Interaction between silicone and EPDM rubbers through functionalization and its effect on properties of the blend

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Silicone rubber was functionalized with acrylamide (AM) to effect interaction with sulfonated EPDM. I.r. spectroscopic studies confirm the dipole–dipole interactions between this graft copolymer (AM-*g*-silicone) and sulfonated EPDM (S-EPDM) through the splitting of the carbonyl stretching and N–H stretching peaks. Physical property measurements show that the functionalized blend has a higher tensile strength, modulus and swelling resistance and lower elongation at break. The thermal stability and ageing behaviour of the new blends are improved owing to an increase in the activation energy of degradation. Finally, dynamic measurements show that the transition temperatures are all increased by 8–10°C and the storage modulus in the temperature range 25–125°C is higher, owing to strong interspecies interactions between the components in the functionalized blends.

(Keywords: silicone rubber; EPDM rubber; functionalization)

INTRODUCTION

Polymer compatibility is an important criterion in the field of polymer blends. There are two types of compatibility referred to in the literature: thermodynamic compatibility and technological compatibility[1]. Thermodynamically compatibilized polymer blends are few in number and difficult to generate. On the other hand, technological compatibilization leads to an enhancement of the properties of blends. In making a large number of industrial polymer blends, technological compatibilization is often employed[1,2]. Various methods to develop a compatible blend include the use of physical and chemical compatibilizers[3,4], suitably functionalized polymers[5,6], polymer pairs having very close solubility parameters[7] and polymer pairs properly functionalized to give a high degree of specific interaction.

Our objective was to develop a blend of silicone and EPDM rubbers through dipole–dipole interactions. Previously, the incompatible nature of the silicone–EPDM blend has been established[8,9]. The steam and moisture resistance of silicone is improved by EPDM and the high temperature properties of EPDM are enhanced by silicone. Also, in our earlier studies we observed that physical compatibilizers like silane-grafted EPR, ethylene–methyl acrylate (EMA) and ethylene–vinyl acetate (EVA) offer better properties over the control blends[8–10]. Hence, this investigation was aimed at further enhancing the interaction between the components. For this purpose, we prepared a blend of sulfonated EPDM (S-EPDM) and acrylamide-grafted silicone rubber, characterized it by i.r. spectroscopy and investigated its physical and dynamic mechanical properties, swelling behaviour and thermal stability.

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EXPERIMENTAL

Materials

Silicone rubber (JSR silicone EH5270, heat-cured type, greyish-white, specific gravity 1.31) was purchased from the Japan Synthetic Rubber Co. Ltd (Japan).

Sulfonated EPDM (ionomer 2590, specific gravity 1.12, Mooney viscosity $ML_{(1+4)}$ at 100°C = 45, average number of SO_3 groups per molecule = 13, 2.7 wt% ionic groups) was supplied by Uniroyal Chemical Co. (USA).

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

Ammonium persulfate, the initiator for the polymerization, soluble in water, was purchased from Aldrich Chemical Co. (USA).

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

Grafting of acrylamide

Silicone (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 i.r. spectroscopy.

Blending

The formulations of the blends are shown in *Table 1*. The two elastomers were blended at 120°C in the Brabender Plasticorder at a 100 rev min^{-1} rotor speed

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Table 1 Physical properties of the blends

Properties	Silicone–EPDM–DCP (50:50:1.5)			AM–*g*–silicone–S–EPDM–DCP (50:50:1.5)		
Tensile strength (MPa)	4.2(0.34)[a]			4.6(0.54)[a]		
Elongation at break (EB) (%)	250(130)[a]			160(40)[a]		
Modulus at 100% elongation (MPa)	2.0			2.5		
V_r	0.25			0.35		
Ageing at 175°C (h)	9	18	36	9	18	36
Retention of tensile strength (%)	35	35	40	55	57	55
Retention of EB (%)	25	14	5	43	36	20
TE index	9	5	2	24	20	11

[a] Results for the unvulcanized compounds

for 10 min. DCP, whenever required, was mixed with the blend in a two-roll mill at room temperature.

Moulding

Rectangular slabs were moulded at 170°C for 10 min under 5 MPa pressure. The specimens containing curative were also postcured at 150°C for 2 h.

I.r. studies

I.r. studies were carried out on thin films using a Perkin–Elmer 843 i.r. spectrophotometer. In order to get better films, low density polyethylene was used as the matrix material[11].

Physical properties

The tensile strength, modulus and elongation at break were measured in a Zwick UTM (model 1445) at a cross-head speed of 500 mm min^{-1} as per ASTM D 412-80. The TE index was defined as the product of the percentage retention of tensile strength and the percentage retention of elongation divided by 100. The volume fraction of rubber (V_r) was determined by swelling the rubber in n-hexane for 48 h and subsequently drying the sample for 24 h in a vacuum oven at 50°C[8].

Thermal analysis

Thermal degradation was studied non-isothermally from ambient temperature to 800°C at a programmed heating rate of 20°C min^{-1} in a nitrogen environment using a model 951 thermogravimetric analyser fitted to a model 9000 thermal analyser from DuPont (USA).

Dynamic mechanical analysis

Dynamic mechanical properties were evaluated using a dynamic mechanical thermal analyser (model MK-II, Polymer Laboratories, UK) in shear mode at a frequency of 10 Hz and at a 64 μm peak to peak strain in the temperature range from −140°C to 200°C with a 2°C min^{-1} temperature rise.

RESULTS AND DISCUSSION

I.r. studies

Figure 1a shows the i.r. spectrum of silicone rubber (poly(dimethylsiloxane) (PDMS)) in the 1800–1500 cm^{-1} region. The absorption peak at 1623 cm^{-1} is attributed to the C=C stretching vibrations of the vinyl groups attached to the silicon atoms ($-SiCH=CH_2$)[12]. However, after reaction with acrylamide monomer in the presence

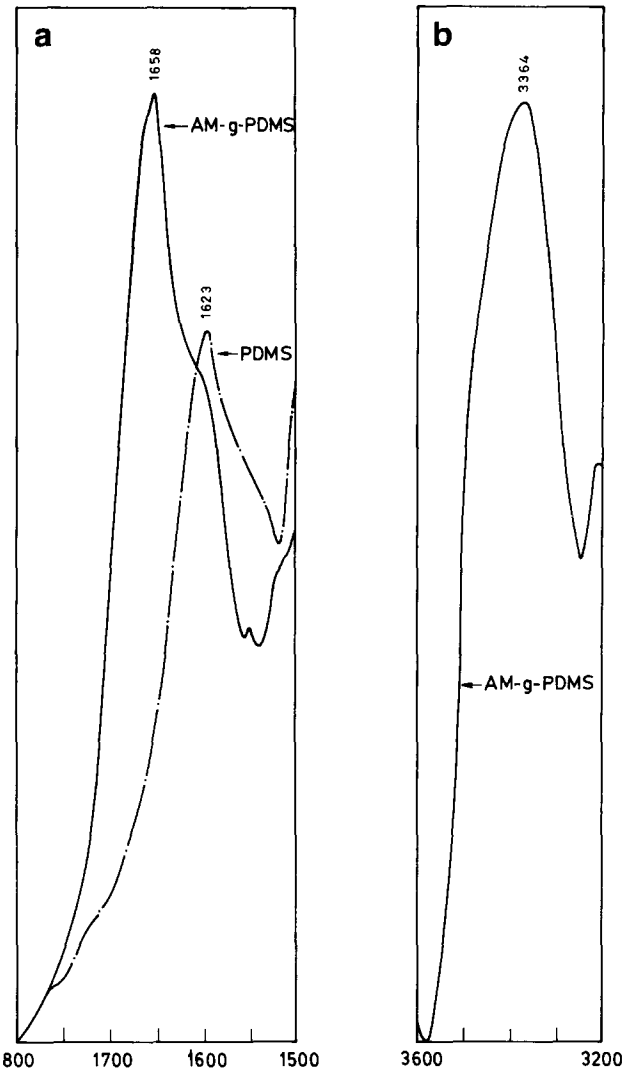


Figure 1 (a) I.r. spectra of silicone and its graft copolymer in the C=C and C=O stretching region. (b) I.r. spectrum of acrylamide-grafted silicone in the amide N–H stretching region

of ammonium persulfate initiator this peak becomes considerably reduced, while a new peak at 1658 cm^{-1} from the C=O stretching vibrations of grafted acrylamide moieties[13] appears. The grafting of acrylamide onto silicone is further supported by a strong and broad peak at 3364 cm^{-1} in the spectrum of acrylamide-grafted silicone (AM-*g*-silicone), as depicted in *Figure 1b*. This broad band is typical of solid-phase, hydrogen-bonded acrylamides, owing to the N–H stretching vibration[12].

When the AM-*g*-silicone is blended with sulfonated EPDM (50:50), a distinct splitting of the carbonyl stretching peak is observed (*Figure 2*). The simulated spectrum of a 1:1 artificial mixture of the two blend components and the difference spectrum of the blend and the simulated artificial mixture are also shown to elaborate this. The latter spectrum shows the distinctive features of the various interactions of the amide carbonyl group of AM-*g*-silicone in the blend. The shifts to lower frequency are caused by hydrogen bonds with either the –NH groups of acrylamide or the $-SO_2OH$ groups of sulfonated EPDM. The shifts to higher frequency may be attributed to the fact that during melt mixing all the hydrogen bonds in AM-*g*-silicone are broken; some of them are involved in the reassociation, but some others

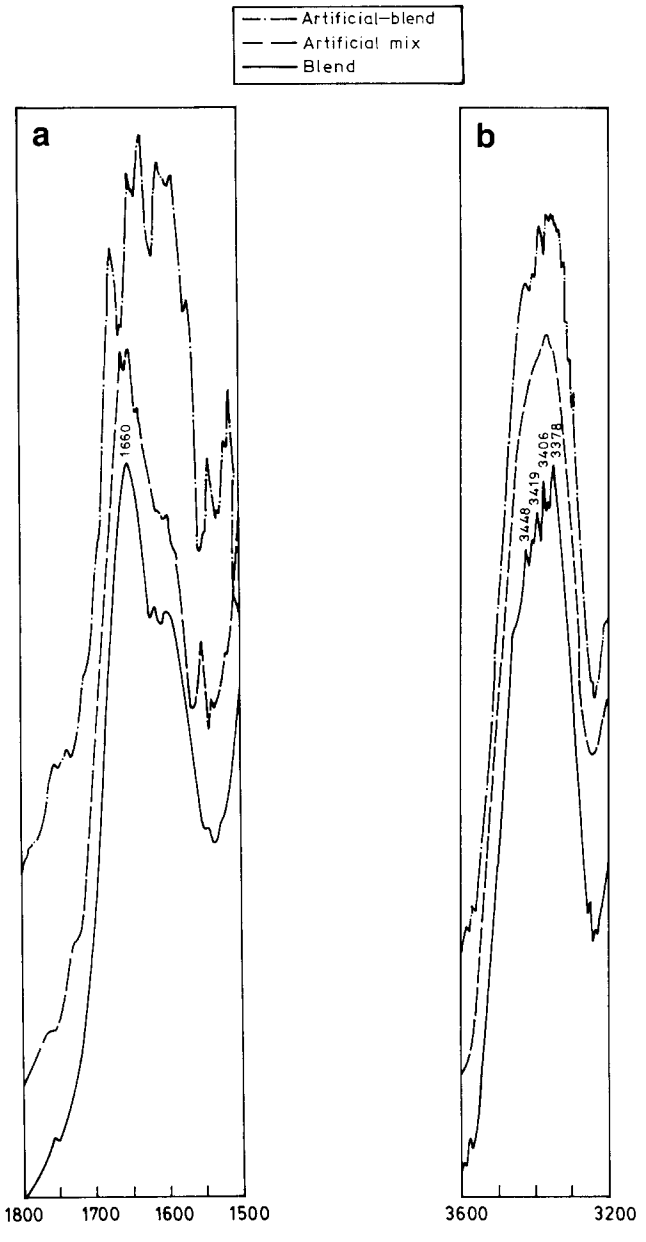
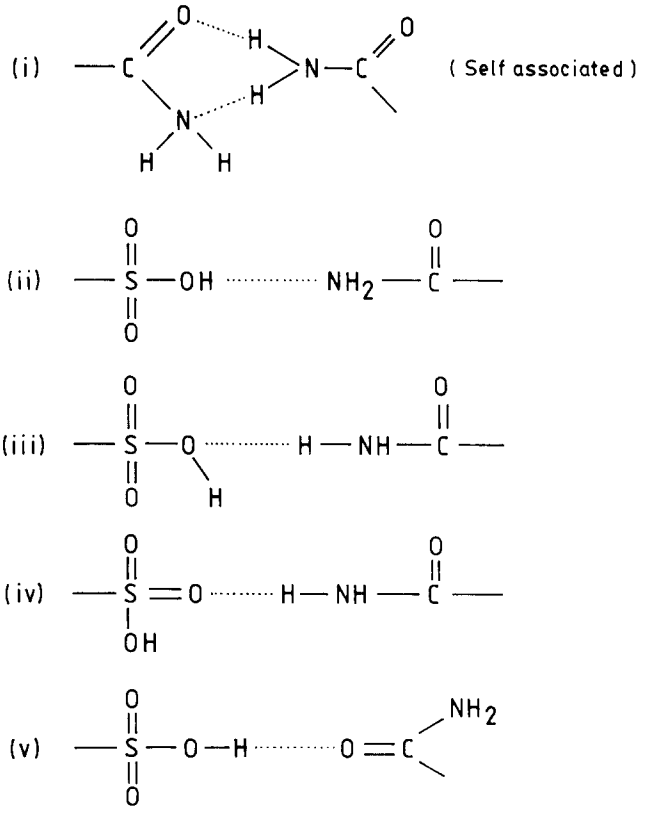


Figure 2 (a) I.r. spectra of the blends in the C=O stretching region. (b) I.r. spectra of the blends in the N–H stretching region



Scheme 1 Schematic diagram of various interactions

remain unassociated owing to hindrance from the non-polar ethylene–propylene chains of the EPDM segments.

The spectra in the 3600–3200 cm^{-1} region (*Figure 2b*), i.e. the N–H stretching region, also reflect similar information. The difference spectrum of the simulated artificial mixture and the blend and the spectrum of the blend show multiple peaks. The various types of possible interaction in the blend of sulfonated EPDM and AM-*g*-silicone are shown schematically in *Scheme 1*.

Effect of functionalization of the base polymers on the physicomechanical properties of the blend

The physical properties of both the vulcanized and unvulcanized blends are reported in *Table 1*. The unvulcanized blend of the functionalized elastomers shows a considerable improvement in the tensile strength (about a 60% rise in tensile strength) over the control blend. However, the elongation at break drastically falls from 130% to 40%. Such behaviour in a binary system with very strong interactions has already been reported[14]. The effects of interaction are also present in the vulcanized blends. The blend of the functionalized species shows a lower elongation at break and a higher modulus, tensile strength and volume fraction of rubber. As reported in the section on i.r. studies, functionalization at the molecular level will induce dipole–dipole interactions and hydrogen bonding. Thus, intermolecular forces will increase, resulting in improved properties.

Ageing behaviour

The interaction between the components is more clear from the ageing studies (*Table 1*). Functionalization improves the retention of tensile strength (55% or more against 35–40% for the control), the retention of elongation at break (40–20% against 25–5% for the control) and the TE index. These improvements may be explained by the fact that weaker molecular chains are protected by the dipole–dipole interactions between the components.

Thermal stability of the vulcanized blends

The results of non-isothermal thermogravimetric analysis are shown in *Figure 3*. The results clearly indicate that the modified blend is superior to the unmodified blend with respect to thermal stability. The activation energy for degradation, calculated using the Freeman–Carrol procedure reported in an earlier paper[10], increases from 49 kcal mol^{-1} to 58 kcal mol^{-1} (1 cal = 4.2 J). The decomposition peaks ($T_{max,1}$ and $T_{max,2}$) also shift considerably (from 473°C to 488°C and from 520°C to 536°C, respectively). The improvement in thermal stability is mainly caused by the increase in the activation energy of degradation, arising from strong interactions among the components.

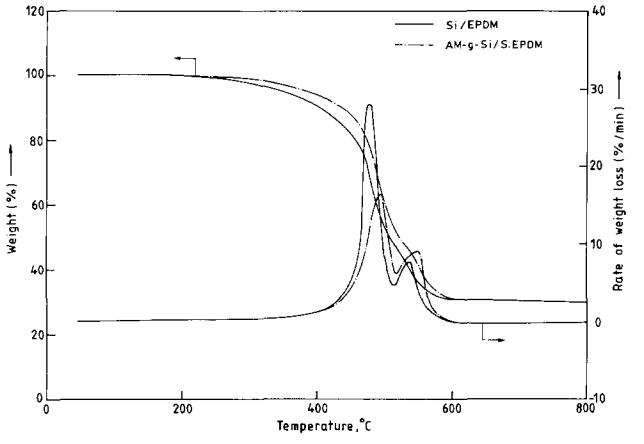


Figure 3 Thermogravimetric and differential thermogravimetric curves of the blends

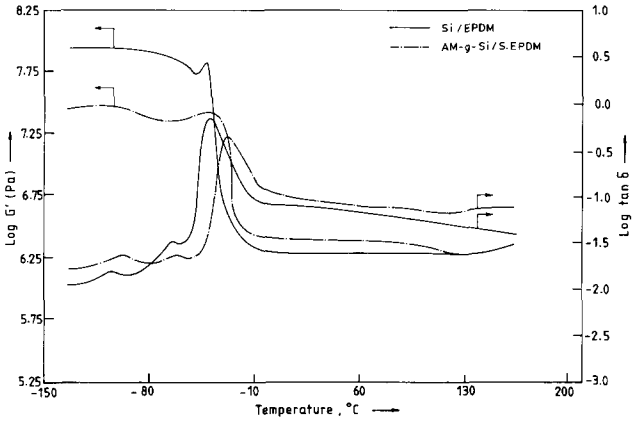


Figure 4 Storage modulus and loss tangent behaviour of the blends

Dynamic mechanical analysis

The results of the dynamic measurements are shown in *Figure 4*. The functionalized vulcanized blend shows all three loss tangent peaks shown by the reference blend. The loss tangent peaks and the associated molecular phenomena for silicone rubber, EPDM and their blend have been discussed by the authors previously[9]. Thus, the loss tangent peak at $-107°C$ for the reference blend is ascribed to the glass transition of silicone, the peak at $-65°C$ is ascribed to the onset of crystallization in the silicone phase and the peak at $-34°C$ is ascribed to the glass transition of EPDM and the crystal melting of silicone. The only difference is that the temperatures of the peak positions are 8–10°C higher in the modified blend. This also reflects the higher level of interchain attraction or intermolecular forces which need to be overcome by various chemical groups or chain segments of the blend to attain mobility. However, the functionalized blend has a significantly lower storage modulus than the reference blend in the temperature range from below the glass transition to the crystallization temperature of silicone.

The driving force for crystallization of the silicone rubber is insufficient to overcome the interspecies interactions, and thus segregation of the chain segments is not possible. So, the functionalized blend cannot crystallize and the product is less dense in the above-mentioned temperature range. However, at temperatures beyond this the dipole–dipole interactions and hydrogen bonds are retained in the functionalized blend, and the reference vulcanized blend lacks both crystallinity and polar interactions. Thus, the functionalized blend has denser packing and higher modulus. At elevated temperatures ($>125°C$), these intermolecular bonds break to a considerable degree and the storage moduli of both blends are identical.

CONCLUSIONS

A 50:50 blend of acrylamide-grafted silicone rubber and sulfonated EPDM was investigated. The grafting reaction of silicone rubber reduces the concentration of vinyl groups, as evidenced from the lowering of the absorbance at $1623\,cm^{-1}$ and the appearance of a peak at $1658\,cm^{-1}$ from the C=O stretching vibration of grafted acrylamide moieties. Interactions between AM-*g*-silicone and S-EPDM are inferred from the splitting of the C=O stretching peak in the blend.

The functionalized blend has a higher modulus, tensile strength, V_r, ageing resistance and thermal stability than the unmodified blend, reflecting the presence of strong intermolecular forces. These are also indicated in the higher transition temperature and higher storage modulus at elevated temperature in the dynamic mechanical spectrum of the functionalized blend.

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