PREDICTION OF SERVICE LIFE OF RUBBER PRODUCTS BASED ON ARRHENIUS THEORY

Joy Joseph, Jacob K.Varkey and Manoj Kurian Jacob

Rubber Research Institute of India, Kottayam-686 009, Kerala, India

Received: 06 December 2018 Accepted: 09 April 2019

Joseph, J., Varkey, K.J., Jacob, M.K. (2019). Prediction of service life of rubber products based on Arrhenius theory. *Rubber Science*, **32**(1): 83-93.

Different types of rubbers have different ageing properties. Service life of rubber products is determined by the differences in ageing properties of the rubbers used in the products and the conditions to which the products are exposed to during their service life. The present work is an attempt to predict the service life of products made up of nitrile rubber (NBR), ethylene propyle diene (EPDM) rubber and NR based on the Arrhenius theory. Logarithm of days in air to reduce the tensile strength to least serviceable level of 10 MPa for NBR and EPDM and 20 MPa for NR were plotted against 1/T where 'T' is the temperature in Kelvin scale. When the results were extrapolated to 1/T for room temperature (3.3 x 10^{-3}), we got log days for room temperature as 7.5 for NBR. This indicates that the product made out of the formulation used can give a service life of 1808 days in air. In a similar way it was predicted that the service life of the NBR product of the formulation studied was only 992 days in sea water. Similarly the service life of EPDM and NR of the formulation used in the present study was estimated as 2208 days and 633 days, respectively in air, and that in sea water was estimated to be 854 days and 81 days, respectively.

Key words: Ageing, Ethylene propylene diene rubber, Natural rubber, Nitrile rubber, Service life, Tensile strength

INTRODUCTION

Different types of rubbers like natural rubber (NR), Ehylene Propylene Diene rubber (EPDM), Nitrile butadiene rubber (NBR) *etc*. are widely used in manufacturing thousands of rubber products (Stevensan, 1990). Various types of synthetic rubbers are being used in places where natural rubber (NR) fails to give service (Eby, 1979). Though many synthetic rubbers are available in the global market NBR, EPDM, Silicone and SBR are some of the most widely used synthetic rubbers in non-tyre sector (Celina *et al.*, 2005).

Though NR is the most widely used polymer in rubber products some of the properties like ageing resistance to air and sea water make NR unsuitable for certain products (Gent, 1992; Shlyapnikov 1996; Suits, 2001). In such situations NR has to be replaced by other types of rubber. In this context it is worthwhile to predict the service life offered by a product under specific conditions, made out of rubber. The present work is an attempt to predict the service life of products based on NBR, EPDM and NR.

Nitrile rubber, also known as Buna-N, Perbunan, acrylonitrile butadiene rubber, and NBR, is a synthetic rubber copolymer of acrylonitrile (ACN) and butadiene. Trade names include Nipol, Krynac and Europrene. NBR is a family of unsaturated copolymers

Correspondence: Joy Joseph (Email: joyjoseph@rubberboard.org.in)

of 2-propenenitrile and various butadiene monomers (1,2-butadiene and 1,3-butadiene) (Bernstein, 2009). Although its physical and chemical properties vary depending on the polymer's composition of nitrile, this form of synthetic rubber is generally resistant to oil, fuel, and other chemicals (the more nitrile within the polymer, the higher the resistance to oils but the lower the flexibility of the material) (Hsuan *et al.*, 1993).

It is used in the automotive and aeronautical industry to make fuel and oil handling hoses, seals, and grommets, since ordinary rubbers cannot be used (Kelen, 1983). It is used in the nuclear industry to make protective gloves. NBR's ability to withstand a range of temperatures from –40 to 108°C (–40 to 226°F) makes it an ideal material for aeronautical applications (Hsuan, 1998). NBR is also used to create molded goods, footwear, adhesives, sealants, sponges, expanded foams, and floor mats (Roland, 2009).

Its chemical resistance makes NBR a useful material for different types of gloves (Chapman *et al.*, 2009). Nitrile rubber is more resistant than natural rubber to oils and acids, and has superior strength, but has inferior flexibility (Mott, 2001). Nitrile gloves are therefore more puncture-resistant than NR gloves, especially if the latter are degraded by exposure to chemicals or ozone. Nitrile rubber is less likely to cause an allergic reaction than NR.

EPDM exhibits satisfactory compatibility with fireproof hydraulic fluids, ketones, hot and cold water, and alkalis. However it exhibits unsatisfactory compatibility with most oils, gasoline, kerosene, aromatic and aliphatic hydro carbons, halogenated solvents, and concentrated acids.

The main properties of EPDM are its outstanding heat, ozone, and weather resistance (Wang *et al*., 2003). The resistance to polar substances is also good. It has excellent electrical insulating properties. It has good resistance to ketones, ordinary diluted acids, and alkalis.

Hevea brasiliensis, which is generally known as para rubber tree is the major commercial source of NR which produces 99 per cent of the world's NR demand. Natural rubber however has been found in latices of over 2000 species of plants belonging to 311 genera of 77 families (George *et al*., 2000).

Various types of rubbers are being used in making components of ships and submarines. However, many components fail on contact with sea water for longer periods. In this context it is necessary to predict the service life offered by a product under specific conditions, made out of various types of rubber.

In this work a study was conducted on standard rubber vulcanizates subjecting them to natural degradation. The rate of degradation reaction based on Arrhenius theory was employed for prediction of service life of vulcanizates.

MATERIALS AND METHODS

The natural rubber latex for the study was collected from the research farm of Rubber Research Institute of India, Kottayam, Kerala. Nitrile rubber and EPDM rubber (90% ethylene content) used for this study were supplied by M/s. Jofex enterprises, Kottayam. Compounding ingredients such as zinc oxide (ZnO), stearic acid, TDQ, CBS, sulphur, *etc*. used in this study were supplied by M/s. Bayer (India) Ltd. Naphthenic oil was supplied by M/s. Samira Chemicals Pvt. Ltd, Kottayam and carbon black (HAF) was supplied by M/s. Vision Enterprises, Mumbai.

The latex collected from the research farm was diluted with water to remove unwanted non rubber constituents and coagulated using 0.5 per cent formic acid and pressed into sheets. The pressed coagula were washed and dried at 60^0C to get dry NR. Nitrile rubber and EPDM rubber were used as such. Sea water required for the work was collected from Wellington island sea, India.

COMPOUND PREPARATION

NBR, EPDM and NR were compounded separately in a laboratory model two roll mill (David Bridge) of size 15x30 cm as per the formulations given in Table 1, 6 and 7, respectively. The cure characteristics of the compounds were determined using Rubber Process Analyser (RPA 2000) at 150^0C according to ASTM D 5289 procedure.

Table 1. **Formulation of NBR compound**

Ingredients	Parts per hundred (Phr)
NBR	100
ZnO	5
Stearic Acid	1
TDQ	1
HAF black	40
DOP	4
DCP	2
Sulphur	1

Preparation of test samples

Test samples were prepared by compression molding according to ASTM D 3182 procedure using an electrically heated hydraulic press heated to 150 ^{0}C under a pressure of 100kg/cm^{2}and applying optimum cure time.

DETERMINATION OF VULCANIZATE PROPERTIES

Tensile properties (ASTM D 412-06)

The three parameters (Modulus, Tensile strength, Elongation at break) were determined according to the ASTM standards, using dumbbell shaped test piece. The test pieces were punched out from the molded sheets using C- type die, along the mill grain direction of the vulcanized sheets. The test was carried out in a Zwick Universal Testing machine (UTM) model 1474 AT (25±2)^{0}C. The dumbbell specimen was placed in the grip of the testing machine, taking care to adjust the specimen symmetrically to distribute tension uniformly over the cross-section. The speed shall be 500 mm/min. The force at the elongation specified for the test and at the time of rupture was recorded. The modulus at 100, 200 and 300 per cent and elongation at break were also noted.

Preparation of sample

NBR, EPDM and NR vulcanizates were cut for tensile strength test as per ASTM standards and were kept for ageing in air as well as in sea water for one, three and five days and the tensile strengths were measured. The experiments were conducted at three temperatures *viz*. 70^0C, 80^0C and 90^0C. The service life was predicted by applying Arrhenius equation.

Theory

Arrhenius equation is expressed as

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

Taking natural logarithm

$\ln k = \ln A - E/RT$

Where k is the rate constant and E is the activation energy. T is the temperature on Kelvin scale and R is a constant. A is an exponential factor, a constant for each chemical reaction.

Rearranging $\ln k = -E/R\,(1/T) + \ln A$

This equation is similar to the equation $y = mx + c$

Therefore when we plot ln k against 1/T we get a straight line which can be used for predicting service life of rubber products (Thomas, 2014).

In our study k is life in days and T is temperature of the environment in Kelvin scale which is expressed as t + 273 =T. Therefore by plotting properties like tensile strength against life in days we get the number of days to reach the degradation reaction to reach least serviceable tensile strength. When we plot log life in days against 1/T we can arrive at service life by extrapolating the graph to 1/T for room temperature. From this we can get the service life of the product made out of the formulation used. For all calculations room temperature is taken as 30^{0}C.

RESULTS AND DISCUSSION

Tensile strengths of vulcanized rubber samples were measured by using Universal testing machine. We need a minimum of three points for drawing a plot. Hence we have measured the tensile strengths of NBR rubber samples aged at three temperatures 70^{0}C, 80^{0}C and 90^{0}C for one day, three days and five days. For NBR and EPDM, the minimum serviceable tensile strength is 10 MPa and that for NR is 20 MPa. That means a tensile strength below 10 MPa is not desirable for a good service for NBR and EPDM products. For NR, the minimum serviceable tensile strength is considered as 20 MPa. The tensile strengths of NBR vulcanisates aged at 70^{0}C, 80^{0}C and 90^{0}C in air for one, three and five days are shown in Table 2.

Table 2. **Tensile strengths of NBR vulcanisates aged in air at different temperatures**

Days	Tensile strength (MPa)		
of ageing	70^{0}C	80^{0}C	90^{0}C
1	17.69	18.50	15.81
3	17.05	16.00	10.33
5	16.40	13.71	5.10

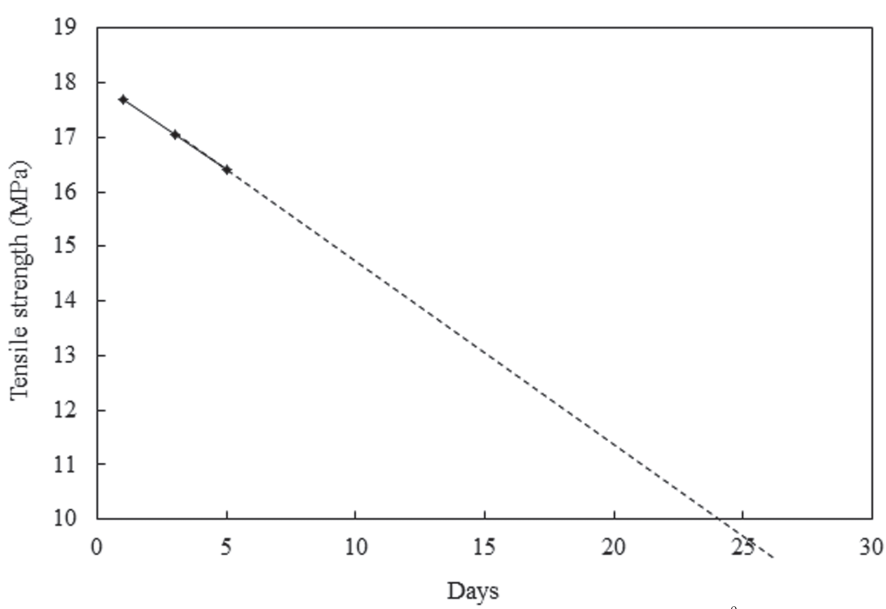

Fig. 1. Plot of tensile strengths against number of ageing days at 70^{0}C in air

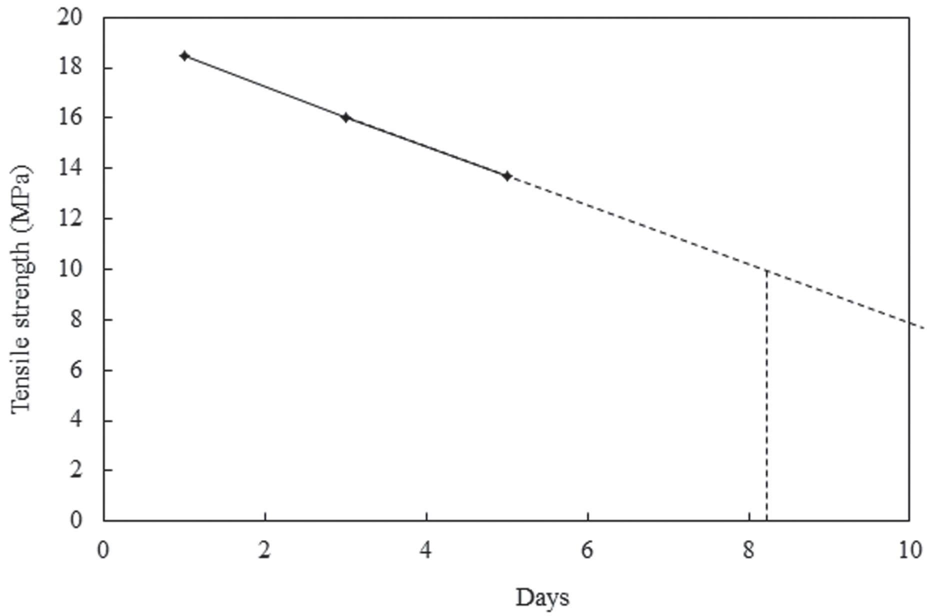

Fig. 2. Plot of tensile strengths against number of ageing days at 80^0C in air

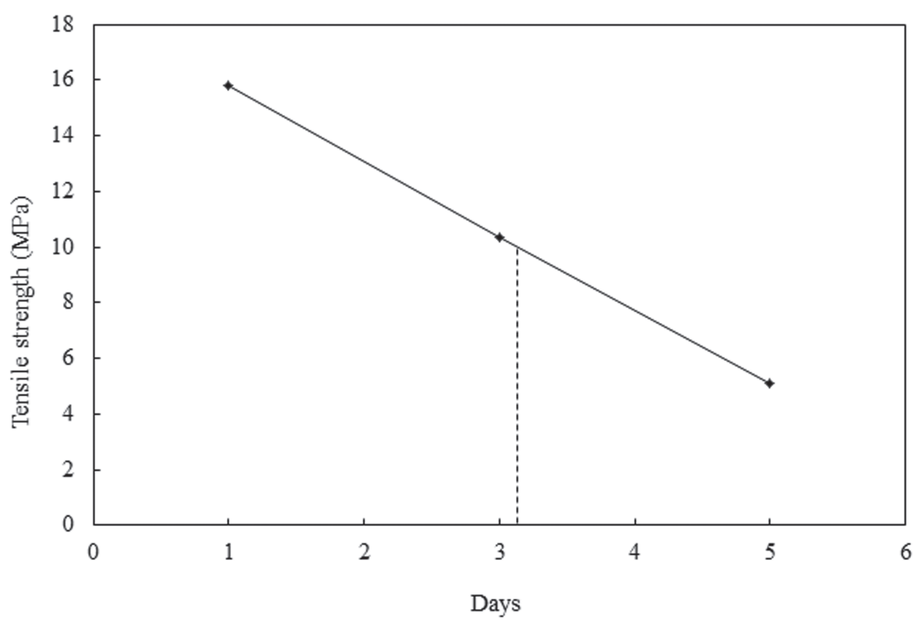

Fig. 3. Plot of tensile strengths against number of ageing days at 90°C in air

Table 3. **Logarithmic functions of days and 1/T**

Temperature (t) ^{0}C	t + 273 = T Kelvin	1/T x 10^{-3}	Days to reach 10 MPa	ln days
70	343	2.9	24	3.18
80	353	2.83	8.1	2.09
90	363	2.73	3.1	1.13

The tensile strengths were plotted against the number of ageing days (1, 3 and 5) and the plot was extrapolated to minimum service tensile strength of 10 MPa and the plot is shown in Figure 1. When the graph is extrapolated to tensile strength of 10 MPa, the number of days to reach the agreeable level of tensile is 24. Similarly, the tensile strengths at 80^{0}C in air were plotted against the number of ageing days and the plot was extrapolated to minimum service tensile strength of 10 MPa and the plot is shown in

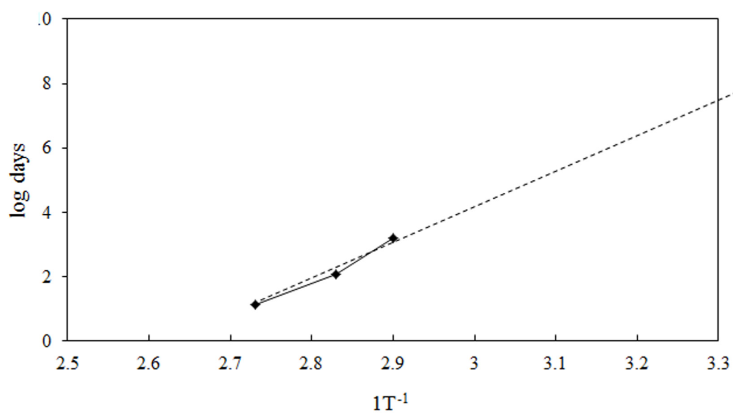

Fig. 4. Plot of log days against 1/T for NBR in air

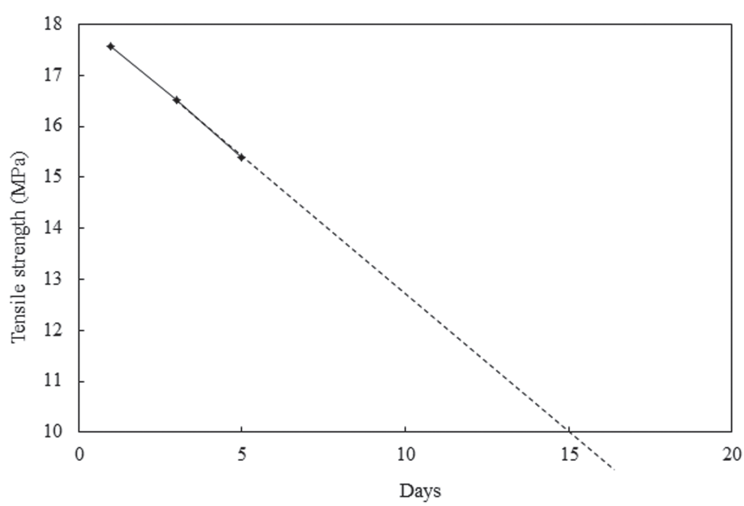

Fig. 5. Tensile strength values of NBR samples at 70^{0}C in sea water

Table 4. **Tensile strengths of NBR samples aged in sea water at different temperatures**

Days of ageing	Tensile strength(MPa)		
	70^0C	80^0C	90^0C
1	17.56	18.96	13.20
3	16.51	15.11	8.79
5	15.40	11.02	4.13

Table 5. **Logarithmic functions of days and 1/K**

Temperature (t) ^{0}C (Sea water)	1/T x 10^{-3}	Days to reach 10 MPa	ln days
70	2.9	15	2.71
80	2.83	5.6	1.72
90	2.73	2.4	0.88

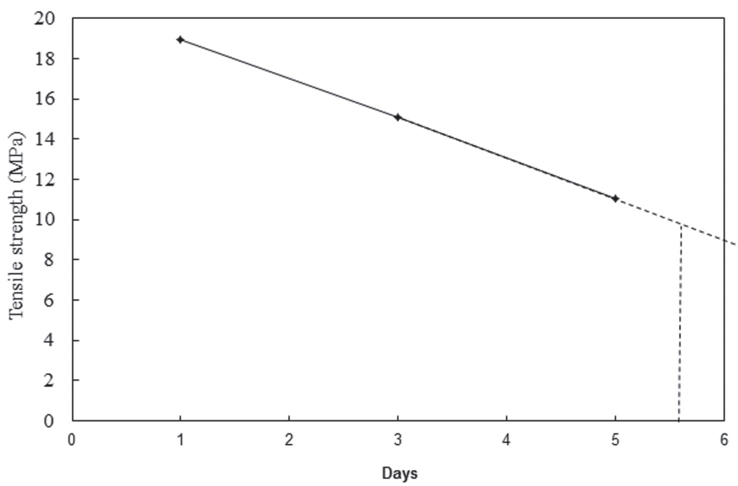

Fig. 6. Tensile strength values of NBR samples at 80^0C in sea water

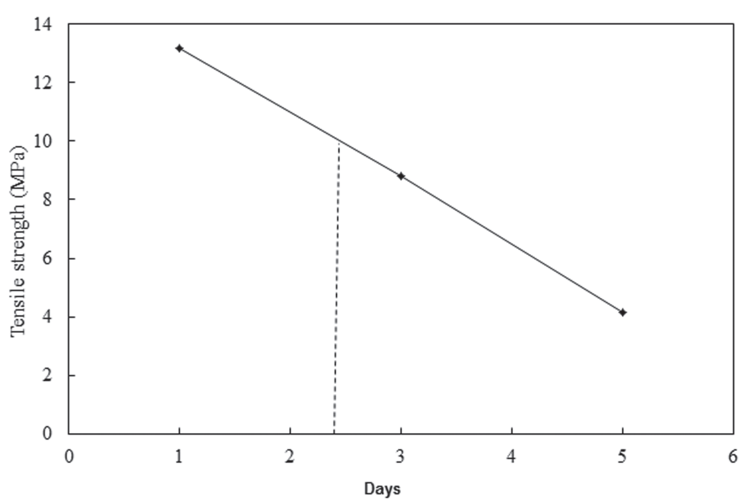

Fig. 7. Tensile strength values of NBR samples at 90^0C in sea water

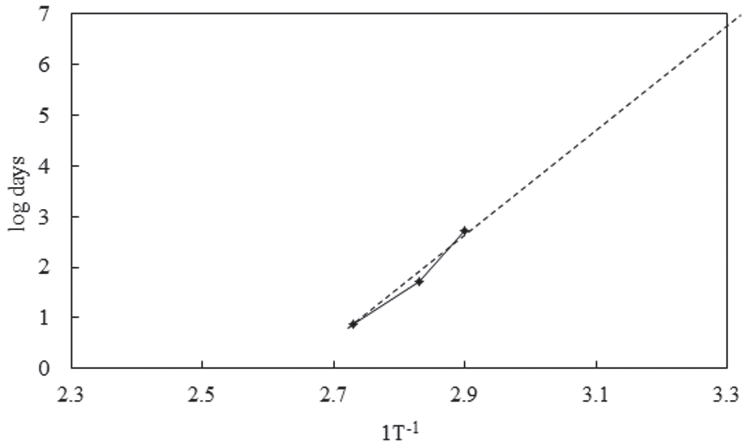

Fig. 8. Plot of Log days against 1/K - in sea water for NBR

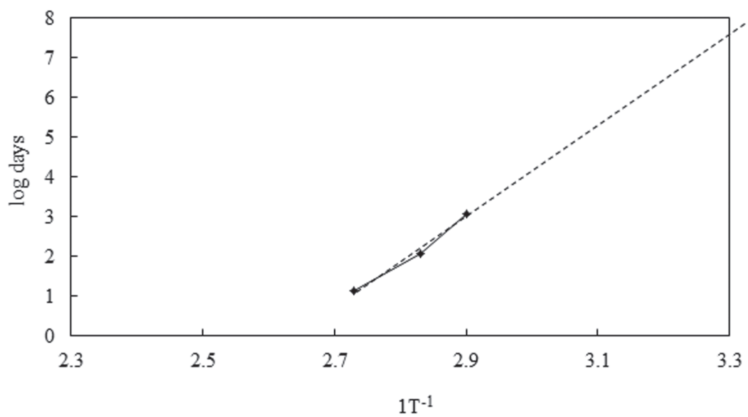

Fig. 9. Plot of log days against 1/T for EPDM in air

Figure 2. When the graph is extrapolated to tensile strength of 10 MPa, the number of days to reach the agreeable level of tensile is 8.1 as per the plot. In the same manner the tensile strengths at 90^0C in air were plotted against the number of ageing days and the plot was extrapolated to minimum service tensile strength of 10 MPa and the plot is shown in Figure 3. When the graph is extrapolated to tensile strength of 10 MPa, the number of days to reach the agreeable level of tensile is 3.1 as per the graph.

The logarithmic functions of days for minimum serviceable tensile strengths obtained from the graph and 1/T are shown in Table 3. Log days were plotted against 1/T and the plot is shown in Figure 4. When the graph is extrapolated to 1/T for room temperature (3.3×10^{-3}) we got log days as 7.5. Similarly, the experiment was repeated with sea water ageing and the tensile strengths at 70^0C, 80^0C and 90^0C are shown in Table 4.

Tensile strength values of NBR samples aged at 70^0C, 80^0C and 90^0C in sea water were plotted against days of ageing and is shown in Figure 5, 6 and 7. The logarithmic functions of days and 1/T in sea water are shown in Table 5. Log days were plotted against 1/T in sea water and the plot is shown in Figure 8. When the graph is extrapolated to 1/T for room temperature (3.3 x 10^{-3}) we get log days as 6.9.

Similarly, the experiments were repeated for EPDM and NR. Plot of log days against 1/T for EPDM in air and sea water are shown in Figure 9 and 10 and the plot for NR in air and sea water are shown in Figure 11 and 12.

Table 6. **Formulation for EPDM rubber compound**

Ingredients	Parts per hundred (Phr)
EPDM	100
ZnO	5
Stearic Acid	1
HAF black	40
Napthenieic oil	4
MBTS	3
TMTD	1
Sulphur	1.5

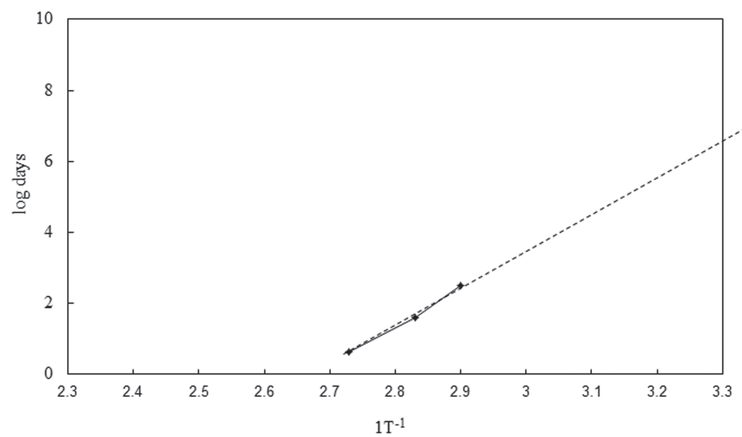

Fig. 10. Plot of log days against 1/T for EPDM in sea water

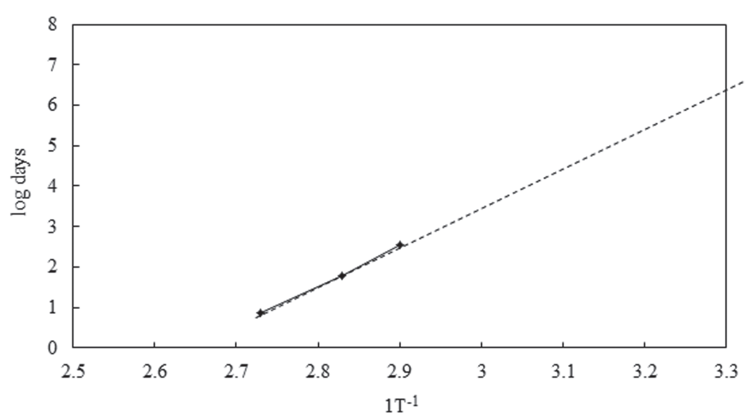

Fig. 11. Plot of log days against 1/T for NR in air

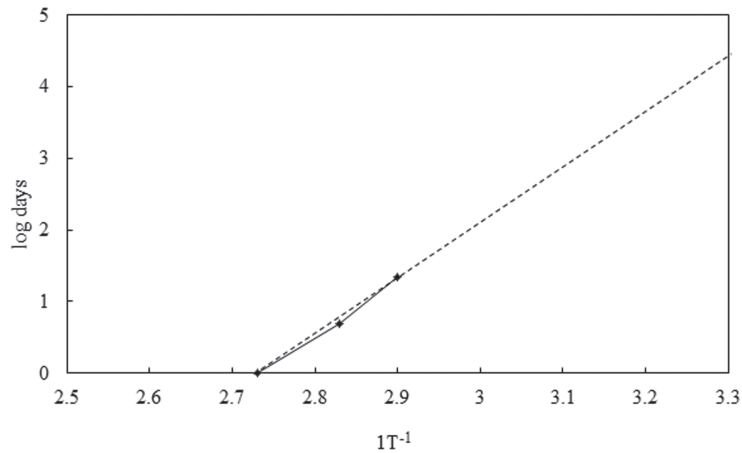

Fig. 12.Plot of log days against 1/T for NR in sea water

Table 7. **Formulation for natural rubber compound**

Ingredients	Parts per hundred (Phr)
Natural rubber	100
ZnO	5
Stearic Acid	2
TDQ	1
HAF black	40
Napthenieic oil	4
CBS	1
Sulphur	3

CONCLUSION

Different test samples of NBR, EPDM and NR were subjected to ageing at different temperatures in air and sea water. When tensile strengths under different temperatures in air were plotted against number of days of ageing and extrapolated to an agreeable tensile strength of 10 MPa we got the number of days required to reach the agreeable tensile strength. When log days in air to reach tensile of 10 MPa for the NBR samples were plotted against 1/T and extrapolated to 1/T for room temperature (3.3×10^{-3}) we got log days for room temperature as 7.5. From this we get serviceable days as 1808 days. This shows that an NBR product made out of the present formulation can give a service life of 1808 days in air.

Similarly, when log days in sea water to reach tensile of 10 MPa are plotted against 1/T and extrapolated to 1/T for room temperature (3.3×10^{-3}) we got log days for room temperature as 6.9. From this we get serviceable days as 992 days. This shows that an NBR product made out of the present formulation can give a service life of only 992 days in sea water.

In a similar way the experiment was repeated with EPDM and NR samples and found that a product made out of EPDM rubber of the formulation studied can give a service life of 2208 days in air and 854 days in sea water and an NR product of the formulation studied can give a service life of 633 days in air and 81 days in sea water.

The result was found to be in tune with actual results. It was found that the submarine beadings made out of NBR and EPDM are giving service life nearly up to three years where as that made by NR was giving only three months life.

REFERENCES

Bernstein, R. and Gillen, K.T. (2009). Predicting the lifetime of Fluorosilicone O-rings. *Polymer Degradation and Stability*, **94**(12): 2107-2113.

Celina, M., Gillen, K.T. and Assink, R.K. (2005). Accelerated ageing and lifetime prediction. Review of Non-Arrhenius behavior due to two competing processes. *Polymer Degradation and Stability*, **90**(3): 395-404.

Chapman, R. E., Butry, D.T., Huang, A.L and Thomas, D.S. (2009). *Benefits and costs of research: A case study of improved service life prediction*. NIST Technical Note 1650, National Institute of Standards and Technology, Gaithersburg, U.S. 199 p.

Eby, R.K. (1979). *Durability of macromolecular materials.* American Chemical Society, Washington, D.C., pp. 11-12.

George, B., Alex, R. and Mathew, N.M. (2000). Modified forms of natural rubber. In: *Natural Rubber Agromanagement and Crop Processing (*Eds. P.J. George and C.Kuruvilla Jacob). Rubber Research Institute of India, Kottayam, India, pp. 453-470.

George, B., Alex, R. and Mathew, N.M. (2000). Modified forms of natural rubber. In: *Natural Rubber Agromanagement and Crop Processing (*Eds. P.J. George and C.Kuruvilla Jacob),Rubber Research Institute of India, Kottayam, India. pp. 453-470.

Hsuan, Y.G. and Guan, Z. (1997). Evaluation of the oxidation behavior of polyethylene geomembranes using oxidative induction time tests. In: Oxidative Behaviour of Materials by Thermal Analytical Techniques, (Eds. A.T. Riga and G.H.Patterson), ASTM International, West Conshohocken, PA., pp. 76-90.

Hsuan, Y.G. and Koerner, R.M. (1993). Can outdoor degradation be predicted by laboratory acceleration weathering. Geotechnical Fabrics Report, **11**(8): 12-16.

Hsuan, Y.G. and Koerner, R.M. (1998). Antioxidant depletion lifetime in high density polyethylene geomembranes.*Journal of Geotechnical and Geoenvironmental Engineering*, **124**(6): 532-541.

Kelen, T. (1983). Polymer Degradation**,** Van Nostrand Reinhold Co., New York, 211 p.

Mott, P.H. and Roland, C.M. (2001). Ageing of natural rubber in air and seawater. *Rubber Chemistry and Technology*, **74**(1): 79-88.

Roland, C.M. (2009). Vagaries of elastomer service life prediction. Plastics, Rubber and Composites., Macromolecular Engineering, **38**(8): 349-354.

Shlyapnikov, Y.A. Kiryushkin, S.G. and Marin, A.P (1996). *Antioxidative Stabilization of Polymers*. Taylor and Francis, London, 245 p.

Suits, L.D. and Hsuan, Y.G. (2003).Assessing the photo-degradation of geosynthetics by outdoor exposure and laboratory weatherometers. *Geotextiles and Geomembranes,* **21**(2): 111-122.

Thomas, D.S. (2014). Economic impact of improved service-life prediction for seams in low-slope EPDM roofing. In: *Ideas to Impact: How Building Economic Standards Keep you on track, (*Eds. R. Chapman and M. Goodkind). ASTM International, West Conshohocken, PA, pp. 127-148.

Wang, W. and Qu, B. (2003). Photo and thermo-oxidative degradation of photocrosslinked ethylene-propylene-diene terpolymer. *Polymer Degradation and Stability*, **81**(3): 531-537.