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A New Comparison of Sheet and Crumb Rubber Part III. Vulcanisate Properties for an ISAF Tread Mix

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Complementary samples of RSS CV and crumb SMR CV covering the Mooney viscosity range ca. *50–85 were prepared from five lots of monoclonal latex. ISAF tread compounds were mixed from these samples and the physical properties of vulcanised test-pieces determined. The major difference between the vulcanisates was the greater stiffness or modulus of the samples based on RSS CV. This was apparent in both extension and compression and under static and dynamic conditions. Comparable differences were also apparent between the various monoclonal samples of both sheet and crumb rubber. There is limited evidence that these differences were due to variations in the degree of black reinforcement rather than variations in the extent of chemical crosslinking. Little or no difference was found between RSS CV and SMR CV vulcanisates in studies of tensile strength, rebound resilience, Goodrich heat build-up and resistance to fatigue and abrasion.*

Data are given here for the properties of vulcanisates produced from ISAF black-loaded mixes, the preparation and further processing of which were discussed in *Part II* of this series[1]. Some limited data are also included for corresponding gum vulcanisates.

EXPERIMENTAL

Considerable disparities in cure behaviour between RSS CV and SMR CV, both in general and between the individual samples, were observed for the highly sensitive ACS 1 cure system in *Part I* of this series[2]. These results are reproduced in *Table 1.* Much smaller differences generally exist in a fully compounded tread stock[3] and such differences were found to be negligible in the present study as shown by the data of *Part II*, also reproduced in *Table 1.*

In view of this, a single cure condition of 20 min at 150°C, corresponding to Monsanto rheometer t_c' (98), was used to prepare all the vulcanised test-pieces, with the exception of the bonded test-pieces for the determination of dynamic shear modulus. These were cured for 25 min at 150°C, the extra time being necessary to compensate for the effect of the cold metal inserts. The following vulcanisate properties were measured, at 23°C unless otherwise indicated:

- Hardness in IRHD (ISO 1818)
- Tensile strength and modulus, both unaged and after air-oven ageing for three days at 100°C (ISO 37). Ten dumb-bells were tested and the results expressed as mean and standard deviation. Average values for the latter, also expressed as coefficients of variation, are:

	Unaged		Aged	
	S.D.	CV (%)	S.D.	CV (%)
TS (MPa)	0.35	1.2	0.66	3.7
EB (%)	9	1.6	12	3.6
M50 (MPa)	0.04	2.9	0.12	5.6
M100 (MPa)	0.07	3.0	—	—
M200 (MPa)	0.19	3.2	0.53	5.4
M300 (MPa)	0.29	2.6	—	—

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TABLE 1 CURE RATE PARAMETERS OF SMR CV AND RSS CV

Parameter	SMR CV RRIM 600	SMR CV RRIM 623	SMR CV RRIM 628	SMR CV RRIM 701	SMR CV PR 261	RSS CV RRIM 600	RSS CV RRIM 623	RSS CV RRIM 628	RSS CV RRIM 701	RSS CV PR 261
Mix properties of ACS 1 cure system										
MOD value[a], 140°C (kg/cm^2)	4 82	5 45	4 95	4 78	4 90	5 92	5 91	6 22	5 54	5 43
Monsanto rheometer, 160°C, 3° arc										
$M_{HR} - M_L$ (torque units)[b]	27 5	30 7	28 0	26 7	28 1	30 6	33 2	32 7	30 4	30 2
Scorch time, t_{s2} (min)	2 8	2 3	2 5	2 1	2 8	1 7	1 9	1 8	2 2	2 2
Cure time, t_c (90) (min)	13 3	11 3	12 8	11 6	13 0	9 5	9 6	9 2	10 1	10 9
Mix properties of tread compound										
Monsanto rheometer, 150°C, 1° arc										
$M_{HR} - M_L$ (torque units)	28 3	29 4	28 5	27 7	26 7	28 9[c]	29 3	28 6	27 4	27 4
Scorch time, t_{s1} (min)	4 3	3 9	3 9	4 2	4 6	3 2[c]	3 7	4 2	4 0	4 6
Cure time, t_c (90) (min)	14 2	14 0	14 7	15 1	15 7	12 9[c]	14 0	15 0	14 3	15 3
Cure time, t_c (95) (min)	16 3	16 3	17 1	17 5	18 1	15 1[c]	16 4	17 4	16 6	17 6

[a]Vulcanisate modulus parameter[8]

[b]1 torque unit 0 11 Nm

[c]Data appear atypical

- Fatigue life to failure for rings cycled at 5 Hz from 0% to 100% extension (ISO 6943). Six rings were tested and the results expressed as median, mode and standard deviation. For the latter, the mean value over all samples was 42 kc, equivalent to a coefficient of variation of 16%. Since fatigue at constant *strain* is involved, fatigue life is effectively increased by concurrent stress relaxation or set of the ring. To monitor the relative effect, if any, of such relaxation, set was determined after initially cycling for 10 kc.
- Abrasion resistance according to the DIN method (ISO 4649). Mean values for three test-pieces were obtained. The experimental error was of the order of ±3 mm^3.
- Rebound resilience according to the Dunlop tripsometer procedure (BS 903 Part A8) using 8 mm-thick test-pieces. Mean values for two test-pieces were quoted. Differences between these two values ranged from 0.1 to 1.7 units.
- Heat build-up as assessed by the Goodrich flexometer (ISO 4666/3) with the following test conditions: pre-stress 1.0 MPa, stroke 5.72 mm, frequency 30 Hz, 30 min run. Mean values of two tests are quoted, for initial static deflection (ISD), initial dynamic deflection (IDD), temperature rise (ΔT) and percentage permanent set.
- Dynamic shear modulus, G, and loss angle, δ, at a frequency of 1 Hz and at 8 strain amplitudes over the range 0.35%–15%. A 'double sandwich' bonded test-piece prepared by transfer moulding (BS 903 Part A24) was used[4].

The possible attribution of variations in vulcanisate stiffness to differences in the degree of black reinforcement, rather than simple variations in crosslinking, prompted a limited study of the analogous gum systems of the formulation shown in *Table 2*. These were prepared by mill mixing. Measurements were made of the viscosity change on mixing, cure behaviour and vulcanisate modulus by both standard stress/strain tests on dumb-bells and compression of Goodrich flexometer test-pieces.

TABLE 2. FORMULATION FOR GUM VULCANISATES

Compound	Parts by weight
Natural rubber	100
Zinc oxide	5
Stearic acid	3
IPPD[a]	2
Sulphur	2.5
TBBS[b]	0.5

[a] Antidegradant, accelerator, N-Isopropyl-N′-phenyl-*p*-phenylenediamine, Permanax IPPD (Vulnax International).

[b] N-*t*-Butylbenzothiazole-2-sulphenamide, Santocure NS (Monsanto).

RESULTS

In studies of this type, where relatively small differences in vulcanisate properties are to be examined, a factor frequently overlooked is the potentially large influence of small between-batch variations in carbon black content. Such variations are almost inevitable in the course of compounding. Their existence may be indicated by differences in the weights of batches discharged from the mixer, but, provided the black has been properly dispersed, quantitative estimates can readily be obtained from measurements of vulcanisate density. Relevant data for the mixes studied here are given in *Table 3*, with various parameters plotted against density in *Figure 1*. While the precision of the density data is hardly adequate for this analysis[5], the range in black content is likely to be in the region of 2–3 p.p.h.r.

Two conclusions can be drawn from these data and the plots in *Figure 1*. Firstly, variations in the batch weights of discharged mixes are not indicative of differences in black content of the vulcanisates. However, the batch weights of the sheet samples were consistently lower than for the crumb rubbers. This was

TABLE 3. BETWEEN-BATCH VARIATION IN BLACK LEVEL

Item	SMR CV					RSS CV					Mean		
	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	SMR CV	RSS CV	All
Masterbatch preparation													
Dump weight (g)	1 276	1 275	1 274	1 272	1 275	1 267	1 271	1 270	1 270	1 270	1 274.4	1 269.6	1 272.0
Vulcanisate properties													
Calculated black level (p.p.h.r.)[a]	44.6	45.0	46.2	44.2	44.6	45.4	45.4	46.2	44.6	43.8	44.9	45.1	45.0
Density (mg/m^3)	1.108	1.109	1.112	1.107	1.108	1.110	1.110	1.112	1.108	1.106	1.1088	1.1092	1.1090
Hardness (IRHD)	64	65	65	63	64	68	67	66	65	65	64.2	66.2	—
Modulus at 100% elongation (MPa)	2.50	2.30	2.31	2.17	2.06	2.50	2.47	2.44	2.25	2.35	2.27	2.40	—

[a]On the assumption that overall mean density can be equated to 45 p.p.h.r. carbon black.

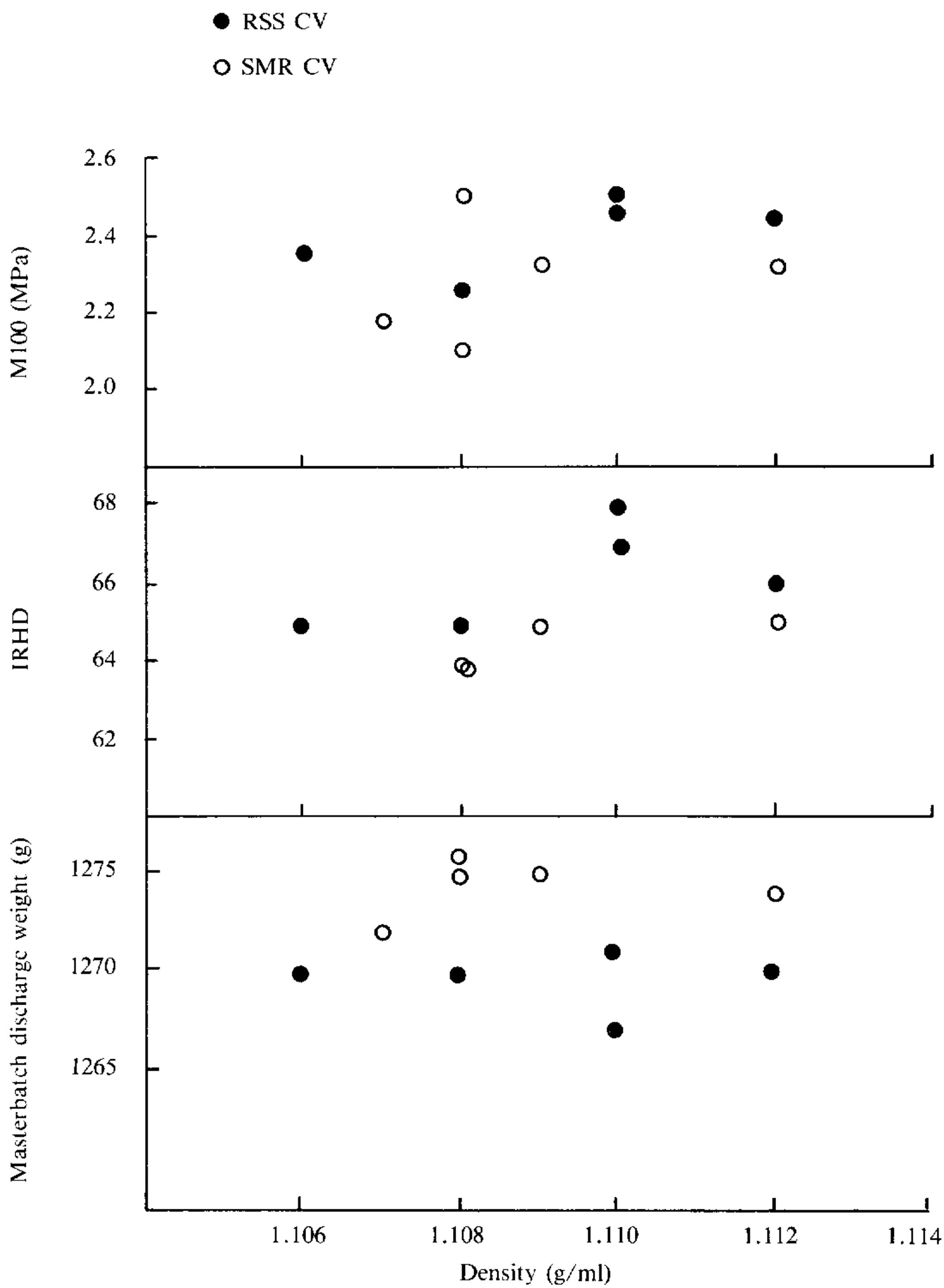

Figure 1. Mix and vulcanisate properties as a function of vulcanisate density.

possibly due to slower incorporation of black into the sheet rubber, with a consequent increased risk of mechanical loss. Secondly, and more importantly, the fluctuations in vulcanisate properties — both within and between types of rubber — were not the immediate consequence of variations in black level. Such variations will not therefore be taken into account in the detailed consideration of vulcanisate properties which follows later in this paper.

Test data and further analyses following the approach of the previous parts of this series[1,2] are given in *Tables 4–9*. Tensile stress-strain data are included in *Tables 4* and *5*. Modulus is rather greater for the sheet rubbers when either the overall mean values or data for the individual clonal samples are considered. The difference is *ca.* 6%, and is independent of extension ratio over the range 50%–300%. Hence, the shape of the stress-strain curve and the onset of strain-induced crystallisation, as reflected in the ratio M300/M50, is not dependent on the type of rubber. A plot of M300/M50 *versus* M50 is given in *Figure 2*.

Both the overall range in modulus of *ca.* 20% and the coefficient of variation of *ca.* 6.5% are about twice those of 10% and 3% respectively found for rheometer torque rise, $\Delta M = M_{HR}-M_L$. Furthermore, as shown in *Figure 3*, the correlation between M50 and ΔM, while significant, shows scatter well beyond that anticipated from the experimental errors; for M300 there is no significant correlation with ΔM. In view of the high temperature involved, ΔM is determined by the degree of crosslinking rather than stiffening due to filler, it would seem likely that these differences in modulus do not stem simply from crosslinking variations, but that the degree of reinforcement is also a factor. Variations in hardness were more similar to the variations in ΔM than to those in modulus, but imprecision of the hardness measurements precluded more detailed assessments. The slightly higher modulus for RSS CV compared with SMR CV is not associated with a significantly higher tensile strength and it should be noted that the *overall* range and coefficient of variation are only 7% and 2% respectively for both tensile strength and elongation at break.

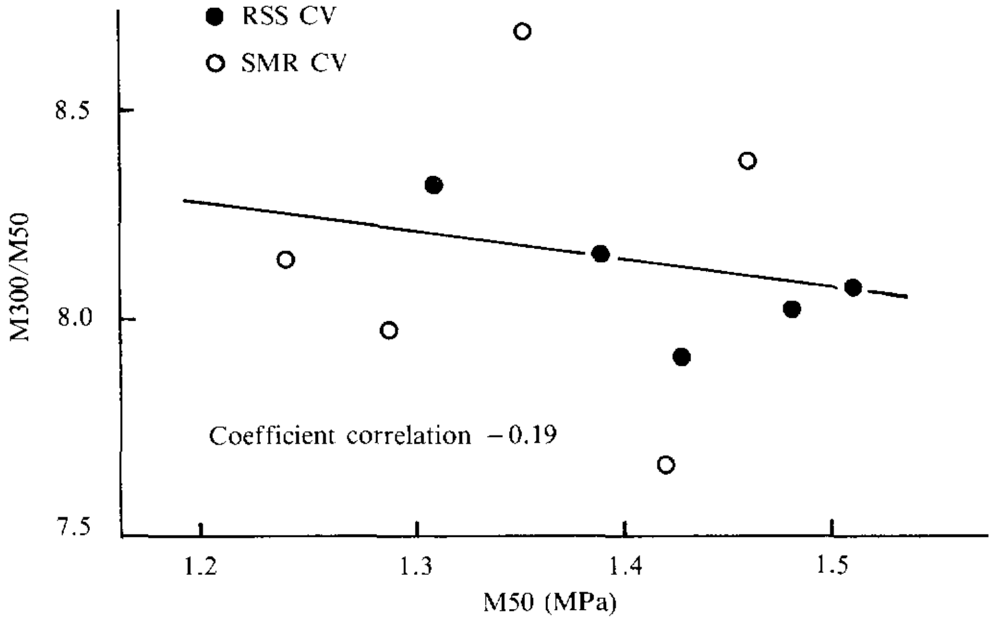

Figure 2. Relation between high- and low-extension modulus of the test vulcanisates.

TABLE 4. UNAGED VULCANISATE PROPERTIES OF TREAD COMPOUNDS[a]

Property	SMR CV RRIM 600	SMR CV RRIM 623	SMR CV RRIM 628	SMR CV RRIM 701	SMR CV PR 261	RSS CV RRIM 600	RSS CV RRIM 623	RSS CV RRIM 628	RSS CV RRIM 701	RSS CV PR 261
Density (mg/m^3)	1.108	1.109	1.112	1.107	1.108	1.110	1.110	1.112	1.108	1.106
Hardness (IRHD)	64	65	65	63	64	68	67	66	65	65
Tensile strength[b] (MPa)	28.6	27.6	29.1	27.4	27.6	28.5	28.6	29.4	28.3	28.9
Elongation at break[b] (%)	575	570	595	585	595	555	570	595	595	570
Modulus at 50% elongation[b], M50 (MPa)	1.46	1.42	1.35	1.29	1.24	1.51	1.48	1.39	1.31	1.43
Modulus at 100% elongation[b], M100 (MPa)	2.50	2.30	2.31	2.17	2.06	2.50	2.47	2.44	2.25	2.35
Modulus at 200% elongation[b], M200 (MPa)	6.52	5.67	6.03	5.40	5.20	6.32	6.26	6.35	5.76	5.87
Modulus at 300% elongation[b], M300[b] (MPa)	12.2	10.9	11.7	10.3	10.1	12.2	11.9	11.9	10.9	11.4
Abrasion loss, DIN method[c] (mm^3)	181	182	176	182	180	179	178	178	176	172
Ring fatigue[d], 0%–100% elongation (kc to failure)										
Median	231	244	266	204	206	253	245	239	—	265
Mode	262	283	270	221	218	328	245	244	—	277
Set at 10 kc (%)	7.2	6.4	6.4	6.8	6.0	5.4	7.3	6.8	7.1	5.9

[a]Cured 20 min/150°C

[b]Mean for 10 dumb-bells

[c]ISO 4649

[d]ISO 6943. Mean for 6 rings

TABLE 5. FURTHER ANALYSIS OF THE DATA OF TABLE 4

Property	RSS CV		SMR CV		Δ(RSS CV — SMR CV)						
	Mean	S.D.	Mean	S.D.	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	Mean	S.D.
Hardness (IRHD)	66.2	1.3	64.2	0.8	+4	+2	+1	+2	+1	+2.0	1.2
Tensile strength (MPa)	28.7	0.4	28.1	0.7	−0.1	+1.0	+0.3	+0.9	+1.3	+0.7	0.6
Elongation at break (%)	577	18	584	11	−20	0	0	+10	−25	−7	15
M50 (MPa)	1.42	0.08	1.35	0.09	+0.05	+0.06	+0.04	+0.02	+0.19	+0.07	0.07
M100 (MPa)	2.40	0.10	2.27	0.17	0	+0.17	+0.13	+0.08	+0.29	+0.13	0.11
M200 (MPa)	6.11	0.28	5.76	0.52	−0.20	+0.59	+0.32	+0.36	+0.67	+0.35	0.34
M300 (MPa)	11.7	0.5	11.0	0.9	0	+1.0	+0.2	+0.6	+1.3	+0.6	0.5
Abrasion loss, DIN method (mm^3)	177	3	180	2	−2	−4	+2	−6	−8	−3.6	3.8
Ring fatigue (0%–100% elongation *(kc to failure)*											
Median	251	11	230	26	+22	+1	−27	—	+59	+14	36
Mode	274	39	251	30	+66	−38	−26	—	+59	+15	55
Set at 10 kc (%)	6.5	0.8	6.6	0.5	−1.8	+0.9	+0.4	+0.3	−0.1	+0.1	1.0

TABLE 6. AGED TENSILE STRESS/STRAIN PROPERTIES FOR TREAD VULCANISATES

Property	SMR CV					RSS CV				
	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261
Vulcanisate properties after ageing 3 days/100°C										
TS, mean (MPa)	17.5	17.9	17.7	16.2	18.5	19.3	18.0	18.0	17.6	18.5
EB, mean (%)	315	355	335	335	345	325	330	320	320	325
M50, mean (MPa)	2.15	1.96	2.02	1.98	1.94	2.37	2.05	2.15	2.09	2.10
M200, mean (MPa)	10.1	9.22	9.70	9.11	9.11	11.2	9.86	10.2	10.0	9.99
Retention of properties after ageing										
TS (%)	61	65	61	59	67	68	63	61	62	64
EB (%)	55	62	56	57	58	59	58	54	54	57
M50 (%)	147	138	150	154	157	157	139	155	159	147
M200 (%)	155	163	161	169	175	178	158	161	174	171

TABLE 7. FURTHER ANALYSIS OF THE DATA OF TABLE 6

Property	RSS CV		SMR CV		Δ(RSS CV — SMR CV)						
	Mean	S.D.	Mean	S.D.	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	Mean	S.D.
Vulcanisate properties after ageing 3 days/100°C											
TS (MPa)	18.3	0.65	17.6	0.85	+1.8	+0.1	+0.3	+1.4	0	+0.7	0.8
EB (%)	324	4	337	15	+10	−25	−15	−15	−20	−13	14
M50 (MPa)	2.15	0.13	2.01	0.08	+0.22	+0.09	+0.13	+0.11	+0.16	+0.14	0.05
M200 (MPa)	10.25	0.54	9.45	0.44	+1.10	+0.64	+0.50	+0.89	+0.88	+0.80	0.23
Retention of properties after ageing											
TS (%)	64	3	63	3	+7	−2	0	+3	−3	—	—
EB (%)	56	2	58	3	+4	−4	−2	−3	−1	—	—
M50 (%)	151	8	149	7	+10	+1	+5	+5	−10	—	—
M200 (%)	168	9	165	8	+23	−5	0	+5	−4	—	—

TABLE 8. DYNAMIC PROPERTIES OF TREAD VULCANISATES

Property	SMR CV RRIM 600	SMR CV RRIM 623	SMR CV RRIM 628	SMR CV RRIM 701	SMR CV PR 261	RSS CV RRIM 600	RSS CV RRIM 623	RSS CV RRIM 628	RSS CV RRIM 701	RSS CV PR 261
Resilience, Dunlop tripsometer (%)	64.0	62.7	64.6	64.3	62.8	63.2	63.9	65.4	63.9	65.3
Goodrich heat build-up										
ISD	0.188	0.176	0.184	0.197	0.183	0.163	0.180	0.166	0.183	0.178
IDD	0.212	0.197	0.204	0.216	0.206	0.191	0.204	0.192	0.204	0.199
ΔT (°C)	77	69	67	67	68	73	69	68	70	65
Set (%)	23.2	19.4	18.3	18.7	18.4	20.0	21.6	17.6	18.1	17.1
Dynamic shear modulus, G (MPa)										
0.35% strain	4.93	4.86	4.61	4.35	4.47	5.13	5.64	5.10	5.41	5.30
0.7% strain	4.38	4.50	4.22	3.88	4.05	4.68	5.05	4.73	4.87	4.64
1.39% strain	3.68	3.69	3.58	3.30	3.41	3.95	4.20	3.92	4.02	3.81
2% strain	3.31	3.33	3.25	3.00	3.11	3.65	3.78	3.50	3.65	3.33
3% strain	2.94	2.97	2.90	2.66	2.77	3.27	3.34	3.11	3.18	2.92
5% strain	2.52	2.55	2.49	2.30	2.38	2.80	2.81	2.66	2.69	2.49
10% strain	2.05	2.05	2.02	1.88	1.94	2.25	2.22	2.09	2.11	2.01
15% strain	1.80	1.79	1.77	1.65	1.70	1.97	1.98	1.86	1.82	1.76
Tan δ										
0.35% strain	0.130	0.121	0.124	0.114	0.137	0.135	0.111	0.124	0.117	0.078
0.7% strain	0.171	0.143	0.158	0.166	0.176	0.172	0.152	0.131	0.150	0.124
1.39% strain	0.209	0.199	0.195	0.205	0.219	0.221	0.195	0.179	0.200	0.172
2% strain	0.226	0.211	0.207	0.219	0.223	0.224	0.206	0.200	0.209	0.196
3% strain	0.230	0.217	0.213	0.229	0.228	0.230	0.213	0.208	0.219	0.209
5% strain	0.226	0.216	0.211	0.226	0.226	0.228	0.216	0.209	0.218	0.210
10% strain	0.201	0.197	0.193	0.202	0.202	0.203	0.197	0.193	0.202	0.192
15% strain	0.181	0.179	0.175	0.181	0.181	0.184	0.182	0.175	0.185	1.173

TABLE 9. FURTHER ANALYSIS OF THE DATA OF TABLE 8

Property	RSS CV		SMR CV		Δ(RSS CV — SMR CV)						
	Mean	S.D.	Mean	S.D.	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	Mean	S.D.
Resilience, Dunlop tripsometer (%)	64.3	1.0	63.7	0.9	−0.8	+1.2	+0.8	−0.4	+2.5	+0.7	1.3
Goodrich heat build-up											
ISD	0.174	0.009	0.186	0.008	−0.025	+0.004	−0.018	0.014	−0.005	−0.012	0.011
IDD	0.198	0.006	0.207	0.007	−0.021	+0.007	−0.012	−0.012	−0.007	−0.009	0.010
ΔT (°C)	69.0	2.9	69.6	4.2	−4	0	+1	+3	−3	0.6	2.9
Set (%)	18.9	1.9	19.6	2.1	−3.2	+2.2	−0.7	−0.6	−1.3	−0.7	1.9
Dynamic shear modulus, G (MPa)											
0.35% strain	5.32	0.22	4.64	0.25	+0.20	+0.78	+0.49	+1.06	+0.83	+0.67	0.33
0.7% strain	4.79	0.17	4.21	0.25	+0.30	+0.55	+0.51	+0.99	+0.59	+0.59	0.25
1.39% strain	3.98	0.14	3.53	0.17	+0.27	+0.51	+0.34	+0.72	+0.40	+0.45	0.18
2% strain	3.58	0.17	3.20	0.14	+0.34	+0.45	+0.25	+0.63	+0.22	+0.38	0.17
3% strain	3.16	0.16	2.85	0.13	+0.33	+0.37	+0.21	+0.52	+0.15	+0.32	0.14
5% strain	2.69	0.13	2.45	0.10	+0.28	+0.26	+0.17	+0.39	+0.11	+0.24	0.11
10% strain	2.14	0.10	1.99	0.08	+0.20	+0.17	+0.07	+0.23	+0.07	+0.15	0.07
15% strain	1.88	0.10	1.74	0.06	+0.17	+0.19	+0.09	+0.17	+0.06	+0.14	0.06
tan δ											
0.35% strain	0.113	0.022	0.125	0.009	+0.005	−0.010	0	+0.003	−0.059	−0.012	0.027
0.7% strain	0.146	0.019	0.163	0.013	+0.001	+0.009	−0.027	−0.016	−0.052	−0.017	0.024
1.39% strain	0.193	0.019	0.205	0.009	+0.012	−0.004	−0.016	−0.005	−0.047	−0.012	0.022
2% strain	0.207	0.011	0.217	0.008	−0.002	−0.005	0.007	0.010	−0.027	−0.010	0.010
3% strain	0.216	0.009	0.223	0.008	0	−0.004	−0.005	−0.010	−0.019	−0.008	0.007
5% strain	0.216	0.008	0.221	0.007	+0.002	0	0.002	−0.008	−0.016	−0.005	0.007
10% strain	0.197	0.005	0.199	0.004	+0.002	0	0	0	−0.010	−0.002	0.005
15% strain	0.180	0.005	0.179	0.003	+0.003	+0.003	0	+0.004	−0.008	0	0.005

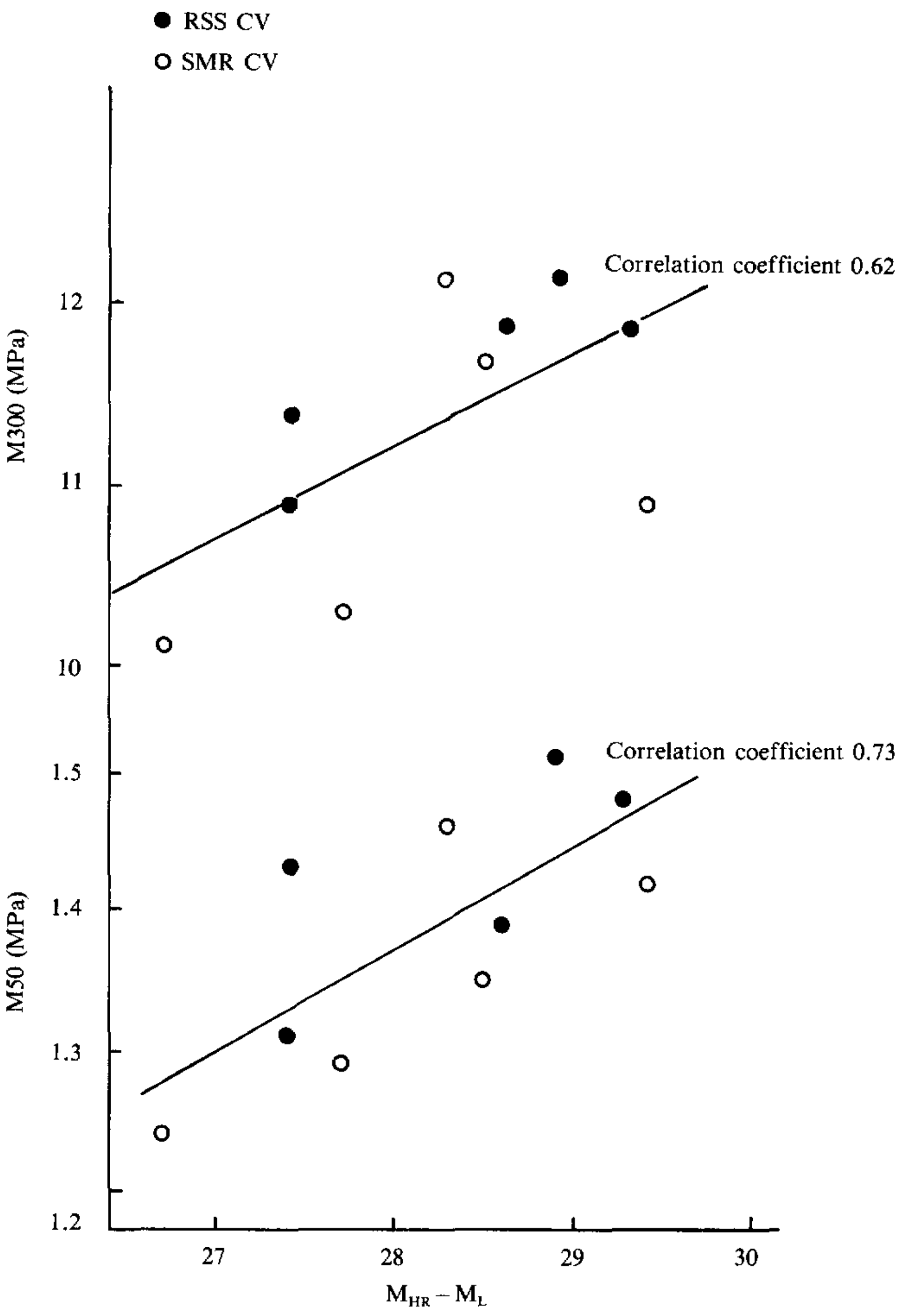

Figure 3. Correlation between vulcanisate modulus and rheometer torque rise.

Data for the strength-related properties, abrasion and fatigue resistance, are also given in *Tables 4* and *5*. In neither case is there evidence for a significant difference between the sheet and crumb materials when considered overall. However, comparison of the data for the individual monoclonal materials suggests very marginal advantages for RSS CV in both abrasion and fatigue resistance. The substantiation of such differences would require a much more extensive study. Aged tensile stress-strain data for one relatively severe ageing condition are given in *Tables 6* and *7*. In broad terms, the differences evident in the unaged properties are present to much the same extent after ageing. Sheet and crumb materials show similar retentions of modulus, tensile strength and elongation at break.

Tables 8 and *9* record 'dynamic properties', comprising rebound resilience, heat build-up behaviour and dynamic shear modulus and loss angle. No significant differences are apparent between sheet and crumb materials for rebound resilience and heat build-up. The results for heat build-up are of interest due to the slightly lower stiffness of an SMR CV vulcanisate, which would have been expected to cause a reduction in the generation of heat[6] during the constant deformation cycle of the Goodrich flexometer test.

At a given temperature, the dynamic properties of a vulcanisate are dependent on both frequency and strain level. Neither of these is overtly specified in a simple rebound resilience test. For the Dunlop tripsometer, a modest

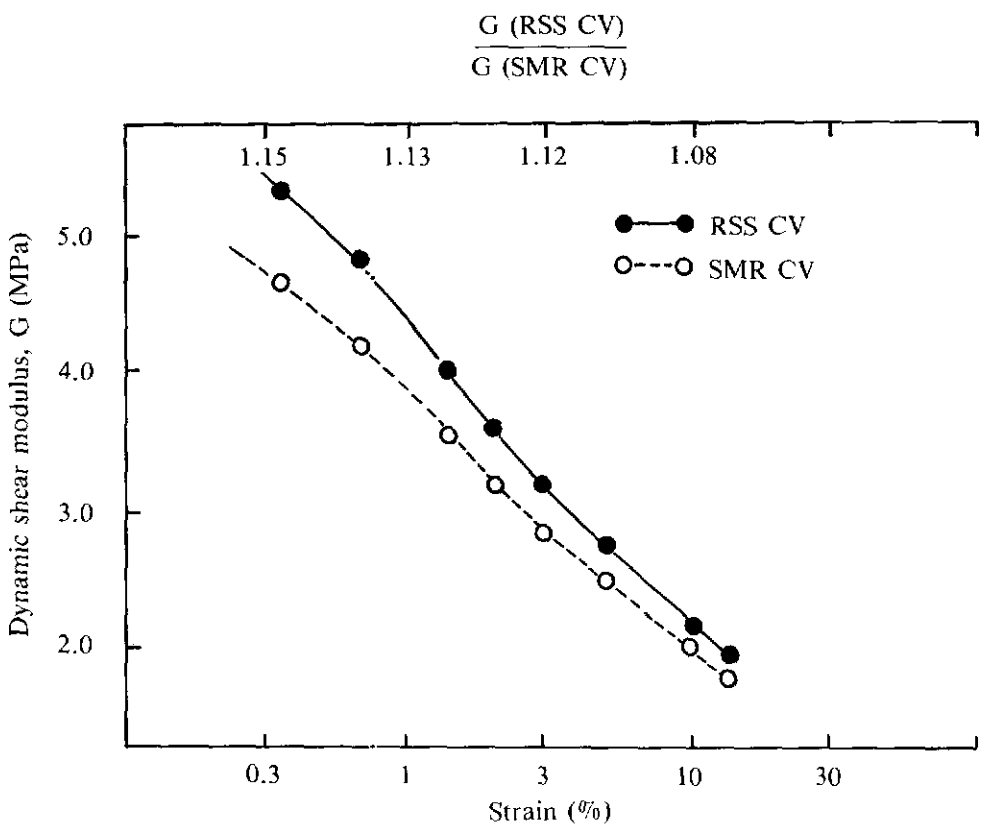

Figure 4. Dynamic modulus as a function of shear strain.

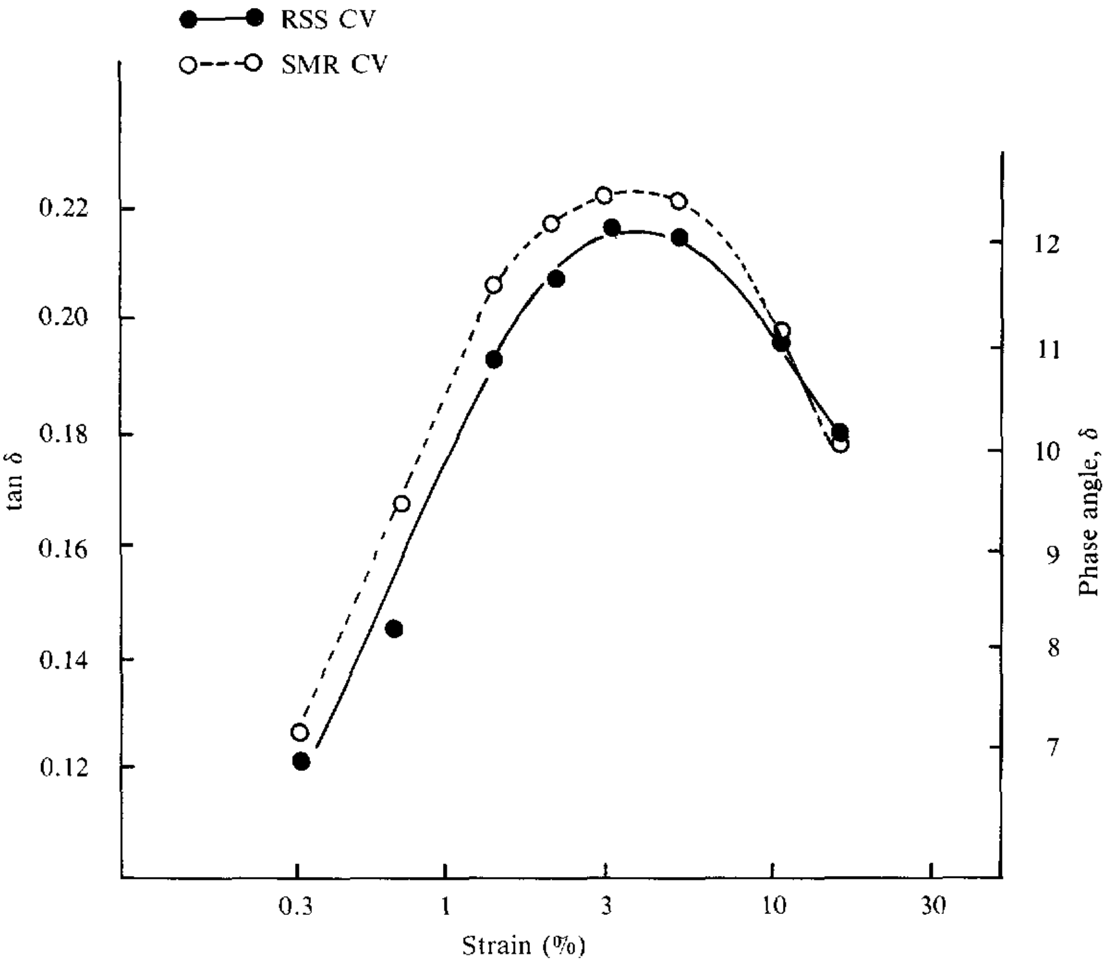

Figure 5. Loss angle as a function of shear strain.

frequency of *ca.* 5 Hz has been suggested[7], while even for relatively stiff black-filled vulcanisates the average strain will be quite high, probably more nearly 10% than 1%. Frequency is specified for the Goodrich flexometer, but the test is in essence a fatigue, *i.e.* a non-equilibrium test, rather than a definitive measure of dynamic behaviour. The latter is however provided by the dynamic shear modulus, *G* and damping, tan δ data of *Tables 8* and *9*. These parameters do differentiate between sheet and crumb materials, both considered individually and as the grade means which are plotted in *Figures 4* and *5*.

The dynamic shear modulus for the sheet rubbers is greater than for the crumb rubbers, an observation which is consistent with the other estimates of stiffness noted previously. As expected, modulus falls with increasing strain, but while the absolute difference between sheet and crumb decreases, the ratio remains nearly constant. Damping also follows the usual pattern with a maximum at moderate strain, in this case 3%–4%. At low strain, the crumb materials display greater damping than the sheet rubbers, but after the maximum, the difference decreases to zero at *ca.* 10%. It should be noted that this approximates to the

TABLE 10. PROPERTIES OF GUM MIXES

Property	SMR CV RRIM 600	SMR CV RRIM 623	SMR CV RRIM 628	SMR CV RRIM 701	SMR CV PR 261	RSS CV RRIM 600	RSS CV RRIM 623	RSS CV RRIM 628	RSS CV RRIM 701	RSS CV PR 261
Mooney viscometer										
V_R[a]	52.5	56.5	84	52	67.5	57	62	87	56	72.5
V_R[b], 100°C	22	25	36	22	33	21	29	41	22	36
Scorch time, t_5, 120° (min)	23.3	21.0	20.3	25.6	24.9	22.3	22.3	23.2	23.4	23.3
Monsanto rheometer, 150°C, 1° arc										
$M_{HR} - M_L$ (torque units)	16.4	17.9	16.6	15.7	15.4	17.5	17.5	15.5	16.7	16.2
Scorch time, t_{s1} (min)	4.7	5.8	5.7	6.4	6.2	5.4	5.6	5.5	5.7	6.0
Cure time, t_c' (90) (min)	13.0	13.7	14.4	14.4	14.7	12.0	13.1	14.5	13.3	13.8
Cure time, t_c' (95) (min)	14.8	15.4	16.3	16.1	16.5	13.5	14.8	16.5	15.0	15.6
Vulcanisate properties										
Tensile modulus[c] (MPa)										
M20	0.275	0.32	0.32	0.26	0.30	0.325	0.315	0.305	0.255	0.275
M50	0.515	0.57	0.585	0.485	0.515	0.58	0.56	0.545	0.47	0.535
M100	0.775	0.865	0.885	0.735	0.78	0.87	0.825	0.805	0.71	0.815
M200	1.265	1.41	1.475	1.215	1.245	1.425	1.365	1.31	1.20	1.335
M300	1.95	2.11	2.23	1.83	1.825	2.23	2.125	1.965	1.76	2.025
Mean	0.96	1.06	1.10	0.91	0.93	1.09	1.04	0.99	0.88	1.00
Compression modulus[d] (MPa)										
M5	0.197	0.211	0.211	0.186	0.191	0.211	0.225	0.199	0.199	0.211
M10	0.420	0.450	0.458	0.401	0.412	0.454	0.487	0.424	0.420	0.450
M15	0.671	0.716	0.728	0.641	0.655	0.722	0.768	0.675	0.667	0.720
M20	0.943	1.018	1.038	0.904	0.939	1.026	1.081	0.963	0.939	1.018
Mean	0.558	0.599	0.609	0.533	0.549	0.603	0.640	0.565	0.556	0.600

[a]Mooney viscosity of raw rubber
[b]Mooney viscosity of gum mix
[c]Mean for 15, 20 min/150°C
[d]Obtained on Goodrich heat build-up test piece, cured 20 min/150°C; stress for 5%–20% compression

TABLE 11. FURTHER ANALYSIS OF THE DATA OF TABLE 10

Property	RSS CV		SMR CV		Δ(RSS CV — SMR CV)						
	Mean	S.D.	Mean	S.D.	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	Mean	S.D.
Mix properties											
Mooney viscometer											
V_c, 100°C	29.8	8.7	27.6	6.5	−1	+4	+5	0	+3	+2.2	2.6
Scorch time, t_5, 120°C (min)	22.9	0.6	23.0	2.3	−1.0	+1.3	+2.9	−2.2	−1.6	−0.1	2.1
Monsanto rheometer, 150°C, 1° arc											
$M_{HR}-M_L$ (torque units)	16.7	0.9	16.4	1.0	+1.1	−0.4	−1.1	+1.0	+0.8	+0.3	1.0
Scorch time, t_{s1} (min)	5.6	0.2	5.8	0.7	+0.7	−0.2	−0.2	−0.7	−0.2	−0.1	0.5
Cure time, t_c' (90) (min)	13.3	0.9	14.0	0.7	−1.0	−0.6	+0.1	−1.1	−0.9	−0.7	0.5
Cure time, t_c' (95) (min)	15.1	1.1	15.8	0.7	−1.3	−0.6	+0.2	−1.1	−0.9	−0.7	0.6
Vulcanisate properties											
Tensile modulus (MPa)											
M20	0.295	0.029	0.295	0.027	+0.050	−0.005	−0.015	−0.005	−0.025	0.000	0.029
M50	0.538	0.042	0.534	0.042	+0.065	−0.01	−0.04	−0.015	+0.02	+0.004	0.040
M100	0.805	0.059	0.808	0.064	+0.095	−0.04	−0.08	−0.025	+0.035	−0.003	0.069
M200	1.327	0.083	1.322	0.114	+0.16	−0.045	−0.165	−0.015	+0.09	+0.005	0.126
M300	2.021	0.177	1.989	0.178	+0.28	+0.015	−0.265	−0.07	+0.2	+0.032	0.217
Compression modulus (MPa)											
M5	0.209	0.011	0.199	0.011	+0.014	+0.014	−0.012	+0.013	+0.020	+0.010	0.012
M10	0.447	0.027	0.428	0.025	+0.034	+0.037	−0.034	+0.019	+0.038	+0.019	0.030
M15	0.710	0.041	0.682	0.038	+0.051	+0.052	−0.053	+0.026	+0.065	+0.028	0.048
M20	1.005	0.056	0.968	0.057	+0.083	+0.063	−0.075	+0.035	+0.079	+0.037	0.065

TABLE 12. VARIOUS MEASURES OF VULCANISATE STIFFNESS FOR GUM STOCKS[a]

Property	SMR CV					RSS CV					Mean	
	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	SMR CV	RSS CV
Mix properties												
Monsanto rheometer, 150°C, 1° arc												
$M_{HR} - M_L$ (torque units)	99	108	100	95	93	106	106	94	101	98	99.0	101.0
Vulcanisate properties												
Tensile modulus (MPa)												
M50	96	106	109	90	96	108	104	102	88	100	99.4	100.4
M100	96	107	110	91	97	108	102	100	88	101	100.2	99.8
M300	96	106	111	92	94	108	103	99	91	101	99.8	100.4
Compression modulus (MPa)												
M5	97	103	103	91	94	103	110	98	98	103	97.6	102.4
M10	96	103	105	92	94	104	110	97	96	103	98.0	102.0
M20	96	103	105	92	95	104	110	98	95	103	98.2	102.0

[a]Normalised such that overall mean = 100

TABLE 13. VARIOUS MEASURES OF VULCANISATE STIFFNESS FOR TREAD STOCKS[a]

Property	SMR CV					RSS CV					Mean		Range		Range (%)
	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	SMR CV	RSS CV	SMR CV	RSS CV	All
Mix properties															
Monsanto rheometer, 160°C, 1° arc															
$M_{HR} - M_L$ (torque units)	100	104	101	98	95	102	104	101	97	97	99.6	100.4	95–104	97–104	9
Vulcanisate properties															
Hardness (IRHD)	98	100	100	99	98	104	103	101	100	100	98.5	101.5	97–100	100–104	7
M50 (MPa)	105	102	97	93	89	109	107	100	94	103	97.5	102.5	89–105	94–109	20
M100 (MPa)	107	99	99	93	88	107	106	104	96	101	97.2	102.8	88–107	96–107	19
M300 (MPa)	107	96	103	91	89	107	105	105	96	100	96.9	103.1	89–107	96–107	18
Goodrich IDD^{-1}	95	103	99	94	98	106	99	105	99	102	97.5	102.5	94–103	99–106	12
Dynamic shear modulus, G (MPa)															
0.7% strain	97	100	94	86	90	104	112	105	108	103	93.6	106.4	86–100	103–112	26
2% strain	98	98	96	89	92	108	112	103	107	98	94.4	105.6	89–98	98–112	23
10% strain	102	99	97	102	102	103	99	97	102	97	99.5	100.5	97–102	97–103	6

[a]Normalised such that overall mean = 100

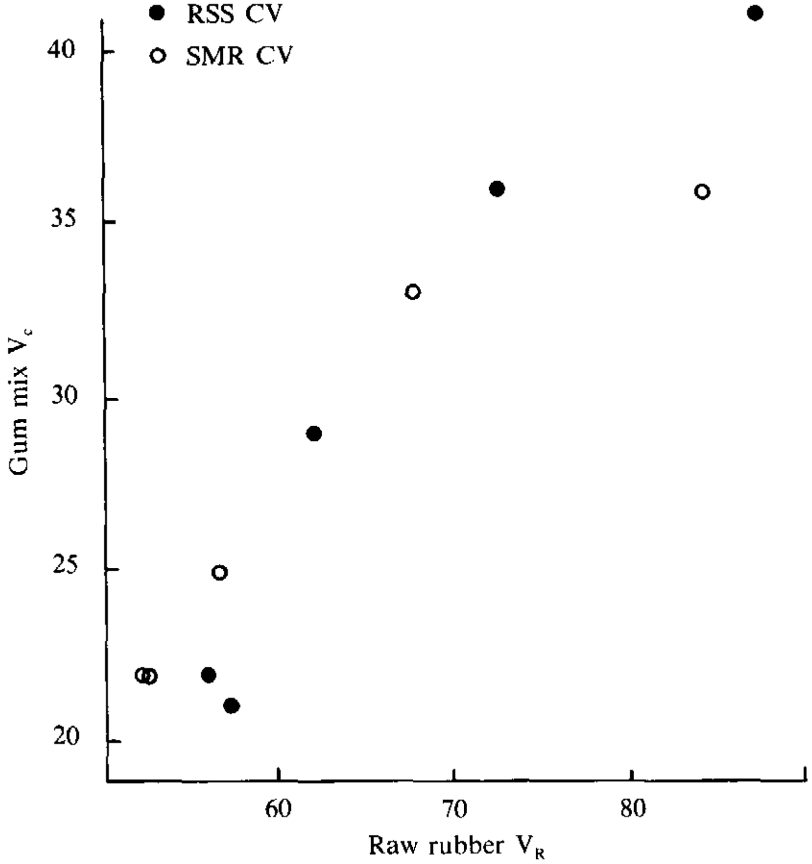

Figure 6. Correlation between viscosities of gum mix and raw rubber.

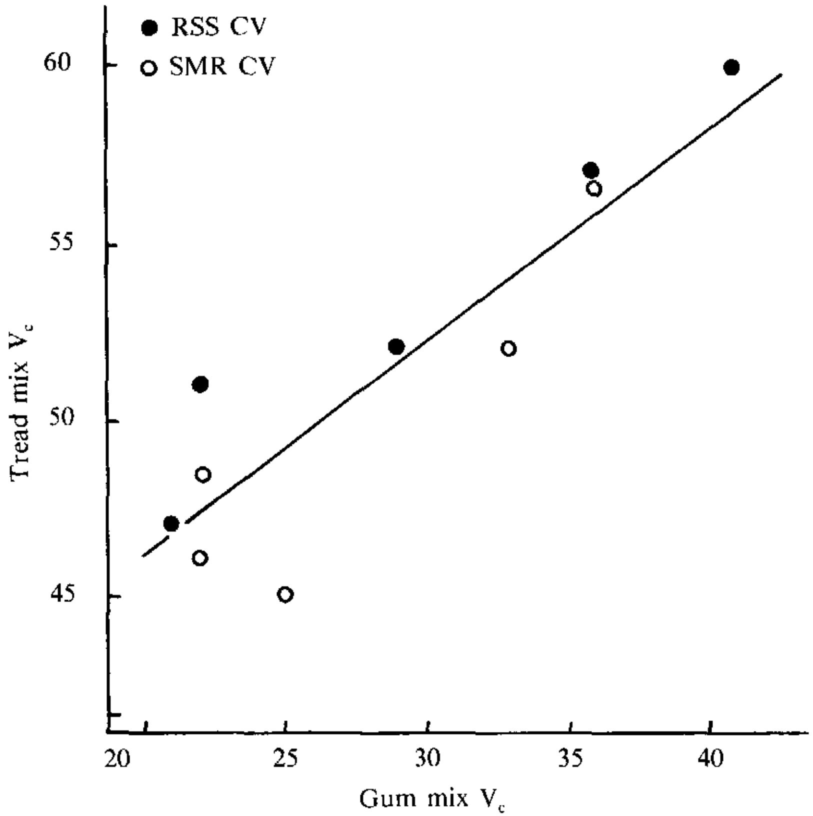

Figure 7. Correlation between viscosities of tread and gum mixes.

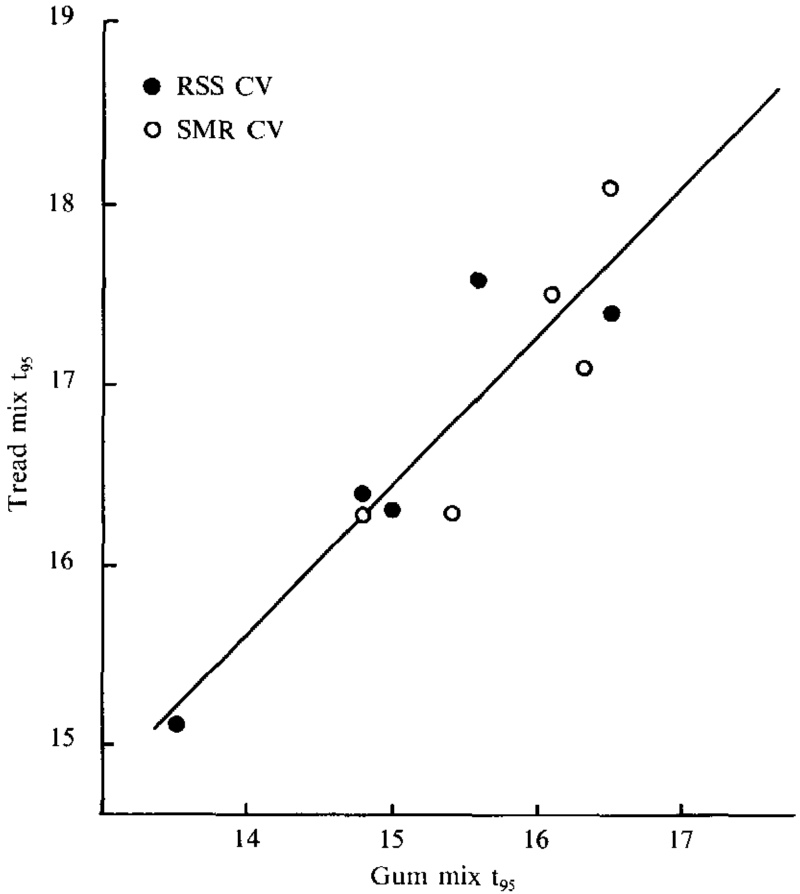

Figure 8. Correlation between Rheometer t'_c (95) values for tread and gum mixes.

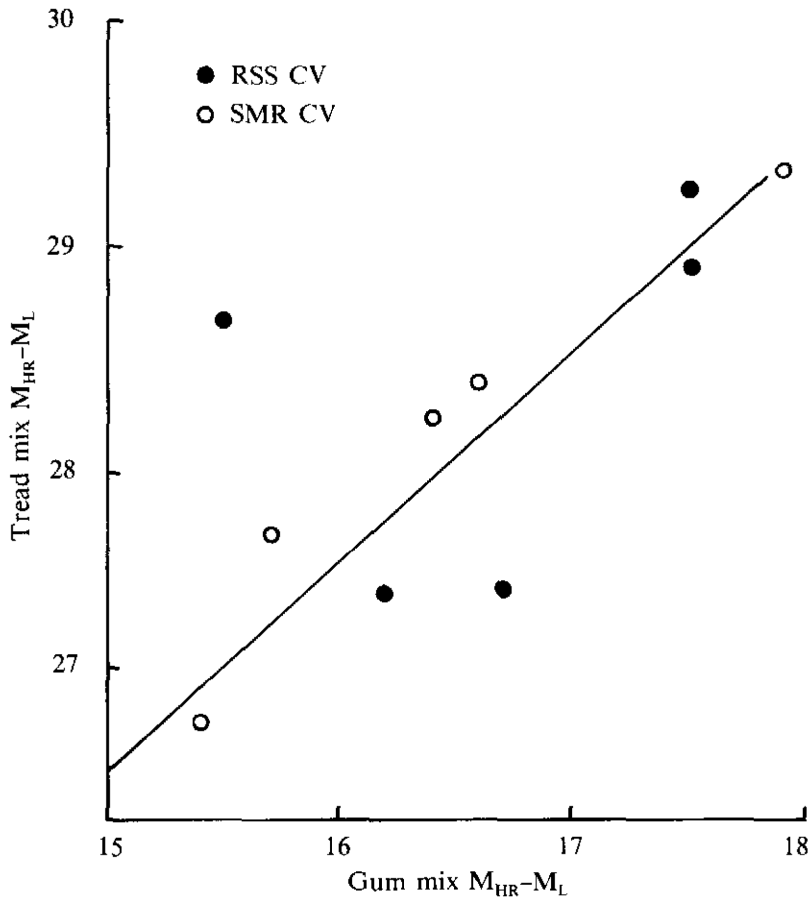

Figure 9. Correlation between torque rise values for tread and gum mixes.

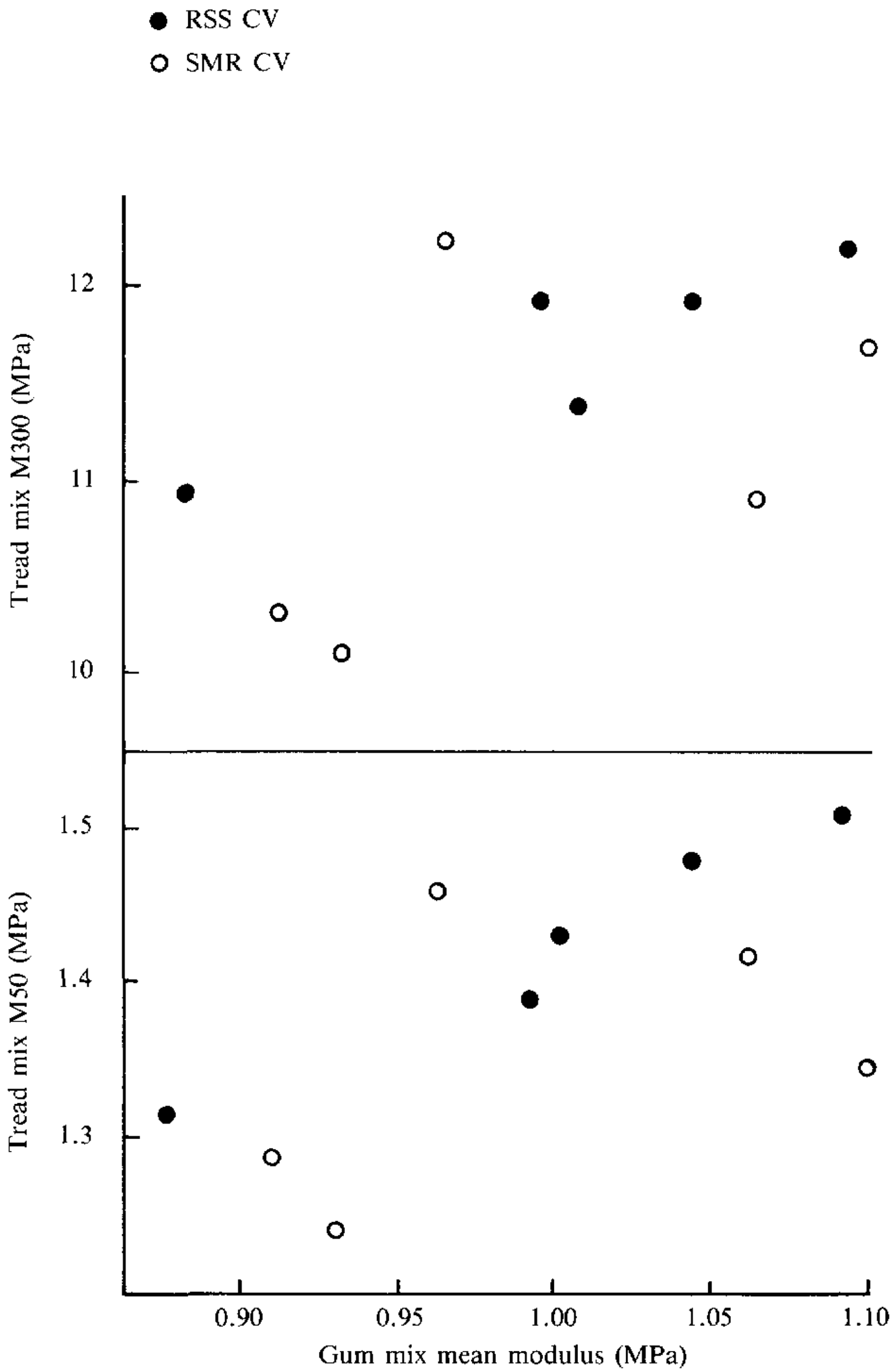

Figure 10. Correlation between M300 and M50 for tread mix and tensile modulus of gum mix.

TABLE 14. CORRELATION BETWEEN PARAMETERS FOR GUM AND TREAD MIXES

Correlation between x	and y	Correlation coefficient	Probability	Coefficient of variation (%) x	y
Gum V_c	Raw rubber V_r	0.95	> 99.9	25.6	19.7
Tread V_c	Gum V_c	0.90	> 99.9	9.5	25.6
Tread t_c' (95)	Gum t_c' (95)	0.91	> 99.9	5.2	6.2
Tread $M_{HR} - M_L$	Gum $M_{HR} - M_L$[a]	0.89	∿99.8	3.3	5.1
Tread M50	Gum mean modulus	0.63	< 95	6.4	7.6
Tread M300	Gum mean modulus	0.59	∿90	6.7	7.6
Tread M50	*Gum compression modulus*	*0.73*	∿97	*6.4*	*5.7*
Tread M300	Gum compression modulus	0.60	∿90	6.7	5.7

[a]RSS CV (RRIM 628) omitted

conditions of frequency and strain for which parity between sheet and crumb is evident in the Dunlop rebound resilience test.

Test data for the study of the gum systems of the formulation shown in *Table 2* are given in *Table 10* and further analysed in *Table 11*. Vulcanisate stiffness is again slightly greater for the sheet materials, but the difference is smaller than for black-filled vulcanisates. This is most clearly shown by the comparison of the normalised data of *Table 12* with the analogous *Table 13* for the tread materials.

More general comparisons between the gum and black-filled materials, without reference to the sheet or crumb nature of the raw rubber, are made in *Figures 6–11* and *Table 14*. Good correlations between the gum and black-filled systems are evident for the viscosity changes during mixing and in the rate and state of cure at 150°C, where the influence of black reinforcement is minimal. However, only very poor correlations exist between the vulcanisate moduli at room temperature.

CONCLUSIONS

The major difference between black-filled vulcanisates derived from sheet and crumb CV rubbers is the greater stiffness or modulus of RSS CV. This is apparent in both extension and compression and under static and dynamic conditions. Analogous differences are not however evident in rheometer torque measurements at curing temperature. Such differences are also not apparent in gum vulcanisates. It seems likely therefore that greater black reinforcement rather than increased crosslinking is achieved with sheet materials. However, it should be noted that while vulcanisates from sheet rubbers show an overall greater stiffness, very comparable differences are apparent *between* the various monoclonal samples of both sheet and crumb rubbers. Little or no enhancement is found for RSS vulcanisates in terms of tensile strength or other strength-related properties such as fatigue and abrasion resistance, consistent with the domination of these properties by strain-induced crystallisation.

Parity between sheet and crumb materials is also found for rebound resilience using the Dunlop tripsometer and for heat build-up in the Goodrich flexometer. Both of these tests are characterised by moderate strain amplitudes. The crumb rubbers show rather higher viscous modulus (higher tan δ) in tests for dynamic shear modulus at amplitudes below 5%. Sheet and crumb CV rubbers show comparable retention of tensile strength and modulus after air-oven ageing at 100°C.

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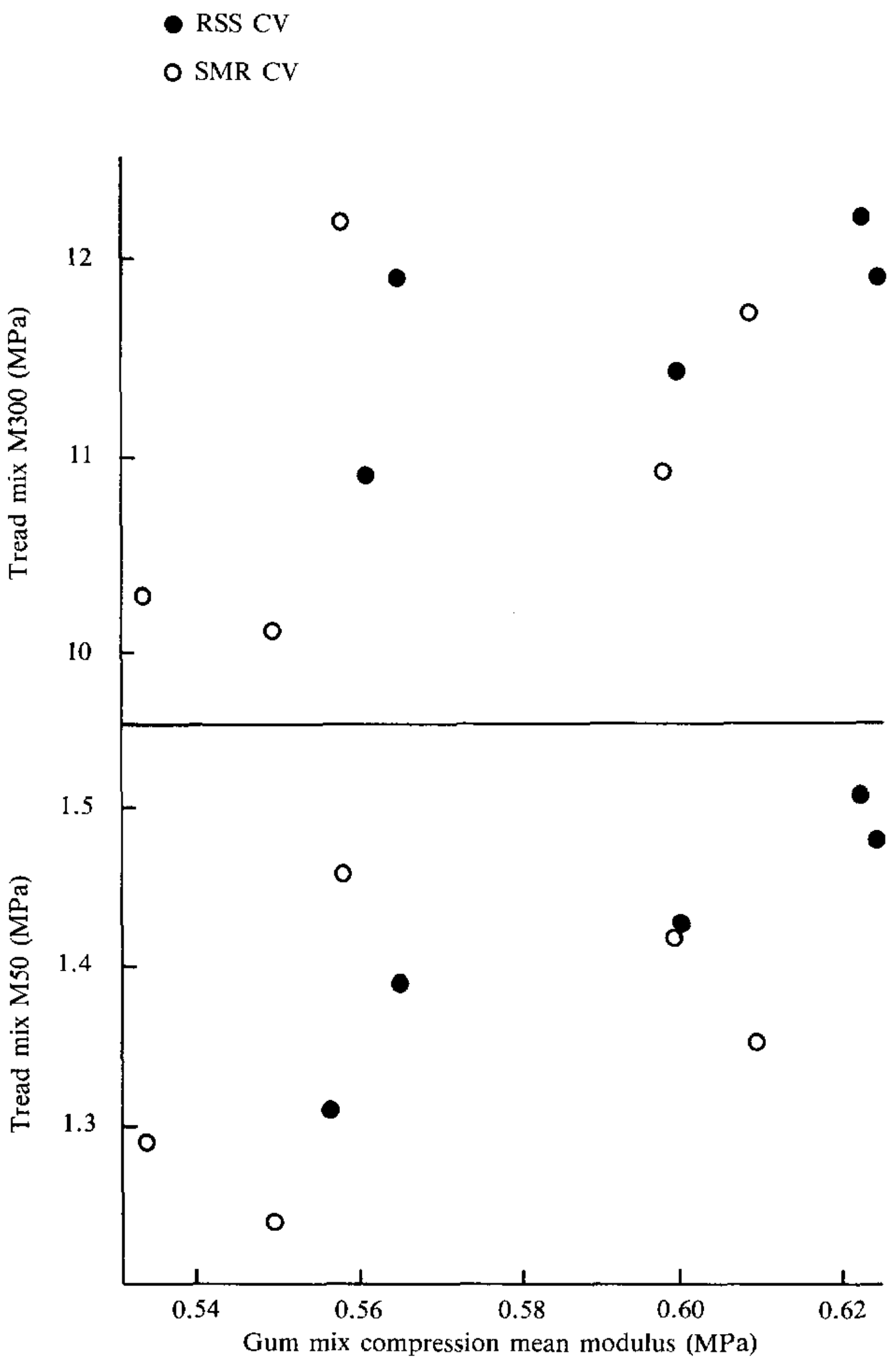

Figure 11. Correlation between M300 and M50 for tread mix and compression stiffness of gum mix.

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