

Wetting Behavior of Functionalized Silicone and EPDM Rubber

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SYNOPSIS

The contact angles and surface energies have been determined for silicone rubber functionalized with amide group and EPDM rubber modified with sulfonic acid and maleic anhydride. The functionalization of the polymers decreases the equilibrium contact angles of water and formamide with an increase in the surface energy. The changes in the surface properties are due to the changes in the concentration of the polar groups as measured by IR spectroscopy. The lap shear measurement on joints of silicone and EPDM rubber indicates an increased strength on modification. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

One of the areas that has drawn attention of polymer scientists today is the development and properties of functionalized polymers. This has become more important when synthesis of new polymers has been found to be very expensive. Functionalized polymers can be generated from the existing polymers. Also a host of new polymers depending on the nature and level of functionalization could be prepared. These polymers are finding a large number of applications, such as compatibilizers in polymer blends, coating, etc. Compared to the number of functionalized polymers available today, their properties are not well understood.

In this paper, we investigated the surface properties of silicone rubber functionalized with amide group and EPDM rubber modified with sulphonic acid and maleic anhydride. Both silicone and EPDM rubbers find a large number of industrial applications.¹ While silicone rubbers have been reported to have surface energy of 19–22 mJ/m² and hence are difficult to wet, a value of 28 mJ/m² has been determined for EPDM rubber.² In our earlier communications, we reported the mechanical, dynamic

mechanical, electrical, and ageing resistance of silicone, EPDM rubbers, and their blends.^{3–5}

Contact angle measurement at a solid–liquid interface is a widely used method for the determination of surface energy of solid polymers. Fowkes⁶ first suggested that the surface energy of a pure phase, γ_a , could be represented as the sum of the contributions from different types of force components, especially the dispersion and polar components.

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

Fowkes⁷ then proposed that the geometric mean of the dispersion force components was a reliable measure of the interaction energies at the interface caused by dispersion forces. Thus, the interfacial free energy, γ_{ab} , between phases *a* and *b* are given by

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

where γ_a and γ_b are the surface free energies of phases *a* and *b*, respectively. To account for the effect of nondispersion forces, Owens and Wendt⁸ and Kaelble and Uy⁹ proposed another energy term $2(\gamma_a^p \gamma_b^p)^{1/2}$, by analogy with the work of Fowkes. Here, γ_a^p and γ_b^p are the polar components of the surface free energy of phases *a* and *b*, respectively. Thus,

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

For a solid-liquid system, eq. (3) may be combined with the well-known Young's equation to eliminate the interfacial free energy, giving

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

Here, it is assumed that the spreading pressure is negligible, and s and l represent solid and liquid, respectively. The thermodynamic work of adhesion may also be obtained from the equilibrium contact angle θ and the surface tension of the liquid as follows:

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

Combining eqs. (4) and (5),

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

Various workers including the present authors, have used these equations extensively to understand surface energies of polymeric solids.¹⁰⁻¹²

EXPERIMENTAL

Materials

1. Silicone rubber (JSR silicone EH 5270, heat-cured type, greyish-white, specific gravity 1.31) was procured from the Japan Synthetic Rubber Co. Ltd. (Tokyo, Japan).
2. 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 (Zwolle, Holland).
3. Sulfonated EPDM (ionomer 2590, specific gravity 1.12, Mooney viscosity $ML_{(1+4)}$ at 100°C = 45, average no. of SO_3 groups per molecule = 13.27 wt % ionic groups) was supplied by Uniroyal Chemical Co. (Naugatuck, Connecticut, USA).
4. Maleated EPDM: Royaltuf 465, specific gravity 0.89, total maleic anhydride/acid 1%, Mooney viscosity $ML_{(1+4)}$ at 125°C = 60, iodine value = 17.

5. Acrylamide: Monomer, soluble in water, melting point 85°C.
6. Ammonium persulfate: Initiator for the polymerization, soluble in water, purchased from Aldrich Chemical Co. (Milwaukee, WI).
7. DCP: The curing agent-dicumyl peroxide (DCP) was supplied by Hercules Inc. (USA).

Grafting of Acrylamide onto Silicone

Silicone rubber (100 g), acrylamide (9.00 g), and ammonium persulfate (0.25 g) were premixed in a roll mill. The premix was processed in a Brabender Plasticorder (PLE-330) at 80°C for 15 min at 100 rev min⁻¹. A thin film (about 150 μm thick) of the mix was heated over a boiling water bath for 1 h and left overnight in fresh distilled water at room temperature. The film was allowed to dry in a vacuum oven at 80°C for 2 h. The levels of acrylamide and ammonium persulfate and the reaction conditions were optimized after a series of reactions under different conditions and studies of the grafting level by IR spectroscopy.¹³

IR Studies

IR studies were carried out on thin films using a Perkin-Elmer 843 IR spectrophotometer. To get better films, low-density polyethylene was used as the matrix material.

Contact Angle Measurements

The contact angles were determined using a contact angle meter (Kernco, model GII). The sessile drop method, using water and formamide as probe liquids, was used for contact angle measurements. Each contact angle quoted is the mean of at least five measurements with a maximum error in θ of $\pm 1^\circ$. All investigations were carried out using a polymer plate in vapor-saturated air at $20 \pm 2^\circ\text{C}$ in a closed sample box.

Lap Shear Measurement

Strips of EPDM/modified EPDM (75 × 25 × 2 mm) were cut from the standard sheets. The test assembly was made by sandwiching the silicone rubber and acrylamide-grafted silicone (AM-*g*-silicone) rubber between two EPDM strips to form an overlapped area of 25 × 25 mm toward the ends. Subsequently,

the assembly was hot pressed in a Labo-Press at 150 or 180°C, as required, for 5 min.

Finally, the lap shear test was performed in a Zwick UTM (model 1445) at room temperature $25 \pm 2^\circ\text{C}$ at a crosshead speed of 50 mm/min (ISO-813-1986(E)).

RESULTS AND DISCUSSION

Contact Angle and Surface Energy of Functionalized EPDM and Silicone Rubber

The equilibrium contact angles for EPDM, sulfonated EPDM (SEP), maleated EPDM (MEP), silicone rubber, and AM-*g*-silicone are tabulated in Table I. The values of thermodynamic work of adhesion W_A calculated from eq. (5) are also included in the table. The functionalization of the polymers decreases the equilibrium contact angle for both water and formamide considerably. For example, the contact angles of water and formamide for sulfonated EPDM decrease from 94° to 86° and 82° to 72° , respectively. The reduction is larger in the case of MEP. The decrease of contact angle is from 94° to 75° for water and 82° to 66° for formamide. AM-*g*-silicone shows a change of 6° for water and 7° for formamide from the parent silicone rubber.

The contact angle decreases due to several factors, of which surface polarity is an important one. The

extent of the decrease generally depends on polar component of the surface energy, which is discussed in the next section. It is expected that the polar liquid drops would wet the polar surfaces more, thereby reduce the θ values. Further experiments with a blend of 1, 3, or 5 parts modified polymers and parent polymers (EPDM or silicone) reveal that even a low proportion of former one causes a substantial decrease of the contact angles and improves wettability. For example, 5 parts of MEP lower the contact angle of water from 94° to 86° . The work of adhesion W_A calculated from the θ value increases when the contact angle decreases. Table I indicates that the functionalization by polar groups enhances the work of adhesion: W_A of EPDM goes up from 68 to 92 mJ/m² on maleation and that of silicone from 65 to 73 mJ/m² on grafting with amine. The polar and dispersion force contributions to the surface free energy of the polymers were calculated using eq. (4) and the following values of γ_i^d and γ_i^p for the probe liquids, i.e., water and formamide, respectively:

$$\text{Water: } \gamma_i = 72.8 \text{ mJ/m}^2; \quad \gamma_i^d = 21.8 \text{ mJ/m}^2;$$

$$\gamma_i^p = 51.0 \text{ mJ/m}^2$$

$$\text{Formamide: } \gamma_i = 58.2 \text{ mJ/m}^2; \quad \gamma_i^d = 39.5 \text{ mJ/m}^2;$$

$$\gamma_i^p = 18.7 \text{ mJ/m}^2$$

Table I Values of Contact Angle and Work of Adhesion

Sample:	θ	W_A	θ	W_A
	H ₂ O (deg)	H ₂ O (mJ/m ²)	HCONH ₂ (deg)	HCONH ₂ (mJ/m ²)
EP	94	68	82	66
SEP	86	78	72	76
EP-1SEP ^a	93	69	80	68
EP-3SEP	91	71	77	71
EP-5SEP	88	75	76	72
MEP	75	92	66	82
EP-1MEP	90	73	80	68
EP-3MEP	88	75	76	72
EP-5MEP	86	78	76	72
Si	96	65	86	62
AM- <i>g</i> -Si	90	73	79	69
Si-1-AM- <i>g</i> -Si	94	68	82	66
Si-3-AM- <i>g</i> -Si	92	70	82	66
Si-5-AM- <i>g</i> -Si	92	70	79	70

^a One part of SEP was mixed with EPDM rubber.

Table II Surface Energy of Functionalized EPDM and Silicon Rubber

Sample	γ_s^p (mJ/m ²)	γ_s^d (mJ/m ²)	γ_s (mJ/m ²)
EP	5.52	13.37	18.89
SEP	7.25	17.89	25.14
EP-1SEP ^a	5.38	14.74	20.12
EP-3SEP	5.58	16.38	21.96
EP-5SEP	7.73	14.88	22.61
MEP	15.30	14.77	30.07
EP-1MEP	7.81	12.46	20.27
EP-3MEP	7.73	14.88	22.61
EP-5MEP	9.46	13.22	22.68
Si	5.81	10.85	16.66
AM- <i>g</i> -Si	7.36	13.30	20.66
Si-1-AM- <i>g</i> -Si	5.52	13.37	18.89
Si-3-AM- <i>g</i> -Si	7.14	11.80	18.94
Si-5-AM- <i>g</i> -Si	5.70	14.97	20.67

^a One part of SEP was mixed with EPDM rubber.

From these values, the total surface energy was calculated. The results are tabulated in Table II. It is found that MEP shows the maximum increase of the surface energy, followed by SEP and AM-*g*-silicone, which is due to the increase of both polar and dispersion components of the surface energy. As the modified polymers are incorporated in EPDM or silicone rubber, there is also an increase in the surface energy of the blend. For example, 5 parts of MEP raises the surface energy value by about 20%, which is little higher than the theoretically predicted values from the additive laws. This implies that the surface energy has higher contribution from the modified polymers. It is also interesting that the value of the polar component of MEP is much higher than the other two polymers, whereas the value of the dispersion component of the surface energy is much greater in the case of SEP.

It is well known that the total polarity is generally measured in terms of various groups present in the polymer surface. The presence of polar groups on SEP, MEP, and acrylamide-grafted silicone was confirmed from the IR measurements.^{13,14} On comparing the IR spectra of silicone rubber and AM-*g*-silicone, it is observed that the peak at 1623 cm⁻¹ in silicone rubber, attributed to the $\begin{matrix} \diagup & & \diagdown \\ & C=C & \\ \diagdown & & \diagup \end{matrix}$ stretching vibrations of the vinyl group attached to the silicone atom, is considerably reduced by grafting with acrylamide; while new peaks are generated, one at 1658 cm⁻¹ due to $\begin{matrix} \diagup & & \diagdown \\ & C=O & \\ \diagdown & & \diagup \end{matrix}$ stretching vibration

and another, strong and broad, at 3365 cm⁻¹ due to N—H stretching vibration.

By comparison of MEP and EPDM spectra one can find, generation of three new peaks: a broad band near 1840 cm⁻¹, a sharp medium intensity peak at 1781 cm⁻¹, and a strong peak at 1711 cm⁻¹. The first two bands can be attributed to the asymmetric and symmetric $\begin{matrix} \diagup & & \diagdown \\ & C=O & \\ \diagdown & & \diagup \end{matrix}$ stretching of the 5-membered saturated ring anhydrides whereas the last one may be due to the $\begin{matrix} \diagup & & \diagdown \\ & C=O & \\ \diagdown & & \diagup \end{matrix}$ stretching of H-bonded saturated carboxylic acid.¹⁵ In the case of SEP, new peaks at 1350 and 1155 cm⁻¹ are observed due to asymmetric S(=O)₂ and symmetric S(=O)₂ stretching of —SO₂OH group. The changes in polar and dispersion component of the surface energy can not, however, be correlated with the level and nature of the functional groups.

Lap Shear Strength between Functionalized Silicone and EPDM

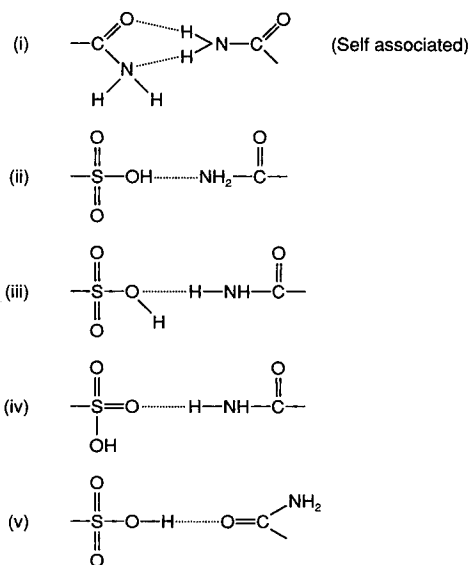
The effect of wetting behavior is further understood from the measurement of lap shear strength of pure and modified joints. For example, silicone and EPDM rubber joined together by hot pressing at 150°C show lap shear strength of 100 MPa (Table III). This increases two to four times when amide grafted silicone is mixed with silicone rubber and SEP or when MEP is added to EPDM at various ratios. Table III indicates that maximum strength

Table III Lap Shear Strength Between Functionalized Silicone and EPDM Rubber

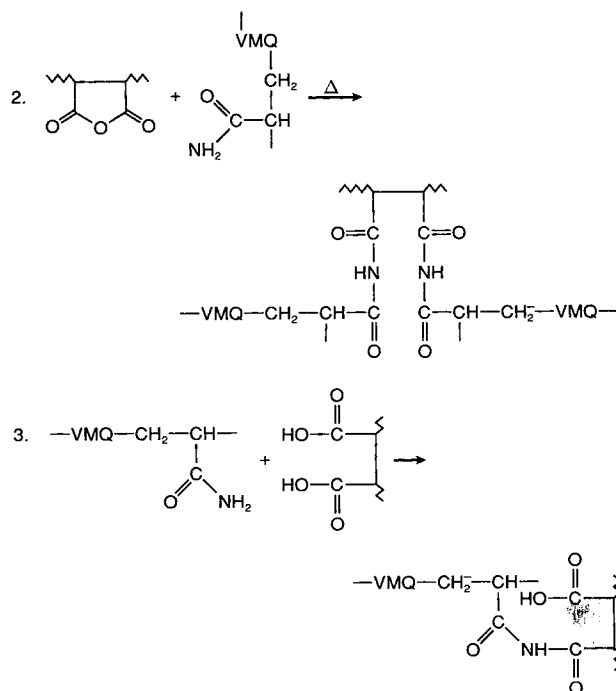
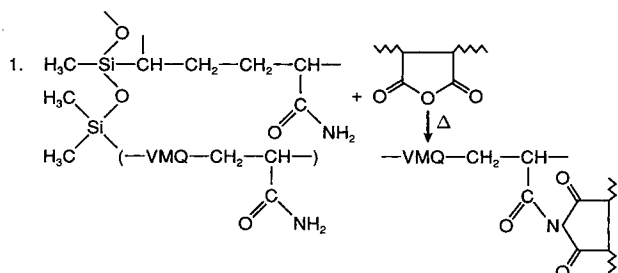
System I	System II	Temperature of Hot Pressing (°C)	Lap Shear Strength (MPa × 10 ⁻²)
EP	Si	180	1.0
EP-1SEP	Si-1-AM- <i>g</i> -Si	150	1.99
EP-3SEP	Si-3-AM- <i>g</i> -Si	150	3.13
EP-5SEP	Si-5-AM- <i>g</i> -Si	150	3.18
EP-1MEP	Si-1-AM- <i>g</i> -Si	150	2.68
EP-3MEP	Si-3-AM- <i>g</i> -Si	150	3.06
EP-5MEP	Si-5-AM- <i>g</i> -Si	150	4.16

(416 MPa) is obtained when 5 parts of modified silicone and MEP are added to the parent polymers. The increase in strength is due to the increased polar component of the surface energy, which gives rise to increased interaction through the interface. The interactions between these components have been further demonstrated with the help of IR studies and reported by us in other communications.^{13,14} Thus, schematically, these can be shown as follows:

(A) For SEP-AM-*g*-silicone system



(B) For MEP-AM-*g*-silicone system



CONCLUSIONS

Surface properties of functionalized EPDM and silicone rubber have been investigated by contact angle measurement, IR, and lap-shear measurement.

Contact angles of water and formamide decrease for the functionalized polymers. The values of the total surface energy for the modified polymers reveal that the maleated EPDM shows the maximum change, followed by sulfonated EPDM, and amide grafted silicone. These are due to the increase of both polar and dispersion components of the surface energy. IR studies clearly indicate the formation of >C=O in maleated EP, >C=O and N-H

functionalities in AM-*g*-Si and —SO₂OH groups in sulfonated EPDM.

The effect of wetting behavior is further confirmed from the lap shear strength measurement of pure and modified joints of EPDM and silicone rubber. The strength of these joints increases two to four times on modification.

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