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High Damping NR/Epoxidised NR Blends

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High damping blends possessing good physical properties are obtained when a lightly filled NR compound is blended with a heavily filled and plasticised epoxidised natural rubber (ENR) compound. The use of a polar plasticiser ensures that the plasticiser is distributed in favour of the more polar ENR phase. Damping is found to vary with the black distribution, being favoured by a large difference between the loading in each phase. The level of damping increases with the proportion of the ENR component in the blend, but the other physical properties worsen. Recovery properties are poor for all blends except those vulcanised by using an efficient vulcanisation cure system. The high level of damping that these materials possess results from the high filler and plasticiser loading in the ENR phase, however, the relatively high T_g *of this component influences how the properties vary with changing temperature. The dynamic loss peak at 5 Hz lies just below 0°C for blends based on ENR-50, and at about –31°C for the blends containing ENR-25. A marked stiffening accompanies this glass transition, limiting the operating range of the materials. ENR-50 based blends give higher damping but have more temperature dependent properties when compared to their ENR-25 analogs.*

Vulcanised rubbers are visco-elastic materials which exhibit the property of hysteresis under dynamic stresses. This energy absorption property is utilised in vibration isolation[1] for example in automotive bushes and mounts or in building bearings for earthquake protection[2]. The amount of energy loss, or damping, is dependent on the temperature and its relationship to the rubber's glass transition temperature (T_g), and also on the formulation of the compound. High damping materials are usually produced using either high T_g rubbers[3] or by using a combination of high filler and plasticiser loadings in a rubber with a low T_g, usually in conjunction with a low curative level[4]. Both approaches result in some property inadequacies; using a high T_g polymer means that the temperature dependence of the dynamic properties is quite large, whilst highly filled and plasticised materials usually possess poor ultimate properties.

A blend between a highly filled and plasticised rubber and a more normally compounded rubber might offer a material with both high damping and good strength properties. However, the choice of plasticiser and polymers is very important since diffusion will occur to produce the equilibrium distribution of plasticiser in the blend, so the plasticiser must have a large partition coefficient in favour of one of the polymers, the highly filled polymer.

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This approach has been demonstrated for blends of highly filled epoxidised natural rubber (ENR-50, 50 mol% epoxidation) and natural rubber (NR)[5]. Diffusion of the plasticiser away from the highly filled ENR-50 phase was avoided by using a polar plasticiser. The equilibrium distribution of such a plasticiser is biased towards the ENR-50 phase as this is the more polar elastomer. Aris[6] used a polymeric ester plasticiser with a distribution coefficient (Kd) in favour of the ENR-50 of 5.35. Although ENR-50 has a high T_g and thus high intrinsic damping[3], it is not this property of the ENR-50 that is important in these particular blends, but the high polarity that promotes the uneven distribution of the polar plasticiser. A high plasticiser loading allows a high filler content in the ENR phase, and these combine to provide the high level of damping.

This study extends the understanding of these new materials by investigating the effect of some of the compounding variables on material properties.

MATERIALS AND METHODS

The rubbers used in this study were natural rubber, NR (SMR CV), 50mol % epoxidised NR, ENR-50 (*Epoxyprene 50*, Guthrie, Malaysia) and 25mol % epoxidised NR, ENR-25 (*Epoxyprene 25*, Guthrie, Malaysia). Rubber chemicals and fillers were standard commercial grade materials; the plasticisers were tributoxyethyl phosphate, TBEP (*Amgard TBEP*, Albright & Wilson, UK) and an alcohol modified polymeric resin plasticiser, *Diolpate 7017* (Kemira Polymers, UK).

Compounding was performed using a BR size Banbury internal mixer. All of the blend materials are produced by crossblending well mixed single polymer masterbatches. This was to ensure that the loading of carbon black in the individual phases of the blend is both known and controlled. Both NR and ENR interact strongly with carbon black and the masterbatches were well mixed; this should ensure that little or no migration of filler occurred during crossblending[7]. To remove absorbed water from the carbon black it was dried at 125°C for 2 h prior to use. This technique was found to minimise black losses during mixing. The single polymer masterbatches were produced using the mix cycles given in *Table 1*, the mix cycle for the NR component is slightly longer so as to give mixes of similar Mooney viscosity (M_L 1 + 4 at 100°C). The large quantities of oil and plasticiser in the ENR phase require a two stage addition of both carbon black and plasticiser and careful control of the ram position and pressure to avoid excessive material losses. Crossblending was performed in the Banbury mixer at a rotor speed of 116 r.p.m. for 2 min, or, for small scale mixes, on a cool two roll mill. The curatives were added on a cool two roll mill. The ENR mixes and the blends show a tendency to band on the back (higher speed) mill roller during milling.

Test pieces were vulcanised at 150°C in a steam heated press to t_{max} as determined by using Monsanto ODR or MDRE rheometers. Metal-rubber bonding of the double shear test pieces used a two-coat system (*Chemlok 205* primer and *Chemlok 220* top coat). These samples were vulcanised by using cold metal pieces in the pre-heated transfer mould and extending the vulcanisation period by 5 min.

The physical properties were obtained by using the relevant international test. The dynamic properties in double shear test

TABLE 1. SINGLE POLYMER MASTERBATCH MIX CYCLES

Time	ENR masterbatch	NR masterbatch
Start	Polymer + calcium stearate	Polymer
30 s	Powders + 1/2 black + 1/4 plasticiser	Powders + 1/2 black
1 1/2 min	1/2 black + 3/4 plasticiser[a]	1/2 black + plasticiser
2 1/2 min	Sweep	Sweep
4 min	Dump	
4 1/2 min		Dump

[a]Ram to neutral for ~ 15 s as plasticiser is absorbed

geometry were determined by using an Instron 1271 test machine. This instrument is actuated by a servo-hydraulic drive and is fitted with an environmental chamber. Test data were collected by using a Schlumber Solartron 1250 frequency response analyser. Room temperature testing was performed on samples conditioned by using a set pre-test strain sequence of 3 cycles of 0%–100% followed by 3 cycles of 0 – ±100% at a frequency of 1 Hz–2 Hz. Testing commenced without further delay, beginning at small strains (0.1%) and increasing strain in stages to a maximum of 20%. The test frequency was 5 Hz.

The temperature sweep tests were performed by first cooling the chamber and sample to approximately – 40°C. This temperature was maintained for 30 min prior to testing to allow thermal equilibrium to be reached. The temperature of the test piece was monitored by use of a thermocouple wire fixed to one of the metal ends of the test piece. The samples were very stiff at this low temperature; strains in excess of 1% caused the instrument overload protection system to function, hence the use of this lower strain for the sweep. The temperature was allowed to increase to room temperature over a period of 2 h–3 h, during which time the test data were obtained. The chamber was then heated in small steps to 40°C, allowing 10 min–20 min for thermal equilibration to occur at each intermediate temperature. Samples only experienced the dynamic strains during the acquisition of the individual datum points.

RESULTS AND DISCUSSION

Effect of Carbon Black Distribution

In his work, Aris[5] used a loading of 50 p.h.r. carbon black in the NR phase and 90 p.p.h.r. carbon black in the ENR-50 phase. The same grade of carbon black was used in the two phases. The loadings of the polymeric ester plasticiser were 5 p.h.r. and 40 p.h.r., respectively. To achieve such a disparate black distribution the blend was produced by crossblending two separately mixed single polymer masterbatches.

A study to determine the effect of the black distribution on the dynamic properties of the

blends was conducted by crossblending single polymer masterbatches of ENR-50 and NR at a polymer ratio of 1 1. As with the earlier work the same carbon black was used in both polymers Two ENR-50 and three NR masterbatches were produced (1, 2 and 4 – 6, *Table 2*) Five compounds (7–11, *Table 3*) were produced by crossblending these masterbatches at a 1 1 polymer ratio and finalising using a sulphur-CBS semi-EV cure system, two analogous single polymer vulcanisates (12 and 13) were also produced (*Table 3*) It is evident that the blends show the high damping of the ENR component Damping is greatest when the difference in black loading in the two phases is greatest (entries 7 and 8 or 9 and 10, *Table 4*) Damping increases with both increased loading in the ENR phase and with decreased loading in the NR phase The blends show a level of damping that is greater than the simple mean of the two component values, suggesting that the ENR phase is continuous Obtaining micrographs to support this thesis proved impossible due to the black loadings defeating attempts to obtain contrast between the two phases

A second set of blends with a higher loading of carbon black in the ENR-50 was used to investigate the effect of cure system (Compound 3, *Table 2*) A range of curative loadings within the semi-EV cure system employed by Aris[5] and a fully efficient cure system were used to produce these blends (*Table 5*) The static physical properties of these blends are generally good (*Table 6*), the tensile strengths are close to 20 MPa whilst the extensions at break are greater than 500%. The semi-EV cure system gives poor compression set at 70°C (> 40%), that of the EV cure is considerably better.

Changing the polymer ratio could change the blend morphology, and thus the properties of the blend Blends were produced at 1 1 and 6 4 volume ratios (NR.ENR masterbatches, *Tables 7* to *9*) As expected, the loss angle is reduced as the proportion of the NR masterbatch is increased (also compare blend 16, *Table 6* with blends 21 and 22, *Table 9*) Care must be taken in interpreting the dynamic data as the loss angle has an inverse relationship with the dynamic modulus, however, the EV vulcanisates appear to be giving higher loss angles The compression set of the blends cured using the conventional and semi-EV cure systems was poor (*Table 9*), whilst that of the EV system blends was good The TMTD/TBBS system was shown by Gelling and Metherell to give ENR vulcanisates with good compression set[8] The tensile properties of blends 25–28 were inferior to those of the other blends, to maximise the tensile strength the proportion of the NR masterbatch needs to be high

Temperature Variation of Dynamic Properties

The use of the high T_g ENR-50 in these blends is likely to confer a high rate of change on the dynamic properties of the material with temperature, particularly as the temperature is reduced below ambient. This is evident in *Figure 1*, which shows the ratio of the dynamic modulus (G') at a given temperature to that at 23°C Blend 28 (▼, *Figure 1*) shows a significant stiffening even at 0°C, with a seven-fold increase in dynamic modulus at –10°C and a twelve-fold increase at –20°C These changes are accompanied by changes in loss angle (*Figure 2*), the loss peak is at –2°C and the loss tangent falls rapidly with temperature below this point, being only a third of the room

TABLE 2 SINGLE POLYMER MASTERBATCH FORMULATIONS I

Mix Number	Formulation 1	2	3	4	5	6
SMR CV				100	100	100
ENR-50	100	100	100			
N 330 BLACK	90	100	110	30	45	55
Diolpate 7017	40	40	40	5	5	5
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
TMQ[a]	2	2	2	2	2	2
Calcium stearate	3	3	3			
Mix wt	242	252	262	144	159	169
Mix vol. (cm^3)	194.3	199.9	205.4	136.6	143 9	149 5
Specific gravity	1.245	1.261	1.275	1.062	1 105	1 13

[a]Poly-2,2,4-trimetyl-1,2-dihydroquinoline *e.g. Felectol H* (Monsanto)

TABLE 3. CROSSBLEND FORMULATIONS I

Masterbatch	Formulation 7	8	9	10	11	12	13
4					67		
1	121		121				242
2		126		126	126		
5	79 5	79.5				159	
6			84.5	84.5			
Polymer ratio	1 1	1:1	1:1	1:1	1:1		
Mix volume ratio	4.6	4:6	4:6	4:6	4:6		
Sulphur	1.2	1.2	1.2	1.2	1.2	1.2	1.2
CBS[a]	1.2	1.2	1.2	1.2	1.2	1.2	1.2

[a]N-Cyclohexyl-2-benzthiazole sulphenamide

TABLE 4. DYNAMIC PROPERTIES (10% STRAIN, 5 Hz AT 23°C)

Dynamic properties	Formulation						
	7	8	9	10	11	12	13
Black ratio[a]	45:90	55:90	30:100	45:100	55:100	45	90
G'(MPa)	2.44	2.22	2.19	2.69	2.54	1.47	3 71
Loss angle,	19.3	18.6	19.8	19.5	19.3	8.26	22.9
Tan(δ)	0.350	0.337	0.360	0.354	0.350	0.145	0.422

[a]NR: ENR, p.h.r. black in each phase. Black loading in the case of single polymer vulcanisates 12 and 13

TABLE 5. CROSSBLEND FORMULATIONS II

Masterbatch	Formulation				
	14	15	16	17	18
3	131	131	131	131	131
4	72	72	72	72	72
Polymer ratio	1:1	1:1	1:1	1:1	1:1
Mix volume ratio	4:6	4:6	4:6	4:6	4:6
Sulphur	0.75	1	1.2	1.5	0.4
CBS[a]	0.75	1	1.2	1.5	6

[a]N-Cyclohexyl-2-benzthiazole sulphenamide

temperature value at –20°C. A plasticiser with a lower T_g would reduce the temperature dependence of the properties of a single polymer ENR vulcanisate, but in these blends the plasticisers were selected primarily on the basis of their partition between the two polymers, a criterion which greatly reduces the number potential plasticisers.

Perceived applications for these compound require the component to operate over a temperature range of –20°C to 30°C, for example as automotive damping materials for use in northern Europe or northern America. The ENR-50 T_g, and thus the change in material properties, occurs at a temperature which is well within this range. Thus the NR/ENR-50 blends may not be suitable for use as high damping materials in these regions. ENR-25 is the 25mol % epoxidised analogue of ENR-50 and therefore has a lower T_g[9]. Blends of NR with ENR-25 would be expected to have a dynamic loss peak at a lower temperature than the analogous NR/ENR-50 blends. The lower level of epoxidation results in a lower polarity polymer and this reduces the plasticiser Kd to

TABLE 6. PHYSICAL PROPERTIES

Properties	Formulation 14	15	16	17	18
Cure system[a]	SEV	SEV	SEV	SEV	EV
Tensile strength (MPa)	16.8	18.8	19	21	18.1
Extension at break (%)	595	570	540	505	525
M300 (MPa)	8.15	10	10.9	12.9	9.92
MR 100 (MPa)	1.28	1.72	1.97	2.52	1.7
Hardness (IRHD)	66	70	71	75	73
Compression set (1 day at 70°C)	57	54	52	44	26
Compression set (3 days at 23°C)		27	22	19	25
G' (MPa[b])	2.14	2.21	2.45	3.08	2.31
Loss angle	22.5	22.3	21.9	20.3	23.4
Tan(δ)	0.414	0.41	0.402	0.37	0.433

[a]SEV: semi-EV cure system, accelerator: sulphur ratio ~ 1:1; EV: efficient cure system accelerator: sulphur ratio ~ 5:1

[b]Dynamic properties determined at 10% strain, 5 Hz at 23°C.

TABLE 7. SINGLE POLYMER MASTERBATCH FORMULATIONS II

Mixes	Formulation 19	20
SMR CV	100	
ENR-50		100
N 330 BLACK	30	110
Diolpate 7017	6	45
Zinc oxide	5	5
Stearic acid	2	2
TMQ[a]	2	2
Calcium stearate		3
Mix wt.	145	267
Mix vol. (cm^3)	136.6	210.4
Specific gravity	1.061	1.269

[a]Poly-2,2,4-trimetyl-1,2-dihydroquinoline *e.g.*, *Felectol H* (Monsanto)

3.82[6], which will mean that the degree of plasticisation of the ENR phase is reduced.

The ENR-25 blend analogous to 26 (*Table 9*) was prepared and found to bleed the *Diolpate* plasticiser on storage. Reducing the *Diolpate* level in the blend may alleviate this problem, but additional plasticisation of the ENR-25 would then be required. TBEP has a much lower T_g than *Diolpate 7017* (–114°C *vs.* –88°C) but similar Kd between NR and ENR-25[6]. A partial substitution of *7017* with TBEP was used for the ENR-25 blends giving a mix with a slightly reduced plasticiser loading to offset the better plasticisation of the TBEP (blend 30, *Table 10*). The TBEP was compounded into the ENR masterbatch, but some will diffuse into the NR component during crossblending. Three levels of curative

TABLE 8 CROSSBLEND FORMULATIONS III

Masterbatch	Formulation							
	21	22	23	24	25	26	27	28
19	88.5	101.5	88.5	101.5	88.5	101 5	88.5	101.5
20	104	80.1	104	80.1	104	80.1	104	80.1
Polymer ratio	61:39	70:30	61:39	70:30	61:39	70:30	61:39	70:30
Mix volume ratio	1:1	6:4	1:1	6:4	1:1	6:4	1:1	6:4
Sulphur	1.2	1.2	2	2	0.2	0.2	0.3	0.3
CBS[a]	1.2	1.2	0.4	0.4			4.5	4.5
TMTD[b]					1.3	1.3		
TBBS[c]					2	2		

[a]N-Cyclohexyl-2-benzthiazole sulphenamide

[b]Tetramethylthiuram disulphide

[c]N-tert-Butyl-2- benzothiazylsulphenamide

TABLE 9. PHYSICAL PROPERTIES II

Properties	Formulation							
	21	22	23	24	25	26	27	28
Blend mix volume ratio	1:1	6 4	1:1	6:4	1:1	6:4	1 1	6:4
Cure system	SEV	SEV	CON	CON	EV	EV	EV	EV
Tensile strength (MPa)	20.3	22.5	14.8	16.5	18	20	16.7	19.2
Extension at break (%)	550	580	470	560	570	580	600	630
M 300 (MPa)	10.2	10.2	9.07	7.66	8.93	8.79	7.13	7.11
MR 100 (MPa)	1.96	1.88	1.82	1.46	1.74	1.63	1 29	1.23
Hardness (IRHD)	67	63	67	62	65	64	61	58
Compression set (1 day at 70°C)	38	32	40	38	24	22	24	23
Compression set (3 days at 23°C)	18	18	23	21	22	21	23	21
G' (MPa[a])	1.69	1.58	1.49	1.46	1.69	1.53	1.53	1.42
Loss angle	22.1	19.6	24.4	21.9	24	22	23.7	22.8
Tan (δ)	0.407	0.357	0.454	0.402	0.445	0.405	0.44	0.421

[a]Dynamic properties determined at 10% strain, 5 Hz at 23°C

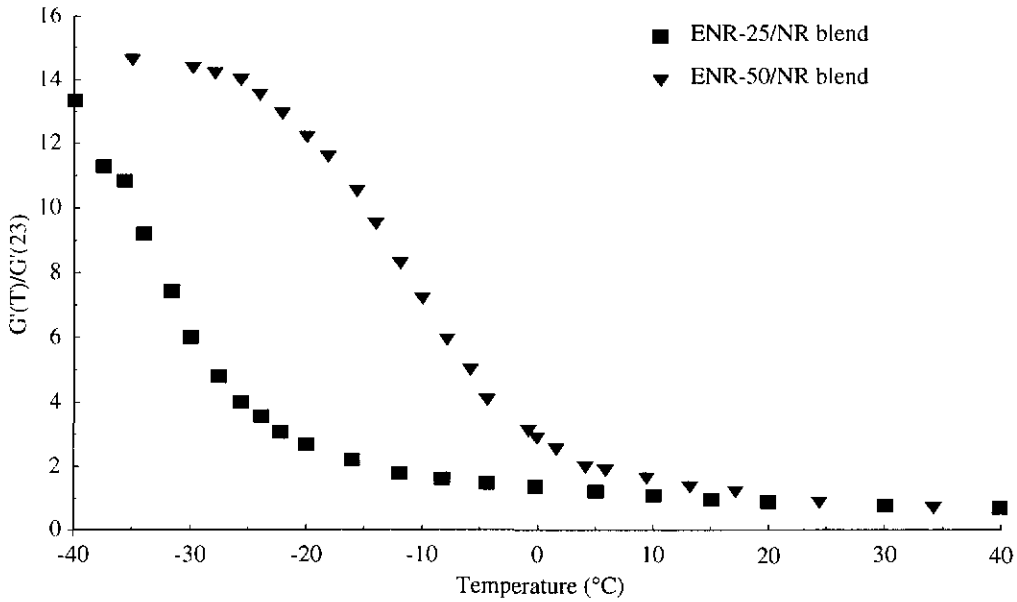

Figure 1. Instron DMTA of ENR-50 and ENR-25 blends: Change of real modulus with temperature at 5 Hz and 1% strain, normalised to 23°C.

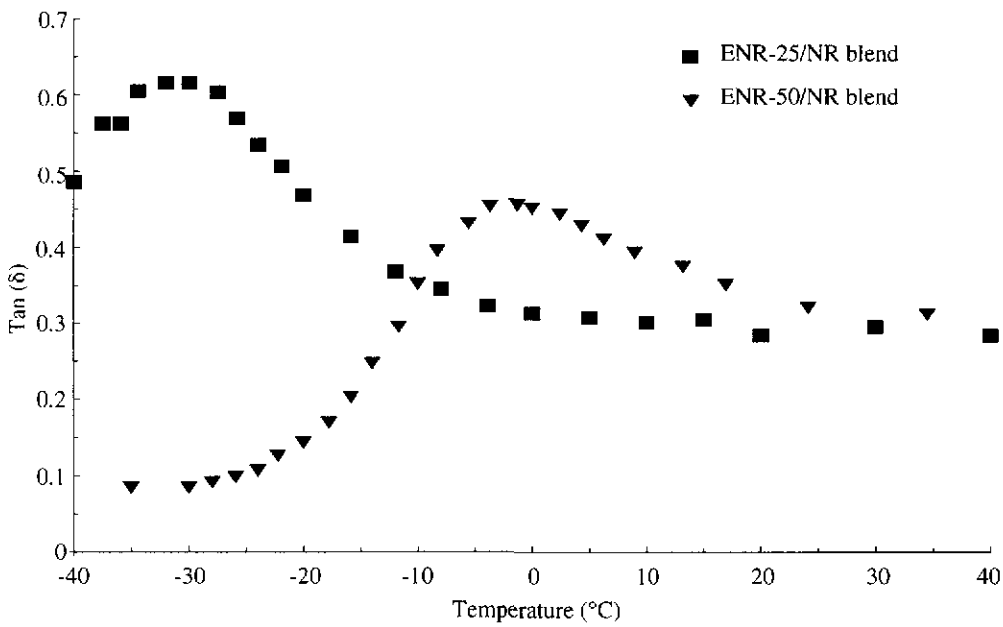

Figure 2. Instron DMTA of ENR-50 and ENR-25 blends: Variation of tangent (δ) with temperature at 5 Hz and 1% strain.

TABLE 10 SINGLE POLYMER MASTERBATCH FORMULATIONS III

Mixes	Formulation 29	30
SMR CV	100	
ENR-25		100
N 330 BLACK	30	110
Diolpate 7017	6	30
Zinc oxide	5	5
Stearic acid	2	2
TMQ[a]	2	2
Calcium stearate		3
TBEP		12
Mix wt	145	264
Mix vol (cm^3)	136.6	207 4
Specific gravity	1 061	1 273

[a]Poly-2,2,4-trimetyl-1,2-dihydroquinoline *e g Felectol H*

were used (*Table 11*), these gave hardness values ranging from 49 IRHD to 55 IRHD, tensile strengths of at least 19 MPa, but somewhat lower loss angles than the ENR-50 analogue at about 18° (blend 33, *Table 12 vs* Blend 26, *Table 9*) Dynamic stiffness and compression set were also lower for blend 33, the ENR-25 blend. No plasticiser bleeding was observed up to six months after vulcanisation.

The lower T_g of the ENR-25, together with a possible influence of the lower T_g of the TBEP, does provide a solution to the temperature dependence of the properties. The increase in dynamic modulus is moved along the temperature axis by about –20°C (■, *Figure 1*), the loss angle peak occurring at –31°C (■, *Figure 2*). The temperature dependence of both of these properties is very low over the range 40°C – 15°C, but does increase below this temperature. However, even at –30°C the increase in dynamic stiffness over the room temperature value is only by a factor of 6. The ENR-25 blends would appear to offer a solution for low temperature applications, albeit with slightly lower damping.

CONCLUSIONS

Blends of normally compounded natural rubber compounds with highly filled and plasticised epoxidised natural rubber compounds produce materials which possess good physical properties, particularly tensile and recovery properties, yet give high levels of damping. The potential for plasticiser diffusion out of the ENR phase is avoided by the use of polar plasticisers with high affinities for the ENR phase. The relatively high T_g of ENR-50 means that its blends show a quite marked temperature dependence of the dynamic properties below ambient temperatures, but give high loss angles and good strength properties. A reduction in the temperature dependence is found for blends of ENR-25 with NR, although this is accompanied with a reduction in the level of damping. High damping is favoured by a large difference in the black loading of the two polymers and by a high proportion of ENR in the blend. This latter factor gives lower ultimate strength properties.

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TABLE 11. CROSSBLEND FORMULATIONS IV

Masterbatch	Formulation 31	32	33
29	101.5	101.5	101.5
30	79.2	79.2	79.2
Polymer ratio	70:30	70:30	70:30
Mix volume ratio	6:4	6:4	6:4
Sulphur	0.13	0.16	0.19
TMTD[a]	0.85	1.04	1.24
TBBS[b]	1.3	1.6	1.9

[a]Tetramethylthiuram disulphide

[b]N-tert-Butyl-2-benzothiazylsulphenamide

TABLE 12. PHYSICAL PROPERTIES II

Properties	Formulation 31	32	33
Tensile strength (MPa)	19	21.5	22.3
Extension at break (%)	715	665	640
MR 100 (MPa)	0.962	1.28	1.4
Hardness (IRHD)	49	53	55
Compression set (1 day at 70°C)	26	21	18
Compression set (3 days at 23°C)	20	14	12
G' (MPa)[a]	1.04	1.1	1.18
Loss angle	18.5	18	17.7
Tan(δ)	0.335	0.326	0.32

[a]Dynamic properties determined at 10% strain, 5 Hz at 23° C

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