JOURNAL OF MATERIALS SCIENCE 29 (1994) 2431–2435

Morphology and ageing behaviour of silicone–EPDM blends

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The silicone–EPDM system has been studied with blend ratios (silicone:EPDM) of 50:50, 40:60 and 30:70. The first set of blends was prepared by roll-mixing of the elastomers and curative whereas in the second set, DCP-cured powder of EPDM, prepared in a Brabender plasticorder, was mixed with silicone rubber and DCP in a roll mill. A comparison of blends show that the second set exhibits inferior properties as compared to the first set. Specimens were also aged at 150 and 175 °C for various periods. The physical properties of the aged specimens show a reversal in trend, i.e. the second set of specimens shows better physical properties on ageing. The strengthening of the silicone phase by use of a different curative (Perkadox 14/40) in the 50:50 blend of the second set shows a beneficial action on ageing. Morphology studies with SEM confirm the two-phase structure for both sets of blends. In both cases phase separation occurs with ageing, but the continuous phase for the second set of blends maintains its continuity for a higher period than the corresponding specimens of the first set.

1. Introduction

Morphology plays an important role in determining the mechanical properties of a polymer blend. Depending on the actual morphology, different models such as a mechanical coupling model, a self-consistent model, and a model based on limits or bounds on the modulus have been proposed by various investigators [1–4]. Dickie [5] has given a concise discussion of various models and methods to calculate different parameters related to blends. Alternatively, Kolarik *et al.* [6] have correlated mechanical properties with the structural integrity of the phases in a blend. Elastomer blends used in industrial applications are also well known for their superior properties compared to individual elastomers [7]. Previous work on silicone–EPDM blends clearly signifies the role of morphology in the ageing behaviour and dynamic properties [8,9]. In the present work we have attempted to develop a three-dimensional connectivity in the silicone phase while using a minimum amount of this elastomer in blends of silicone and EPDM.

It was presumed that the effect of ageing will be less harmful if the more stable component forms the continuous phase, because such specimens will be in a position to take more deformation without structural disintegration. At this point an analogy has been drawn with different crystal structures formed by identical spheres. In such structures, both the spheres and the void space will be three-dimensionally connected. The fractional amount of space occupied by the spheres in the total compact structure is determined for cubic, body-centred and face-centred structures as 0.52, 0.68 and 0.74 respectively. With any of the above structures, an attempt to increase the void space will result in complete breakdown of the connected structure of the spheres, where upon they will be surrounded by void space. This reveals that three-dimensional connectivity in the silicone phase could be obtained with a relatively small quantity of this material if it takes the role of the void space.

To obtain the above-mentioned type of morphology, advantage can be taken from the fact that the low-viscous phase tends to form the continuous phase and the high-viscous phase tends to form the dispersed phase [7]. Silicone rubber is very low-viscous and to arrest the flow of the EPDM phase, crosslinked particles of the same were used. Once the desired morphology is attained, the composite will be able to maintain its elongation property after ageing through deformation of the relatively unaffected continuous phase.

2. Experimental procedure

2.1. Materials

The EPDM used was Keltan 520 (DSM, Holland) with ethylene content 55 mol %, diene content 4.5 mol % and density 0.86. The silicone rubber was Silastic 1625 (Dow Corning), type VMQ (i.e. vinyl methyl-based silicone) with specific gravity 1.28–25 °C; curing agents were dicumyl peroxide (DCP) (Hercules Inc., USA) and bis(t-butylperoxy-i-propyl) benzene (Perkadox 14/40) (40% active material).

2.2. Mixing and vulcanization

A complete list of the mixes used in the present investigation is given in Table I. Cured particles of EPDM were formed in a Brabender plasticorder (PLE

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TABLE I Formulation of mixes

Mix	EPDM (parts)	Silicone (parts)	Powder A (parts)[a]	DCP (parts)	Perkadox 14/40 (parts)
A	50	50	–	1.5	–
B	60	40	–	1.5	–
C	70	30	–	1.5	–
D	–	50	50	0.75	–
E	–	40	60	0.60	–
F	–	30	70	0.45	–
G	–	50	50	–	1.88

[a] Powder A is EPDM 100 parts, DCP 1.5 phr mixed at 100 r.p.m. and 170 °C in a Brabender plasticorder as described in section 2.

330). First of all EPDM was compounded with 1.5 phr DCP in a roll mill and this batch was fed to the plasticorder at 170 °C. The plasticorder was run for 10 min at 100 r.p.m. and the final product obtained was cured particles of EPDM (powder A). Mixing for the first set of mixes (mixes A, B and C) was done in a roll mill. For the second set (mixes D, E, F and G) the curative was first mixed with silicone rubber in a roll mill and then it was further compounded with an appropriate amount of powder A in the same roll mill. The specimens were vulcanized in a hot platen hydraulic press at 170 °C and at 5 MPa pressure for 10 min. Post-curing was done for 2 h at 150 °C in a temperature-controlled air-circulated ageing oven (model FC 712, Blue M Electric Co., Blue Island, Illinois).

2.3. Ageing

Heat-ageing of the specimens was carried out using both tensile and tear samples in a test-tube ageing tester (Seisaku-SHO Ltd, Toyoseiki, Japan) at 150 and 175 °C.

2.4. Physical property measurements

Tensile strength, tear strength and hardness were measured for both unaged and aged specimens according to ASTM D 412-80, D 424-81 and D 2240, respectively, in a computerized Zwick UTM (Model 1445) at a crosshead speed of 500 mm min^{-1}.

2.5. SEM studies

The morphologies of the unaged and aged specimens were studied using tensile-fractured surfaces of the blends in a Cam Scan Series II scanning electron microscope after coating the surface with a thin layer of gold in a sputter machine.

3. Results and discussion

3.1. Physical properties

Physical properties of the blends are shown in Table II. The modulus (at 100% elongation) and hardness of the specimens are found to be independent of the method of preparation of the blends, but depend on the composition. Both hardness and modulus decrease as the EPDM content increases. A remarkable variation in tensile strength, elongation at break and tear strength is observed depending on the method of preparation of the blend. The first set of blends (conventional ones, i.e. mixes A, B and C) have considerably higher tensile strength, elongation at break and tear strength than the corresponding blends of the second set (mixes D, E and F).

In the conventional method of blend preparation the two components are blended in the uncured state and thus are flowable; thus some diffusion at the interface is possible which leads to a relatively strong interface. On the other hand, blending for the particulate blends is done with cured particles of EPDM which will not show any flowability. This causes a weak interface. The above observations can be explained on the basis of interfacial strength, distribution of the load between two phases, interface failure and stress concentration. The modulus remains the same for corresponding specimens of the two sets, which indicates that in both cases the load is effectively transferred from one phase to the other through the interface. In other words, along any cross-section of the specimen the load will be more or less uniformly distributed. The low tensile strength and elongation at break for specimens of the second set suggest stress-concentration in one of the phases, probably in the continuous phase following interface failure.

3.2. Effect of ageing

To assess the ageing behaviour of the blends, retention of elongation and TE index [10] (the product of tensile strength retained and elongation retained expressed as a percentage) are reported for the aged specimens in Table III. The results show significant drop in retention of elongation and TE index even after 9 h ageing, and at ageing periods beyond 18 h the specimens lose almost all their useful properties. However, the relative position of the two sets of the blends is altered. Aged specimens of the second (i.e. particulate blends, where EPDM is incorporated as cured particles; mixes D, E and F) show a higher TE index and retention of elongation than corresponding specimens of first set.

The changes in hardness of the specimens with ageing time follow a complex pattern. Although the hardness increases with ageing, its dependence on ageing time is not the same for the two sets. With a particular ageing time, the first set shows a higher

TABLE II Mechanical properties of vulcanizates

Mix	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% elongation (MPa)	Tear strength (N cm^{-1})	Hardness (Shore A)
A	6.0	350	1.4	140	51
B	5.5	400	1.2	151	50
C	4.8	343	1.15	99	49
D	2.2	170	1.4	97	51
E	1.5	130	1.3	98	48
F	1.2	110	1.15	64	51
G	2.3	150	1.5	81	51

TABLE III Ageing behaviour of blends at 175 °C

Mix	Retention of elongation (%)						TE Index						Hardness (Shore A)					
	0 h	9 h	18 h	36 h	72 h	144 h	0 h	9 h	18 h	36 h	72 h	144 h	0 h	9 h	18 h	36 h	72 h	144 h
A	100	15	6.6	4.86	4.29	5.14	100	3.3	1.74	2.8	3.38	4.68	51	60	65	72	80	85
B	100	12.5	4.25	3.25	3.5	3.25	100	3.01	1.37	1.22	3.625	2.96	52	58	59	62[a]	80	84
C	100	12.83	5.54	3.5	4.08	2.04	100	3.29	2.25	2.11	3.91	1.61	50	56	58	60[a]	65[a]	85
D	100	50	22.35	12.94	9.41	5.88	100	34.1	13.2	8.47	6.84	5.35	51	55	62	65	65	78
E	100	61.54	16.92	10.76	7.69	6.15	100	50.05	11.73	8.54	8.15	7.79	50	53	55	58	62	70
F	100	57.27	2.0	10	6.35	6.54	100	51.39	17.09	11.28	7.89	9.46	48	52	53	58	61	67

[a] Surface breakdown occurred during measurement.

hardness than corresponding specimens of second set. Again at higher ageing time, some specimens of the first set show surface breakdown while measuring hardness (indicated in Table III). It is seen that the second set of specimens has superior ageing properties with regard to elongation and hardness. To understand the complex behaviour of hardness change with ageing, hardness was measured as a function of ageing time for 1.5 phr DCP-cured specimens of silicone and EPDM. The results are reported in Table IV. Silicone rubber shows a slow rise in hardness with ageing time, whereas EPDM shows a slight reduction in hardness. On further ageing, the rise in hardness is not significant. Ultimately the surface of the EPDM sample hardens at 36 h while the bulk of the specimen remains soft, as evidenced from the fact that although the surface of EPDM breaks during hardness measurement, the measured value of hardness is considerably low. This phenomenon of surface hardening and its breakdown is observed with the specimens containing higher amounts of EPDM in the first set (mixes B and C).

TABLE IV Ageing behaviour of silicone and EPDM at 175 °C

Specimen	Hardness (Shore A)				
	0 h	5 h	9 h	18 h	36 h
Silicone	58	59	61	62	63
EPDM	49	47	48	49	52[a]

[a] Surface breakdown occurred during measurement.

3.3. Role of Perkadox 14/40 in the silicone phase

The role of morphology and its stability on the physical properties and ageing behaviour of silicone–EPDM has been reported earlier [8]. A different morphology was developed in a Brabenden Plasticorder (PLE 330) using a compatibilizer and a two-stage curing technique. Physical property measurements (e.g. modulus at 100% elongation and volume fraction of rubber in the swollen gel) confirmed that DCP offers a higher extent of crosslinking to EPDM, and Perkadox offers a higher crosslinking to silicone at identical dosage. Thus it was argued that if in the composite structure silicone is cured with Perkadox and EPDM is cured with DCP, the composite will be more stable at high temperature. Also the tight network structure in the silicone phase which surrounds the EPDM particles is expected to act as a better barrier for diffusion of oxygen to the EPDM phase. In the previous section it was observed that within the initial 9 h of ageing at 175 °C, the properties fall off drastically: in other words, the ageing process is quite fast at this temperature, so to get a thorough picture of ageing a lower ageing temperature (150 °C) was also tried. The study of the present section is confined to 50/50 blends (mixes D and G) only and the results are shown in Table V. The ageing behaviour of the specimens indicates the beneficial action of strengthening the silicone phase. The effect is more pronounced at 150 °C and at relatively low ageing periods. In fact Perkadox-cured specimens show some improvement in properties on initial ageing.

3.4. SEM observations

SEM observations of unaged specimens show that a finer dispersion of phases occurs in the conventional

TABLE V Effect of curative system in silicone phase on the ageing behaviour of 50/50 blend

Ageing time (h)	Ageing temperature (°C)	Tensile strength (% retention)		Elongation at break (% retention)		Tear strength (N cm^{-1})		Hardness (Shore A)	
		Mix D	Mix G	Mix D	Mix G	Mix D	Mix G	Mix D	Mix G
0	–	100	100	100	100	97	81	51	51
5	150	88.24	72.26	86.23	50.55	73	54	51	51
	175	86.47	111.68	67.2	105.6	94	106	53	52
9	150	60.00	99.27	30.55	78.79	59	101	52	53
	175	60.50	59.12	34.09	38.44	47	48	55	55
18	150	61.76	88.32	40.71	62.18	42	66	53	53
	175	22.35	27.01	13.21	15.86	48	51	62	62
36	150	52.94	73.72	33.93	48.92	55	60	54	55
	175	12.94	26.28	8.47	15.31	40	42	65	62
72	150	31.18	45.99	16.58	26.40	45	42	57	57
	175	9.41	14.6	6.84	9.82	–	–	65	65
144	150	14.12	18.98	9.3	12.34	47	44	62	63
	175	5.88	14.6	5.35	12.44	–	–	78	78

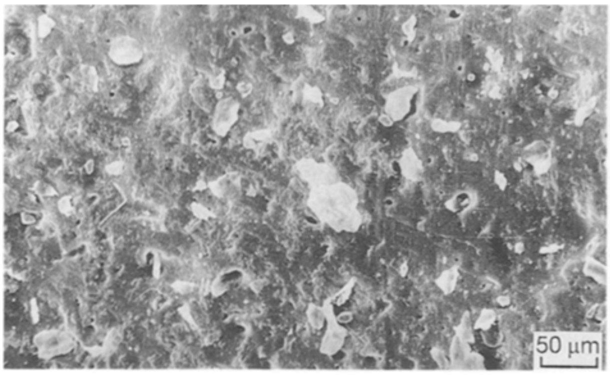

Figure 1 SEM photograph of 50:50 particulate blend (mix D).

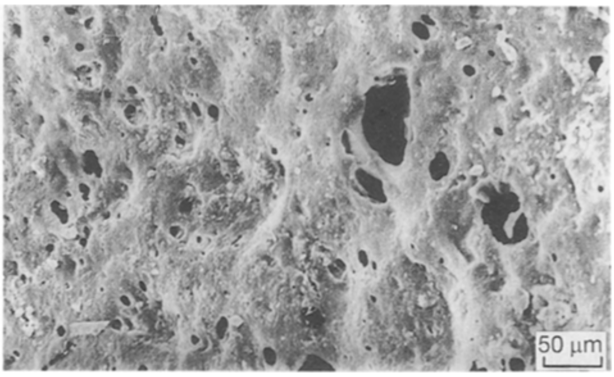

Figure 3 SEM photograph of 50:50 particulate blend (mix D), aged for 9 h at 175 °C.

Figure 2 SEM photograph of 50:50 conventional blend (mix A).

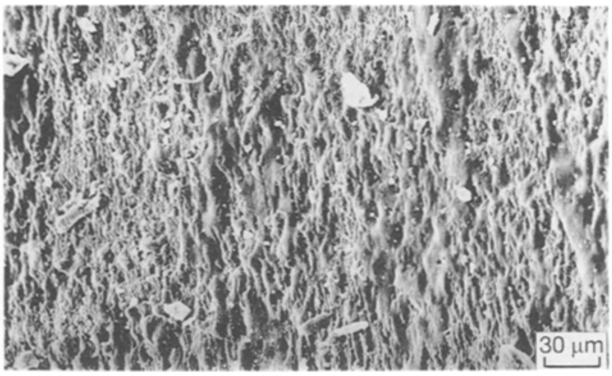

Figure 4 SEM photograph of 50:50 conventional blend (mix A), aged for 9 h at 175 °C.

blends than in the particulate blends (Figs 1 and 2). Ageing of the specimens also shows that phase separation occurs in both cases (Figs 3 and 4). Poor adhesion between silicone and EPDM phases is also evident from the fact that along the fractured surface particles come out of the structure, leaving behind equivalent vacuoles in the particulate blends. This explains the source of stress concentration and subsequent premature failure of the particulate blends, as explained in a previous section. Such behaviour is understandable from the incompatible natures of the two elastomers and the lack of flow at the interface during processing as the EPDM particles are crosslinked.

The most important observation is that although phase domains in the conventional blends merge, the particulate blends show that a continuous matrix surrounds the particles. The improved ageing properties of the particulate blends discussed so far can be explained on the basis of the above observation. The continuous phase being silicone, it is resistant to heat-ageing and maintains its rubberiness. The improved performance is due to the ability of the composite structure to deform under load through deformation of the continuous phase, while still maintaining structural integrity.

4. Conclusions

1. The physical properties of a blend depend very much on the method of the blend preparation. The controlling parameter is the morphology of the blend.
2. Ageing behaviour is influenced by the morphology of a blend.
3. Continuity of the heat-resistant phase and its strengthening adds to high-temperature stability of the blend.

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Received 13 January
and accepted 8 October 1993