Influence of Curative, Filler, Compatibilizer, Domain Size, and Blend Ratio on the Dynamic Mechanical Properties of Silicone–EPDM Blends

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SYNOPSIS

Dynamic property measurements show two loss tangent peaks for silicone rubber at about −95°C and −20°C, and one peak for EPDM at about −30°C. DSC studies confirm that the first loss tangent peak of silicone rubber is caused by its glass transition and the other is caused by crystalline melting of silicone. Measurements with blends reveal the individual characters of the components in the blends. Large differences in the solubility parameter between them also explains the incompatible nature. The effects of curative, blend ratio, and ageing are found on the glass-transition temperature and also on the storage modulus and loss tangent. Although filler does not change the glass-transition temperature, it changes the dynamic properties. Silane-grafted EPR shows an optimum concentration as a compatibiliser, resulting in improved mechanical properties of the blends. The domain size of the blends also reduces with the introduction of the compatibilizer. Imposition of restriction on the domains by partial curing during mixing results in materials with higher storage modulus. The morphology study indicates an interpenetrating network structure for these restricted domain blends. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The dynamic mechanical method is very useful for structural analysis of viscoelastic materials and their blends via their dynamic moduli and damping. Changes in these parameters are studied as a function of temperature and impressed frequency. The dynamic method is extremely sensitive in detecting changes in internal molecular mobility and for understanding phase structure and morphology.[1,2] Sensitivity of different measurement techniques toward the glass transitions in mixture depends on the physical dimensions of the phases.[3] Dynamic mechanical measurement has the advantage of being capable of detecting smaller phases than differential calorimetry.[4] Compatibilisers, which can be incor-

porated separately or can be generated by *in situ* reactions, are known to cause finer dispersion or even homogenisation of the blends.[5–10] Dynamic measurements are very helpful to get an insight into the single phase or multiphase structure of the blend.[6,10]

The present work aims at characterizing silicone rubber, EPDM, and its blends in respect to the effects of nature and dosage of curative, filler, and compatibiliser, restriction of the domains in the phase structure while mixing, and ageing on the dynamic mechanical properties.

The silicone–EPDM blends are also important from the commercial point of view, as they find applications in wire and cable insulation, gaskets, and seals at elevated temperature. These materials are characterized by good processing behaviour, high volume resistivity, and dielectric breakdown voltage, and low compression set.[11] EPDM has very good damping characteristics and silicone rubber has excellent heat resistance. The dynamic properties of

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these blends, although important in many applications, have not been studied. Improvement in tensile strength of EPDM–silicone rubber blends by interfacial coupling has been reported.[12] A detailed discussion on silicone-based thermoplastic elastomers is also available,[13] but they have not been commercially explored so far.

EXPERIMENTAL

Materials

Silicone Rubber. Silastic 1625 (Dow Corning), type—VMQ (i.e., vinyl–methyl based silicone), specific gravity 1.28 (25°C) was obtained from Fort Gloster Industries Ltd., India.

EPDM Rubber. Keltan 520 (ethylene content 55 mol %, diene content 4.5 mol % (DCPD), density 0.86) was also supplied by Fort Gloster Industries Ltd., India.

Compatibiliser. Silane-grafted EPR was developed in our laboratory following the procedure by Sen et al.[14]

Peroxide I. Dicumyl peroxide, obtained from Hercules Incorporated, USA.

Peroxide II. Perkadox 14/40 ([bis(t-butylperoxy-i-propyl)benzene] 40% active material) obtained from Fort Gloster Industries Ltd., India.

Filler 1. HAF black, a reinforcing filler, was procured from Philips Carbon Black Ltd., Durgapur, India.

Filler 2. Vulcasil S, a reinforcing silica filler, was obtained from M/s. Bayer India Ltd., Bombay, India.

Mixing and Vulcanization

A complete list of mixes and their composition are given in Table I. Blending was done in a Brabender

Table I   Composition of the Mixes

Mix No.	Silicone	EPDM	Silane-Grafted EPR (phr)	HAF (phr)	Silica (phr)	DCP (phr)	Perkadox 14/40 (phr)
A	100	0	—	—	—	0.5	—
B	50	50	—	—	—	0.5	—
C	—	100	—	—	—	0.5	—
D	100	—	—	—	—	—	1.25
E	50	50	—	—	—	—	1.25
F	—	100	—	—	—	—	1.25
G	100	—	—	—	—	1.5	—
H	75	25	—	—	—	1.5	—
I	50	50	—	—	—	1.5	—
J	25	75	—	—	—	1.5	—
K	—	100	—	—	—	1.5	—
L	50	50	—	15	15	1.5	—
M	50	50	3	—	—	1.5	—
N	50	50	5	—	—	1.5	—
O	50	50	8	—	—	1.5	—
P	50	50	10	—	—	1.5	—
Q	50	50	15	—	—	1.5	—
R	50	50	—	—	—	0.5 + 1.0 (1)	—
S	50	50	—	—	—	0.25 + 1.25 (3)	—
T	50	50	—	—	—	0.13 + 1.37 (3)	—

Samples R, S, and T were cured in two-stage process as described in Experimental section. The last number under DCP indicates the amount added in the second stage mixing. The figures in the parenthesis indicate mixing time in the first stage.

Plasticorder (PLE 330) at 120°C for 5 min at a rotor speed of 100 rpm. Compatibiliser was also mixed in the Brabender at the same temperature and speed over a period of 5 min. Compatibiliser was mixed with silicone rubber first and the masterbatch obtained was blended with the desired amount of EPDM in the Brabender Plasticorder for 5 min as before. Silica and HAF black were mixed with EPDM in a roll mill and the masterbatch was blended with silicone rubber in the Brabender under identical conditions. In the single-stage curative mixing process that generally followed, curative was mixed in a two-roll mill. In few cases, part of the curative was mixed in a Brabender at 120°C for various periods to ensure a certain degree of cure, and the balance was mixed at room temperature in a roll mill. Curing was done in a hot-platen hydraulic press at a pressure of 5 MPa at 170°C for 10 min. Post curing was done at 150°C for 2 h in a temperature-controlled air-circulated ageing oven (Model No. FC 712, Blue M. Electric Co., Blue Island, IL, USA). A few samples (mix A to F, Table I) were cured at 150°C for 1 h.

Tensile Testing

Tensile strength, modulus and elongation at break were measured per ASTM D 412-80 in a computerised Zwick UTM (1445) at a crosshead speed of 500 mm/min. The dumbbell-shaped specimens were obtained from vulcanized sheet.

Etching and Ageing

Etching was done on vulcanised sheets using 1 : 1 HNO_3 and heating over boiling water bath for a period of 2 h. Then, the samples were thoroughly washed with water, rinsed with acetone, and dried overnight in a vacuum oven at 50°C. Ageing was done in a Test Tube Ageing Tester (Seisaku–SHO Ltd., Toyoseiki, Japan) at 175°C for periods of 6, 18, and 36 h.

Morphology Study

Morphology of the blends was studied by SEM (Cam Scan Series II model, Scanning Electron Microscope). The surface of the specimens was studied. Samples included unaged, aged, and etched specimens of the vulcanisates. Some of the specimens were also studied with a Philips Scanning Electron Microscope (PSEM 500).

DSC Study

The differential-scanning calorimetry study was done for the raw polymers of silicone rubber and EPDM using a 910 Differential Scanning Calorimeter attached to a Dupont 9000 Thermal Analyser. Scanning was done from −150°C to +100°C at the rate of 20°C/min. Low temperature was attained by liquid nitrogen.

Dynamic Property Measurements

Dynamic mechanical properties were evaluated using DMTA (model No. MK-II, Polymer Laboratories, UK). Testing was done in shear mode. In shear configuration, a plate was affixed to the drive clamp and two sample pieces were sandwiched between this with studs mounted on the fixed clamps. Frequencies selected were 3, 10, and 30 Hz. The strain selected was 64 μ peak-to-peak. However, results at 10 Hz have been reported. The experiments were carried out from −140°C to +100°C at a rate of 2°C/min. Low temperature was attained by slow cooling with liquid nitrogen. Once the desired temperature was attained, the samples were reclamped to take care of the shrinkage of the samples at low temperatures, particularly below glass-transition temperature of the sample. At this stage the sample was again cooled to the desired low temperature. The heater was automatically started and the data was recorded on computer.

RESULTS AND DISCUSSION

Tan δ vs. temperature and storage modulus vs. temperature of silicone and EPDM are shown in Figures 1(a,b), respectively. Glass-transition temperatures were determined from the tan δ peak temperatures. Silicone vulcanizates (mixes A, D, and G) show two peaks, one at a temperature of about −92°C to −95°C and the other at about −16°C to −20°C depending on the curative system and its dosage [Fig. 1(a)]. Tan δ peak value corresponding to the low-temperature peak lies in the range of 0.013–0.027 and for the other peak it is 0.14–0.16. Urban and Stewart[15] provided DMA plots of silicone rubber before and after plasma surface modification that indicates peak tan δ value of about 0.14 for untreated and about 0.2 after plasma treatment. The first peak in the tan δ–temperature plot of silicone vulcanisates, occurring in the neighbourhood of −92°C, corresponds to true glass-transition temperature.
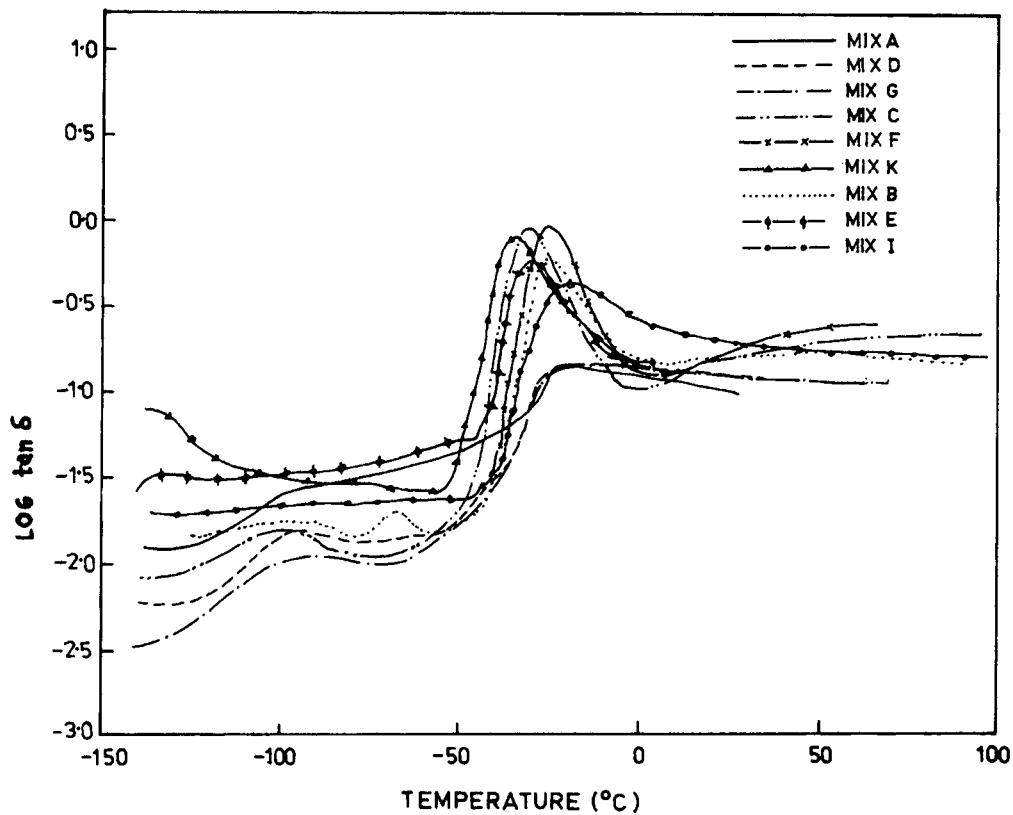
Figure 1(a) Effect of curative and curative dosage on loss tangent. Mixes A, D and G contain only silicone rubber; B, E and I are 50-50 blends and C, F and K contain only EPDM. Each of the above systems were cured with 0.5 phr DCP, 1.25 phr perkadox (14/40) and 1.5 phr DCP respectively.
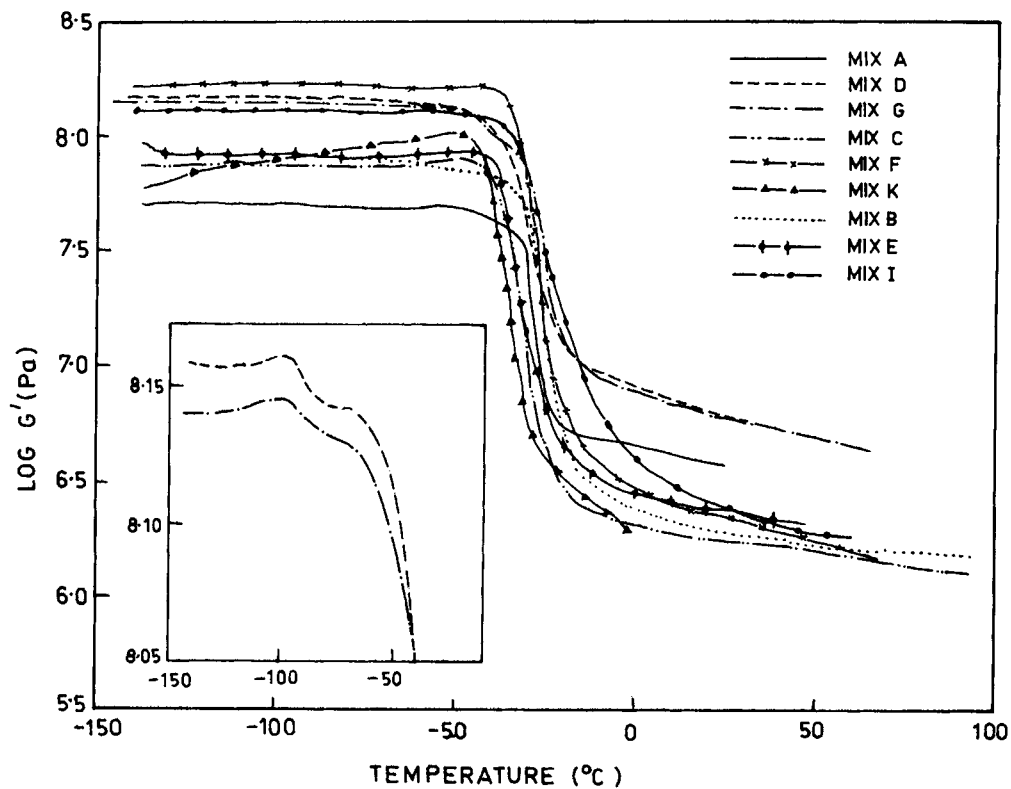

Figure 1(b) Effect of curative and curative dosage on storage modulus.

The other peak, occurring in the range −16°C to −20°C, is believed to be caused by crystalline melting of silicone. DSC studies and the available literature also confirm this view.[16] DSC trace (Fig. 2) of unvulcanized silicone indicates glass transition at −121.5°C, a crystallization peak at −93.5°C, and a melting endotherm with the peak at −40°C (Fig. 2).

The tan δ–temperature plot of EPDM [Fig. 1(a), mixes C, F, and K] shows a prominent peak in the temperature range of −28°C to −34°C and the peak tan δ value is of the order of 0.83–0.95. DSC studies of raw EPDM indicate glass transition at −44.5°C (Fig. 2).

Glass-transition temperatures obtained from dynamic measurements are found to be higher than those measured from DSC. Available literature also supports a variation of glass-transition temperature as high as 10–20°C for the same polymer depending on the method of measurement and on the thermal history of the sample.[17]

Storage modulus for silicone was found to fall at the glass-transition zone and also at the melting zone [Fig. 1(b)]. A drop in the value of storage modulus at the glass-transition temperature was understood only after careful magnification of log-modulus scale. Change in the modulus in the melting zone was prominent. For EPDM, change in modulus occurs only at the transition zone.

The effect of blend ratio, curative, filler, compatibiliser, and domain structure on the dynamic properties of the blends are discussed in the following sections.

Effect of Curative and Curative Dosage

The effect of nature and dosage of curative on tan δ peak temperature is shown in Fig. 1(a) and more clearly in Table II. Glass-transition temperature of silicone rubber cured with DCP (mix A) is slightly higher than the perkadox cured system (mix D) at equivalent dose. Loss-tangent peak value is also higher for the DCP-cured system. The second peak occurs at a lower temperature for the DCP-cured system compared to the other system. Tan δ values corresponding to this peak are more or less equal.

As DCP dosage is increased from 0.5 phr (mix A) to 1.5 phr (mix G), glass-transition temperature is found to increase slightly but tan δ decreases significantly (Table II). The second peak correspond-
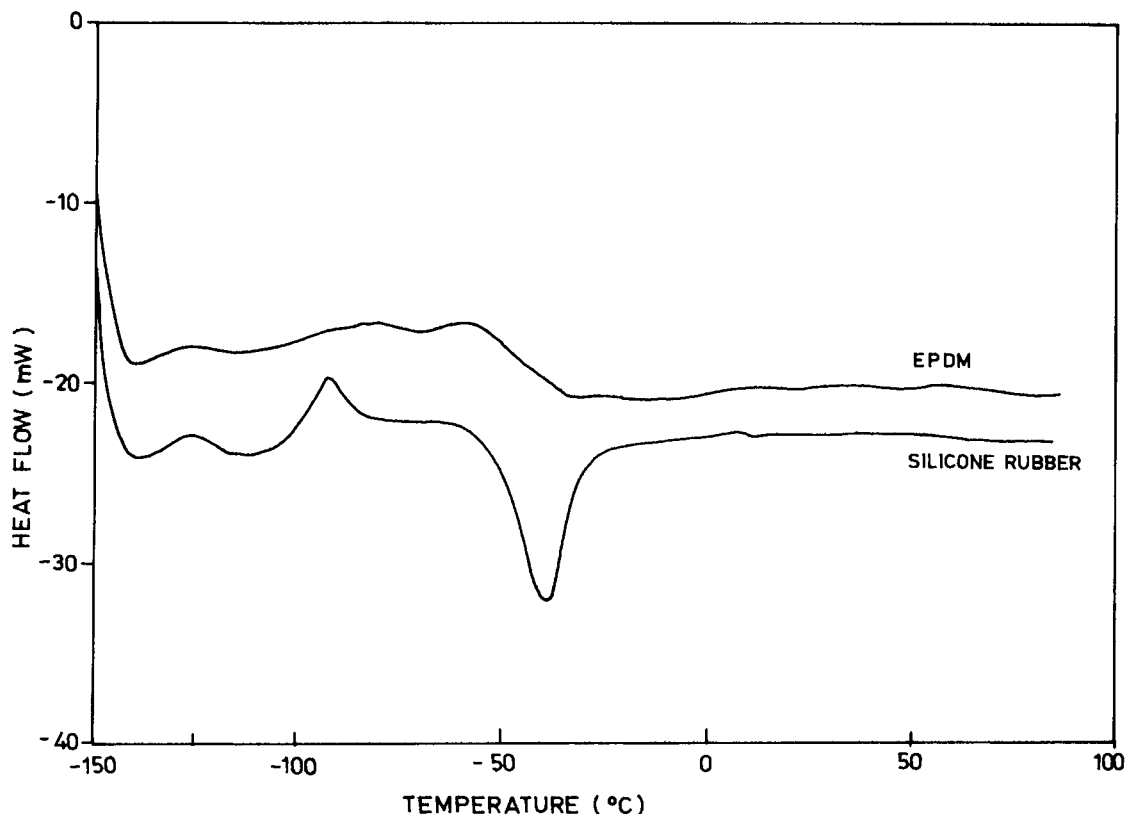

Figure 2   DSC thermogram of raw silicone rubber and EPDM.

Table II   Effect of Curative and Curative Dosage on Glass-Transition Temperature and Storage Modulus of Silicone, EPDM, and Their 50/50 Blend

| Composition | | | | | | |
| Elastomer | Curative | | | | | |
Silicone/EPDM (parts)	Perkadox/(40% active phr)/DCP	T_{g_1} (°C)	Tan δ_1	T_{g_2} (°C)	Tan δ_2	G' at 25°C (MPa)
100/0	1.25/0	−95.5	0.016	−17.5	0.15	5.17
100/0	0/0.5	−94.5	0.027	−21	0.15	4.07
100/0	0/1.5	−92	0.013	−16	0.15	6.03
50/50	1.25/0	−97.5	0.018	−28	0.55	2.14
50/50	0/0.5	−93	0.017	−25	0.57	1.91
50/50	0/1.5	−97.5	0.016	−22	0.44	2.4
0/100	1.25/0			−31	0.92	2.09
0/100	0/0.5			−32	0.95	1.78
0/100	0/1.5			−34	0.83	2.13

T_{g_1}: Glass-transition temperature of silicone.
Tan δ_1: Tan δ at T_{g_1}
T_{g_2}: Glass transition of EPDM or tan δ peak temperature caused by melting of silicone, or a tan δ peak temperature caused by both of the above.
Tan δ_2: Tan δ at T_{g_2}
G': Storage modulus.

ing to the 1.5 phr DCP-cured system occurs at about 5°C higher than that of the 0.5 phr DCP-cured system, and peak tan δ value are found to fall marginally.

Storage modulus of silicone rubber [Fig. 1(b)] at 25°C for the perkadox cured system (mix D) is higher than the corresponding DCP-cured system (mix A and Table II). Samples cured with 1.5 phr DCP (mix G) are found to have higher storage modulus than the corresponding sample cured with 0.5 phr DCP (mix A), both in the glassy and rubbery zones.

EPDM cured with 0.5 phr active perkadox (mix F) has a glass-transition temperature slightly higher than the corresponding DCP-cured (mix C) system [Fig. 1(a) and Table II]. Tan δ value for the DCP-cured system is marginally higher. But perkadox curing offers higher storage modulus. The 1.5 phr DCP-cured system (mix K) is found to have a glass-transition temperature slightly lower than that of the 0.5 phr DCP-cured system (mix A). The peak value of tan δ for the 1.5 phr DCP-cured system is somewhat lower than the 0.5 phr DCP-cured system.

For a 50/50 blend of silicone/EPDM, both the glass transitions of silicone and EPDM are observable. For the perkadox cured (mix E) system, both the glass transitions occur at lower temperature than the corresponding DCP-cured system [Fig. 1(a)]. The tan δ value corresponding to silicone peak is

higher for the perkadox-cured system, but tan δ value corresponding to EPDM peak is lower for this system. With the higher DCP dose, the glass-transition temperature is found to increase marginally and tan δ decreases. The storage modulus at 25°C of the perkadox cured system (mix E) is higher than the DCP-cured system and an increase in DCP dose (mix I), the storage modulus increases [Fig. 1(b) and Table II]. The changes in the values of tan δ and storage modulus are explained with the help of crosslink density in the following section.

Effect of Blend Ratio

Blends of silicone–EPDM show two peaks in the tan δ–temperature plots [Fig. 3(a) and Table III]. The low-temperature peak is due to silicone and it is not very prominent. The other peak that occurs at a higher temperature and more prominently is caused by glass transition of EPDM and crystalline melting of silicone.

In the blends (mixes H, I, and J), the glass transition of the silicone component occurs at a lower temperature than that of pure silicone vulcanisate (mix G). Loss-tangent peak value is also higher for the blends. The second peak in the tan δ–temperature plot occurs at a temperature in between the glass-transition temperature of EPDM and the sec-
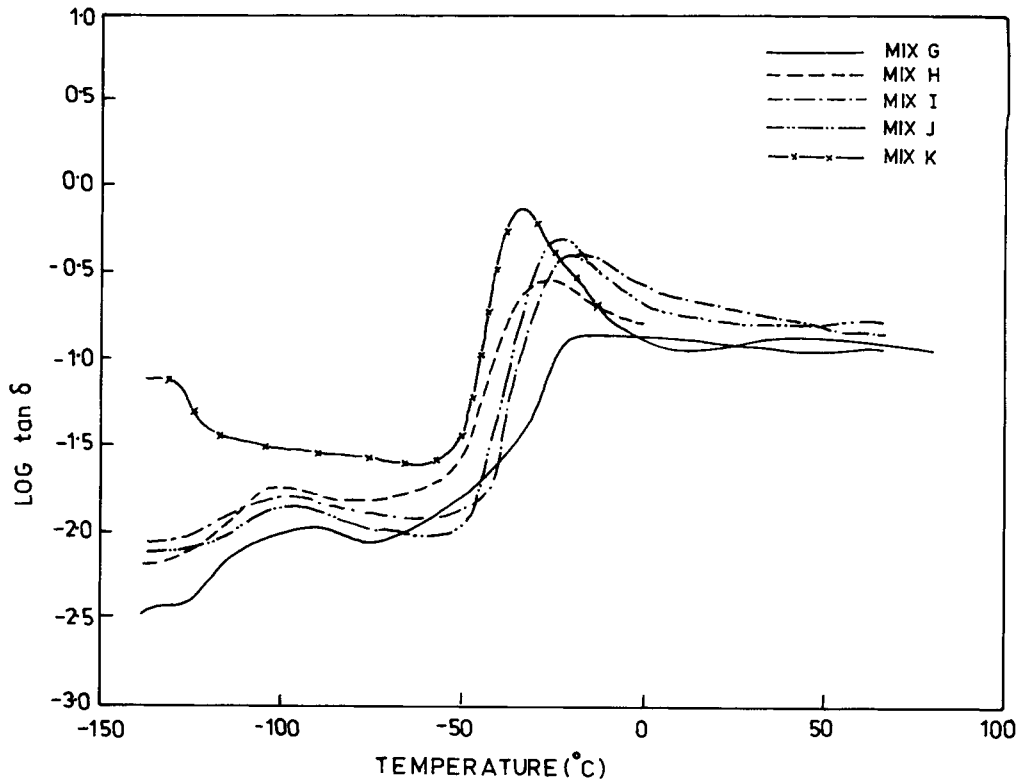
Figure 3(a)   Effect of blending on loss tangent. Mixes G, H, I, J, and K have blend ratios of 100/0, 75/25, 50/50, 25/75, and 0/100 of silicone/EPDM.
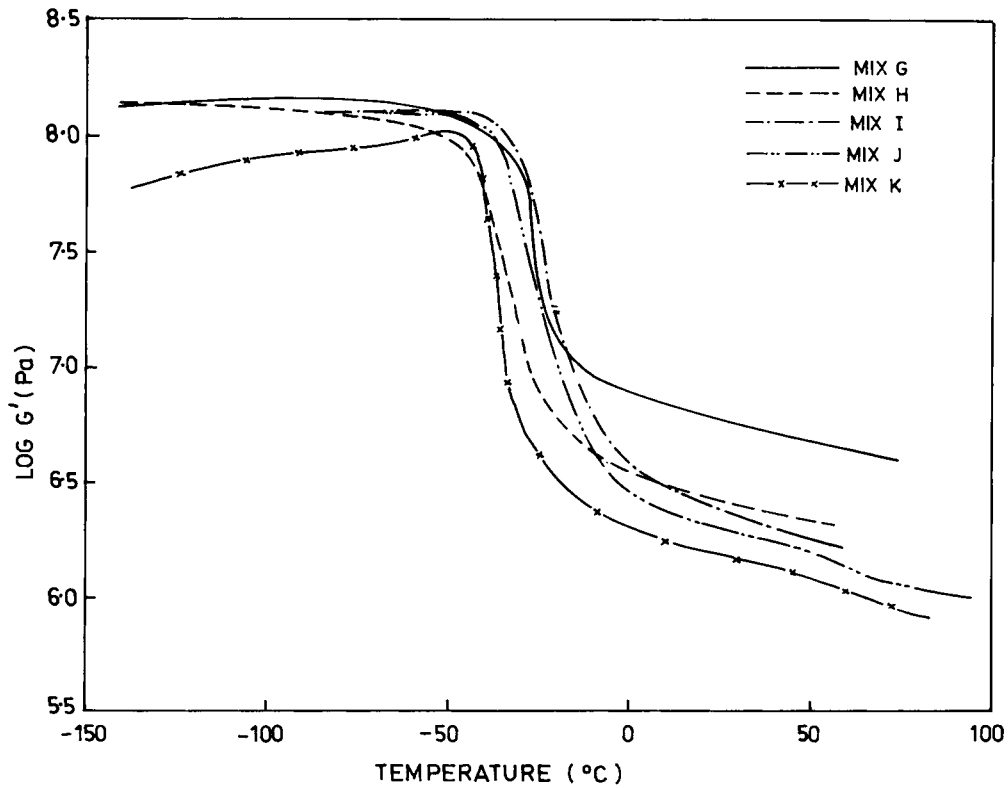

Figure 3(b)   Effect of blending on storage modulus. Mixes G, H, I, J, and K have blend ratios of 100/0, 75/25, 50/50, 25/75, and 0/100 of silicone/EPDM.

Table III   Effect of Blend Ratio on the Glass-Transition Temperature and Storage Modulus of Silicone, EPDM, and Their Blends

Composition							
Silicone (parts)	EPDM (parts)	DCP (phr)	T_{g_1}[a] (°C)	Tan δ_1[a]	T_{g_2}[a] (°C)	Tan δ_2[a]	G′ at 25°C[a] (MPa)
100	0	1.5	−92	0.013	−16	0.147	6.03
75	25	1.5	−100	0.018	−26	0.307	3.28
50	50	1.5	−97.5	0.016	−22	0.445	2.4
25	75	1.5	−103	0.014	−23.5	0.52	2.29
0	100	1.5			−34	0.835	2.13

[a] Symbols are same as explained at the footnote of Table II.

ond peak of silicone. With an increase in EPDM content, tan δ peak value increases.

The storage modulus of EPDM in the glassy zone is much lower than the silicone and its blend [Fig. 3(b)]. At room temperature and above, the storage modulus decreases with increase in EPDM content. Similar behaviour of composition dependence for blends has been reported by Kolarik et al.[18] They find for polyethylene/EPDM and polypropylene/EPDM systems, loss maxima increases in proportion to the EPDM content and the storage moduli decreases with EPDM content because of lower modulus.

Effect of Ageing

The purpose of studying these systems is to improve the ageing resistance of EPDM rubber. Hence, a

detailed study on the effect of ageing on dynamic mechanical properties has been undertaken.

Silicone samples cured with 1.5 phr DCP (mix G) were heat aged for 6, 18, and 36 h. Glass-transition temperature (T_g) does not change with heat-ageing time [Fig. 4(a) and Table IV]. Tan δ peak value at T_g is found to increase slowly with ageing time and finally falls. The second peak of silicone rubber caused by crystalline melting is found to occur gradually at lower temperature as heat ageing is continued up to 36 h. Tan δ corresponding to the second peak initially increases with heat ageing as observed from the value for a 6-h-aged sample. With further heat ageing it gradually falls. In the glassy region, storage modulus for heat-aged samples is lower than the unaged sample [Fig. 4(a)]. In fact, up to 18-h heat ageing, the storage modulus continues to fall, and then the trend is reversed. The stor-

Table IV   Effect of Aging Time at 175°C on Glass-Transition Temperature and Storage Modulus of Silicone, EPDM, and Their Blends

Composition Silicone/EPDM	Aging Time (h)	T_{g_1}[a] (°C)	Tan δ_1[a]	T_{g_2}[a] (°C)	Tan δ_2[a]	G′ at 25°C (MPa)
100/0	0	−92	0.013	−16	0.147	6.03
	6	−93	0.016	−20	0.15	4.73
	18	−91	0.02	−21	0.132	6.03
	36	−93	0.016	−22	0.13	6.24
50/50	0	−97.5	0.016	−22	0.445	2.4
	6	−98	0.014	−27	0.5	2.06
	18	−98	0.015	−26	0.49	2.72
	36	−99	0.021	−26	0.495	3.24
0/100	0			−34	0.835	1.53
	6			−23	0.77	1.26
	18			−25	0.765	1.15
	36			−23	0.675	1.82

[a] Symbols are same as noted at the footnote of Table II.
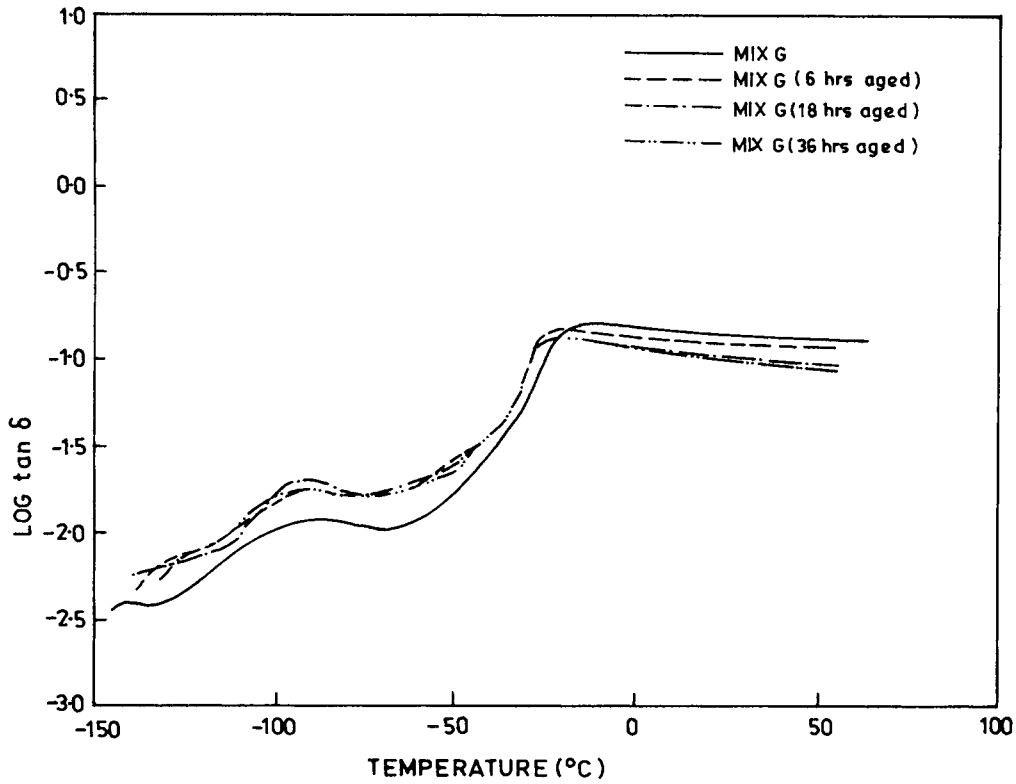
Figure 4 (a)   Effect of ageing on loss tangent of silicone vulcanisate. Samples were cured with 1.5 phr DCP.
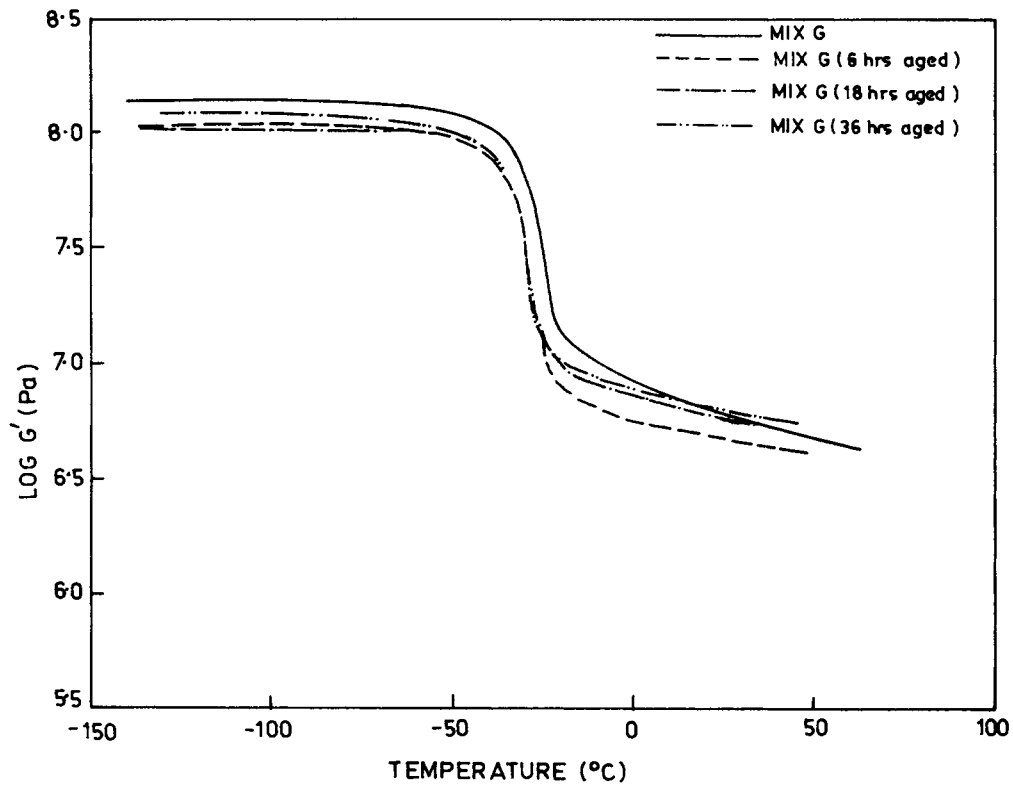

Figure 4 (b)   Effect of ageing on storage modulus of silicone vulcanisate. Samples were cured with 1.5 phr DCP.

age modulus increases with further ageing time. At temperatures beyond the second tan δ peak temperature, storage modulus is found to be higher as the ageing period is increased from 6 to 36 h. The unaged sample shows highest modulus immediately after the second tan δ peak temperature but its value falls rapidly, and after 10°C the storage modulus of 36-h aged sample becomes higher and at 35°C it reaches the storage modulus value of the sample aged for 18 h.

For the 50/50 blend of silicone/EPDM (mix I), the tan δ peak temperature corresponding to the glass transition of silicone does not change with ageing time [Fig. 5(a) and Table IV]. Peak value of tan δ remains constant up to 18 h ageing and then for 36-h aged sample the value increases slightly. The other peak of the aged samples corresponding to the glass transition of EPDM occurs at a temperature of about 5°C lower than that of unaged sample. Corresponding tan δ values for aged samples are slightly higher than the unaged sample.

Storage modulus in the glassy zone increases with increasing ageing time up to 18 h ageing and then decreases significantly as ageing is continued to 36 h [Fig. 5(b)]. In the rubbery zone, storage modulus decreases with initial aging. Beyond 6 h of aging, it increases with any further aging time.

On initial aging for 6 h, the glass-transition temperature of EPDM (mix K) enhances by 10°C and with further heat ageing T_g remains at this point [Fig. 6(a) and Table IV]. Tan δ at T_g is found to decrease with heat ageing. Storage modulus in the glassy region first increases and then it falls with ageing time [Fig. 6(b)]. At 25°C, storage modulus is found to decrease with heat ageing up to 18 h and then it increases with further heat ageing.

Effect of Filler

Dynamic properties of a filled system of 50/50 silicone/EPDM was evaluated. Glass-transition temperatures of the filled blend (mix L) do not shift from that of the unfilled blend (mix I). Loss-tangent peak values at both the glass transitions reduce as filler is incorporated [Fig. 7(a)].

Storage modulus for the filled system is found to be higher both at the glassy state and also at room temperature (25°C, rubbery state) [Fig. 7(b)] as expected.

General behaviour of filled systems have been reported by Payne and Scott.[19] They reported a large increase in storage modulus for filled systems and tan δ peak is lowered and broadened.

Effect of Compatibiliser

The effect of compatibiliser on glass transition and storage modulus of a 50/50 blend of silicone/EPDM is shown in Figs. 8(a) and 8(b) and also in Table V. As the compatibiliser concentration is increased (mixes M to Q), the glass-transition temperature caused by EPDM occurs at higher temperature and the T_g increases up to 5% compatibiliser concentration. With further addition of compatibiliser, the T_g of the sample decreases [Fig. 8(a)]. Tan δ value also shows a maxima at 5% compatibiliser concentration and then decreases. The low temperature peak due to silicone is observable with compositions having 3% and 5% compatibiliser. With 8% and 10% compatibiliser the silicone peak is not observable. At 15% compatibiliser again a peak in the range of the glass transition of silicone becomes visible. These observations confirm the beneficial action of the compatibiliser. Main-chain structure of silane-grafted EPR is very close to that of EPDM. The only exception is that EPDM contains 4.5 mol % DCPD randomly distributed in its backbone. Additionally, silane-grafted EPR contains pendant groups arising from trimethoxy vinyl silane.[14] This unique feature of the compatibiliser makes it an ideal interfacial agent where the main chain will tend to remain with the EPDM phase and the pendant groups will try to align with the silicone phase. Figure 9(a,b) show the homogenising action of the compatibiliser.

Storage modulus at 25°C is found to decrease with compatibiliser concentration up to 5% compatibiliser and then steadily increases with an increased dose of compatibiliser [Fig. 8(b) and Table V]. Storage modulus in the glassy region does not follow any well-defined trend. The specimen having 5% compatibiliser has the lowest storage modulus followed by the specimen containing 3% compatibiliser. Others have storage modulus higher than the system containing no compatibiliser. The specimens containing 15% compatibiliser have the highest storage modulus.

Effect of Restricted Domain Structure

These samples have interpenetrating type network structure that prevents phase separation. This material has remarkably higher modulus. The interpenetrating structure is developed during dynamic vulcanization. The shear rate results in intimate mixing of the two phases in the form of thin layers and these layers are subsequently crosslinked with the crosslinking also occurring between the phases.
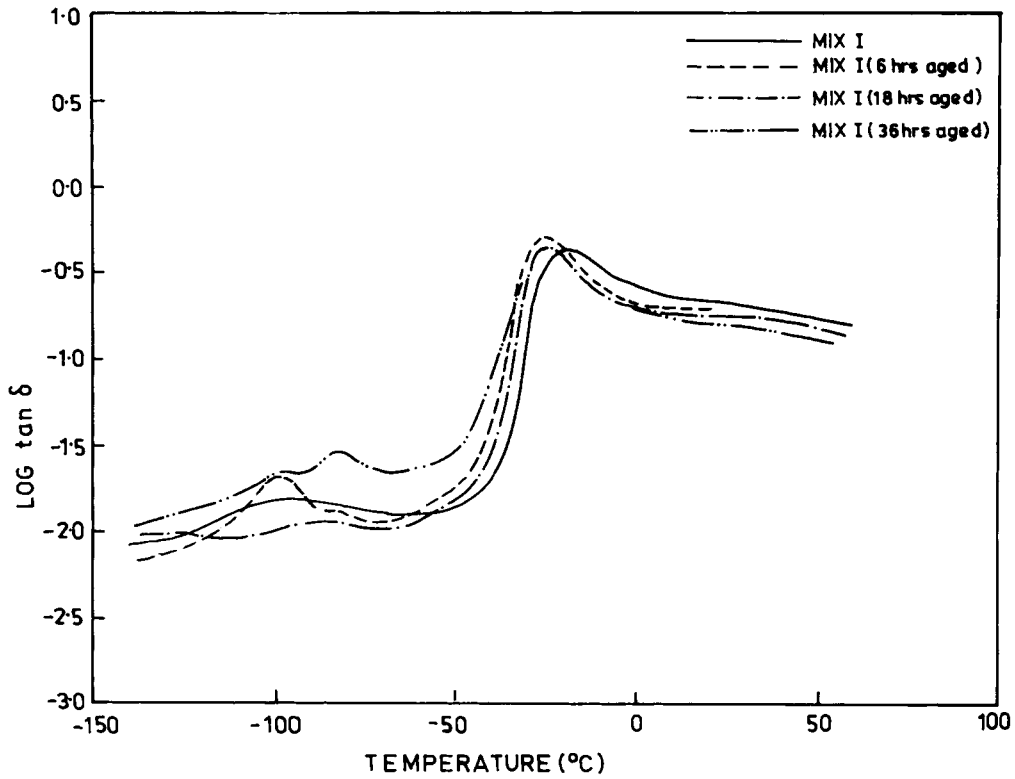
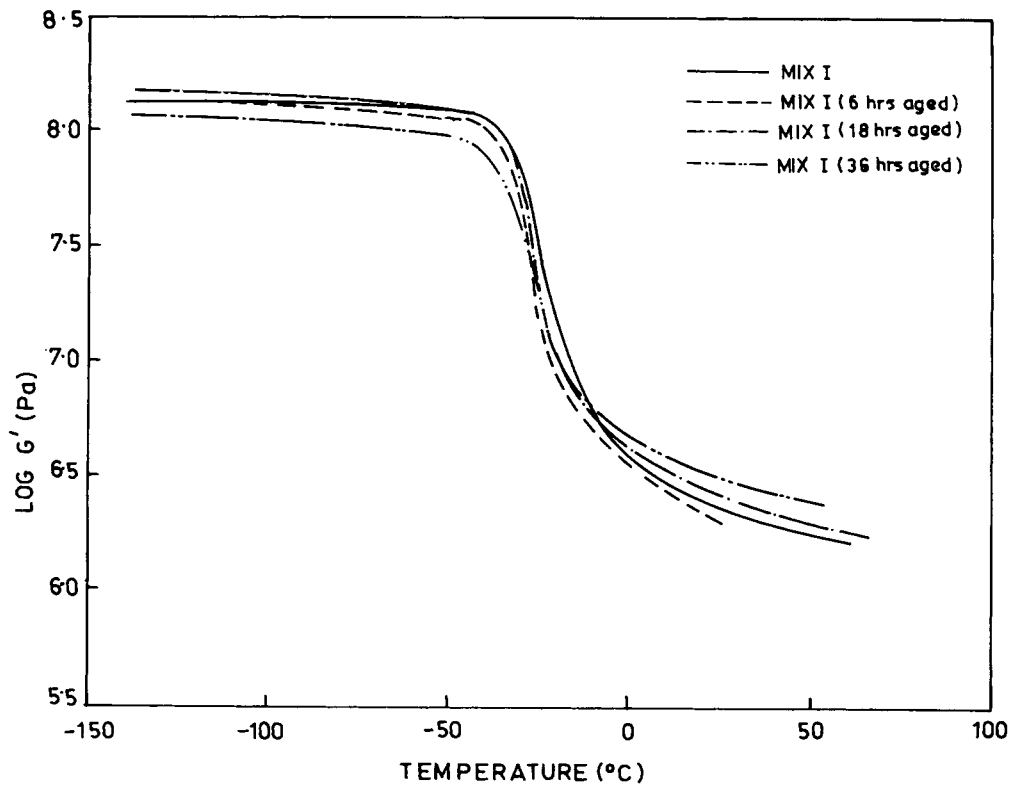**Figure 5(a)**   Effect of aging on loss tangent of 50/50 blend of silicone/EPDM, cured with 1.5 phr DCP.

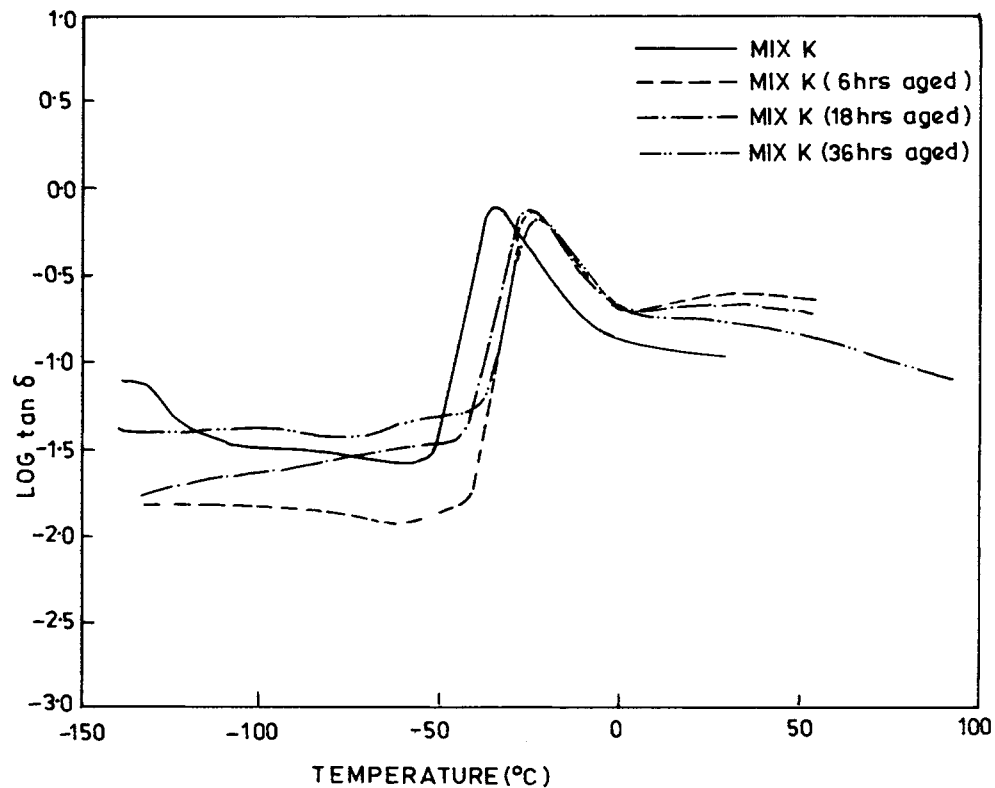**Figure 5(b)**   Effect of aging on storage modulus of 50/50 blend of silicone/EPDM, cured with 1.5 phr DCP.

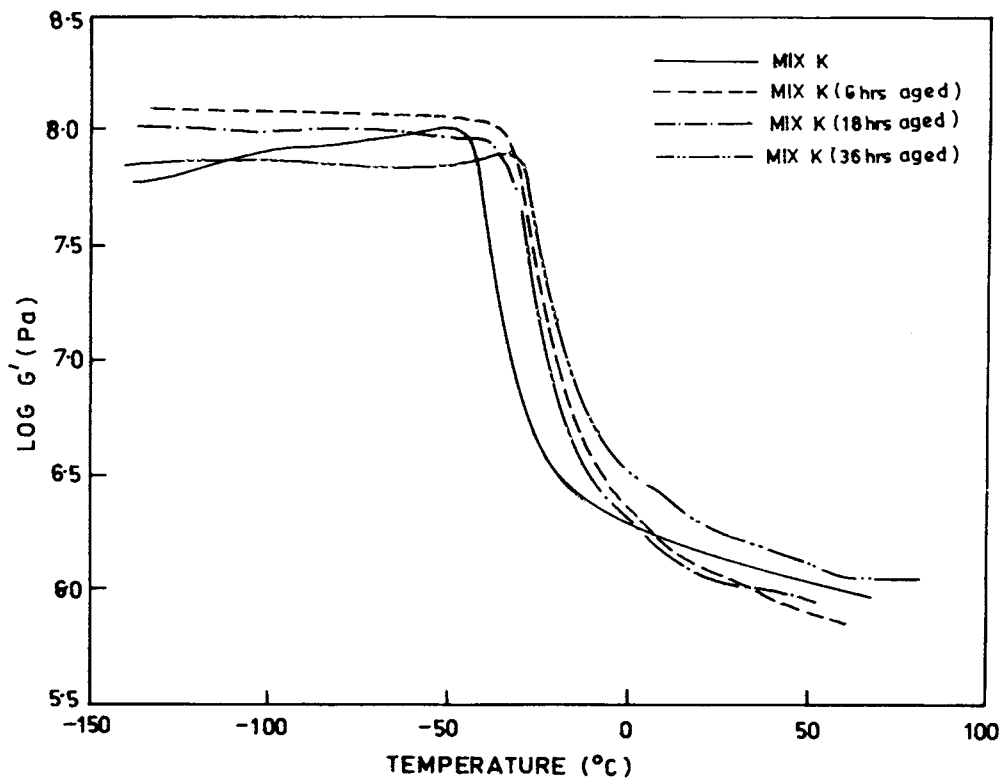**Figure 6(a)**   Effect of aging on loss tangent of 1.5 phr DCP cured EPDM vulcanisate.

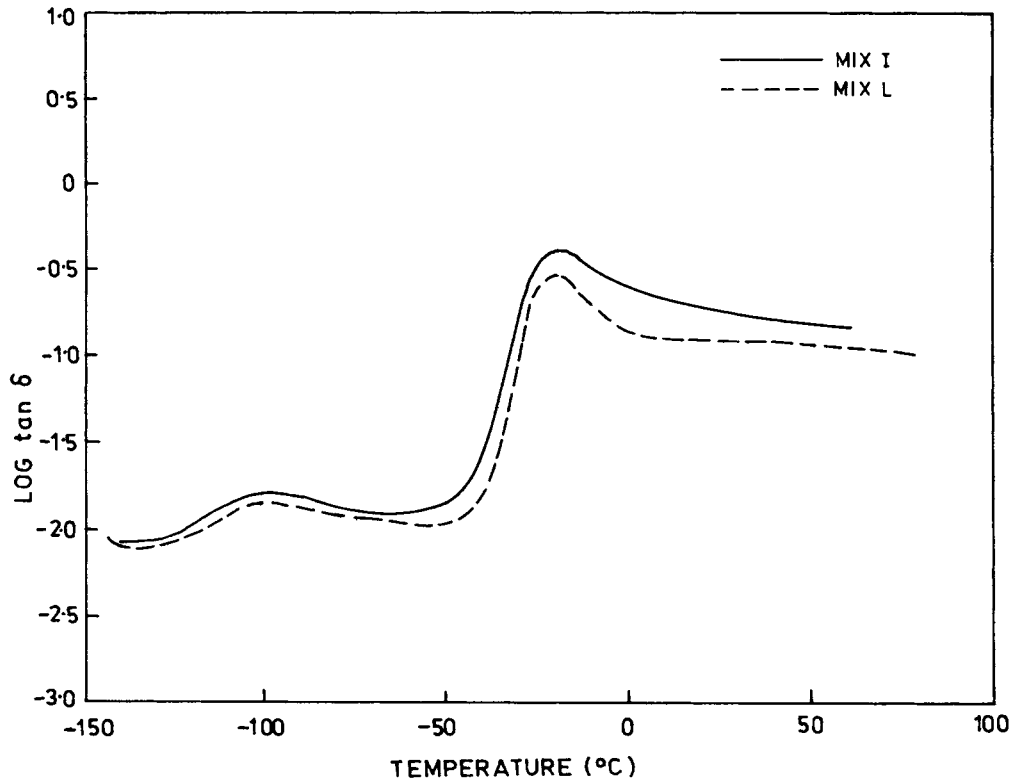**Figure 6(b)**   Effect of aging on storage modulus of 1.5 phr DCP cured EPDM vulcanisate.

Figure 7 (a)   Effect of filler on loss tangent of 50/50 blend of silicone/EPDM. Mix L contains 15 phr silica and 15 phr HAF black. Mix I is unfilled.
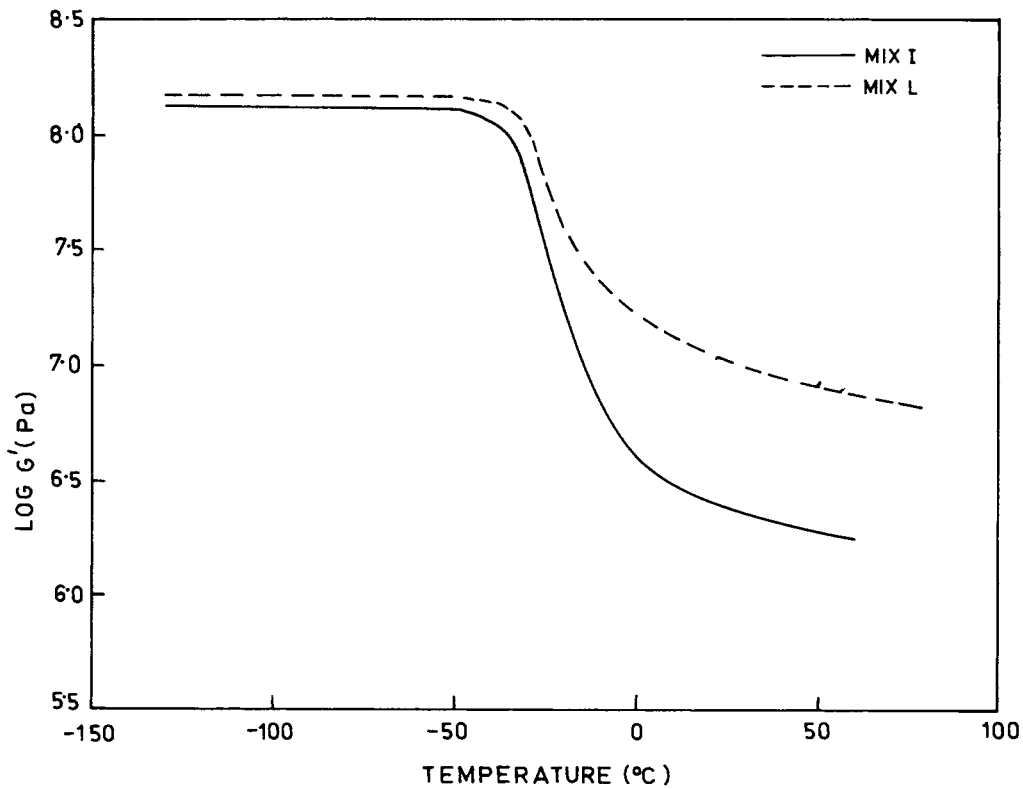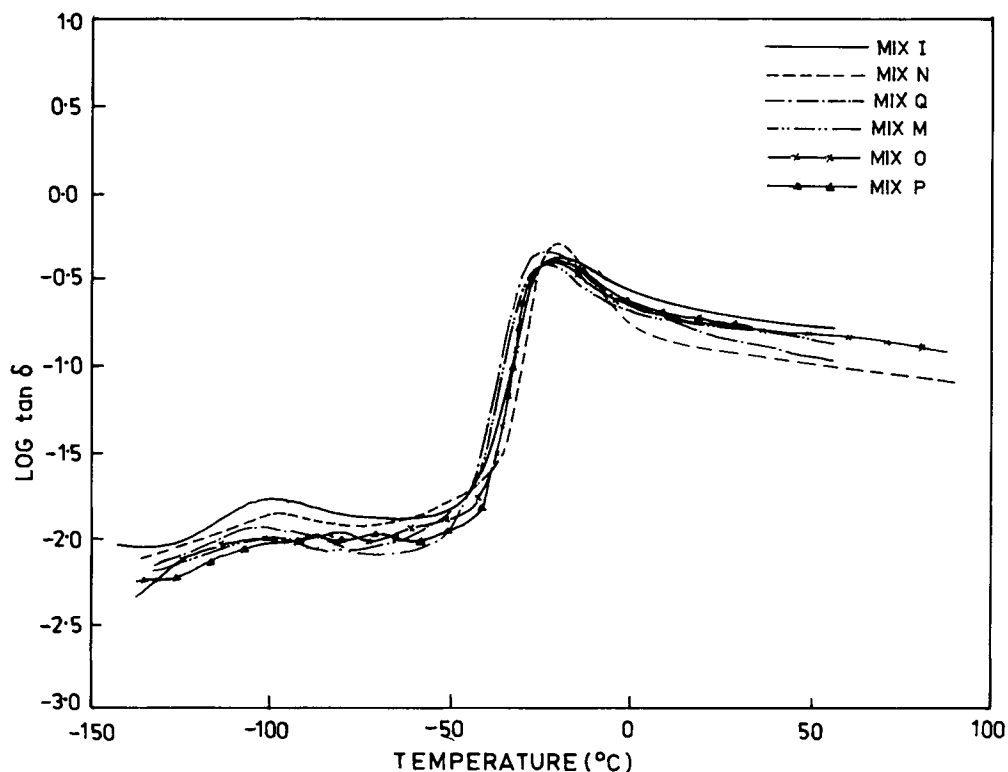

Figure 7 (b)   Effect of filler on storage modulus of 50/50 blend of silicone/EPDM. Mix L contains 15 phr silica and 15 phr HAF black. Mix I is unfilled.

Figure 8(a)   Effect of compatibiliser on loss tangent of 50/50 blend of silicone/EPDM. Mixes I, M, N, O, P, and Q contain, respectively, 0, 3, 5, 8, 10, and 15 phr compatibiliser.
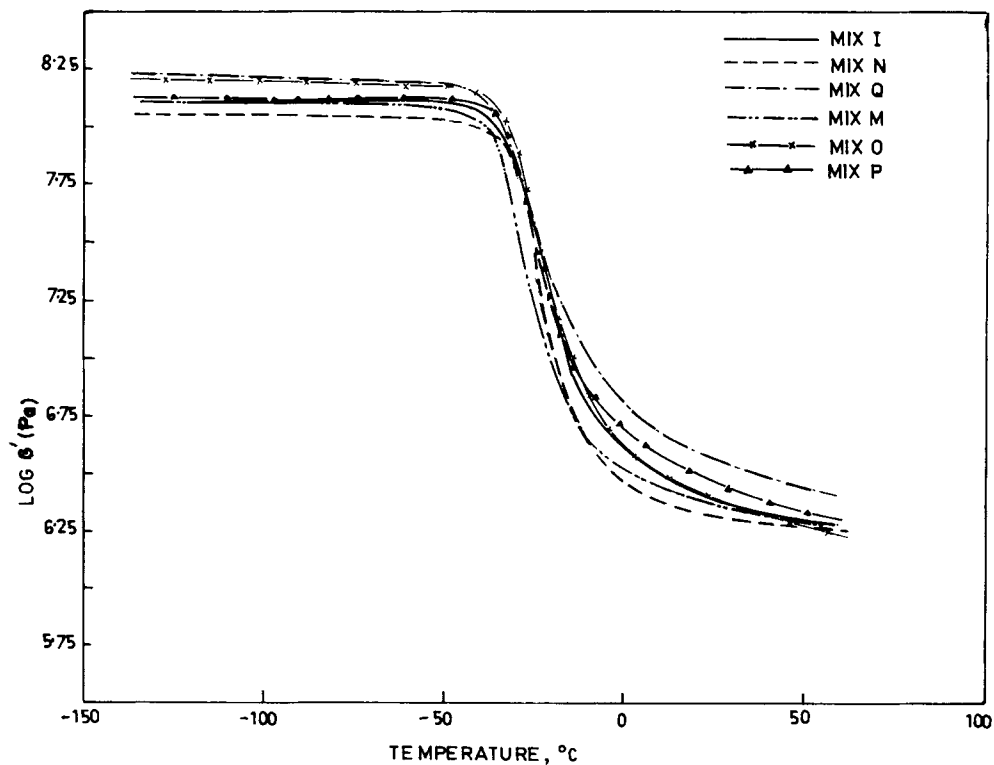

Figure 8(b)   Effect of compatibiliser on storage modulus of 50/50 blend of silicone/ EPDM. Mixes I, M, N, O, P, and Q contain, respectively, 0, 3, 5, 8, 10, and 15 phr, compatibiliser.
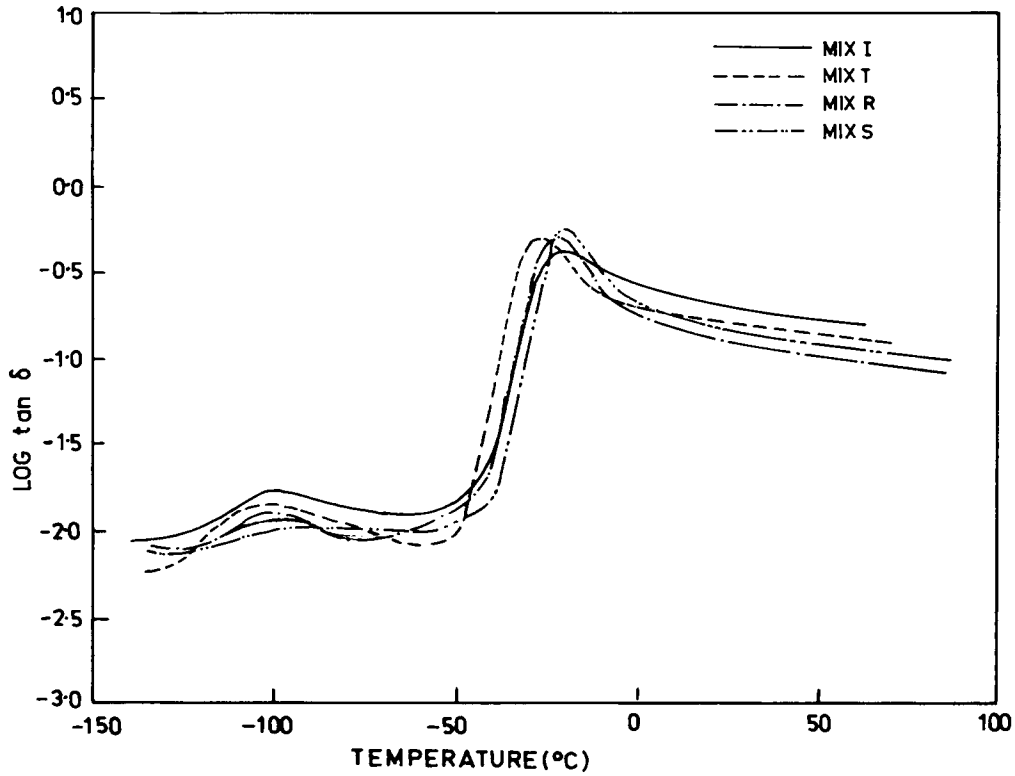
Figure 9(a) Effect of restricting the domains on the loss tangent of 50/50 blend of silicone/EPDM. First stage curing of mixes I, R, S, and T was done for 0, 1, 3, and 3 min and the corresponding DCP doses were 0, 0.5, 0.25, and 0.13 phr, respectively.
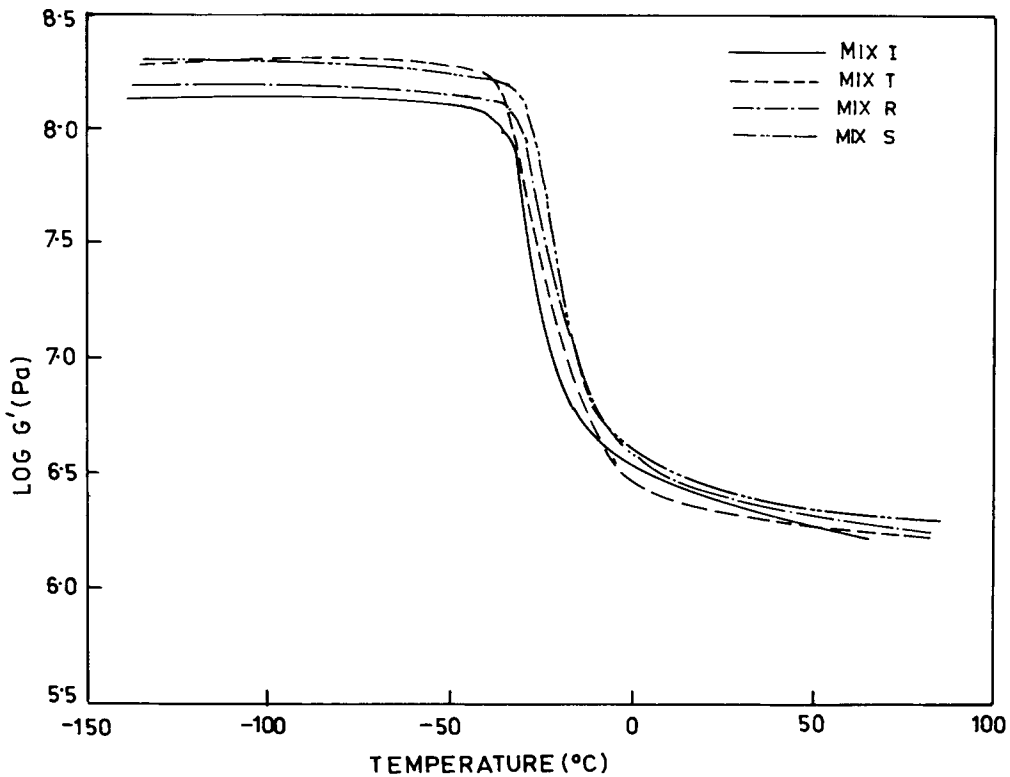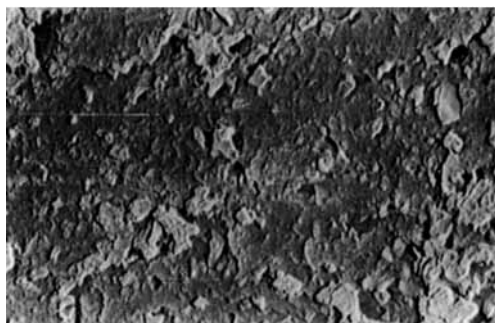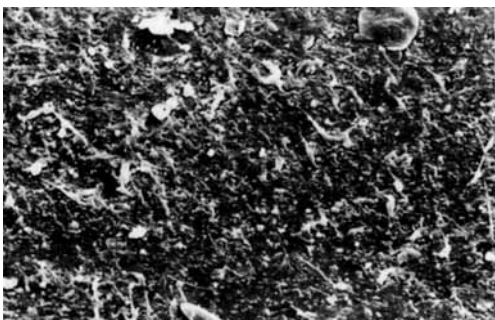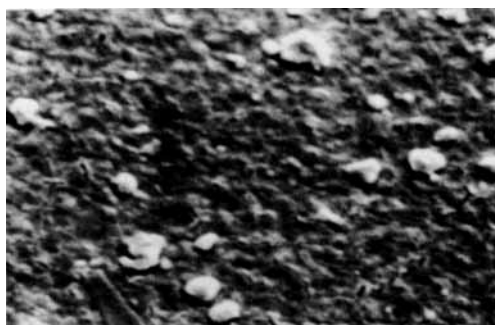

Figure 9(b) Effect of restricting the domains on the storage modulus of 50/50 blend of silicone/EPDM. First stage curing of mixes I, R, S, and T was done for 0, 1, 3, and 3 min and the corresponding DCP dose was 0, 0.5, 0.25, and 0.13 phr, respectively.

(a)

(b)

(c)

Figure 10 (a) SEM micrograph of a 50/50 blend of silicone/EPDM (mix I). Magnification ×1000. (b) SEM micrograph of a specimen containing 5 parts compatibilizer (mix N). Magnification ×600. (c) SEM micrograph of a restricted domain specimen (mix S). Magnification ×4000.

After a certain degree of cure, the material gels resulting in a constant morphology and a restricted domain structure may be generated for the mixes R, S, & T (Table I). SEM study of the specimen, mix S [Fig. 9(c)], clearly indicates generation of a co-continuous structure.

The storage modulus in the rubbery zone shows a typical trend. At 25°C, samples cured dynamically with 0.5 phr DCP for 1 min and with 0.125 phr for 3 min have lower storage modulus than that of the one-stage sample [Fig. 10(b)]. After 50°C, they are found to rearrange in a way that the sample having higher modulus at 100% elongation also shows higher storage modulus. Thus, the sample cured dynamically with 0.25 phr DCP has the highest storage modulus and the sample prepared by one stage vulcanisation has the lowest storage modulus. In the glassy zone, restricted domain specimens have higher storage modulus than the simple vulcanizate. However, in this region storage modulus does not follow the relative trend of the 100% modulus of the specimens.

The low temperature tan δ peak caused by silicone was found with the specimen having relatively low modulus at 100% elongation (e.g., the sample vulcanized dynamically with 0.125 phr DCP for 3 min). The sample having intermediate modulus (i.e., the dynamically vulcanized specimen with 0.5 phr DCP for 1 min) does not show a clear peak and the other specimen, dynamically vulcanised for 3 min with 0.125 phr DCP (having highest small strain modulus), shows no peak at all [Fig. 10(a)]. The other peak for the restricted-domain structure specimens occurs at the same temperature as the simple vulcanisate. The only exception to this is the specimen vulcanised dynamically for 3 min with 0.125 phr DCP, for which the peak occurs at a temperature about 5°C lower than the other. Tan δ maxima for all the restricted domain samples are higher than the one-stage vulcanisate.

CONCLUSIONS

Miscibility of polymers can be studied from dynamic mechanical measurements. The incompatible nature of silicone–EPDM pair is reflected in the glass transitions and other dynamic properties of the blend, where the behaviour of the individual components is clearly present.

Dynamic properties are influenced by nature and dosage of curative, blend ratio, filler, and ageing of the blends.

Silane-grafted EPR, being active toward both silicone rubber and EPDM, acts as a compatibiliser and at some optimum concentration the loss-tangent curve shows one peak caused by a crystalline melting of silicone and glass transition of EPDM.

DSC study helps to understand different molecular processes involved corresponding to the peaks

**Table V Effect of Compatibiliser on the Glass-Transition
Temperature and Storage Modulus of 50/50 Blend of Silicone/EPDM**

Compatibiliser Dosage (phr)	T_{g_1}[a] (°C)	Tan δ_1[a]	T_{g_2}[a] (°C)	Tan δ_2[a]	G' at 25°C (MPa)
0	−97.5	0.016	−22	0.445	2.4
3	−101.5	0.015	−21	0.445	2.34
5	−100	0.01	−20.5	0.492	2.04
8	—	—	−21	0.447	2.38
10	—	—	−22	0.412	2.82
15	−102	0.012	−22	0.385	3.55

[a] Symbols are same as explained at the footnote of Table II.

in the loss-tangent curve and is complimentary to dynamic measurements.

A two-stage curing process, where the first step is intended to impose restriction on the domains while mixing, results in vulcanisates with higher storage modulus and their general behaviour is closer to the specimens containing compatibiliser.

Morphology study with scanning electron microscope indicates homogenising action of compatibiliser and co-continuous structure of the two-stage vulcanisates.

REFERENCES

1. John D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., John Wiley & Sons, New York, 1980, p. 3.
2. W. J. MacKnight, F. E. Karasz, and J. R. Fried in *Polymer Blends*, Vol. 1, Chap. 3, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978.
3. J. Stoelting, F. E. Karasz, and W. J. MacKnight, *Polym. Eng. Sci.*, **10**, 133–138 (1970).
4. J. W. Schurer, A. deBoer, and G. Challa, *Polymer*, **16**, 201–204 (1975).
5. C. C. Chen, E. Fontan, K. Min, and J. L. White, *Polym. Eng. Sci.*, **28**, 69–80 (1988).
6. W. H. Christiansen, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **34**, 537–548 (1987).
7. J. C. Huarng, K. Min, and J. L. White, *Poly. Eng. Sci.*, **28**, 1085–1094 (1988).
8. M. Xanthos, *Poly. Eng. Sci.*, **28**, 1392–1400 (1988).
9. M. Saleem and W. E. Baker, *J. Appl. Polym. Sci.*, **39**, 655 (1990).
10. Namita Roychowdhury, T. K. Chaki, and Anil K. Bhowmick, *Thermochimica. Acta.*, **176**, 149 (1991).
11. Technical Literature, JSR JENIX E, Japan Synthetic Rubber.
12. J. M. Mitchell, *Rubber Plast. News.*, **3**, 18 (1985) in *Handbook of Elastomers: New Developments and Technology*, C. Michael Roland, Anil K. Bhowmick, and Howard L. Stephens, Eds., Marcel Dekker, New York, 1988, p. 209.
13. Anil K. Bhowmick and Howard L. Stephens in *Handbook of Elastomers: New Developments and Technology* Anil K. Bhowmick and Howard L. Stephens, Eds., Marcel Dekker, New York, 1988, p. 436.
14. A. K. Sen, B. Mukherjee, A. S. Bhattacharya, P. P. De, and A. K. Bhowmick, *J. Appl. Polym. Sci.*, **44**, 1153–1164 (1992).
15. Marek W. Urban and Mark T. Stewart, *J. Appl. Polym. Sci.*, **39**, 265 (1990).
16. Bacon Ke, in, *Encyclopedia of Polymer Sci. and Tech.*, Vol. 5, Norbert M. Bikales, Ed., Interscience Publishers, New York, 1966, p. 52.
17. Ryong-Joon Roe in *Encyclopedia of Polymer Science and Eng.*, Vol. 7, H. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, Eds., John Wiley & Sons, N. Y. 1990, p. 535.
18. J. Kolarik, G. L. Agrawal, Z. Krulis, and J. Kovar, *Polym. Composites*, **7**, (1986).
19. A. R. Payne and J. R. Scott, *Engineering Design with Rubber*, Interscience Publishers, New York, 1960.