

Self-vulcanizable ternary rubber blend based on epoxidized natural rubber, carboxylated nitrile rubber and polychloroprene rubber: 1. Effect of blend ratio, moulding time and fillers on miscibility

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Miscibility of the self-vulcanizable ternary blend based on epoxidized natural rubber (ENR), neoprene and carboxylated nitrile rubber (XNBR) depends on blend ratio. Miscibility is attained at an ENR content of 75 parts per 100 parts of neoprene/XNBR blend, irrespective of the neoprene/XNBR blend ratio. At lower ENR content, miscibility depends on neoprene/XNBR blend ratio. At a fixed ENR content, the higher the neoprene content in the neoprene/XNBR blend, the lower is the miscibility in the ternary blend system. Reinforcing fillers, such as silica and carbon black, cause phase separation in a miscible ternary blend. Variation in moulding time does not alter the miscibility, but shifts the glass transition temperature due to change in crosslink density.

(Keywords: epoxidized natural rubber; carboxylated nitrile rubber; polychloroprene rubber; ternary blend; miscible blend)

INTRODUCTION

De and co-workers¹⁻⁶ have developed novel self-vulcanizable rubber blends based on rubbers with appropriate reactive groups. Such blends are vulcanizable during moulding by the blend constituents themselves in the absence of any external vulcanizing agent. Examples are blends based on epoxidized natural rubber (ENR) and carboxylated nitrile rubber (XNBR)^{1,2}, polychloroprene (neoprene) and XNBR³, chlorosulphonated polyethylene (hypalon) and XNBR⁴, and ENR and hypalon⁵. It has also been observed that the miscibility of these binary blends depends on the blend ratio, concentration and nature of reactive groups and moulding conditions⁶. Three examples are worth mentioning in this context. The binary blend neoprene/XNBR is immiscible in all compositions³. On the other hand ENR/neoprene⁷ is partially miscible and ENR/XNBR² blend is miscible at any composition. There are a few examples in which two of the binary pairs (A + B and A + C) are miscible but the third binary (B + C) is not⁸⁻¹⁰. It is of interest to investigate how to prepare a miscible blend on addition of A to the immiscible binary (B + C) blend. In the present series of rubber-rubber blends it is of interest to learn how much ENR needs to be added to the binary (neoprene/XNBR) blend to create a self-vulcanizable miscible ternary blend.

In an earlier communication¹¹ we have reported that epoxidized natural rubber acts as a compatibilizer when added to an immiscible blend of neoprene and XNBR to form a 1/1/1 miscible ternary blend. In the present paper we report the results of our investigations into the dependence of miscibility of such ternary blends on blend composition, moulding time and filler.

There are examples of a third component in a ternary blend acting as a polymeric compatibilizer for an incompatible or immiscible binary system. Lee and Chen¹² reported that chlorinated polyethylene, with ethylene segments similar to ethylene propylene diene (EPDM) rubber and chlorinated sequences similar to poly(vinyl chloride) (PVC), serves as a compatibilizer for the binary blend of EPDM/PVC just like the effect of chlorinated polyethylene on PVC/polyethylene blends^{13,14}. Blends of poly(caprolactone) (PCL) and PVC and PCL and chlorinated PVC (CPVC) are miscible at any composition¹⁰. However, PVC and CPVC are immiscible¹⁵. It has been shown by Ameduri and Prud'homme¹⁵ that the addition of PCL to a PVC/CPVC mixture allows observation of a single glass transition temperature (T_g), at PCL contents >40% at high PVC/CPVC ratios and at PCL contents > ~26% at low PVC/CPVC ratio. Min *et al.*¹⁶ have identified a ternary miscible system based on poly(methyl methacrylate)/poly(epichlorohydrine)/poly(ethylene oxide). There is no published report of a self-vulcanizable ternary rubber blend.

EXPERIMENTAL

Epoxidized natural rubber (ENR) with 50 mol% epoxidation was obtained from the Malaysian Rubber Producers' Research Association, UK. Carboxylated nitrile rubber, containing a high level of carboxylated monomer and a medium level of bound acrylonitrile (Krynac 221) was obtained from Polysar Ltd, Canada. Neoprene AD was obtained from DuPont Ltd, UK. Vulcasil S (precipitated silica) was obtained from Bayer (India) Ltd, Bombay.

Formulations of the blends are shown in Table 1. ENR and XNBR were separately masticated for ~ 1 min each and neoprene for ~ 2 min, on a 14×6 in. two roll mixing mill. Neoprene and XNBR were blended first and then ENR was added and blended further. The total mixing time was about 8 min. The temperature rise during mixing was 2°C and the rolls were kept cool by circulation of cold water.

The blends were moulded for 60 min at 150°C in a laboratory-size moulding press.

Dynamic mechanical analyses (d.m.a.) were made using Toyo-Baldwin Rheovibron model DDV-III EP at a strain amplitude of 0.0025 cm and a frequency of 3.5 Hz. The procedure was to cool the sample to -100°C and

record the measurements during the warm-up. The temperature rise was 1°C min^{-1} .

Differential scanning calorimetry (d.s.c.) studies were made on a DuPont thermal analyser model 910 in a nitrogen atmosphere. The T_g of the sample was taken as the mid-point of the step in the scan, run at a heating rate of $20^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

Miscibility of the ternary blend based on ENR/neoprene/XNBR depends on blend composition. At constant neoprene/XNBR ratio, an increase in ENR concentration increases the miscibility. Figures 1–3 show the effect of

Table 1 Formulation of blends

Component	Blend designation												
	A	B	K	C	J	D	E	F	M	G	L	H	I
Neoprene AD (wt%)	75	75	75	75	75	50	50	50	25	25	25	25	25
XNBR (Krynac 221) (wt%)	25	25	25	25	25	50	50	50	75	75	75	75	75
ENR (phr) ^a	75	50	37.5	25	12.5	75	50	25	87.5	75	62.5	50	25

^a Unit: parts per 100 g of neoprene/XNBR blend

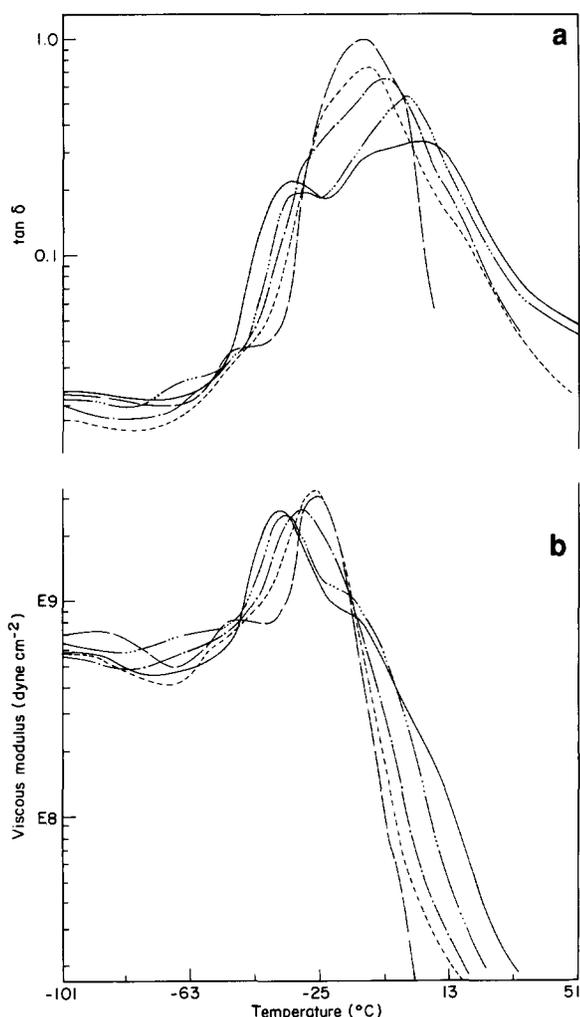


Figure 1 Dynamic mechanical spectra of the ternary blend showing the effect of ENR content on a fixed neoprene/XNBR ratio of 75/25: (a) $\tan \delta$ versus temperature; (b) viscous modulus versus temperature. ENR content (blend designation): —, 12.5 phr (J); - - - -, 25.0 phr (C); — · — ·, 37.5 phr (K); — · — · — ·, 50.0 phr (B); — — — —, 75.0 phr (A)

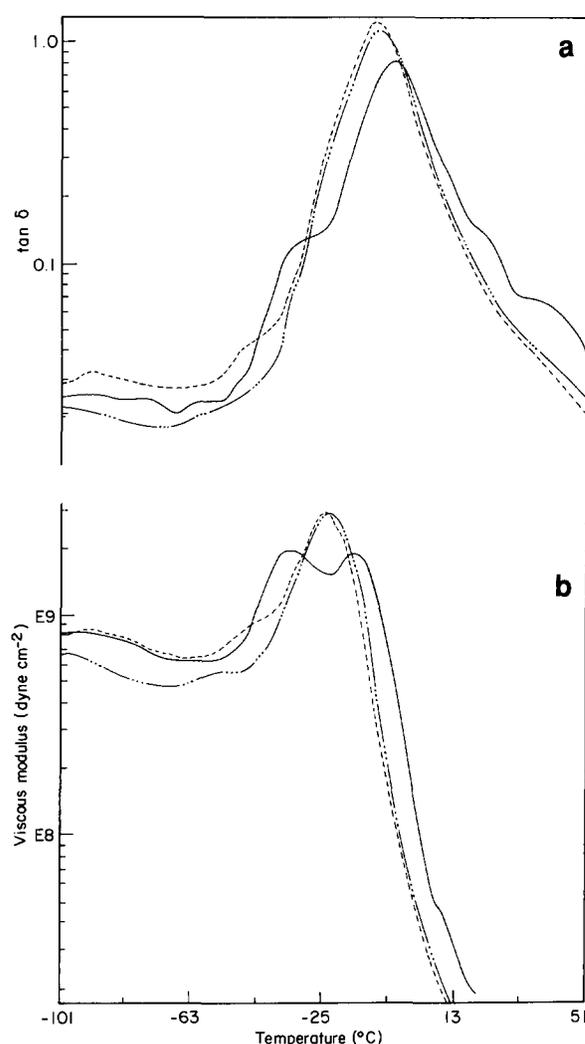


Figure 2 Dynamic mechanical spectra of the ternary blend showing the effect of ENR content on a fixed neoprene/XNBR ratio of 50/50: (a) $\tan \delta$ versus temperature; (b) viscous modulus versus temperature. ENR content (blend designation): —, 75 phr (D); — · — ·, 50 phr (E); — — — —, 25 phr (F)

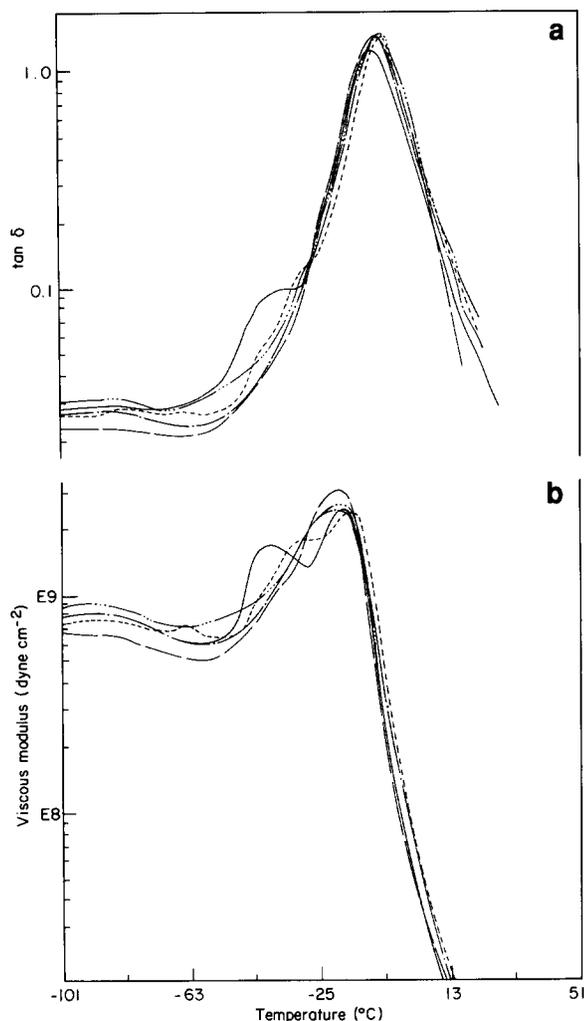


Figure 3 Dynamic mechanical spectra of the ternary blend showing the effect of ENR content on a fixed neoprene/XNBR ratio of 25/75: (a) $\tan \delta$ versus temperature; (b) viscous modulus versus temperature. ENR content (blend designation): —, 25.0 phr (I); ---, 50.0 phr (H); - · - · - ·, 62.5 phr (L); - · - · - ·, 75.0 phr (G); —, 87.5 phr (M)

ENR content at constant neoprene/XNBR ratio on $\tan \delta$ and viscous modulus plots of the ternary blends. At 75/25 ratio of neoprene/XNBR, an ENR concentration up to 25 parts per hundred parts neoprene/XNBR blend (phr) does not result in a miscible ternary blend. In fact two T_g s were observed, corresponding to two phases, i.e. neoprene/ENR and XNBR/ENR. When ENR content increases to 37.5 phr and above, the miscibility improves in the sense that instead of two peaks a single broad peak was observed. As ENR content in the blend increases from 50 to 75 phr the broad peak is replaced by a sharp peak, indicating enhanced miscibility.

Similar observations were made when neoprene content in the binary blend neoprene/XNBR decreases for example from blend composition 50/50 to 25/75. However, when neoprene content decreases in the blend, instead of a broad peak a sharp peak was observed, indicating enhanced miscibility.

Figure 4 shows that at an ENR content of 75 phr the ternary blend becomes a miscible system irrespective of the binary neoprene/XNBR composition. However, the miscibility is greater when the neoprene content is less in the binary neoprene/XNBR blend as evident from the sharp $\tan \delta$ peak. Results are summarized in Table 2.

Results of d.s.c. studies (Figure 5) also provide

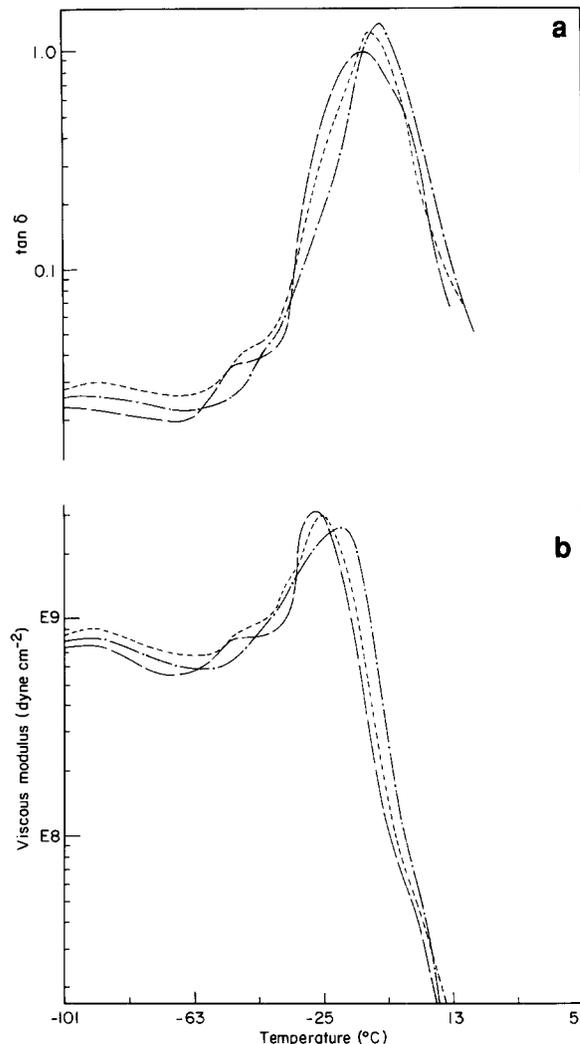


Figure 4 Dynamic mechanical spectra of ternary blend showing the effect of a 75 phr content of ENR on different neoprene/XNBR ratios of: —, 75/25 (blend A); ---, 50/50 (blend D); —, 25/75 (blend G): (a) $\tan \delta$ versus temperature; (b) viscous modulus versus temperature

supportive evidence for the conclusions drawn from d.m.a. studies. Results of d.s.c. studies are summarized in Table 2. It is evident that miscibility in a particular blend is manifested in the occurrence of sharp transition in the T_g zone. Accordingly, an immiscible system provides no clear-cut single transition, while a miscible system provides a single transition. For example, blend G is a miscible system showing a sharp T_g at -18°C , while blend C is an immiscible system showing two T_g s at -40°C and -18°C and blend H is an example of a partially miscible system wherein the two transitions merge with each other and no clear-cut transition is observed.

In the ternary blends, the broadening in the T_g is due to microlevel inhomogeneity. Microheterogeneity can be attributed to partial interpenetrating network formation involving thermovulcanized neoprene and crosslinked ENR/XNBR phases and also to density fluctuations¹⁷. The phase separation behaviour of interpenetrating polymer networks (IPNs) has been reported earlier¹⁸⁻²⁰. It has been reported that due to microheterogeneity the glass transition of the IPN may be very broad, extending the range between the glass transitions of two homopolymers²¹.

Table 2 Glass transition temperatures (T_g) of various ternary blends obtained from d.m.a. and d.s.c. studies

Blend designation	Blend composition	T_g ($^{\circ}\text{C}$) from d.m.a.			T_g ($^{\circ}\text{C}$) from d.s.c.
		$\tan \delta$	Loss modulus		
A	75/25/75	-11	-27		-26
B	75/25/50	-11	-27		^a
K	75/25/37.5	-5	-30		-
C	75/25/25	-29, -1	-35, shoulder at -19		-40, -18
J	75/25/12.5	-33, +8	-38, shoulder at -19		-
D	50/50/75	-10	-25		-19
E	50/50/50	-10	-24		-16
F	50/50/25	-29, -5	-37, -17		^a
M	25/75/87.5	-9	-19		-
G	25/75/75	-7	-19		-18
L	25/75/62.5	-9	-20		-
H	25/75/50	-7	-30, shoulder at -17		^a
I	25/75/25	-37 to -29, -10	-40, -20		^a

^aNo clear-out transition

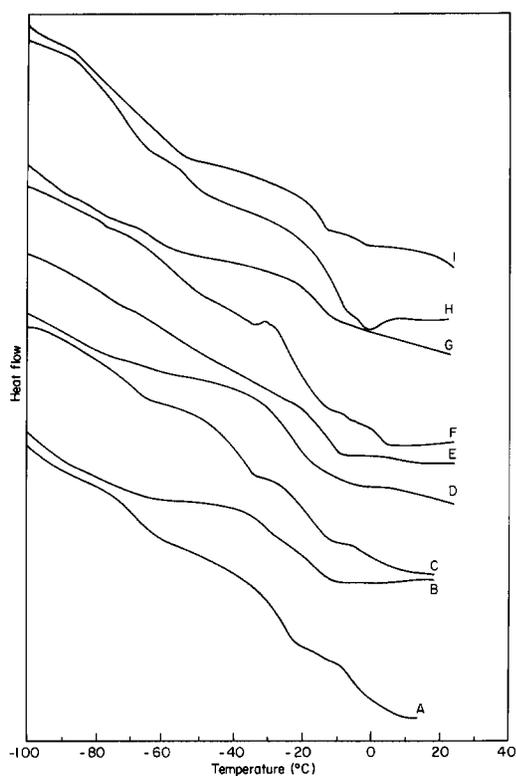


Figure 5 D.s.c. thermograms of ternary blends. Blend composition as given in Table 1

The effect of crosslink density on miscibility of such blends was then studied. In self-vulcanizable blends crosslink density can be varied by changing the moulding time²³. The aim was to check whether miscibility of the immiscible blend could be improved by moulding for a longer time and similarly whether a miscible system could be made immiscible if moulded for a shorter time.

Figure 6 shows the effect of moulding time on variation of $\tan \delta$ and viscous modulus with temperature for a miscible system (blend G) and an immiscible system (blend C). When the moulding time is reduced from 60 min to 15 min in a miscible system, miscibility is not affected. However, the $\tan \delta$ peak is shifted to a lower

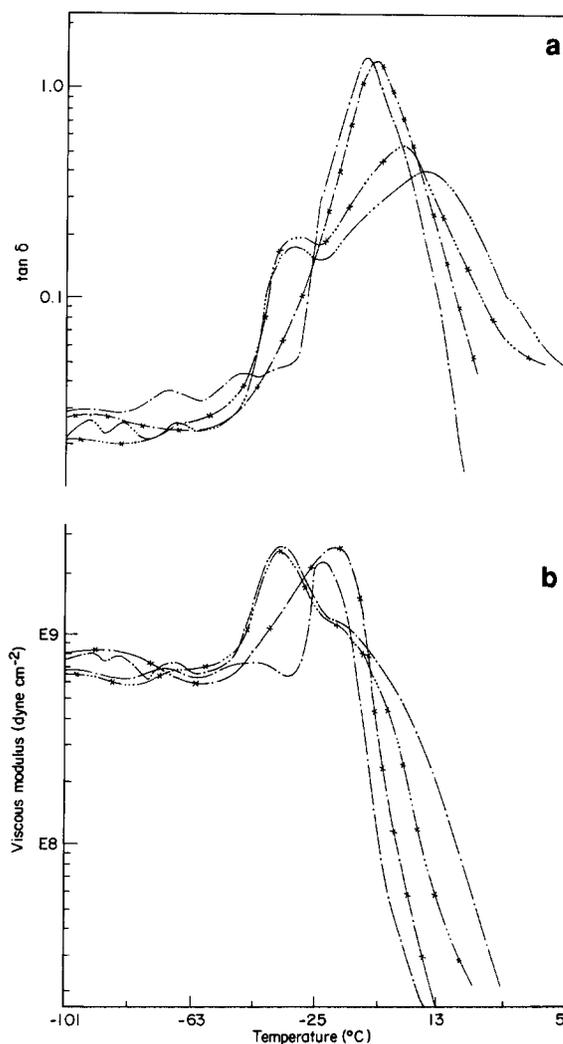
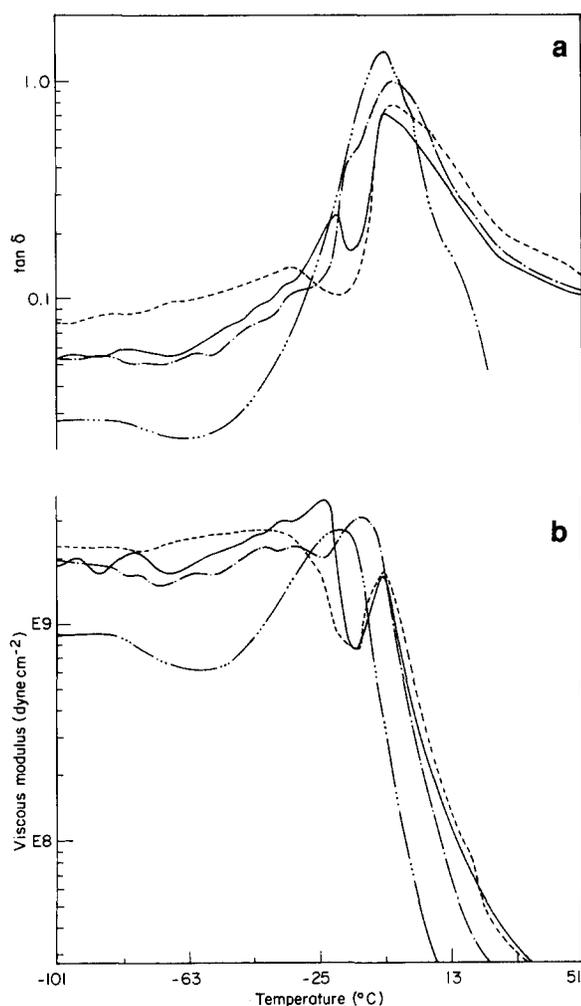


Figure 6 Dynamic mechanical spectra of ternary blends (G and C) showing the effect of moulding time on T_g behaviour: (a) $\tan \delta$ versus temperature; (b) viscous modulus versus temperature. Curing times: blend G, —, 15 min, *-*-, 60 min; blend C, *...*, 60 min, —...—, 120 min

Table 3 Effect of fillers on glass transition temperature (T_g) of miscible ternary blend G of neoprene/XNBR/ENR

Blend designation	Filler type	T_g (°C)		
		$\tan \delta$	Loss modulus	T_g (°C) from d.s.c.
G ^a	—	—7	—19	—18
GIS40	ISAF black	—33, —5	—33, —7	^b
GSi40	Silica	—21, —7	—23, —7	—40, —22
GSR40	SRF black	—5, shoulder at —16	—13	—19

^aUnfilled; value from Table 2^bNo clear-cut transition**Figure 7** Dynamic mechanical spectra of the miscible ternary blend G filled with ISAF black, SRF black and precipitated silica. Filler loading was 40 parts per hundred parts of rubber in each case: (a) $\tan \delta$ versus temperature; (b) viscous modulus versus temperature. —··—, Blend G; —, ISAF black + G; —·—, SRF black + G; —·—, silica + G

temperature due to lower crosslink density at 15 min moulding as compared to 60 min moulding. For the immiscible system, when the moulding time is increased to 120 min the miscibility does not change, but the $\tan \delta$ peak is shifted to a higher temperature due to higher crosslink density at 120 min moulding as compared to 60 min moulding. The lowering of the damping level and broadening of the damping peak due to an increase of crosslinking has been reported previously²².

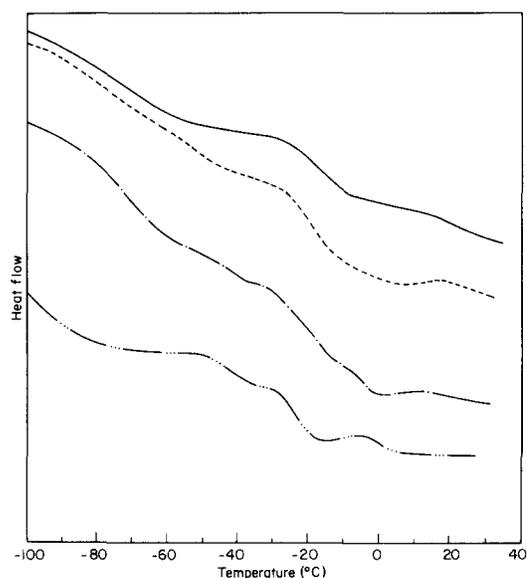
**Figure 8** D.s.c. thermograms of the miscible ternary blend G filled with ISAF black, SRF black and precipitated silica. Filler loading was 40 parts per hundred parts of rubber in each case. —, Blend G; —·—, SRF black + G; —·—, ISAF black + G; —·—, silica + G

Figure 7 shows the dynamic mechanical spectra of the miscible ternary blend system (blend G) filled with three fillers, namely silica, intermediate super abrasion furnace (ISAF) black and semi-reinforcing furnace (SRF) black. The miscibility of the ternary blend was altered as is evident from the two peaks in both $\tan \delta$ and viscous modulus plots in the case of blends with ISAF black (at -33°C and -5°C) and silica (at -21°C and -7°C). However, in the case of blends with SRF black a single peak at -5°C and a hump at -16°C were observed. It is evident that reinforcing fillers, such as ISAF black and silica, cause phase separation in a miscible ternary blend, presumably due to variations in the affinity of the filler to different rubbers. SRF black is less reinforcing and accordingly rubber-filler interaction will be less and the effect of the filler on miscibility will be less pronounced.

D.s.c. results showing the effect of different fillers on 25/75/75 neoprene/XNBR/ENR blend (blend G) are shown in Figure 8. It is evident that the addition of SRF black broadens the transition with no clear-cut glass transition. ISAF black also broadens the transition zone. Silica filler shows two transitions at -40°C and -22°C . It is evident that reinforcing fillers affect the miscibility of the self-vulcanizable ternary blend, as evidenced by the d.m.a. and thermal analysis studies (see Table 3). However, it is to be noted that transitions in d.s.c. studies are not as conclusive as those of d.m.a. results.

CONCLUSIONS

In the ternary blend of ENR/neoprene/XNBR, miscibility is attained at an ENR content of 75 parts per 100 parts of neoprene/XNBR blend, irrespective of neoprene/XNBR blend ratio. At lower ENR content miscibility depends on neoprene/XNBR blend ratio.

Reinforcing fillers like ISAF black and silica cause phase separation in a miscible ternary blend. SRF black does not have a pronounced effect on miscibility.

Increase in moulding time shifts the glass transition to a higher temperature due to increase in crosslink density without affecting the miscibility.

REFERENCES

- 1 Alex, R., De, P. P. and De, S. K. *J. Polym. Sci., Polym. Lett. Edn* 1989, **27**, 361
- 2 Alex, R., De, P. P. and De, S. K. *Polym. Commun.* 1990, **31**, 118
- 3 Mukhopadhyay, S. and De, S. K. *J. Appl. Polym. Sci.* in press
- 4 Mukhopadhyay, S., De, P. P. and De, S. K. *J. Appl. Polym. Sci.* in press
- 5 Mukhopadhyay, S., Chaki, T. K. and De, S. K. *J. Polym. Sci., Polym. Lett. Edn* 1990, **28**, 25
- 6 Mukhopadhyay, S. and De, S. K. *Polymer* 1991, **32**, 1223
- 7 Alex, R., De, P. P. and De, S. K. *Kautsch. Gummi Kunst.* in press
- 8 Shah, V. S., Keitz, J. D., Paul, D. R. and Barlow, J. W. *J. Appl. Polym. Sci.* 1986, **32**, 3863
- 9 Kwei, T. K., Frisch, H. L., Radizan, W. and Vogel, S. *Macromolecules* 1977, **10**, 157
- 10 Wang, Y. Y. and Chen, S. A. *Polym. Eng. Sci.* 1981, **21**, 47
- 11 Alex, R., De, P. P. and De, S. K. *Polym. Commun.* 1990, **31**, 366
- 12 Lee, Y.-D. and Chen, C.-M. *J. Appl. Polym. Sci.* 1987, **33**, 1231
- 13 Locke, C. E. and Paul, D. R. *Polym. Eng. Sci.* 1973, **13** (4), 308
- 14 Paul, D. R., Locke, C. E. and Vinson, C. E. *Polym. Eng. Sci.* 1973, **13** (3), 2092
- 15 Ameduri, B. and Prud'homme, R. E. *Polymer* 1988, **29**, 1052
- 16 Min, K. E., Chiou, J. S., Barlow, J. W. and Paul, D. R. *Polymer* 1987, **28**, 1721
- 17 Macknight, W. J., Karasz, F. E. and Fried, J. R. in 'Polymer Blends' (Eds D. R. Paul and S. Newman), Academic Press, New York, 1975, Ch. 5
- 18 Houston, D. J. and Zia, Y. *J. Appl. Polym. Sci.* 1983, **28**, 3849
- 19 Sperling, L. H. *Polym. Eng. Sci.* 1985, **25** (9), 517
- 20 Nielsen, L. E. 'Mechanical Properties of Polymers and Composites', Marcel Dekker, New York, 1974
- 21 Sperling, L. H. 'Interpenetrating Polymer Networks and Related Materials', Plenum Press, New York, 1981
- 22 Prud'homme, R. E. *Polym. Eng. Sci.* 1982, **22**, 90
- 23 Alex, R., De, P. P., Mathew, N. M. and De, S. K. *Plast. Rubber Process Applic.* 1990, **14**, 223