

Surface Properties of EPDM, Silicone Rubber, and Their Blend During Aging

ANIL K. BHOWMICK,* J. KONAR, S. KOLE, and S. NARAYANAN

Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India

SYNOPSIS

Surface energy of EPDM, silicone rubber, and their 50 : 50 (by weight) blend during aging was determined by contact angle measurement using water and formamide as the probe liquids. The surface energy increases initially with aging time. The results are explained on the basis of the polar component of the surface energy. Blending offers a good degree of protection toward aging of EPDM rubber. The generation of polar groups during aging is confirmed by IR and ESCA investigations. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Surface modification as a technology has been employed in various ways for many years. For example, halogenation, etching, grafting, oxidation, etc., are well-known techniques. However, the breadth and the magnitude of its application have grown significantly during the last decade and a great emphasis has been placed recently on understanding the science and technology and its relationship to the behavior of the modified surface. Chan¹ reviewed surface modification and characterization by various techniques. Waddell et al.² described modification of elastomer and fiber surfaces by chemical, photochemical, and physical techniques. The literature search clearly reveals that there is a further scope to work in this area, as new properties can be imparted to existing polymers. With this view in mind, earlier we reported surface properties of polymers modified by dibutyl maleate, vinyl trimethoxysilane,³ and by triallyl cyanurate in the presence of an electron beam.⁴ The surface modification of elastomers by corona, plasma, high energy radiation, halogenation, etching, oxidation, etc., has been discussed. However, other processes are described in the patent literature.^{2,5,6} The modification of a rubber surface by blending and subsequent aging has not been mentioned in the literature. During our

work on silicon-EPDM blends, we found that the aging properties of EPDM could be significantly improved by blending with silicone.⁷ To understand the mechanism, we have investigated the surface properties by contact angle, IR, and electron spectroscopy for chemical analysis (ESCA) measurement of a 50 : 50 blend of silicone : EPDM rubber during aging and compared the results with those of the pure components.

The surface energy of solid polymers by contact angle measurement is a widely used method. Fowkes⁸ proposed that the surface energy of a pure phase (γ_a) is a sum of the contribution from the dispersion (γ_a^d) and polar (γ_a^p) components such that

$$\gamma_a = \gamma_a^d + \gamma_a^p \quad (1)$$

He further suggested that the interaction energy at the interface (γ_{ab}) having dispersion force components can be accounted for by the following expression,

$$\gamma_{ab} = \gamma_a + \gamma_b - 2(\gamma_a^d \gamma_b^d)^{1/2} \quad (2)$$

where γ_a and γ_b are the surface free energies of the phases *a* and *b*, respectively. Owens and Wendt⁹ and Kaelble and Uy¹⁰ later introduced another energy term for the polar component as

$$\gamma_{ab} = \gamma_a + \gamma_b - 2(\gamma_a^d \gamma_b^d)^{1/2} - 2(\gamma_a^p \gamma_b^p)^{1/2} \quad (3)$$

* To whom correspondence should be addressed.

Table I Values of Contact Angle and Work of Adhesion

Status	θ						W_a (mJ/m ²)					
	EPDM		Silicone		50 : 50 Blend		EPDM		Silicone		50 : 50 Blend	
	F	W	F	W	F	W	F	W	F	W	F	W
Unaged	75	87	93	105	90	95	73	77	55	54	58	66
Air aging												
For 3 h	77	80	92	94	92	90	71	85	56	68	56	73
For 9 h	78	70	93	90	94	90	70	98	55	73	54	73
For 24 h	77	67	97	104	101	102	72	101	51	55	47	58
For 48 h	81	86	92	100	112	107	67	78	56	60	36	51

Air aging was carried out at 175°C.

Combining eq. (3) with Young's equation for a solid-liquid system, we obtain

$$\cos \theta = -1 + \frac{2(\gamma_s^d \gamma_l^d)^{1/2}}{\gamma_l} + \frac{2(\gamma_s^p \gamma_l^p)^{1/2}}{\gamma_l} \quad (4)$$

assuming spreading pressure to be negligible and s and l represent solid and liquid, respectively, and θ represents the contact angle of the liquid with the solid surface. The work of adhesion could also be obtained from the equilibrium contact angle θ as follows:

$$W_a = \gamma_l(1 + \cos \theta) \quad (5)$$

or

$$W_a = 2(\gamma_s^d \gamma_l^d)^{1/2} + 2(\gamma_s^p \gamma_l^p)^{1/2} \quad (6)$$

These equations have been used extensively to understand the surface energetics of the polymeric solids.

During surface modification, various types of changes, including structural, take place. X-ray photoelectron spectroscopy is probably the most useful technique for quantitative surface analysis.¹¹⁻¹³ These changes have been reviewed extensively in the literature.¹ The present authors have also used this technique to understand tack, diffusion, milling, and aging of rubbers. IR spectroscopy¹⁴ can also be used to understand the chemical composition of the modified surface, although chemical changes in a thin surface layer are missed because of its deep penetration.

EXPERIMENTAL

Materials

Silicone rubber: JSR EH 5270V, type VMQ (i.e. vinyl methyl based silicone), density 1.31 g/mL, vinyl

content = 0.45%, $M_n = 1 \times 10^5$ g/gmol, Mooney viscosity, ML_{1+4} at 100°C = 33, provided by Japan Synthetic Rubber Co., Japan.

EPDM rubber: Keltan 520-DCPD containing rubber, density 0.86 g/mL, diene content = 4.5 mol %, viscosity average mol wt = 1.93×10^5 g/gmol, ethylene propylene ratio = 58/42 mol/mol, supplied by DSM Chemical, Holland.

Dicumyl peroxide (DCP): DiCup obtained from Hercules Inc., U.S.A.

Mixing and Molding

Blending of silicone and EPDM rubbers was carried out in a Brabender Plasticorder PLE-330 at 120°C for 5 min at 100 rpm rotor speed. Silicone rubber, EPDM rubber, and the 50 : 50 (by weight ratio) blend of silicone and EPDM rubbers were mixed with 1.5 phr DCP on an open roll mill at 25°C. The samples were cured at 170°C for 10 min between smooth-surface molds in a hydraulically operated press, and then postcured for 2 h at 150°C in an oven. A blend of silicone and EPDM rubber produced by the above mixing and molding procedures was incompatible in nature.⁷

Air Aging

Air aging of the vulcanized rubbers (0.5-mm thick) was carried out in a test tube aging tester (Seisaku-SHO Ltd., Toyoseiki, Japan) at 175°C for various times. A few samples were also aged at different temperatures (165, 175, 185, and 195°C) for 3 h.

Contact Angle Measurement

The sessile drop method using water and formamide as the probe liquids was adopted for contact angle

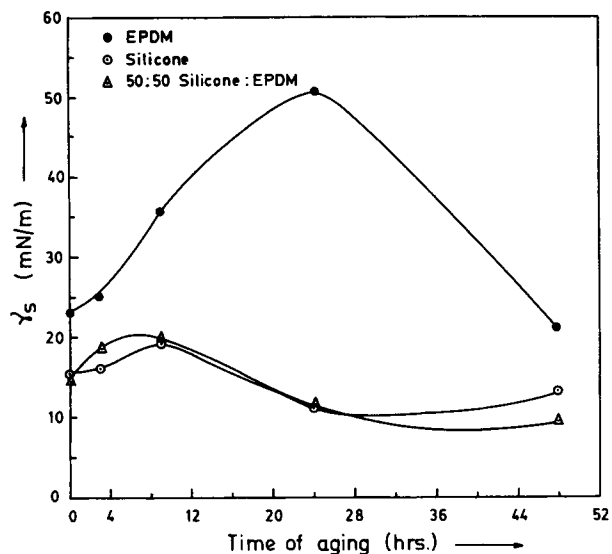


Figure 1 Change of surface energy against time of aging at 175°C: (●) EPDM; (○) silicone; (△) 50 : 50 silicone : EPDM.

measurements. The experiments were carried out on a polymer plate having dimensions of $10 \times 10 \times 0.5$ mm in vapor saturated air at $20 \pm 2^\circ\text{C}$ in a closed box of the Contact Angle Meter (Kernco Model G-II). Each value reported is the mean of at least five measurements with a maximum error in θ of $\pm 2^\circ$.

IR Measurement

IR studies were carried on thin molded films (0.5 mm) of rubber using a Perkin-Elmer spectrophotometer (Model 883).

ESCA

ESCA measurements were carried out on rectangular samples ($20 \times 8 \times 0.5$ mm) by using a VG

Scientific ESCA Lab MK-II spectrometer employing exciting radiation of 1486.6 eV (AlK_{α}). The working pressure in the spectrometer was 4.3×10^{-9} torr, and the electron take-off angle with respect to the polymer surface was 90° . All spectra recorded were referenced to the C1s peak for neutral carbon, assigned a value of 285.0 eV. Each specimen was analyzed by a combination of a 1250 eV survey and 25-eV high resolution scans for different peaks. The peak area was divided by the atomic sensitivity factor of the respective element to calculate the concentration of carbon, oxygen, and silicone.

RESULTS AND DISCUSSION

Surface Energy of Rubber and Rubber Blends

The equilibrium contact angles of silicone, EPDM, and a 50 : 50 blend of Si : EPDM using water and formamide as the probe liquids are reported in Table I. The contact angle of water on unaged rubbers is higher than that of formamide. As expected, the probe liquids on silicone are spread the least. On aging, at 175°C, the contact angle of water gradually decreases with aging time and then increases at 48 h of aging. Formamide does not follow a systematic trend. The thermodynamic work of adhesion W_A , calculated from eq. (5) is also included in the same table. These values show a similar but opposite trend to those of contact angles. For example, W_A increases from 77 to 101 mJ/m^2 up to 24 h of aging and then decreases to 78 mJ/m^2 at 48-h aging of the EPDM surface; the contact angle shows a minima at 67° for 24-h aging. The work of adhesion is lower on the silicone surface. The highest value of W_a is found on the EPDM surface aged for 24 h at 175°C using water as the probe liquid. In most cases, the work of adhesion values of the blend and the silicone surface before and after aging are comparable. The re-

Table II Surface Energy (mJ/m^2) of EPDM, Silicone Rubber and Their Blend Before and After Aging at 175°C

Sample	EPDM			Silicone			50 : 50 Blend		
	γ_s^p	γ_s^d	γ_s	γ_s^p	γ_s^d	γ_s	γ_s^p	γ_s^d	γ_s
Unaged	7.95	15.05	23.00	1.86	13.62	15.47	8.73	6.74	15.47
Air aging									
For 3 h	17.06	8.02	25.08	10.95	4.79	15.74	15.68	3.05	18.73
For 9 h	33.49	2.59	36.08	16.40	2.54	18.96	17.19	2.11	19.30
For 24 h	50.55	0.67	51.22	4.80	6.54	11.34	8.32	3.09	11.41
For 48 h	12.60	8.47	21.07	5.50	8.15	13.65	9.23	0.65	9.88

Table III Values of Surface Energy (mJ/m²) at Various Temperatures for 3-h Aging

Sample (°C)	EPDM			Silicone			50 : 50 Blend		
	γ_s^p	γ_s^d	γ_s	γ_s^p	γ_s^d	γ_s	γ_s^p	γ_s^d	γ_s
165	a	a	a	19.90	0.70	20.60	27.45	0.21	27.66
175	17.06	8.02	25.08	10.95	4.79	15.74	15.68	3.05	18.73
185	11.92	9.38	21.30	24.87	1.25	26.12	19.65	1.04	20.69
195	12.39	17.38	29.77	37.64	0.03	37.67	41.87	0.03	41.90

(a) Tacky surface; measurement is difficult.

duction in contact angle due to aging has been reported by several workers.^{15,16} It is also interesting to note that the contact angle values of the 50 : 50 blend are close to the silicone surface even after aging. As discussed later, the changes in the contact angles are related to the changes in the surface energy of the solids caused by the changes in the surface chemistry due to aging.

The total surface energy and its dispersion and polar force contribution to all the samples was calculated using eq. (4) and the following values of γ_l^d and γ_l^p for the probe liquids. Water: $\gamma_l = 72.8$ mJ/m²; $\gamma_l^d = 21.8$ mJ/m²; $\gamma_l^p = 51.0$ mJ/m². Formamide: $\gamma_l = 58.2$ mJ/m²; $\gamma_l^d = 39.5$ mJ/m²; $\gamma_l^p = 18.7$ mJ/m². The surface energy values are plotted against time of aging in Figure 1. Table II reports the values of the individual contributions. For all the rubbers, the surface energy increases with an increase of time of aging in the initial stage and then decreases. The peak value after which there is a decrease in the surface energy is 9 h for the silicone and blends and 24 h for the EPDM rubber. Also, it is interesting to note that by blending 50 parts silicone with 50 parts EPDM (by weight), the surface energy values in the initial stages of aging are similar and these are lowered for the blends at longer times of aging. It may be noted that the surface energy value for silicone rubber reported in the literature^{17,18} is 19–22 mJ/m² and for EPDM rubber it is 28 mJ/m². To investigate the reasons, the dispersion and polar force contributions were examined. It is clear from Table II that the polar contribution increases: from 7.95 mJ/m² for the unaged sample of EPDM to 50.55 mJ/m² for a 24-h aged sample, a sixfold increase; from 1.86 mJ/m² for the unaged sample of silicone rubber to 16.40 mJ/m² for the 9-h aged sample, a ninefold increase; and from 8.73 mJ/m² for the blend to 17.19 mJ/m² for the 9-h aged sample. These values decrease on continued aging. The dispersion component, on the other hand, shows a decrease in general before the final increase. It is also notable that the ratio γ_s^d/γ_s^p is 1.89 for unaged EPDM, 7.32 for unaged silicone rub-

ber, and 0.77 for unaged blend. This ratio is lowered on aging. For example, this becomes 0.013 for 24-h aging of EPDM, 0.16 for 9-h aging of silicone, and 0.12 for 9-h aging of the blend. These results clearly indicate that the polar groups are generated on the surface during aging, resulting in an increased surface energy. On prolonged air aging for 48 h, the decrease in the polar components and the overall surface energy may be the result of the loss of small molecules from the surface.

Values of surface energy of samples aged for 3 h at 165, 175, 185, and 195°C are given in Table III in order to understand the effect of temperatures. EPDM generates a tacky surface at 165°C aging and hence, the surface energy could not be determined accurately. With an increase in temperature from

Table IV Results of IR Analysis of EPDM, Silicone Rubber, and Their Blend Before and After Aging at 175°C

Sample	Absorbance Ratio	Time (h)		
		0	24	48
EPDM	A_{1742}/A_{1473}	—	1.38	1.34
	A_{1366}/A_{1473}	0.98	0.94	1.32
	A_{1155}/A_{1473}	0.43	0.47	0.54
	A_{871}/A_{1473}	0.09	0.21	—
Silicone	A_{1741}/A_{1070}	1.13	1.48	1.28
	A_{1401}/A_{1070}	1.58	1.21	1.69
	$A_{1590-1610}/A_{1070}$	1.82	1.46	1.42
	A_{1248}/A_{1070}	1.65	1.12	1.09
	A_{827}/A_{1070}	0.81	0.87	0.90
Blend				
	EPDM	A_{1353}/A_{1475}	0.99	0.84
	A_{1152}/A_{1475}	0.62	0.62	0.71
	A_{870}/A_{1475}	0.56	0.49	0.67
Silicone	A_{1618}/A_{1087}	1.29	1.76	1.68
	A_{1420}/A_{1087}	1.89	1.15	1.27
	A_{1237}/A_{1087}	1.16	1.13	0.97

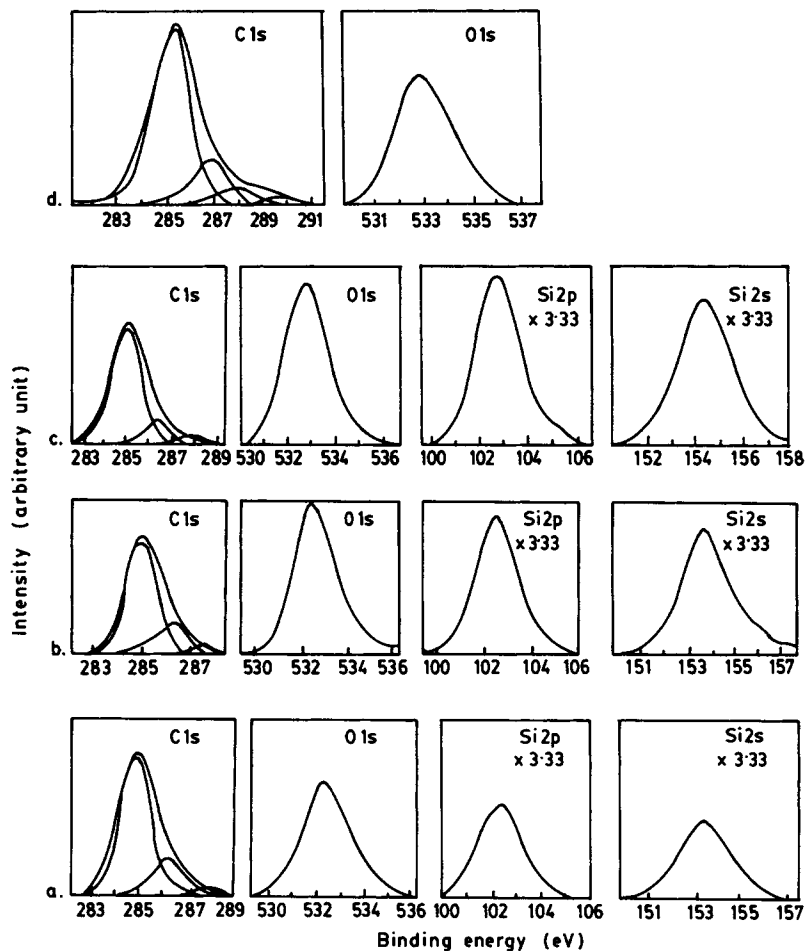


Figure 2 C1s, O1s, Si2s, and Si2p spectra of: (a) unaged 50 : 50 silicone : EPDM blend; (b) 50 : 50 silicone : EPDM blend aged for 9 h at 175°C; (c) silicone rubber aged for 9 h at 175°C; and (d) EPDM aged for 9 h at 175°C.

175°C, the polar component of the surface energy γ_s^p decreases, while γ_s^d increases. The net result is that the surface energy becomes minimum at 185°C. The silicone rubber surface, on the other hand, shows a minimum value at 175°C aging (15.74 mJ/m²). γ_s^p decreases before a final increase. The trend of γ_s^d values is just the reverse: 50 : 50 blend displays similar characteristics to silicone rubber. The increase of γ_s^p at higher temperatures (185 and 195°C) in the case of silicone clearly indicates oxidation of the surface; the decrease of γ_s^p for EPDM reveals probably further modification and a loss of small molecules.

IR Investigation

IR spectra of aged and unaged samples of silicone, EPDM, and their 50 : 50 blend were analyzed. The peaks of interest are: 1742 and 1155 cm⁻¹ due to

C=O stretching; 1366 cm⁻¹ due to chain branching; 871 cm⁻¹ due to C=CH; 1473 cm⁻¹ due to the —CH₂— stretching for EPDM rubber; 1741 cm⁻¹ (C=O stretching); 1401 cm⁻¹ (CH₂ in plane deformation); 1590–1610 cm⁻¹ (C=C stretching), 1248 cm⁻¹ [due to symmetric deformation vibration of CH₃ group in Si (CH₃)_n]; and 1080 cm⁻¹.

(Si—O stretching) for silicone rubber.¹⁹ The changes in these values with respect to 1473 cm⁻¹ in the case of EPDM and with respect to 1070 cm⁻¹ in the case of silicone, assuming that the absorbances at 1473 and 1070 cm⁻¹ remain constant, are reported in Table IV. With increased oxidation, A_{1742}/A_{1473} and A_{1155}/A_{1473} of EPDM increase significantly, indicating generation of polar C=O groups. At the same time there is chain branching and some double bond formation. Similarly, silicone rubber shows marginal increase in C=O functionality, and reduction of C=C and Si(CH₃)_n on oxidation. These results are in ac-

Table V Peak Position and Area of C1s, O1s, Si2p, and Si2s and Concentration of C, O, and Si on Surface

Sample	C1s		O1s		Si2p		Si2s		Concentration (%)		
	Peak Position (eV)	Area	Peak Position (eV)	Area	Peak Position (eV)	Area	Peak Position (eV)	Area	C	O	Si
50 : 50 unaged	—	126.60	532.4	110.40	102.2	27.60	153.6	31.74	66.9	20.7	12.4
		(rel. area %)									
	285.0	83.8									
	286.5	14.8									
50 : 50 9-h air aged	—	107.95	532.6	150.15	102.4	41.50	153.7	46.60	53.9	27.5	18.5
		(rel. area %)									
	285.0	80.5									
	286.5	15.0									
Silicone 9-h air aged	—	115.05	532.7	123.15	102.8	54.40	154.2	55.10	55.1	21.1	23.8
		(rel. area %)									
	285.0	85.9									
	286.5	12.4									
EPDM 9-h air aged	—	191.80	532.9	156.75	—	—	—	—	79.2	20.7	—
		(rel. area %)									
	285.0	71.3									
	286.7	17.7									
	288.2	7.8									
	289.7	3.2									

cordance with surface energy values up to 24 h of aging reported earlier. The characteristic peaks due to EPDM (1353, 1152, and 870 cm^{-1}) and silicone (1618, 1420, and 1237 cm^{-1}) in the 50 : 50 blend, except the one at 1712 cm^{-1} which is common for both, were analyzed and the results are reported in Table IV. There is a clear indication of increased polar functionalities, mainly due to C=O function, although the changes in the absorbance ratio are less compared to that of the contact angles. For example, during aging at 175°C for 48 h, there is about a 25% increase of A_{1152}/A_{1473} for the control EPDM, while a 15% increase of the same ratio is registered for the EPDM in the blend. Clearly, the EPDM in the blend is protected from oxidation by the presence of silicone rubber. IR analysis of oxidized rubbers have been reported in the literature and the present data are in accord with those trends due to oxidation.

ESCA Spectra

ESCA spectra in the 0–1250 eV binding energy were taken for various samples for unaged and 9-h aged 50 : 50 blend, 9-h aged silicone, and 9-h aged EPDM.

C1s, O1s, Si2p, and Si2s regions are expanded and shown in Figure 2. The individual peak position and peak area and the concentration of carbon, oxygen, and silicone are reported in Table V. The C1s peak appears at 285-eV binding energy for the unaged 50 : 50 blend. There are additional peaks observed on a curve fitting at 286.5 eV (shift of 1.5 eV) and 288.1 eV (shift of 3.1 eV), which may be ascribed to C—O and C=O, respectively. On air aging of the blend, there is a peak at 286.5 eV (shift of 1.5 eV) due to C—O and a shift of the peak at 288.1 to 287.6 eV with increased peak area. Similarly, the aged silicone surface reveals peaks at 285.0, 286.5, and 288.0 eV and aged EPDM at 285.0, 286.7, 288.2, and 289.7 eV

(due to $\begin{array}{c} \text{O} \\ || \\ \text{C}-\text{C}-\text{O} \end{array}$ groups). Clearly, the aging in-

duces oxidation and incorporates polar functionalities. This is also corroborated from the appearance of the peaks at O1s. In order to quantify, C1s peaks are curve fitted. It is observed that the relative area percent, which is proportional to the concentration of a particular chemical species, changes due to oxidation. The total peak area of O1s also increases

due to oxidation. Silicone peaks at Si2p and Si2s appear at 102 and 153.5 eV, respectively, in the blend. The surface composition given in Table V shows that the surface of the blend, as prepared, is already enriched in the silicone component. It is interesting to note that the peak area of silicone increases from 31.74 to 46.6 units (47% increase) on aging for 9 h at 175°C. It can be inferred that the silicone diffuses onto the surface during aging. The total concentration of silicone is 18.5% after aging as compared to 12.4% on the unaged surface. Concomittantly, there is approximately a 7% increase in the oxygen concentration (from 20.7 to 27.5%). The C1s concentration, however, is lowered by about 13%. These results are in general agreement with the contact angle values and IR observations.

CONCLUSIONS

Surface properties of EPDM, silicone rubber, and their 50 : 50 blend during aging have been investigated by contact angle measurement, IR, and ESCA spectroscopies.

The contact angle of water decreases with aging time and then increases for all the rubbers. As a result, the work of adhesion and the surface energy follow a similar but opposite trend to those of contact angle. The peak at which the surface energy becomes maximum occurs at 24-h aging for EPDM, and 9 h for silicone rubber and the blend, all aged at 175°C. The increase in surface energy is due to a six- to ninefold increase of the polar force component of the surface energy. In a 50 : 50 blend of these two rubbers, the changes in surface energy of EPDM due to oxidation are prevented by diffusion of silicone rubber. Aging at higher temperature (195°C) increases surface energy values further.

IR studies clearly indicate the formation of C=O functionalities of EPDM during aging. There is a marginal increase in the same for the silicone rubber. ESCA measurements further corroborate the IR observation and reveal the increased concentration of silicone rubber on the surface in the blend during aging and general increase of oxygen concentration for EPDM, silicone rubber, and the blend on aging.

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