12

Improving resistance to low temperature crystallization in NR/ENR-25 blends

Benny George, Jianhe Liao† and Sally Groves§*
**Rubber Research Institute of India;*
†Chinese Academy of Tropical Agricultural Sciences;
§Tun Abdul Razak Research Centre, MRPRA, UK

12.1 INTRODUCTION

The automobile rubber products manufacturing industry has expressed a long-standing need for high damping rubbers which combine good physical properties with a low dependence of dynamic properties on temperature. Elastomers with inherently high damping have a high dependence of properties on temperature because the damping derives from relatively high glass transition temperatures (T_g). An alternative approach of using natural rubber (NR) with high levels of carbon black and oil but relatively low crosslink densities limits' the degree of damping attainable and gives rather poor physical properties.

Previous work has demonstrated the advantage of using a blend of normally filled NR with highly filled and plasticized 25 mole% epoxidized NR (ENR-25) [1]. The NR component provides good physical properties whilst the ENR-25 phase provides high damping. These blends are required to provide good performance at both high and low temperatures. The use of efficient (EV) or semi-EV sulphur cure systems, in which the levels of accelerator are greater than those of sulphur, and appropriate antioxidants should provide resistance to change in prop-

Blends of Natural Rubber. Edited by Andrew J. Tinker and Kevin P. Jones.
Published in 1998 by Chapman & Hall, London. ISBN 0 412 819406

erties at elevated temperatures [2]. However, low temperature properties of NR/ENR-25 blends can be affected by the stiffening of the NR phase due to crystallization. These blends are particularly prone to such stiffening, because the polarity of the ENR phase tends to attract the curatives to itself and leaves the NR with a low crosslink density (Chapter 10). ENR is not so susceptible to crystallization at low temperatures due to the inhibiting effects of the epoxide groups [3]. One method to overcome NR crystallization is to use a conventional sulphur vulcanization system, which imparts chain modification in NR. However this conflicts with the requirement of low sulphur levels in the ENR phase, which is prone to attack by sulphur acids [4, 5].

It had been reported that the incorporation of small amounts of high vinyl polybutadiene (Hv-BR) in NR increases the inhibition time for crystallization and decreases the rate of subsequent crystallization [6]. Therefore, the effect of incorporating Hv-BR into the NR phase of NR/ENR-25 blends as a means towards reducing low temperature crystallization was examined.

For a given cure system, the degree to which separate elastomers in a blend are vulcanized will have a profound effect on both damping and physical properties. The ideal situation for the blend described herein would be a moderate crosslink density in the NR achieved by a semi-EV cure system and a lower crosslink density in the ENR-25 achieved by an EV cure system, thereby ensuring high damping and good ageing resistance. Because the ENR is polar it is difficult to achieve a lower crosslink density in this phase because of the tendency of curatives to preferentially locate in the more polar elastomer of a blend (Chapter 5). However, earlier work had shown that a S/TBBS cure system gives satisfactory properties (Chapter 10). The approach described herein used factorial design methods for determining the S/TBBS level which provides optimum properties.

12.2 EFFECT OF INCORPORATING HV-BR INTO NR/ENR-25 BLENDS

The miscibility of NR and Hv-BR has been established in previous work [6, 7]. The closely related work [6] indicated that a Hv-BR content of 10% is sufficient to significantly inhibit the rate of crystallization of NR with little effect on physical properties. In this work it was decided to restrict the level of Hv-BR in the NR phase of NR/ENR-25 blends to 10% for this reason.

Blends of NR/Hv-BR with ENR-25 were studied by Dynamic Mechanical Thermal Analysis (DMTA) over the temperature range −100°–0 °C in order to confirm that the blend consisted of only two separate phases. Figure 12.1 shows the DMTA thermogram of a NR/Hv-BR/

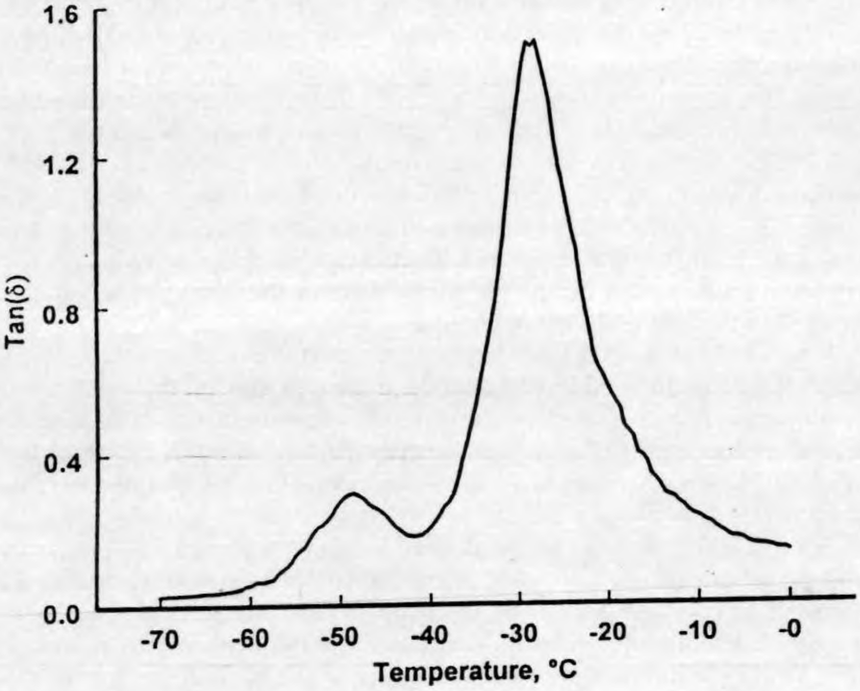

Figure 12.1 DMTA thermogram of a 45:5:50 NR/Hv-BR/ENR-25 gum vulcanizate at 1 Hz.

ENR-25 gum vulcanizate prepared in the ratio 45:5:50. A maximum in the loss peak corresponds to a distinct T_g. It is clear from the figure that NR and Hv-BR form a miscible phase represented by a single T_g at −48 °C. ENR-25 exhibits a separate T_g at −29 °C. A separate Hv-BR phase would be manifested as a further loss maximum between −10 °C and 0 °C.

Having established the miscibility of this grade of Hv-BR with NR, filled tri-blend vulcanizates were prepared with the aim of investigating the low temperature crystallization of the NR/Hv-BR phase. Vulcanizates were prepared according to the formulations listed in Table 12.1 by first mixing separate NR/Hv-BR and ENR-25 masterbatches in an internal mixer then cross-blending these masterbatches and adding curatives in a single mix cycle.

Samples were cured to rheometer t_{95} at 150 °C. The degree of crystallization in the NR/Hv-BR phase of tri-blends after periods in an unstrained state at −26 °C was determined by differential scanning calorimetry (DSC). The rate of crystallization in NR is at a maximum at this temperature [8]. The results of the DSC study are shown in

Table 12.1 Formulations of masterbatches used in preparation of blends containing Hv-BR, phr[a]

SMR CV	100	90	–
Hv-BR (VI-1979)[b]	–	10	–
ENR-25[c]	–	–	100
N326 carbon black	30	30	100
Dioplate 7017[d]	6	6	30
TBEP	–	–	12
Zinc oxide	5	5	5
Stearic acid	2	2	2
TMQ	2	2	2
Calcium stearate	–	–	3

[a] Subsequently crossblended at a 1:1 volume ratio, finalized with 0.3 phr S, 2 phr TMTD and 3 phr TBBS
[b] Buna VI 1979 (70 ± 3% 1,2, content), Bayer, France
[c] Epoxyprene-25, Kumpulan Guthrie Berhad, Malaysia
[d] A polymeric ester, Kemira Polymers, Stockport, Cheshire, UK

Figure 12.2 and indicate that the rate of crystallization in NR/Hv-BR and NR/Hv-BR/ENR-25 blends is slower than that of comparable NR and NR/ENR control vulcanizates.

In addition, the DSC study also provides insight into the crosslink density of the NR phase in the blends. Increased crosslink densities are

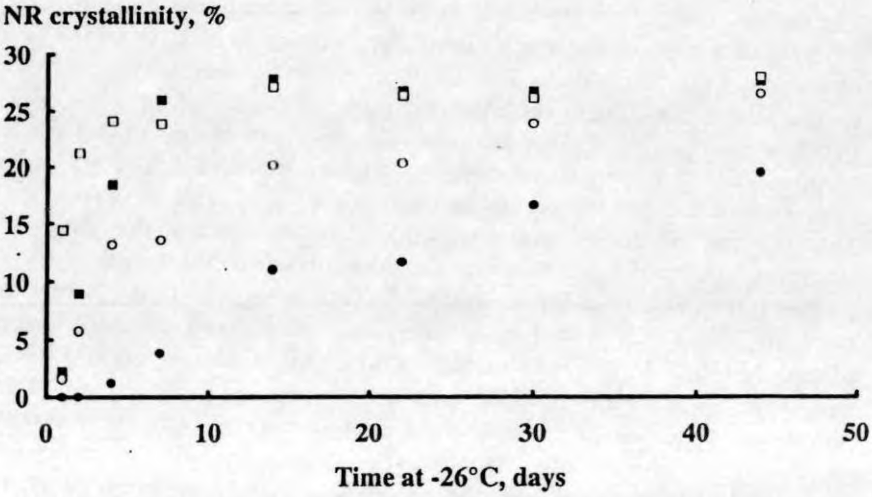

Figure 12.2 Comparison of the degree of crystallization in the NR (NR/Hv-BR) phase of NR (■), NR/Hv-BR (●), NR/ENR-25 (□) and NR/Hv-BR/ENR-25 (○) vulcanizates at −26 °C.

known to reduce crystallization rates [8]. The data imply faster rates in the NR/ENR and NR/Hv-BR/ENR blends with respect to a single polymer NR vulcanizate. This indicates that the crosslink density in the NR phase of the NR(NR/Hv-BR)/ENR-25 blends is lower than that of the control NR single polymer vulcanizate, and reinforces the suggestion that ENR tends to scavenge curatives in this blend system.

The susceptibility of these vulcanizates to low temperature crystallization in a strained state has been determined by measuring the loss of stress associated with the onset of crystallization. Strained samples were kept at −26 °C over a time period similar to the DSC study. The results of the study are shown in Figure 12.3 and confirm that crystallization of NR/Hv-BR and NR/Hv-BR/ENR-25 blends is slower than the corresponding vulcanizates not containing Hv-BR.

In order to assess the effect of incorporating Hv-BR into NR/ENR-25 blends on properties, both NR/ENR-25 and NR/Hv-BR/ENR-25 vulcanizates were prepared to the masterbatch formulations in Table 12.1 but cured with 0.3 phr sulphur and 4 phr TBBS. Test results shown in Table 12.2 indicate that the properties of the blend containing Hv-BR are similar to those of the binary blend. The lower tear strength of the tri-blend may be attributed, at least in part, to a higher modulus apparently due to higher crosslink density.

Ozone resistance tests performed at 40 °C, 20% strain and 50 pphm ozone showed a substantial reduction in cracks (by 70%) in the tri-blend.

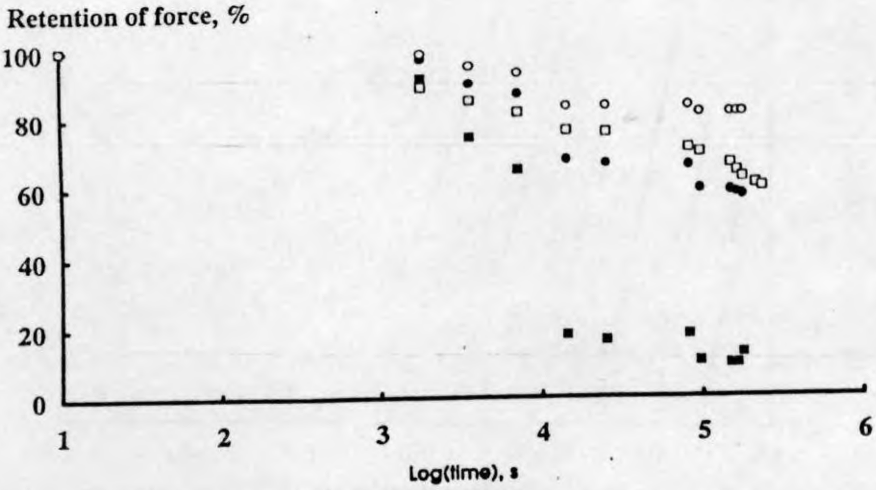

Figure 12.3 Stress relaxation of NR (■), NR/Hv-BR (●), NR/ENR-25 (□) and NR/Hv-BR/ENR-25 (○) vulcanizates at −26 °C.

Table 12.2 Comparison of the properties of NR/ENR-25 and NR/Hv-BR/ENR-25 vulcanizates

Property	*NR/ENR-25*	*NR/HV-Br/ENR-25*
Mooney viscosity[a]	48	49
t_{95}, min[b]	18.5	15.0
M_H–M_L, dNm	12.6	16.3
Hardness, IRHD	60	64
Tensile strength, MPa	20.1	20.6
Elongation at break, %	450	450
MR100, MPa	1.9	2.4
Crescent tear strength, N/mm	71	44
Compression set, 1 d/70 °C, %	21	23
Compression set, 3 d/23 °C, %	11	11
Loss angle, 5 Hz/5%, °	18.5	17.8

[a] ML(1+4) 100 °C
[b] Monsanto MDR2000E rheometer at 150 °C

12.3 CURATIVE LEVEL OPTIMIZATION

Previous work had shown that a number of vulcanization systems give good physical properties and high loss angles for NR/Hv-BR/ENR-25 blends (Chapter 10). All were derived from formulations known to be suitable for ENR-50 vulcanizates [4,5]. A S/TBBS system was found most appropriate, but it is possible to further improve properties by optimizing the sulphur/accelerator level. A two-level factorial designed experiment [9,10] was performed to investigate the widest range of S/TBBS levels within an EV to semi-EV range. The masterbatch formulations are shown in Table 12.3 and the levels of sulphur and TBBS used in the design are given in Table 12.4 which also includes compound

Table 12.3 Masterbatch formulations, phr

SMR CV	90	–
Hv-BR (VI 1979)	10	–
ENR-25	–	100
Zinc oxide	5	5
Stearic acid	2	2
TMQ	2	2
Calcium stearate	–	3
N326 carbon black	30	99
Diolpate 7017	6	34
TBEP	–	11

Table 12.4 Sulphur, TBBS levels and compound properties from the designed experiment

Mix no.	*Sulphur (phr)*	*TBBS (phr)*	*M_H–M_L (dNm)*	*t_{95} at 150 °C (min)*
1	0.32 (−1)	4.06 (+1)	9.8	37.5
2	0.85 (0)	1.50 (−1.414)	10.0	10.0
3	0.85 (0)	3.00 (0)	12.2	13.0
4	1.38 (+1)	4.06 (+1)	15.8	12.0
5	0.32 (−1)	1.94 (−1)	7.9	21.3
6	0.85 (0)	3.00 (0)	12.5	12.5
7	0.85 (0)	3.00 (0)	14.1	13.0
8	0.85 (0)	4.50 (+1.414)	14.2	18.0
9	1.38 (+1)	1.94 (−1)	13.5	9.0
10	0.10 (−1.414)	3.00 (0)	5.8	48.5
11	0.85 (0)	3.00 (0)	12.7	13.3
12	1.60 (+1.414)	3.00 (0)	15.5	9.3

Figures in brackets refer to the variable level in design units

properties. The separately mixed masterbatches were cross-blended at 1:1 volume ratio and finalized in a single-stage in an internal mixer.

Vulcanizates were prepared by curing to rheometer t_{max} at 150 °C and the resulting properties are shown in Table 12.5.

Table 12.5 Properties of NR/Hv-BR/ENR-25 vulcanizates from the designed experiment

Mix no.	*MR 100 (MPa)*	*T.S. (MPa)*	*E.B. (%)*	*Ring[a] fatigue (kc)*	*Cres. tear (N/mm)*	*Compression set (%)*		*δ (°) 5% 5 Hz*	*Hard. (IRHD)*
						3d/23 °C	*1d/70 °C*		
1	1.37	22.6	590	63	84	9	11	17.8	56
2	1.42	24.7	665	87	121	11	23	16.4	56
3	1.96	24.5	580	55	85	8	15	15.4	59
4	2.74	21.8	425	14	60	7	18	14.6	64
5	1.07	20.8	665	58	96	13	17	16.5	51
6	1.95	22.7	535	43	83	9	17	15.2	60
7	2.07	24.7	555	52	83	9	15	16.8	61
8	2.49	22.5	465	33	78	8	13	15.7	63
9	2.11	25.3	580	85	115	10	28	16.5	62
10	0.80	14.1	635	99	39	19	21	19.1	45
11	2.14	23.9	530	54	83	8	15	16.3	61
12	2.85	22.8	485	37	81	8	23	15.7	64

[a] 0–100% strain, 5 Hz, kc to failure

Response equations which relate the compound properties to design variables were generated using a commercial modelling program and are shown below:

Hardness, IRHD $= 60.2 + 5.7\ (S) + 2.1\ (TBBS) - 2.6\ (S)^2$

Tensile strength, MPa $= 24.2 + 2.1\ (S) - 2.4\ (S)^2$

Elongation at break, % $= 559.4 - 57.7\ (S) - 63.9\ (TBBS)$

Compression set, °

1 day at 70 °C, % $= 16.2 + 2.6\ (S) - 3.8\ (TBBS) + 2.7\ (S)^2$

Cresent tear strength, N/mm $= 84.0 - 21.1\ (TBBS) - 15.4\ (S)(TBBS)$

Loss angle, 5%, 5 Hz, $= 16.3 - 1.0\ (S)$

Hardness increase at −26 °C

after 28 days, IRHD $= 18.9 - 10.2\ (S) - 4.4\ (TBBS)$

Rate of hardness increase

at −26 °C, IRHD per day $= 0.73 - 1.04\ (S) - 0.41\ (TBBS) + 0.62\ (S)^2$

where (S) and (TBBS) are the levels of curatives in design units.

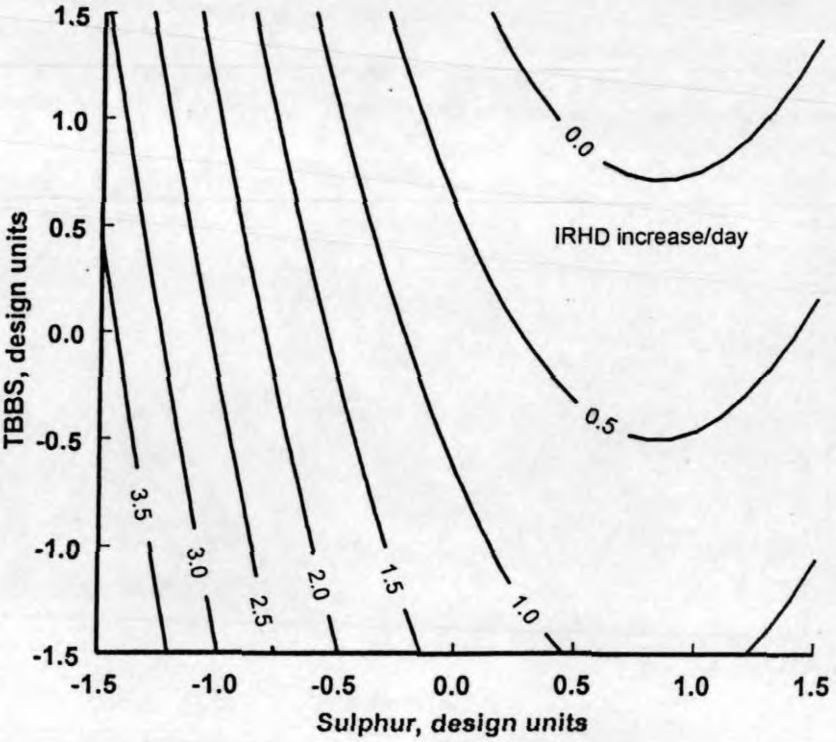

Figure 12.4 Dependence of rate of hardness increase at −26 °C on sulphur and

The response equations in general indicate the expected trend in properties with crosslink level and type. For example, loss angle is reduced by increasing the sulphur level, i.e. total number of crosslinks. Crescent tear strength is more dependent on crosslink type; increasing the TBBS level, i.e. decreasing polysulphide crosslinks, decreases tear strength.

Contour plots may be generated from the response equations and show the response of properties to changes in sulphur and TBBS level. Figures 12.4 and 12.5 show the dependence of rate of hardness increase at −26 °C and compression set respectively, with sulphur and TBBS levels given in design units.

The figures serve to demonstrate the difficulty in achieving desirable values for two different properties as they indicate different design regions (S/TBBS levels) in which the most desirable properties are found, in this example resistance to low temperature crystallization and low compression set. The use of desirability functions in conjunction with response equations is the usual method of determining the most appropriate levels of variables to provide optimum properties [11]. For this

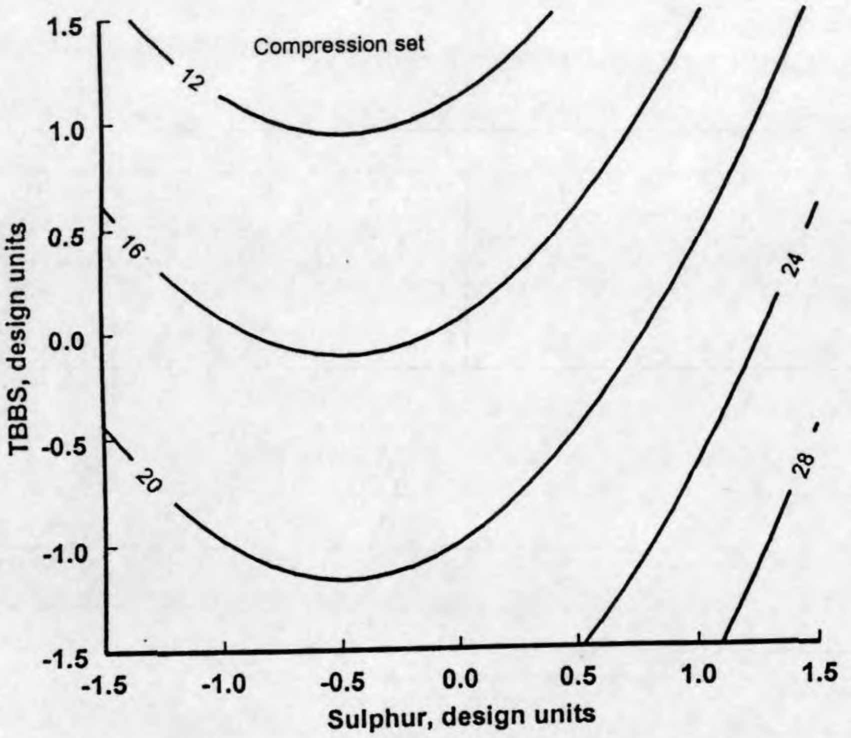

Figure 12.5 Dependence of compression set (one day at 70 °C) on sulphur and TBBS levels in NR/Hv-BR/ENR-25 vulcanizates.

relatively simple two-variable system, superimposing contour plots allows a desirable region to be defined with a suitable degree of accuracy. This procedure was followed for all properties and the outcome indicated a S/TBBS level of 0.4/3.0 phr is the most appropriate for NR/ Hv-BR/ENR-25 blends with high damping, low compression set and resistance to changes of properties at low temperature.

12.4 CONCLUSIONS

Both DSC and stress relaxation measurements demonstrate that NR/Hv-BR/ENR-25 blends have improved resistance to crystallization at low temperatures. Physical testing of bi- and tri-blends demonstrates that the addition of 10% Hv-BR does not severely affect the blend properties. A designed experiment to determine the optimum levels of curatives indicates that S and TBBS levels of 0.4 and 3.0 phr respectively are the most desirable in terms of overall vulcanizate properties.

12.5 REFERENCES

1 Brown, P.S. (1996) High damping NR/ENR blends. *Journal of Natural Rubber Research*, submitted for publication.

2 Crowther, B.G., Lewis, P.M. and Metherell, C. (1988) Chapter 6, Compounding, *Natural Rubber Science and Technology* (ed. A.D. Roberts). Oxford University Press, Oxford, p. 180.

3 Davies, C.K.L., Wolfe, S.V., Gelling, I.R. and Thomas, A.G. (1983) Strain crystallization in random copolymers produced by epoxidation of cis 1,4-polyisoprene. *Polymer*, **24**, 107–113.

4 Gelling, I.R. and Metherell, C. (1993) Vulcanisation systems for ENR-50. *Journal of Natural Rubber Research*, **8**(1), 37–56.

5 Gelling, I.R. and Morrison, N.J. (1985) Sulphur vulcanization and oxidative ageing of epoxidised natural rubber. *Rubber Chemistry and Technology*, **58**(2), 243–257.

6 Brown, P.S., Cook, S., Groves, S.A., Lewan, M.V. and Tinker, A.J. (1993) Natural rubber blends. Paper No. 127 presented at a meeting of the American Chemical Society, Rubber Division, Orlando, Florida, October 26–29.

7 Roland, C.M. (1988) Interactions in a miscible polymer blend. *Rubber Chemistry and Technology*, **61**(5), 866–878.

8 Stevenson, A. (1988) Chapter 18, Low temperature crystallization of natural rubber, in *Natural Rubber Science and Technology* (ed. A.D. Roberts). Oxford University Press, Oxford, 853–891.

9 Freakley, P.K. (1985) *Rubber Processing and Product Organisation*. Plenum Press, New York.

10 Davies, O.L. and Goldsmith, P.L. (1972) *Statistical Methods in Research and Production*. Oliver and Boyd, Edinburgh.

11 Derringer, G.C. (1983) A statistical methodology for designing elastomer formulations to meet performance specifications. *Kautschuk und Gummi Kunststoffe*, **35**(9), 349–352.