

## Thermal and Thermo-Mechanical Behavior of Butyl based Rubber Exposed to Silicon Oil at Elevated Temperature

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**Summary:** Silica reinforced rubbers are used as chemical resistant seals at high temperature. In this study the effect of alkali and silicon oil on the thermal and thermo-mechanical properties of the silica reinforced butyl rubber exposed as an interface between two liquid media at elevated temperature is investigated. Rubber bladder containing alkaline solution was immersed in silicon oil at 195±5°C for multiple cycles and loss in its thermal, thermo-mechanical and mechanical properties were studied by TGA, DMA and Tinius Olsen Testing Machine supported by FTIR and Optical microscopy. It was observed that the thermal and thermo-mechanical properties of butyl rubber were negatively affected due to leaching out of silica filler embedded in an organic matrix at elevated temperature. The thermal stability of exposed rubber was decreased around 200°C and the loss of storage modulus was observed up to 99.5% at -59°C.

Key words: Butyl rubber, Silica reinforcement, Silicon oil, Thermo-mechanical, DMA, Rubber bladder.

### Introduction

Rubbers are natural or synthetic polymeric materials which are elastic at room temperature. Their high and reversible extensibility and damping properties distinguish them from other materials [1]. The cross linking of polymeric composites such as rubbers play the primary role in controlling their properties. Butyl rubber is of prime importance due to its wide ranging applications. Butyl rubber is a copolymer of isobutylene with a few percent of isoprene (0.5-3%) [2]. Uncured butyl rubber is thermoplastic but may be cross-linked or vulcanized using sulfur. The physical properties of butyl rubber can be improved tremendously by cross linking. The cross linked butyl rubbers exhibit wide utility because of their improved physical properties. The butyl rubber is extensively used in various applications, especially where resistance to air permeation is required. General applications of butyl rubber include oil seals, heat resistant parts, inner tires and tubes, cable insulation, vibration dampers, pharmaceutical stoppers, automotive parts protective clothing and gas masks [3-5].

Besides cross linking, additives and fillers play an important role in controlling the physical properties of butyl rubber. The physical properties of butyl rubber composite with silica can be easily tailored using a number of additives and fillers, used as plasticizers, colorants, stabilizers and flame retardants. The transport of solvents through polymers is influenced by several factors such as the physical and chemical structure of the polymer, cross linking density, shape and size of solvent molecules,

temperature and the type and concentration of fillers [6]. The degradation of butyl rubber has been extensively studied under different conditions namely thermal, thermo-oxidative, mechanical, catalytic, chemical, electro-chemical and radiation induced ozonolysis [7-20]. Sorption and diffusion of kerosene oil were investigated through butyl rubber composites reinforced with different concentration of titanium carbide ceramic [21]. The thermal ageing effects were also studied by keeping the samples in the hot air oven for 7 days at 70°C [22]. The trends of mechanical properties such as tensile strength, modulus at 300% elongation and strain at break were also compared. In comparison to unfilled samples, micron-sized filler reinforced systems exhibit higher ageing resistance. Natural rubber (NR) and carboxylated styrene butadiene rubber lattices and their blends were studied by thermo gravimetric method [23]. The properties of aged samples were found to decrease due to chain depletion. Water absorption properties of water-swallowable rubber (WSR) were also investigated [24]. It is found that the degree of water absorption, water absorption rate and the degree of weight loss were increased while tensile strength and elongation at break decreased with increasing quantity of super absorbent polymer (SAP) in the blends. The effect of thermal aging on mechanical properties of vulcanized natural rubber and Chitosan blend (NR/CS) were examined [25], which showed reduced swelling rate due to the tortuosity of the path and the reduced transport area in blended samples. In order to realize the full potential of the applications of butyl elastomer, it is

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necessary to have knowledge of its limitations, especially with regard to its degradation under various conditions. In this study we have tried to identify the structural behavior and thermo-mechanical behavior of butyl rubber under acute temperature and strong alkaline interfacial exposures.

## Results and Discussion

### FT-IR Analysis

To record the FT-IR spectrum, both the samples, i.e. oil exposed and unexposed were mixed with KBr and pressed into pellets for measurement. All the specimens were sufficiently thin to be within a range where the Beer-Lambert law is obeyed. Silica siloxane in butyl rubber composite exhibits IR in the range of 1260-1000  $\text{cm}^{-1}$  [26]. The stretching and bending vibrations for Si-O-Si, Si-OH, Si-O and Si-O-C were observed in the range of 1200-1000  $\text{cm}^{-1}$ . The bands at 1023 and 1104  $\text{cm}^{-1}$  were attributed to the linear and cyclic asymmetric and symmetric stretching. A band at 801  $\text{cm}^{-1}$  confirms the presence of Si-O bond. Before reaction Si-O-Si and Si-O-C bands appeared in the region 1023 and 1104  $\text{cm}^{-1}$  respectively and -Si-C- is in the region of 801  $\text{cm}^{-1}$ . Butyl rubber peaks at 2929 and 1240  $\text{cm}^{-1}$  are due to the methyl stretching and rocking respectively. In both unexposed and exposed rubber, the peak positions are not changed but the peak intensities are decreased in the oil exposed rubber which indicates the loss of silica from the rubber matrix. (Fig. 1)

### Thermogravimetric Analysis

Thermal decomposition of the two rubber samples was studied to investigate their thermal stability, purity and fragmentation pattern in the temperature range 50-1000 °C. Kinetic parameters such as activation energy ( $E_a$ ), order of reaction ( $n$ ), enthalpy ( $H$ ) and entropy ( $S$ ) were calculated using Horowitz [27] and Coats methods [28]. Unexposed rubber followed a single step decomposition pattern as shown in Fig. 2 which showed a 68.3% weight loss in temperature range 400-550°C with the order of 1.17 and the activation energy of 102.58 kJ/mole. The enthalpy of the reaction is 98.45 kJ/mole whereas entropy is 205.21 J/mole K. The exposed rubber is just stable up to 190°C and then decomposes in two steps. First decomposition occurs

from 195-395 °C with a 48.5% weight loss. This step required activation energy of 24.6 kJ/mole with the order of reaction as 0.94. The second decomposition step which occurred from 405-515°C showed a 33.77 % weight loss with the order of 0.98 and activation energy as 105.42 kJ/mole. The enthalpy of the two steps is 21.9 and 101.42 kJ/mole whereas the entropy is -112.71 and 234.98 J/mole K respectively as shown in Table-1. The results reflect that in exposed rubber at some elevated temperature, the filler contents of the rubber matrix has leached out hence resulting in loss of thermal stability of an embedded organic network of the composite moiety.

### Dynamic Thermo-mechanical Analysis

Fig. 3 shows the comparative curve of storage modulus of the two samples. The graph clearly indicates that the elastic strength of unexposed rubber is very high as compared to exposed rubber. The storage modulus of unexposed rubber at -59.9°C is  $2.8 \times 10^9$  Pa while that of exposed rubber is  $1.16 \times 10^8$  Pa. This shows that elastic strength of unexposed rubber is 4.09% higher than exposed rubber. As the 1 hour boiling of silica reinforced butyl rubber intact with a ternary mixture of  $\text{N}_2\text{H}_4$ -NaOH- $\text{H}_2\text{O}$  at 195°C has adverse effect on the thermo-mechanical properties. The strong damaging media, i.e. silicon oil destroys the chains of silica and has a dramatic negative effect on the strength of material by directly affecting the reinforcement. Similarly it is observed from the Fig. 4 that the loss modulus of unexposed rubber is also high as compared to the exposed rubber. At -59.9°C the loss modulus is decreased from  $1.14 \times 10^9$  Pa to  $5.27 \times 10^6$  Pa which is clearly showing that an exposure to oil decreased the viscosity of the material and as a result the loss modulus was also decreased. The maxima of  $\tan\delta$  curves shows that the glass transition temperature of unexposed rubber is around -45.69°C while after an exposure to damaging media it is shifted to -75.88°C (Fig. 5). The high glass transition of rubber reflects its high mechanical strength. The silicon oil treatment destroyed the silica filler which complements the TGA results. The study of thermo-mechanical behavior by DMA showed that the mechanical losses observed in the exposed rubber were very high as compared to unexposed rubber.

Table-1: Kinetic parameters for unexposed and exposed composite rubber.

Sample Name	Temp. range (°C)	Activation energy (kJ/mole)	Enthalpy (kJ/mole)	Entropy (J/mole K)	Order of Reaction (n)
Unexposed rubber	400-550	102.58	98.45	205.21	1.17
	195-395	24.6	21.9	-112.71	0.94
Exposed rubber	405-515	105.42	101.42	234.98	0.98

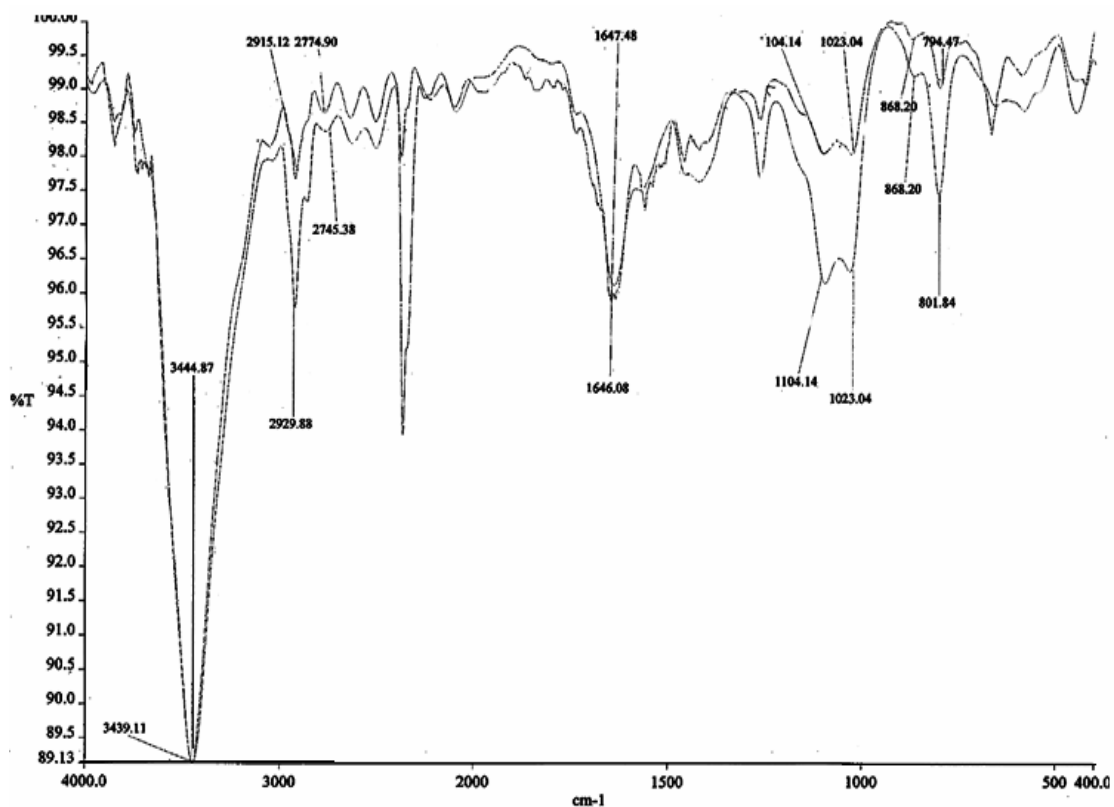


Fig. 1: FTIR spectra of unexposed (Bottom) and exposed butyl rubber (Upper).

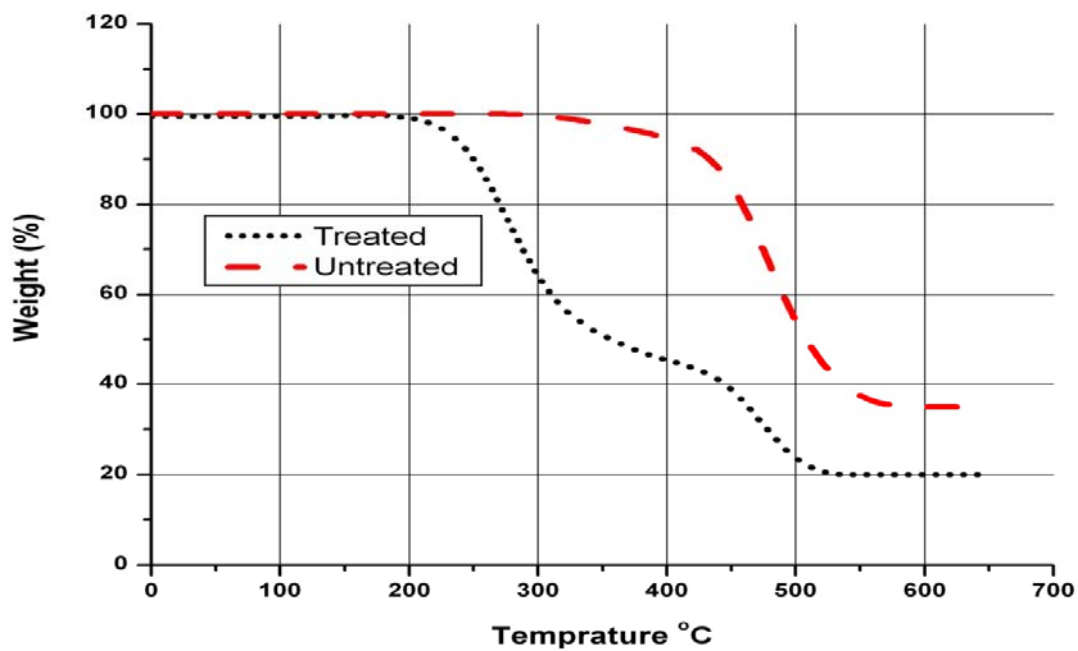


Fig. 2: Thermal decomposition pattern of unexposed and exposed composite rubber.

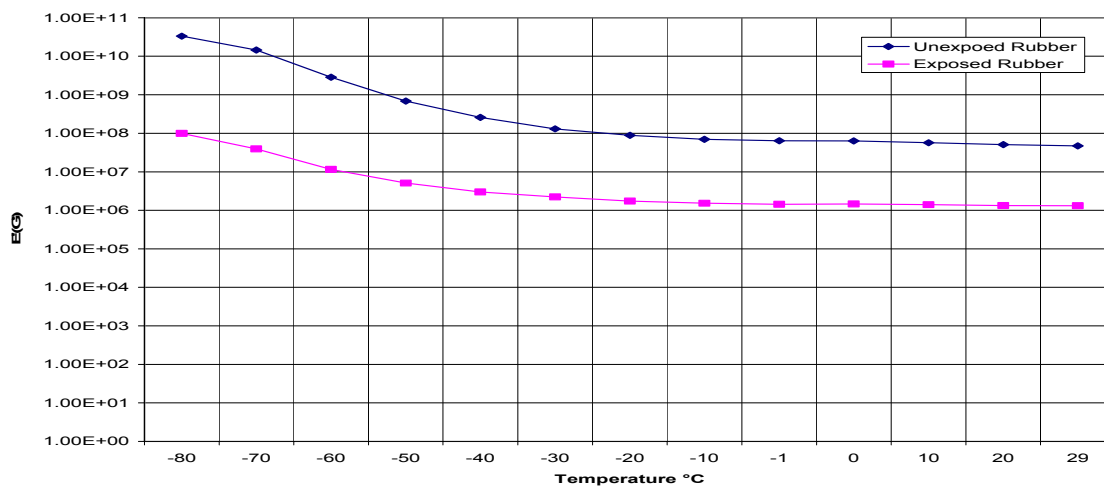


Fig. 3: Storage modulus curve of unexposed and exposed rubbers.

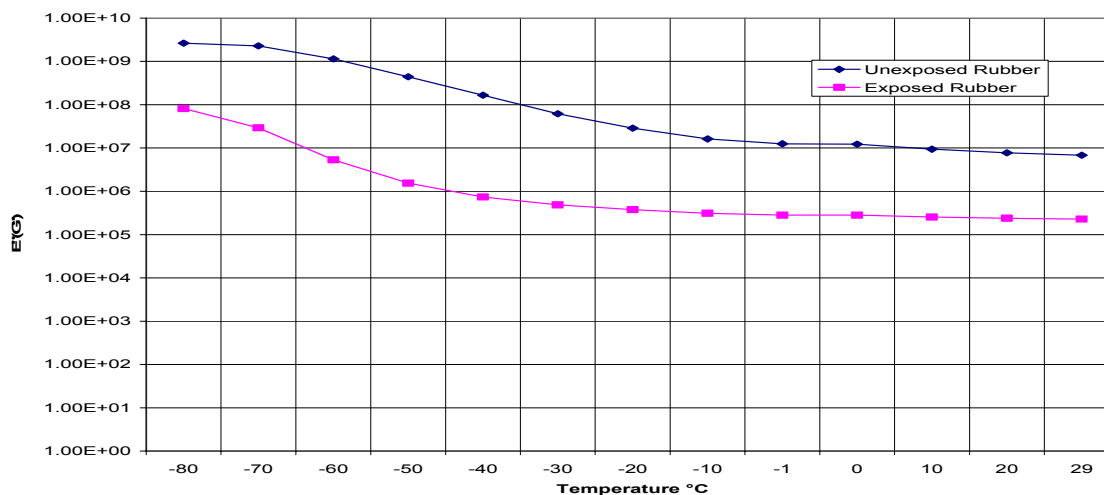


Fig. 4: Loss modulus curve of unexposed and exposed rubbers.

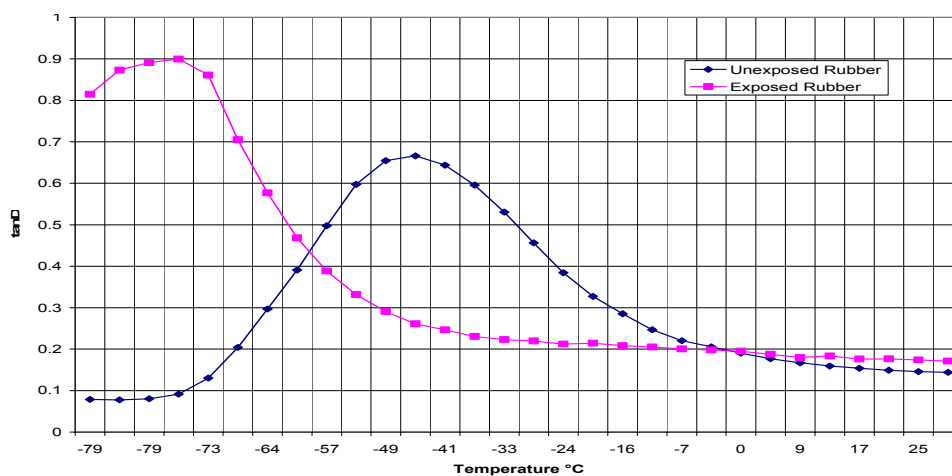


Fig. 5: tanD curves for unexposed and exposed rubbers.

The storage and loss moduli values were also very helpful for the calculation of cross link density (XLD) and viscosity ( $\eta$ ) of rubbers at different temperatures [29]. The crosslink density (XLD) as the molar number of elastically effective network chain per cube centimeter of the material was calculated from the storage modulus region according to Equation:

$$XLD = E' / 3RT$$

$E'$  is the elastic storage modulus,  $R$  is the ideal gas constant and  $T$  is the temperature in K.

The cross link density curves of the exposed and unexposed rubbers (Fig. 6) were clearly showing the strong reinforcement effect of high silica contents in the unexposed rubber.

The cross link density of exposed and unexposed rubbers measured at different temperatures is given in the Table-2. It shows that the difference of XLD of exposed and unexposed rubber at each temperature was manifold reflecting the high strength of unexposed rubber.

Table-2: Cross link density (XLD) of unexposed and exposed rubber.

Sr. No	Temperature °C	XLD unexposed rubber	XLD exposed rubber
1.	-70	3042593	8223
2.	-60	569823.7	2277.251
3.	-50	128951.5	946.2865
4.	-40	45816.14	535.2996
5.	-30	22078.94	364.498
6.	-20	14241.29	278.4359
7.	-10	10788.6	237.3251
8.	-1	9497.888	219.4626
9.	10	8056.744	198.7816
10.	20	7018.529	183.3856

The viscosity of exposed and unexposed rubbers was also calculated according to the Equation:

$$\eta = E'' / 2\pi f$$

$E''$  is the loss modulus and  $f$  is the frequency.

The viscosity of exposed rubber was very low as compared to unexposed rubber clearly showing enhanced strength/stiffness of material before the oil treatment at the elevated temperatures. The high concentration of silica reinforcement in an unexposed rubber increased the viscosity of material by restricting its mobility at interface region.

#### Mechanical Properties of Unexposed and Exposed Composite Rubber

The mechanical properties of exposed and unexposed rubber composites were calculated as

shown in Table-3. The results indicate that mechanical properties of the unexposed rubber are better than exposed rubber due to the high percentage of silica reinforcement that strengthens the rubber matrix and makes it suitable for high temperature pervaporation application of strong alkali.

Table-3: Mechanical properties of unexposed and oil exposed Rubber.

S.No	Sample ID	UTS (MPa)	Elongation (%)	E (MPa)	Hardness (shore)	SiO <sub>2</sub> (%age)
1	Unexposed rubber	12.46	834	1.71	0.85	33
2	Exposed rubber	3.275	461.00	0.66	0.78	18

#### Optical Microscopy

The structural morphology of butyl rubber before and after treatment in silicon oil was observed under an optical microscope. The image A of Fig. 7 clearly shows that the rubber before treatment is comparatively smooth and homogeneous while after an exposure in silicon oil, the voids were developed as seen in the B, C and D optical images of samples (Fig. 7). The silicone oil treatment at this high temperature has a direct effect on the breaking of the filler chains and as a result the pits were developed in the matrix. These developed voids are the clear indication of the loss of the strengthening effect of inorganic reinforcement. The harsh medium destroys the silica and has an adverse effect on the strength of the material. The optical microscope images of the unexposed and exposed rubbers are in very close agreement with the thermal, thermo-mechanical and mechanical response of the material (Fig. 8).

#### Experimental

##### Material and Methods

Butyl rubber bladder received from Jiang Xi Zhongxing Sporting Goods Co. Ltd(China) contained SiO<sub>2</sub> (33%) as filler, butyl rubber content (60%) and hydroxyethyl cellulose (5%) as determined gravimetrically. Various analytical reagents such as acetone, dichloromethane, toluene, hydrazine (98%) and NaOH were purchased from local market and used as received.

Butyl rubber was used as an interface between two liquid media of silicon oil and strong aqueous alkali solution. The rubber was thermally heated up to 195±5°C for 10 to 15 times and its thermal and thermo-mechanical behavior was recorded by different techniques.

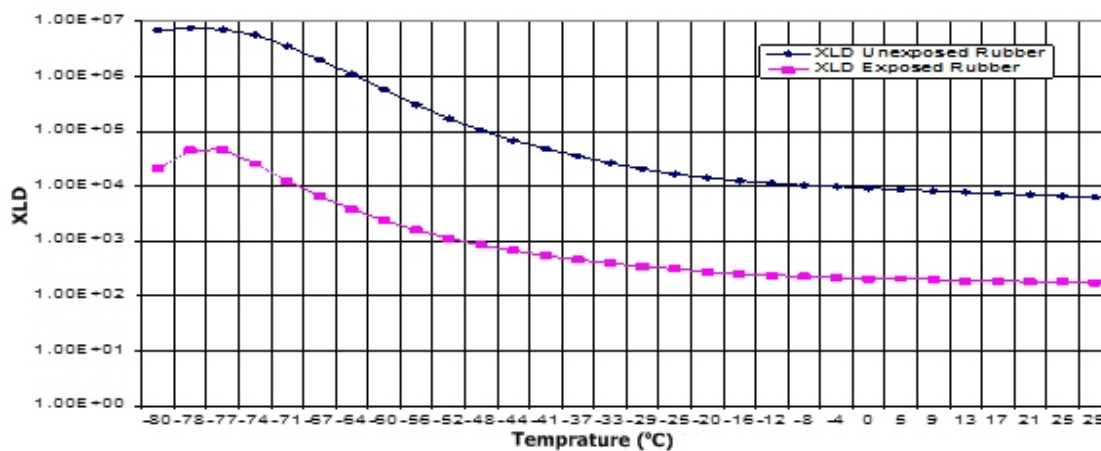


Fig. 6: Cross link density (XLD) of unexposed and exposed rubber.

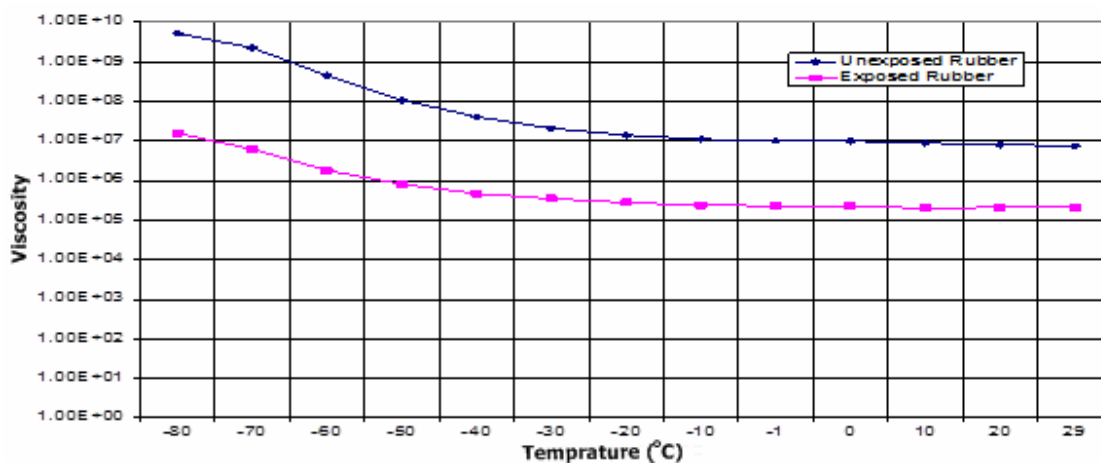


Fig. 7: Viscosity curve of unexposed and exposed rubber.

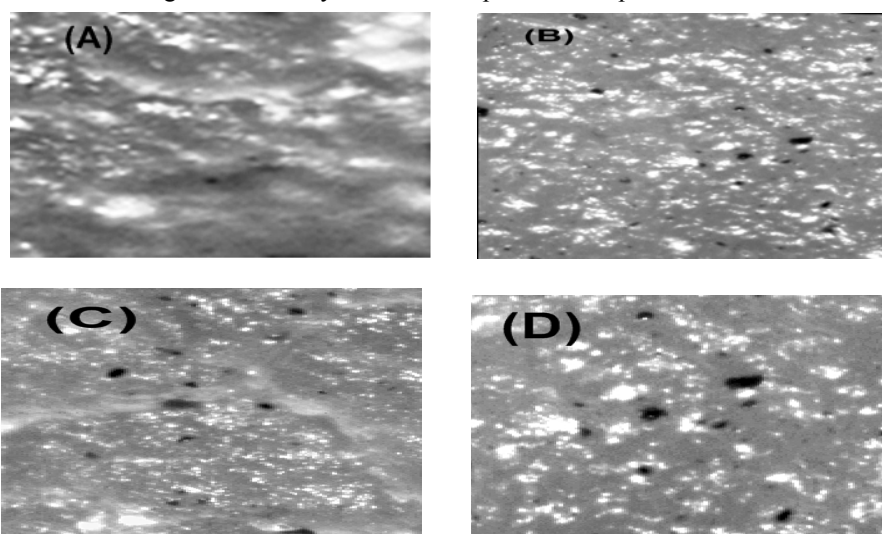


Fig. 8: Optical microscope images of unexposed rubber (A) and exposed rubber (B, C, D).

Silica contents were estimated gravimetrically in a furnace (MF 9-134 HOBERSAL, Spain) at 1000 °C in the air. The IR spectra were recorded on a Fourier Transform Infrared Spectrophotometer (FT-IR) Model IR 1000 Perkin Elmer in the range of 4000-400  $\text{cm}^{-1}$  with scan rate 12 and resolution of 4 $\text{cm}^{-1}$  in KBr mixture. The thermal decomposition studies were carried out on a TGA-7 Thermal Analyzer of Perkin- Elmer. 10-15 mg of sample was taken in a platinum crucible and subjected to the controlled heating rate of 20°C/min under inert atmosphere in the range of 50-1000 °C. Dynamic Viscoelastic trends were studied with the aid of a DMA Model Pyris Diamond DMA from Perkins Elmer at 1Hz at the heating rate of 2°C/min with sample dimension 1.5×10×50 mm. Mechanical properties of exposed composite rubber samples were studied by using a Tinius Olsen testing machine H1KT at speed 100 mm/min having gauge length 35±1mm with load cell 5KN. The sample dimensions were 5×25×150 mm. Hardness of the composite rubber after an exposure in an acute environment was measured with a Deurometer Type A-Instron USA according to ASTM standard D-2240. The thickness of the sample was 5mm and diameter was 5cm. An optical microscope fitted with a camera Model MTV-1362 Mintron interfaced through a computer was used to study the morphology of the rubber. The micrographs were taken at 80x magnification to visualize the drastic effects during the elevated chronic environment.

### Conclusions

The effect of alkaline solution and silicon oil on butyl rubber composite at an elevated temperature of 195°C was investigated. The thermo-mechanical properties of elastomer depend mainly on the silica filler loading. Tensile strength, modulus, elongation and hardness were decreased dramatically with decreasing the concentration of silica. FT-IR spectroscopy revealed that the intensities of the peaks of silica decreased which is a sign of low % age of silica contents in a matrix after an exposure. The thermal analysis showed that the percentage of silica filler was decreased from 33% to 17%. The storage modulus of unexposed rubber at -59.9°C is 4.09 % higher than exposed rubber while at -59.9°C the loss modulus was also decreased from 1.14 x 10<sup>9</sup> Pa to 5.27 x 10<sup>6</sup> Pa. Viscosity and glass transition temperatures were also drastically decreased with an oil treatment at high temperature. The DMA results clearly indicated that the mechanical losses observed in the exposed rubber are very high as compared to unexposed rubber. The optical microscopic images also reflected the damaged surface of treated rubber.

As the breakdown of silica-siloxane linkages occurs, so the interaction between reinforcement and matrix decreased and as a result the thermal and thermo-mechanical properties are lost when exposed in a strong harsh medium. Therefore, the adverse effects of alkaline solution and silicon oil on butyl rubber composite at elevated temperature of 195°C was clearly interpreted by all these techniques.

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