

# Accelerated Hydrothermal Weathering of Silicone Rubber, EPDM, and Their Blends

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## SYNOPSIS

Hydrothermal weathering of the peroxide vulcanized specimens of silicone rubber, EPDM rubber, and their 50 : 50 blend carried out for various durations at different temperatures reveals that silicone is very susceptible to degradation. For example, the modulus, the strength, and the elongation at break consistently fall with aging period. For 72 h of aging at 210°C, it practically loses its rubberiness (elongation < 50%); while EPDM and the 50 : 50 blend maintain more than 100% elongation at break during the times and temperatures. While hydrolytic chain scission is the main degradation mechanism for silicone, EPDM undergoes a predominantly crosslinking reaction. The kinetics study reveals that the better retention of properties of the blends over silicone is due to an increase in the activation energy of degradation in the presence of EPDM rubber, and this protection effect is higher in liquid-phase weathering than in steam-phase weathering. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Silicone rubber is excellent for its high- as well as low-temperature properties and high oxidative resistance,<sup>1</sup> whereas the electrical properties and weather resistance of EPDM rubber are outstanding because of its hydrocarbon nature and saturated backbone.<sup>2</sup> This combination of properties has drawn the attention of researchers to develop suitable blends of silicone rubber and EPDM rubber.<sup>3-5</sup> Our previous work showed that silicone improves air aging behavior and thermal stability of EPDM.<sup>3,6</sup>

The present study aims at improving the high-temperature moisture resistance of silicone rubber by blending it with EPDM. Such modifications will be of great practical importance for applications like underwater cables, high-temperature gaskets, and seals in humid environments where silicone already has some applications. A few viable data at 170°C on the technological properties of silicone rubber justify its deteriorating nature in humid environments.<sup>7</sup> There are also reports of high-temperature behavior of silicone rubber.<sup>8-10</sup> Thus, it becomes necessary to verify the performance of silicone rubber in humid environments over a wide range of

times and temperatures, and improve its performance through its part replacement by EPDM. This article reports the data on steam- and water-resistance of these blends.

## EXPERIMENTAL

### Materials

#### *Silicone Rubber*

JSR EH5270U, type VMQ (i.e., vinyl methyl-based silicone), density 1.31 g/mL; Japan Synthetic Rubber Co., Tokyo (Japan).

#### *EPDM Rubber*

Keltan 520, DCPD containing polymer, density 0.86 g/mL, DSM (Netherlands).

#### *DCP*

Dicumyl peroxide (Di-Cup) from Hercules, Inc., Wilmington, Delaware, USA.

#### *Mixing and Vulcanization*

Blending of silicone rubber with EPDM (50 : 50 by weight) was done at 120°C in a Brabender Plasti-

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corder (PLE-330) for 5 min at 100 rpm. DCP (1.5 phr) was mixed with the individual polymers and the blend in a roll mill at room temperature. Vulcanization was done in a hydraulically operated press (Moore Press) at 170°C and 5 MPa pressure for 10 min as per the usual procedure. The vulcanizates were postcured for 2 h at 150°C in an air-circulated oven.

### Hydrothermal Weathering

Rectangular rubber slabs of 0.5 mm thickness (wt: 5–7 g, depending on the density of the specimen) were weathered one at a time in a pressure vessel. The pressure vessel is essentially a high-pressure autoclave with a vertical cylindrical chamber (80 mm  $\phi$   $\times$  300 mm). Copper gaskets were used to make the joints of the chamber totally fluid-proof. The external jacket of the chamber housed the electrical heating element. The temperature controller worked in the range of set temperature  $\pm$  1°C by an off-on mechanism using a relay device consisting of a contact thermometer.

Fifty percent of the chamber volume was filled with distilled water. For the purpose of exposure in vapor phase, the sample was hanged over the liquid phase. For liquid-phase exposure of the specimen, it was immersed in the water with the help, when necessary, of a glass sink. The inside air was replaced by N<sub>2</sub> (IOLAR 2 grade from Indian Oxygen; oxygen content < 1%) by pressurizing it at 50 atm and releasing the pressure. The process was continued twice and the release valve was locked. The set temperature reached around 2 h once the temperature controller was switched on. The specimen was weathered for the desired period. It was cooled to the ambient temperature for 3 h once the heating was turned off. The specimens were taken out after dismantling the assembly.

### Need for Separate Weathering in Steam and Water

In a particular set of experiments, the temperature and pressure of the system (the saturated steam pressure at the selected temperature) remained constant. Apparently, identical results should be obtained irrespective of liquid-phase or vapor-phase exposure of the specimens, as the chemical potential of saturated steam and the corresponding liquid at its bubbling point are the same. But certain physical phenomena, like the possibility of leaching out of small molecular species by water or the presence of any trace amount of oxygen in the system, influences its chemical environment. Leaching of a product

molecule by water will reduce the rate of reverse reaction, and the point of equilibrium will be shifted towards the right. For hydrocarbon-type polymers, oxygen triggers a series of thermo-oxidative processes. The equilibrium concentration of oxygen in vapor phase and in liquid water phase need not be the same. Again, the O<sub>2</sub> molecules in the liquid medium will approach the specimen surface slowly, as diffusivity, in general, is lower in liquid medium than in the vapor medium. Thus, a kinetically different extent of degradation is expected to occur, depending on the medium. This difference is likely to be reflected in the physical properties of the weathered specimens.

### Drying of the Specimen

The specimens were dried in a vacuum oven at 50°C and 0.1 torr pressure for 24 h to get a constant weight.

### Physical Properties

Physicomechanical properties of the specimens were carried out in a computerized Zwick UTM (model 1445) as per ASTM D 412-80. Tensile strength, elongation at break, and modulus at 50% and 100% elongations were determined. The low-strain elastic modulus was determined from the slope of the tangent drawn at the initial point of the equilibrium stress-strain curve. Hardness was measured in a Shore A durometer as per ASTM D 2240. Equilibrium swelling in n-hexane and, hence, volume fraction of rubber in the swollen gel, was determined following the procedure described previously.<sup>3</sup>

## RESULTS AND DISCUSSION

### Weathering of Silicone Rubber

Results of hydrothermal weathering of silicone rubber are shown in Table I. These indicate that degradation is influenced by time and temperature of exposure and also by the medium. Qualitatively, the extent of degradation can be understood from the drop in modulus, which is caused by the scission of some of the network chains. In view of the extremely high oxidative stability of silicone and consistent decrease of modulus over the prolonged period of weathering, it is certain that hydrolytic chain scission of silicone rubber is taking place. Loss in weight of the weathered specimens also indicates the leaching of oligomeric species, which will definitely be formed in a process of random hydrolytic chain scis-

**Table I** Weathering Behavior of Silicone Rubber

Medium of Weathering	Temp (°C)	Time (h)	Mod (MPa) at the Elongation of		Tensile Strength (MPa)	Elongation at Break (%)	Wt Loss (%)	Hardness (Shore A)
			50%	100%				
Control/ without weathering	—	0	2.7	4.7	5.91	145	0	70
Steam	210	24	2.2	4.3	5.80	150	3.3	65
		48	1.9	3.2	3.50	120	4.2	60
		72	—	—	0.79	40	5.2	48
		96	—	—	0.53	20	5.7	35
	190	48	2.4	4.0	4.70	125	2.7	61
		96	1.5	—	2.20	95	3.5	57
		192	1.2	—	1.95	85	6.4	56
	170	96	2.6	4.5	5.80	135	1.8	60
		192	2.4	4.3	5.40	125	2.1	67
		384	1.8	—	2.30	90	2.9	68
Water	210	24	2.1	3.2	3.25	105	1.5	57
		48	1.7	—	2.11	95	5.2	60
		72	—	—	1.20	40	7.6	55
		96	—	—	0.89	15	9.1	57
	190	48	2.2	—	3.62	95	5.2	65
		96	1.3	—	1.95	70	9.2	64
		192	1.1	—	1.83	55	10.1	62
	170	96	2.5	—	4.20	85	1.8	65
		192	2.2	—	2.90	75	2.9	70
		384	1.4	—	2.10	85	5.6	70

sion. At any particular aging temperature, this weight loss increases with aging period. The weight loss is higher in weathering in water, indicating that water is an effective leachant for the oligomeric species. For the samples in steam phase, the weight loss is due to partial leaching of oligomeric species by the condensing steam.

Temperature is found to have a profound effect on the extent of degradation. The specimens weathered for 72 h at 210°C do not maintain even 50% elongation at break and 25% tensile strength. These values are 95% and 35% for samples weathered in water, and 120% and 60% for weathering in steam for 48 h. The results indicate a higher extent of degradation in water, and the same is also observed at other temperatures. The extent of degradation is lower at lower temperatures. Thus, the specimens aged at 190°C maintained more than 50% elongation at break and 30% tensile strength over the entire range of aging (a maximum of 192 h), and the specimens aged at 170°C for 384 h maintained more than 50% elongation and 35% tensile strength. The

hardness decreases with prolonged aging. The fall in properties is in line with the loss of oligomeric products.

#### Weathering of EPDM Rubber

The results of weathering of EPDM rubber are reported in Table II. The elongation at break is higher than 100% over a range of aging temperatures (170°C to 210°C) and times (maximum: 384 h at 170°C). Further, strength and elongation property after passing through a minima with aging period increase again. The water-aged specimens have better properties than those of the steam-aged specimens. Hardness of the specimens maintains a constant level of higher value. However, the weathering process of EPDM rubber seems to be complex, as observed from the modulus values which never deteriorate below a reference value (the same for the un-aged specimen). There is also a gain in weight from 0.1% to 1%. Thus, some reaction is taking place. Little yellowing of the transparent sheets on

**Table II** Weathering Behavior of EPDM Rubber

Medium of Weathering	Temp (°C)	Time (h)	Mod (MPa) at the Elongation of		Tensile Strength (MPa)	Elongation at Break (%)	Wt Gain (%)	Hardness (Shore A)	Vol Fraction of Rubber (V <sub>r</sub> )	Initial Elastic Modulus (E) (MPa)
			50%	100%						
Control	—		0.6	1.1	1.95	205	—	46	0.39	1.70
Steam	210	24	0.8	1.3	1.65	140	—	52	0.39	1.85
		48	0.8	1.2	1.35	120	0.1	50	0.40	1.82
		72	0.8	1.2	1.25	110	0.5	50	0.40	1.83
		96	0.9	1.4	1.48	115	0.5	51	0.40	1.90
	190	48	0.6	1.2	1.53	140	0.5	50	0.39	1.82
		96	0.7	1.3	1.82	145	0.3	50	0.40	1.87
		192	0.7	1.2	1.67	125	—	51	0.39	1.84
	170	96	0.8	1.3	1.74	155	0.7	50	0.40	1.87
		192	0.8	1.2	1.25	110	0.5	51	0.39	1.86
		384	0.8	1.3	1.65	130	0.3	52	0.39	1.87
Water	210	24	0.9	1.5	1.90	180	0.4	51	0.40	1.93
		48	0.8	1.3	1.81	150	0.3	50	0.39	1.87
		72	0.9	1.3	1.72	150	0.8	50	0.40	1.87
		96	0.9	1.4	1.92	175	0.3	51	0.41	1.90
	190	48	0.9	1.5	1.74	155	1.0	53	0.40	1.95
		96	1.0	1.8	1.85	160	1.0	53	0.41	1.97
		192	0.9	1.5	1.92	185	1.2	54	0.40	1.94
	170	96	0.8	1.5	1.66	130	0.7	52	0.40	1.94
		192	0.9	1.9	1.78	180	1.1	52	0.41	2.03
		384	1.0	1.9	1.87	155	1.2	51	0.41	2.01

aging confirms the formation of chromophoric groups by absorption of oxygen. Although oxidative degradation of EPDM is well-known, the present observations need a more complex model of aging for explanation. Presently, some crosslinking process<sup>11</sup> superimposed by oxygen diffusion controlled degradation process fully explains the observations. The higher change in modulus of the specimens exposed in the liquid phase is due to a lesser extent of oxidative degradation in these specimens, due to lower diffusivity of oxygen in the liquid phase than in the vapor phase.

An analysis of the polymer microstructure, stability of the various chemical bonds and their possible interaction, and the prevailing chemical environment might lead to a clue to the actual chemical steps occurring during the hydrothermal conditioning. In the experimental conditions, the samples are under high hydrostatic pressure. The high temperature of 170–210°C is also significant to activate chemical processes, and the mobility of polymer segments also will be high at elevated temperature.

So, the prevailing conditions will be favorable to trigger pressure-sensitive chemical processes like polymerization or some additional reaction through the unsaturation present in the molecules. Without going into the actual chemical steps, it can be argued that any prevailing unsaturation in the polymer, the strained cyclic ring structure of the diene moiety, chemical activity of different C—H bonds in the ring, and the participation of any trace amount of oxygen in thermo-oxidative processes will contribute to the final property of the aged specimens. The ultimate crosslinking process is also justified by the swelling resistance of the specimens. The aged specimens show marginally higher value for volume fraction of rubber.

#### Weathering of the Blends

Weathering behavior of the 50 : 50 blend is shown in Table III. The results clearly indicate that the presence of EPDM improves the aging behavior significantly. Thus, the elongation at break is always

Table III Weathering Behavior of 50 : 50 Blend

Medium of Weathering	Temp (°C)	Time (h)	Mod (MPa) at the Elongation of		Tensile Strength (MPa)	Elongation at Break (%)	Wt Loss (%)	Hardness (Shore A)	
			50%	100%					
Control	—		1.1	2.0	5.99	355	—	55	
Steam	210	24	1.1	2.0	3.76	210	0.2	57	
		48	1.0	1.7	3.38	245	1.7	55	
		72	0.8	1.4	2.25	165	2.0	55	
		96	0.6	1.2	2.35	200	2.5	50	
	190	48	1.0	1.9	3.07	190	1.4	56	
		96	0.9	1.6	2.51	170	1.7	52	
		192	0.7	1.5	2.30	140	1.8	58	
		384	0.8	1.7	2.50	195	1.7	52	
	Water	210	24	1.1	2.1	6.25	255	0.8	55
			48	1.0	1.9	3.88	225	3.5	60
			72	0.9	1.7	2.99	195	4.3	51
			96	0.7	1.7	2.60	140	6.2	52
190		48	1.0	2.1	4.66	210	3.1	57	
		96	0.9	1.8	4.15	231	5.7	60	
		192	1.0	1.7	3.92	215	7.1	55	
		384	0.9	1.9	3.37	180	3.0	60	
170		96	1.0	2.1	5.39	225	1.3	54	
		192	1.0	2.0	3.29	145	1.7	58	
		384	0.9	1.9	3.37	180	3.0	60	

higher than 100% over the entire range of aging temperatures and times. The tensile strength and modulus values are never below 35% and 55%, respectively. The effect of crosslinking in EPDM phase is observable at low exposure times in liquid mediums. At higher periods, the degradation of silicone takes a decisive role in determining the physico-mechanical properties and, hence, the strength and modulus fall at higher exposure times. This behavior is quite understandable from the degradation behavior of the individual components. The deterioration in strength and modulus is less in the specimens exposed in liquid medium due to a higher level of crosslinking reaction in the EPDM phase of these specimens.

#### Kinetics of Degradation in Steam and H<sub>2</sub>O

The kinetic study was carried out for the vulcanizates of silicone rubber and its 50 : 50 blend with EPDM to make a quantitative analysis of hydrolytic chain scission process of silicone and the extent of protection offered by EPDM to silicone. For this

purpose, equilibrium stress-strain curves were generated using a very low strain rate (0.1 min<sup>-1</sup>). Two different cases of degradation, e.g., degradation of silicone network and that of the 50 : 50 blend were treated separately.

In silicone rubber, the mode of degradation is random hydrolytic chain scission. The extent of reaction ( $p$ ) can be correlated with the probability ( $p_s$ ) that a particular network chain undergoes scission:

$$p_s = 1 - (1 - p)^n \quad (1)$$

where  $n$  is the number of "mers" per network chain.

Thus, the probability ( $p_e$ ) that a particular network chain still remains elastically coupled between two crosslink points is given by:

$$p_e = (1 - p)^n \quad (2)$$

According to the theory of rubber elasticity as described by Flory<sup>12</sup> and Mark,<sup>13</sup> the equilibrium initial elastic modulus ( $E$ ) is given by:

**Table IV Results<sup>a</sup> of Hydrolytic Degradation Kinetics of Silicone in Steam**

Temp (°C)	Time (h)	Initial Elastic Modulus (E) (MPa)	Extent of Reaction (p) <sup>b</sup> × 100	Zero-Order Rate Constant (ka) × 10 <sup>8</sup> (sec <sup>-1</sup> )	Activation Energy (E <sub>a</sub> ) (kcal · mol <sup>-1</sup> )
210	0	5.4	—		
	24	3.5 (3.1)	2.3 (2.8)	25.3 (32.4)	
	48	2.3 (1.8)	4.2 (5.3)		
	72	1.4 (0.9)	6.5 (8.5)		
190	48	4.3 (4.1)	1.1 (1.4)		
	96	3.4 (3.0)	2.3 (2.9)	6.4 (8.1)	29.2 (30)
	192	2.2 (1.8)	4.4 (5.4)		
170	96	4.9 (4.8)	0.5 (0.6)		
	192	4.3 (4.1)	1.1 (1.4)	1.4 (1.9)	
	384	3.6 (3.2)	2.0 (2.6)		

<sup>a</sup> Corresponding results for degradation in liquid medium are given in parentheses.

<sup>b</sup> Calculated using eq. (2).

**Table V Results<sup>a</sup> of Hydrolytic Degradation Kinetics of 50 : 50 Blend in Steam**

Temp (°C)	Time (h)	Initial Elastic Modulus (E) (MPa)	Extent of Reaction (p) <sup>b</sup> × 10 <sup>3</sup>	Zero-Order Rate Constant (ka) × 10 <sup>9</sup> (sec <sup>-1</sup> )	Activation Energy (E <sub>a</sub> ) (kcal · mol <sup>-1</sup> )
210	0	2.30	—		
	24	2.02 (2.12)	1.8 (1.0)		
	48	1.68 (1.91)	4.0 (2.4)	24.1 (14.2)	
	72	1.41 (1.71)	6.1 (3.7)		
	96	1.20 (1.60)	8.1 (4.7)		
	190	48	2.16	0.7 (0.4)	
190	96	2.00	1.7 (1.0)	4.9 (3.1)	36.8 (37)
	192	1.75	3.5 (2.0)		
	170	96	2.25 (2.28)	0.2 (0.1)	
170	192	2.21 (2.25)	0.5 (0.3)	0.7 (0.4)	
	384	2.12 (2.18)	1.1 (0.6)		

<sup>a</sup> Corresponding results for degradation in liquid medium are given in parentheses in the next row.

<sup>b</sup> Calculated using eq. (2).

$$E = 3\nu RT \quad (3)$$

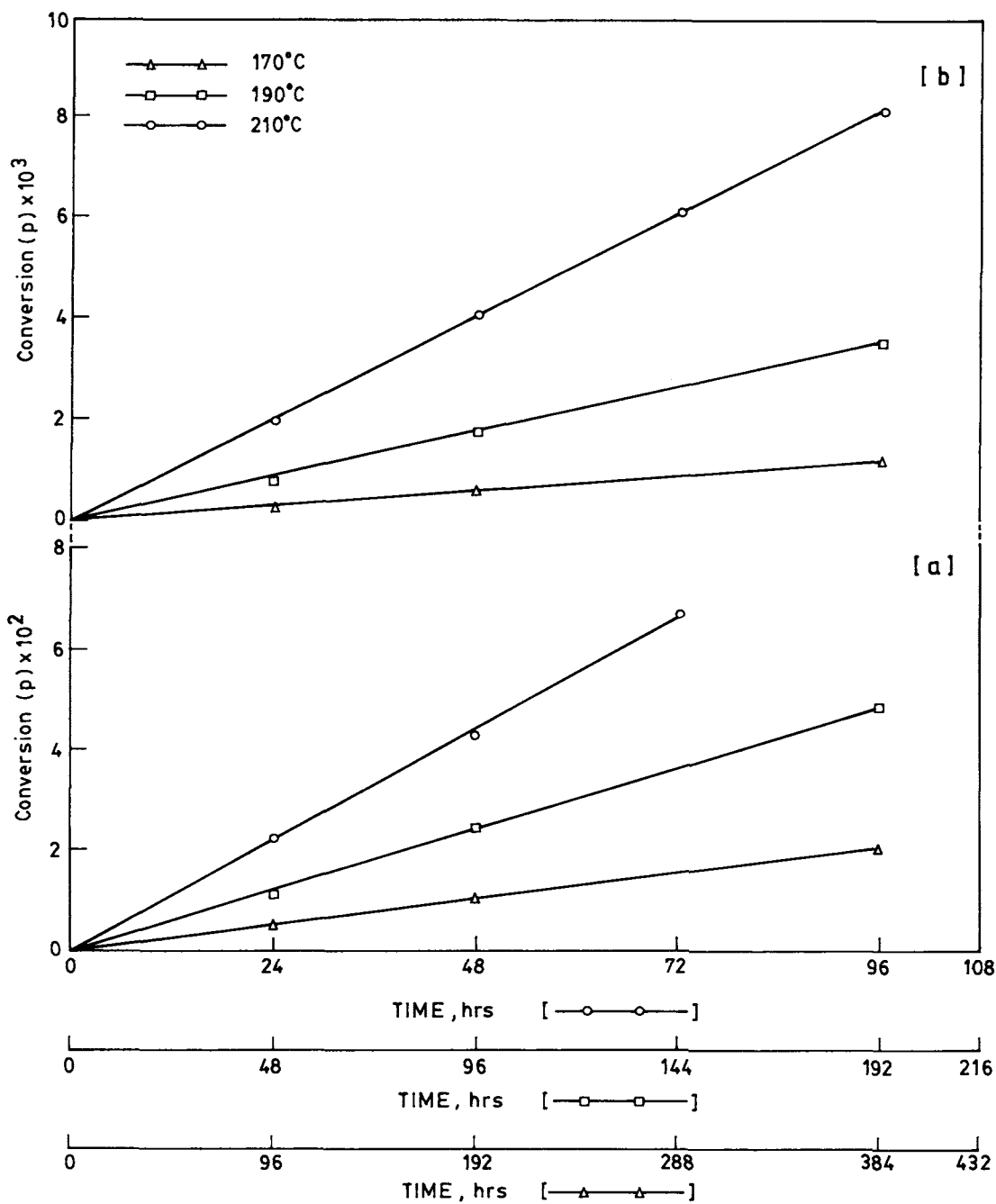
$$p_e = \nu_w/\nu = E_w/E \quad (4)$$

where  $\nu$  = molar density of network chains,  $R$  = universal gas constant, and  $T$  is absolute temperature ( $^{\circ}\text{K}$ ) of measurement.

The value of  $p_e$  [Eq. (2)] is also determined using the following equation:

where the subscript  $w$  refers to weathered specimen.

For the un-aged specimen,  $n$  could be precisely calculated, as the nonideality arising from end-groups would remain at a minimum, from the relations:



**Figure 1** Isothermal conversion-time plots for the steam phase hydrolysis of (a) silicone rubber and (b) 50 : 50 blend of silicone rubber and EPDM.

$$n = M_c/M_0 = \rho/(vM_0)$$

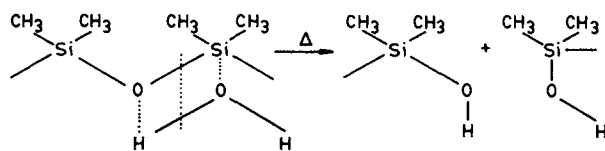
$$= (\rho \cdot 3 RT)/(E \cdot M_0) = (3 \rho RT)/(E \cdot M_0) \quad (5)$$

where  $M_c$  is the mol wt of the network chain between two crosslink points,  $M_0$  is the "mer" molecular wt, and  $\rho$  is the density of the polymer.

The extent of reaction ( $p$ ) was calculated from Eq. (2) using the known values of  $n$  and  $p_e$ .

For 50 : 50 blend, degradation is a combination of hydrolytic chain scission in silicone and predominant crosslinking reaction in EPDM. The crosslinking reaction in EPDM is evident from swelling behavior and initial elastic modulus (Table II). Volume fraction of rubber ( $V_r$ ) in equilibrium swollen gel is never below the reference value (that of un-aged specimen), and most cases, it is marginally higher. Elastic modulus is also on the higher side. All the kinetic parameters were calculated for this blend system through the relations described in the previous paragraph using average value for density and "mer" molecular weight.

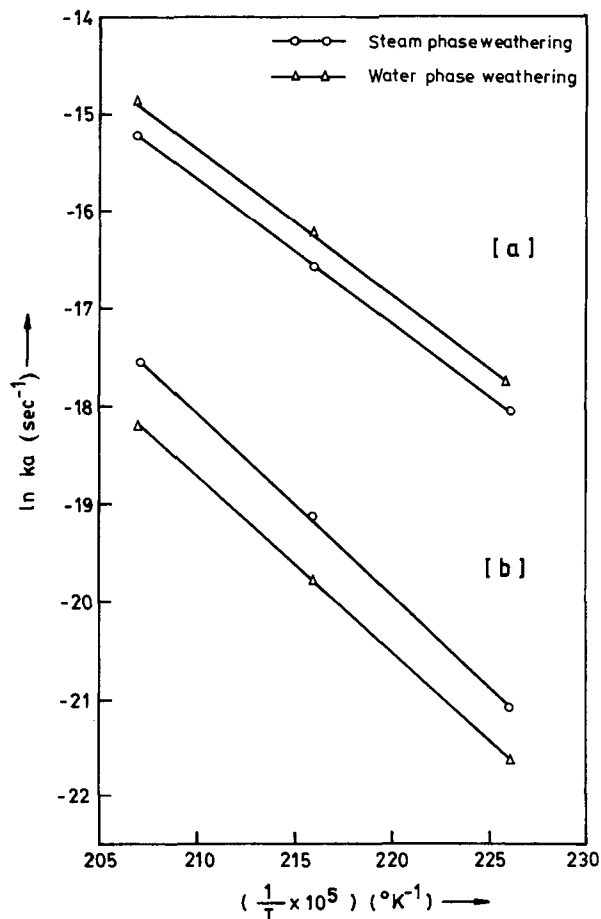
Results of kinetic study for degradation of silicone are shown in Table IV. The isothermal plots [Fig. 1(a)] of conversion-time are straight lines passing through the origin of the co-ordinates, indicating a pseudo zero-order rate process for the hydrolytic degradation of silicone. However, the hydrolytic process can be viewed as a bimolecular process:



The observed zero order could be understood if

we consider the low conversion of  $\text{Si}-\text{O}-\text{Si}$  during the entire degradation process and the moisture content within the vulcanizate in equilibrium with saturated steam. Thus, the kinetics are of pseudo zero-order. The rate constants [Table IV, Fig. 2(a)] are about 25% higher in the case of liquid-phase exposed samples. The activation energy, however, practically remains the same. This reflects the effect of leaching by liquid water of the oligomeric species, which may otherwise participate in the reverse reaction.

For the 50 : 50 blend, the results are shown in Table V. The rate constants for steam-phase degradation are merely 5–10% of the rate constants of silicone degradation in steam. A significant lowering of hydrolytic rate constant by EPDM reflects its



**Figure 2** Arrhenius plot for hydrolytic degradation process of (a) silicone rubber and (b) 50 : 50 blend of silicone rubber and EPDM.

level of protection to silicone in humid environment. The time-conversion plots [Fig. 1(b)] follow a zero-order linear curve. The rate constants [Table V, Fig. 2(b)] in liquid-phase degradation is somewhat lower than those in the steam-phase degradation; this also suggests higher level of crosslinking and/or lower extent of scission reaction in EPDM in the liquid phase. Finally, activation energy is found to increase by  $7 \text{ kcal} \cdot \text{mol}^{-1}$  in the presence of EPDM, and this explains the superior weathering resistance of the blend compared to silicone alone.

## CONCLUSIONS

The present study reveals the excellent weathering resistance of EPDM rubber; it can be used in combination with silicone rubber to extend the applicability of the latter in a humid environment. The following observations reinforce the above views:



1. EPDM and its 50 : 50 blend with silicone maintains its rubbery nature over a wide range of aging periods and temperatures (e.g., 96 h at 210°C and 384 h at 170°C).
2. Silicone loses its elastomeric property after 48-h aging at 210°C and 192-h at 170°C.
3. Chemically, the silicone rubber undergoes hydrolytic chain scission with continued decrease in strength and modulus. Leaching of oligomeric products is also observed.
4. Weathering of EPDM is governed mainly by crosslinking reaction. The modulus never deteriorates below the reference, and the strength and elongation after passing through a minima again improve at higher aging periods.
5. The presence of EPDM increases the activation energy of degradation from 30 to 37 kcal·mol<sup>-1</sup>, and this explains the better weathering resistance of the blend.

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