in DEBEL. He has been working on the toxic emissions studies of materials. Currently, he is working as Chromatography Specialist in Agilent Technologies.



Mr Leeladhar Gaikwad obtained his MSc (Chemistry) from Kuvempu University. He has been working in the area of chromatography and toxic emissions studies. Currently, he is working at the High Energy Materials Research Laboratory.



Mrs Nirmala L. is working as Technical Officer 'A' at DEBEL. She has been working in the areas of rubber testing and degradation studies.



Dr N.S. Kumar obtained his MSc (Chemistry) from Kerala University and PhD (Chemistry) from Sree Chitra Tirunal Institute for Medical Sciences and Technology, Thiruvananthapuram. He has been working in the area of biomaterials, polymers, and also quality management. He has published about 25 research articles in various refereed journal and conferences. He is the Head of the Material Testing

and Quality Assurance Group.