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Influence of chemical interaction on the properties of silicone–EPDM rubber blend

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Acrylamide-grafted silicone (AM-*g*-Si) and maleic anhydride modified EPDM (MA-*g*-EP) were blended in a weight ratio of 50:50 at 35, 70 and 150°C and moulded at the blending temperature in order to understand the effect of interaction on the physical properties. I.r. spectra confirm the chemical bonding between the two rubbers. The tensile strength, the modulus and the swelling resistance increase with the extent of interaction. Ageing studies at 175°C for various times and dynamic thermogravimetry further reveal improved retention of physical properties and thermal stability of the interactive blends. The chemical interaction increases the storage modulus in the rubbery zone.

(Keywords: chemical interaction; rubber blends; physical properties)

INTRODUCTION

Blending polymers has become an interesting way for producing new materials with tailored properties. Unfortunately, most of these materials are incompatible owing to the difference in their viscoelastic properties, surface energy and interactions[1], and the properties are not obtained at the expected levels. Hence, efforts are underway to enhance specific interactions between polymer components. In our earlier communications, we have reported the incompatible nature of 50:50 silicone–EPDM blends[2] and observed that technological compatibility could be achieved by introducing a physical compatibilizer which interacts with both the components[3] or by modifying the components to induce dipole–dipole interactions[4]. In this paper, our objective is to graft silicone rubber with acrylamide and EPDM with maleic anhydride/maleic acid and then to study a 50:50 blend of the modified rubbers in order to understand the effect of chemical interaction between the components on the physico-mechanical properties. Improvement in the physical properties and the morphology, by increasing the interaction between the component polymers, has been reported by several workers[5–10]. The degree of enhancement varies from system to system. In a few cases, however, chemical interaction causes deterioration of the properties, i.e. for natural rubber–polypropylene (PP) blends when the crystallinity of PP is affected[8].

EXPERIMENTAL

Materials

JSR silicone EH5270, heat-cured silicone rubber was supplied by Japan Synthetic Rubber Co. Ltd (Japan). It is greyish white in colour, with a specific gravity of 1.31. It contains occasional vinyl groups (0.45%) for cross-linking purposes.

The maleated EPDM used was Royaltuf 465. It has a specific gravity of 0.89, total maleic anhydride/acid 1%, Mooney viscosity, $ML_{(1+4)}$, of 60 at 125°C, and an iodine value of 17.

The acrylamide monomer was soluble in water, with a melting point of 85°C.

Ammonium persulfate was used as initiator for polymerization. It was soluble in water, and was procured from Aldrich Chemical Co. (USA).

The curing agent, dicumyl peroxide (DCP), was supplied by Hercules Inc. (USA).

Grafting of acrylamide onto silicone and its characteristics

Silicone rubber (100 g), acrylamide (9.00 g) and ammonium persulfate (0.25 g) were premixed in a roll mill. The grafting reaction was carried out in a Brabender Plasticorder (PLE-330) at 80°C and 100 rev min^{-1} rotor speed for 15 min. Unreacted monomer was removed by heating polymer films (150 μm thick) in boiling water for 1 h and leaving the films overnight in fresh distilled water at room temperature. The grafting level was determined from the i.r. spectra.

Mixing and moulding

The amide-grafted silicone and the maleated EPDM were mixed in a Brabender Plasticorder (50:50 weight ratio) at three different temperatures (35, 70 and 150°C) for 15 min and at a rotor speed of 100 rev min^{-1}. DCP (1.5 phr) where required for vulcanization, was mixed on an open roll mill at room temperature.

Moulding was done in a Labo press at 150°C for 10 min at 5 MPa pressure followed by post-curing for 2 h at 150°C in an air-circulated oven. The blends mixed at 35 and 70°C were moulded at 35 and 70°C, respectively,

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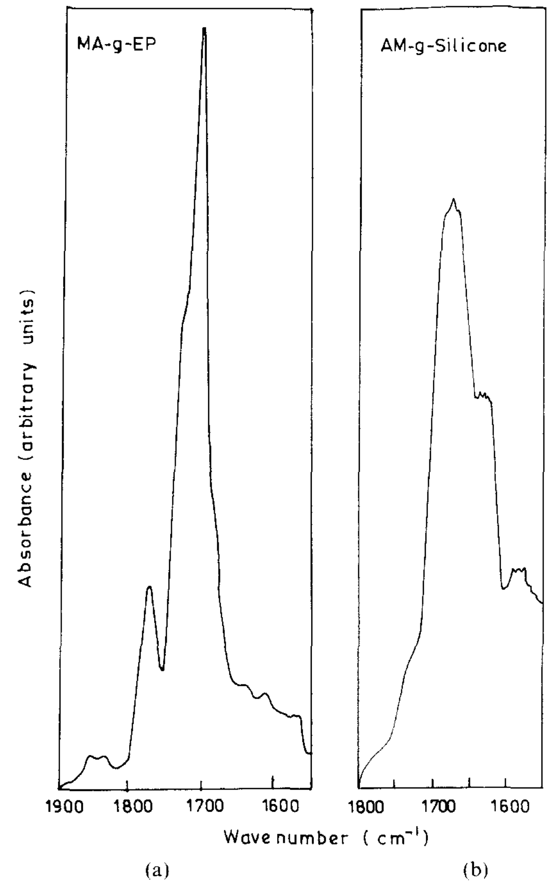


Figure 1 I.r. spectra of the functionalized polymers

for 10 min. For the i.r. study, thin films were also made by a similar procedure, without post-curing.

I.r. study

The i.r. study was carried out on thin films by using a Perkin-Elmer 843 infra-red spectrophotometer.

The grafting level was calculated from the calibration curve prepared from i.r. absorption of silicone films containing different amounts of polyacrylamide. The grafting level was found to be 26 mmol per mol of siloxane.

Physical properties

Physical properties, i.e. tensile strength, modulus and elongation at break, were measured in a Zwick UTM (model 1445) at a crosshead speed of 500 mm min^{-1} as described in ASTM D412-80. Equilibrium swelling of the vulcanizates in n-hexane was determined. The volume fraction of rubber (V_r) in the swollen gel was calculated by using the procedure described previously[2].

Ageing

Ageing of the specimens was performed in a multicell Test Tube Ageing Tester (Seisaku-SHO Ltd, Toyoseiki, Japan) at 175°C for 9, 18 and 36 h.

Thermal analysis

Thermogravimetric analysis was carried out in a 951 Thermogravimetric Analyser (DuPont) from ambient temperature to 800°C at a heating rate of 20°C min^{-1} in a nitrogen environment. Degradation kinetics was studied by the Freeman–Carroll method[11] for the order and activation energy of the degradation process.

Table 1 I.r. absorption peaks (cm^{-1}) observed for the blends and the individual components processed at different temperatures

		Blend (50:50) at		
Am-*g*-Si	MA-*g*-EP	35°C	70°C	150°C
–	1840	1877 (m)	1877 (m)	1875 (w)
	1781	1786 (w)	1780 (w)	1775 (w)
	1711	1710	1709	1700 (w)
–		1680	1675	1672
1660		1663 (m)	1660 (w)	–
Broad band 1640–1620		1624 (m)	1622 (m)	1620 (w)
Broad weak band 1615–1590				

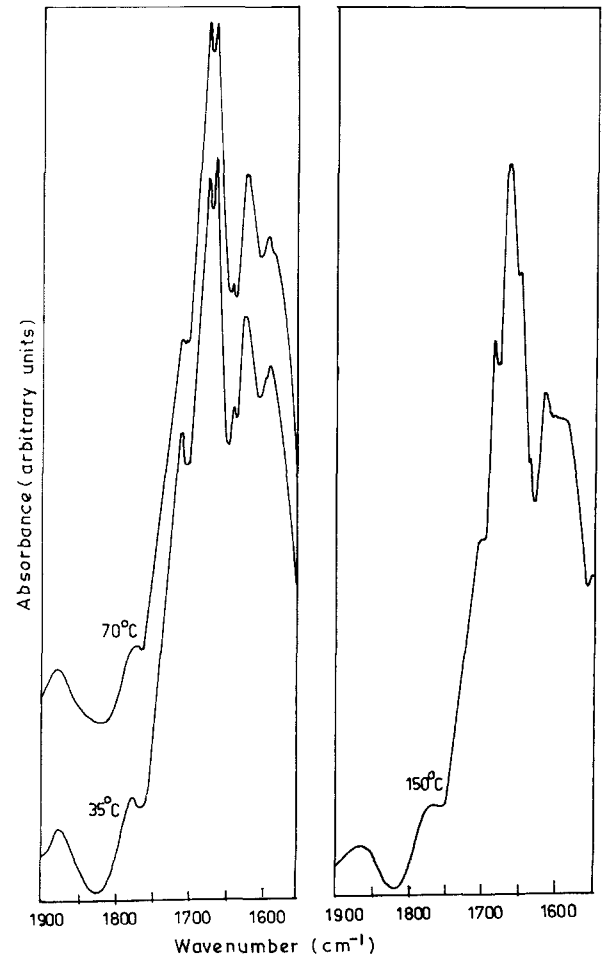


Figure 2 I.r. spectra of the blends prepared at various mixing temperatures

Dynamic mechanical analysis

Dynamic mechanical behaviour was studied in a Dynamic Mechanical Thermal Analyser (model MK-II, Polymer Laboratories, UK) in shear mode at a strain of 2% in the temperature range from −140 to 200°C with temperature rise of 2°C min^{-1}.

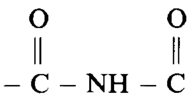
RESULTS AND DISCUSSION

I.r. study

Figure 1a shows the expanded i.r. spectrum of maleated EPDM (MA-*g*-EP) in the 1900–1550 cm^{-1}

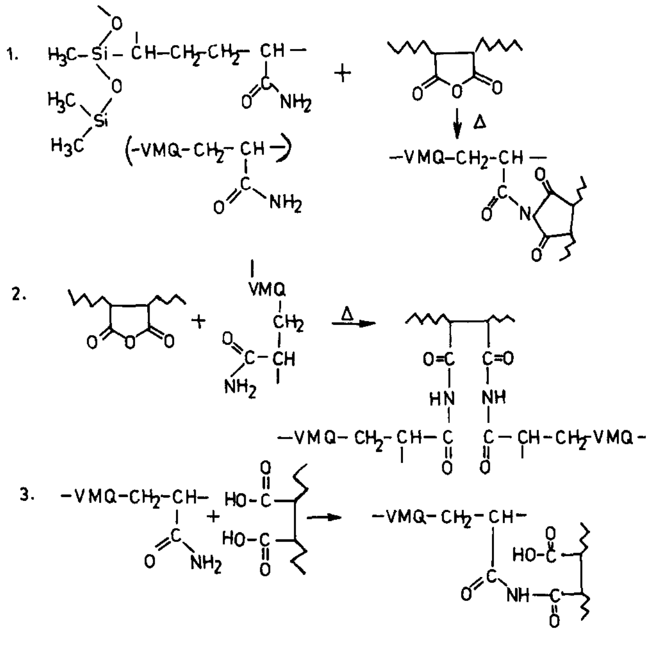
region. The spectrum shows a broad band near 1840 cm^{-1}, a sharp medium intensity peak at 1781 cm^{-1} and a strong peak at 1711 cm^{-1}. The first two bands correspond to the asymmetric and symmetric >C=O stretching of the five-membered saturated-ring anhydrides[12]. The strong peak at 1711 cm^{-1} is due to the >C=O stretching of H-bonded saturated carboxylic acid[12]. The acrylamide grafted silicone rubber (AM-*g*-Si) is characterized by a strong absorption near 1660 cm^{-1} (*Figure 1b*) corresponding to the >C=O stretching vibration of the primary amides in the solid phase[12]. However, the amide II band due to the N–H deformation (1650–1620 cm^{-1} in the solid phase) is missing in the spectra and is probably submerged within the amide I band.

The spectra of the (50 : 50) blend of MA-*g*-EP and AM-*g*-Si at 35, 70 and 150°C show several new peaks. The observed peaks are tabulated in *Table 1* and shown in the expanded spectra (*Figure 2*). In all the cases, the >C=O stretching bands of the anhydride have shifted to higher frequencies (1875 and 1786–1775 cm^{-1}), probably due to the reduction in the extent of interactions of the >C=O groups in the blend. All other bands of MA-*g*-EP and AM-*g*-Si are present in the spectrum of each blend, with a new peak at 1680 cm^{-1} due to the unassociated >C=O stretching of the amide. It is interesting to note that, on increasing the temperature of moulding (to 70 and 150°C from 35°C), the anhydride peak intensity is much reduced. At 150°C, the intensity of >C=O stretching of the associated carboxyl group is greatly reduced and the peak position shifts to a lower frequency (1700 cm^{-1}) as well. The >C=O stretching vibration of the associated H-bonded amide (1660 cm^{-1}) almost disappears and the strongest peak in this spectrum is observed at 1672 cm^{-1}. This peak may be assigned to the asymmetric >C=O stretching band of a diacyl amine group:



$$-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\overset{\overset{\displaystyle O}{\|}}{C}-$$

with another broad band at 1775 cm^{-1} due to the symmetric >C=O stretching[12] of the same group. However, the possible formation of a five-membered cyclic imide cannot be ruled out; if present, this would give bands at 1770 and 1700 cm^{-1} for the symmetric and asymmetric >C=O stretching, respectively[12]. From the above discussion, the following newly formed structures may be assumed when the blend is processed at 150°C (VMQ, an ISO designation for vinyl methyl silicone, has been used in the reaction scheme for abbreviation):



Physical properties

Physical properties of the blends are reported in *Table 2*. The amount of interaction, represented by the volume fraction of rubber in the swollen gel in the case of the uncrosslinked blend, is also given in the table. A comparison of the results of the functionalized blend (sample C) with that of the control sample (D) reveals a

Table 2 Physical properties of the blends

Properties	Sample^a A	B	C	D
Tensile strength (MPa)	0.9	1.7	5.3	4.2
Elongation at break (%)	95	140	175	250
Modulus at 100% (MPa)	–	1.2	2.9	2.0
Volume fraction of rubber, V_r	0.11	0.15	0.37	0.25
Retention of properties after ageing time, t, at 175°C				
Tensile strength (%)				
$t = 9$ h	145	117	72	35
$t = 18$ h	148	125	85	35
$t = 36$ h	110	105	88	40
Elongation at break (%)				
$t = 9$ h	65	55	50	25
$t = 18$ h	40	43	41	14
$t = 36$ h	19	24	31	5
Thermogravimetric analysis				
Activation energy (kcal mol^{-1})	54	58	62	49
$T_{max,1}$ (°C)	482	489	492	473
$T_{max,2}$ (°C)	535	542	547	520

^{a} A, AM-*g*-Si + MA-*g*-EP blended and moulded at 35°C; B, AM-*g*-Si + MA-*g*-EP blended and moulded at 150°C; C, AM-*g*-Si + MA-*g*-EP blended and cured at 150°C; D, control silicone + EPDM blend cured at 150°C. The components were blended in a 50:50 ratio

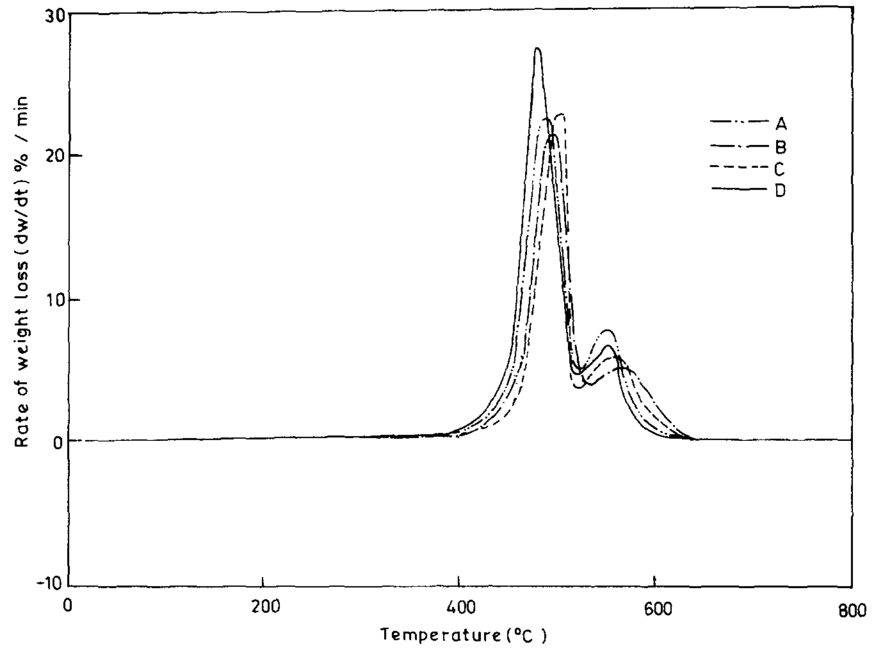


Figure 3 Differential thermogravimetric curves of various blends

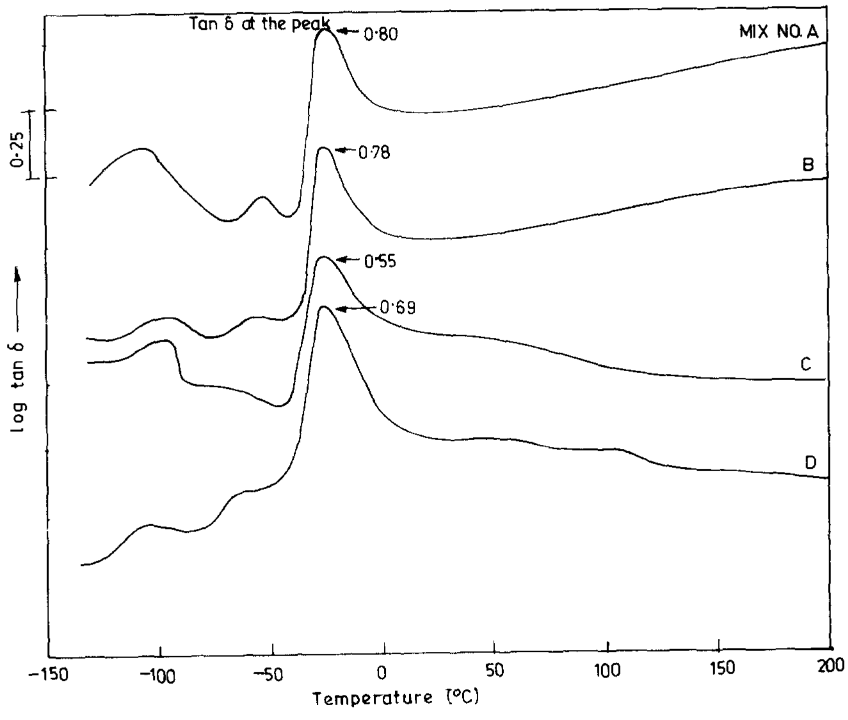


Figure 4 Loss tangent behaviour of various blends

fair increase in modulus (45%) and tensile strength (26%). The elongation at break, however, decreases. Similarly, the higher the interaction, the higher is the tensile strength and modulus (samples A and B). These observations are true for the compounds with and without the curing agent.

Ageing behaviour of the blends is also shown in *Table 2*. The results clearly indicate that the blends prepared with different levels of chemical interaction have remarkably higher ageing resistance over the control blend. For example, there is at least a two-fold increase in the retention of tensile strength of sample C over sample D. The retention of elongation at break is also much better for C at all times of ageing at 175°C. The results for samples without the curing agent at 9 h and 18 h of ageing demonstrate that there is further interaction between the components on ageing, resulting in higher tensile properties. With increasing the ageing time from 9 h to 36 h, the cured modified sample (C) shows an increase in tensile strength and reduction in the elongation at break due to the post-curing reaction.

The results could be explained as follows. The thermal

Table 3 Storage modulus of the various samples

	Storage modulus, G' (MPa) at					
Sample	25°C	50°C	75°C	100°C	125°C	150°C
A	0.95	0.94	0.82	0.74	0.58	0.41
B	1.88	1.76	1.48	1.20	0.91	0.65
C	2.51	2.44	2.39	2.25	2.07	2.05
D	1.99	1.95	1.97	1.99	1.99	2.02

stability of EPDM is lower than that of silicone. By increasing the interaction between the components, EPDM rubber is protected because (1) the chain length may be increased by reaction, (2) the generation of small degraded fragments from EPDM, which help in further degradation by a diffusion mechanism, may be prevented, and (3) silicone may form a protective layer.

Thermogravimetric analysis of the blends further confirms these observations. *Figure 3* shows thermogravimetric curves of the representative blends. The various parameters calculated from the figures are given in *Table 2*. The unfunctionalized blend has lower thermal stability than the blends with chemical interaction. This is also evident from the lower value of the activation energy of the non-functionalized blend, and the lower decomposition temperatures $T_{max,1}$ and $T_{max,2}$ (samples C and D, *Table 2*). As the extent of chemical interaction increases in the AM-*g*-Si and MA-*g*-EP blends, the thermal stability increases, in spite of the low crosslink density of room-temperature interaction of blend A. Considerable increase in thermal stability is probably partly contributed by the dipole–dipole interaction. These polar groups will have some induction effect on the adjacent main-chain atoms and thus will influence the main-chain degradation kinetics. Also, the imide groups forming crosslinks are very resistant to thermal degradation. Again, these functional groups provide multifunctional crosslinking sites. Such crosslinks have the advantage that the chain length between two crosslink points will be low at the same level of crosslinking, and so the possibility of release of a degradation product by main-chain scission may be reduced.

Dynamic mechanical analysis of the blends

Loss tangent data of various blends are shown in *Figure 4*. Sample A shows the general characteristics of an incompatible blend. The loss tangent peak at −109°C is due to the glass transition of silicone and the peak at −23°C is due to a combination of the glass transition of EPDM and the melting of silicone crystallites. A very small hump at about −55°C indicates the amorphous to crystalline transition in silicone[2]. The magnitude of the hump indicates the low level of crystallization which may be due to the presence of polar–polar or chemical interaction. Such behaviour has also been observed in the AM-*g*-Si/sulfonated EPDM system[4].

As the level of interaction is increased (i.e. compare blends A and B and C and D), the glass transition peak of silicone and the hump due to the amorphous to crystalline transition tend to vanish. Instead, a very broad peak at −83°C is observed. This also confirms the chemical reaction between the components. It influences the mobility of the segments and ultimately results in some intermediate mobility with glass transition temperature in between those of the silicone rubber and the EPDM rubber. The height of the second loss tangent peak in this blend also decreases, which indicates that the availability of free EPDM segment is reduced.

The storage modulus values for these blends are reported in *Table 3*. At low temperatures (below the second loss tangent peak), the blend with chemical interaction shows a lower value of the storage modulus than the unfunctionalized blend due to lack of crystallization, as described in a previous paragraph. In this respect, these blends are identical in nature with that having dipole–dipole interaction (AM-*g*-Si/sulfonated EPDM). At room temperature and above, the storage modulus shows a reversal in the trend. The specimen without functional groups has a lower value of the storage modulus and this difference decreases in the region 100–125°C due to thermal breakdown of the dipole–dipole bonds. Beyond this point, the DCP-cured blend C shows some marginal improvement in storage modulus compared to the unfunctionalized blend, owing to the additional crosslinks arising from the chemical interaction between the components.

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