

## ***A New Comparison of Sheet and Crumb Rubber. Part I. Raw Rubber Composition and Rheology***

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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. Standard SMR tests on these rubbers showed small but consistent differences between the sheet and crumb materials. However, with the exception of cure rate, these were considered to be insufficient to be reflected as differences in technical quality between RSS and crumb rubber. In a range of Mooney and capillary flow tests, similar rheological behaviour for sheet and crumb rubbers was observed.*

The advantages of rubber supplied under the Standard Malaysian Rubber (SMR) Scheme in terms of presentation and packaging have been universally acknowledged ever since its inception in 1965. A limited number of consumers have, however, maintained that the technical quality of conventional sheet grades of NR is consistently superior to the new process-crumb rubbers, as evinced in service performance. New process-crumb rubbers now comprise over 99% of SMR production.

In some cases, the comparisons have been inappropriate. For example, RSS 3, which is prepared by the acid coagulation of latex, has been compared with SMR 20, which stems from so-called field coagula such as cup lump. The approximate parity in price of these two grades, which was a feature of the early days of the Scheme, undoubtedly served to promote such technically fallacious comparisons.

Several attempts, both published<sup>1</sup> and unpublished<sup>2,3,4</sup>, have been made to check the veracity of these claims in laboratory tests on comparable materials, notably RSS 1 and SMR L. All such comparisons have, however, been less than ideally based. Either standard commercial materials have been used, in which case it is difficult to ensure that the inevitably limited number of samples tested is truly representative of the grade; or samples of RSS 1

and SMR L produced from a single sample of latex have been tested, a procedure which clearly invites the criticism that the results only relate to specially prepared materials.

However, while these comparisons can be criticised on various grounds, there seems little doubt that, on a laboratory scale at least, differences in vulcanisate properties between latex processed into sheet as RSS 1, or crumb as SMR L, are very small. Differences in mixing and curing behaviour and other aspects of processability are possibly more significant and, more importantly, could favour either grade depending on the processing regime used. A further consideration is that relatively small differences noted in laboratory-scale trials might be manifested to a much greater extent in manufacturing operations or service performance.

The production procedures for RSS 1 and SMR L are undoubtedly different. For RSS 1, the latex is diluted to ca. 10%-15% d.r.c. and acid-coagulated at pH 4.5-5; after washing, the sheeted coagulum is dried in smoke/air for several days at 40°C-75°C. For crumb SMR L, the latex is coagulated at near field d.r.c. (ca. 30%) and at a somewhat higher pH than for sheet; after washing and crumbling/comminuting the granulated coagulum is dried in air for only a few hours at ca. 110°C. Overall, sheet

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rubber is a tougher, more elastic material than SMR L. This is reflected in the general practice whereby sheet is masticated or peptised prior to mixing, while SMR L is often used without premastication.

Further comparative data are presented here for sheet and crumb rubbers prepared by the established production techniques from each of five samples of monoclonal latex. An important additional feature to earlier exercises of this type was the viscosity-stabilisation of the latices by the addition of hydroxylamine neutral sulphate (HNS) before coagulation and further processing. The rubbers tested were therefore samples of SMR CV and 'RSS CV'. The monoclonal latices were selected to ensure a wide range in stabilised viscosity of the final rubber samples. Preparation of these materials was kindly undertaken by the Rubber Research Institute of Malaysia. Details of the procedures used are given in *Table 1*.

In the routine production of SMR CV, 0.15% HNS is used, since this has been found to give adequate viscosity stabilisation. Because of the greater dilution of the latex used in the preparation of RSS CV, a somewhat greater concentration of HNS was necessary and, to ensure consistency, this higher level was used for both RSS CV and SMR CV. These materials are hereafter referred to as 'sheet' and 'crumb' respectively.

The large amount of data obtained for these ten samples of rubber is to be considered under the following categories:

- Raw rubber analysis and rheology
- Processability and curing behaviour
- Vulcanisate properties.

The second and third items will be covered in subsequent papers.

#### EXPERIMENTAL

All tests were performed on rubbers blended on a two-roll mill using the procedure specified for SMR<sup>5</sup>. The SMR parameters: nitrogen content, Plasticity Retention Index (PRI), *etc.*, were determined according to the specific methods. Gel content was determined after immersion in petroleum spirit (distilled and collected at 100°C–120°C) for six days at room temperature. Viscosity testing using the Mooney viscometer included not only measurement of the standard parameter, ML1 + 4 at 100°C, but also the measurements of initial peak torque and relaxation behaviour described previously<sup>6</sup>.

Capillary flow measurements at 100°C were made on most but not all of the samples using an Instron 3211 rheometer. Two capillaries were used, both having diameters (D) of 1.27 mm and lengths (L) of 6.36 mm and

TABLE 1. PREPARATIVE PROCEDURES FOR CRUMB SMR CV AND RSS CV

Item	Preparative procedure for	
	SMR CV	RSS CV
Latex <sup>a</sup> d.r.c. (%)	30	12.5
Additives prior to coagulation	0.4% sodium metabisulphite 0.25% hydroxylamine neutral sulphate	
pH of coagulation <sup>b</sup>	4.8 – 5.0	4.5 – 4.7
Drying	3 h at 100°C	Smokehouse at 40°C–55°C for 4 days followed by air tunnel at 75°C for 4 days

<sup>a</sup>Latex from the following clones was used: RRIM 600, RRIM 623, RRIM 628, RRIM 701, and PR 261.

<sup>b</sup>Using 3% formic acid

50.8 mm respectively. Measured values of total shear stress,  $\tau$ , corrected for end effects by the procedure originally proposed by Bagley<sup>7</sup> were used to calculate the true wall shear stress,  $\tau_w$ :

$$\tau_w = \tau \left[ 1 + \frac{4D}{L} e \right]$$

where the dimensionless parameter,  $e$ , is the total end correction. Shear rates,  $\gamma$ , were calculated from the volume efflux rates but corrections for non-Newtonian flow were not applied. The empirical power-law expression,

$$\tau_w = k\gamma^n$$

was used to relate shear stress and rate where  $n$  is the flow index.

The extrudates were relatively smooth, enabling — at least at the lower shear rates — apparently reliable estimates of area swell to be made by simple measurements of weight and length. These were carried out after relaxing the sample at room temperature.

## RESULTS AND DISCUSSION

Test data are presented not only 'as measured' but also, since the aim of the study was a comparison of sheet and crumb, as mean values for the five samples of each grade, where such a comparison is appropriate. Elsewhere the data are presented as values of  $\Delta$  (RSS – SMR) for the five different clones, together with means and standard deviations for these values.

Data for the SMR specification parameters and certain other qualities are given in *Table 2*, with a further analysis in *Table 3*. Simple inspection of the data, without recourse to detailed statistical analysis, suggests several respects in which sheet and crumb rubbers differ. These can be summarised as follows:

Parameter	RSS CV compared to SMR CV
Viscosity	Slightly higher
PRI	Slightly lower
Nitrogen content	Slightly higher
Gel content	Higher
Cure rate (ACS 1)	Higher

Apart from cure response with the ACS 1 system, it seems highly unlikely that such differences would significantly influence the relative technical performance of sheet and crumb rubbers. Despite the use of a relatively high level of HNS, the values of ASHT  $\Delta P_0$  suggest a lesser degree of viscosity stabilisation with the RSS materials, though this is not always reflected in greater levels of residual HNS, as might have been expected. The small viscosity changes observed in normal storage over a limited period of time (not reported here) are consistent with the ASHT values.

Mooney viscosity data are given in *Table 4* and further analysed in *Table 5*. As anticipated, the slightly higher value of ML5 + 4 of RSS CV produced from a given clone is associated with a rather higher value of  $ML_{max}$ . Furthermore, as noted elsewhere<sup>8</sup>, the ratio  $ML_{max}/ML5 + 4$ , or difference ( $ML_{max} - ML5 + 4$ ), increases as the test temperature is reduced from 110°C to 80°C. However, as shown in *Figure 1*, there is no evidence for an overall discrimination between sheet and crumb rubbers in these respects; both materials conform to a single regression line at a given temperature.

As in the previous study<sup>6</sup>, relaxation of stress following 'instantaneous' arrest of rotor motion was quantified either as  $a$  in,

$$\text{Torque} = kt^{-a}$$

or by,

$$D_1 = ML5 + 4 - (\text{torque after 20s relaxation})$$

$$D_2 = ML5 + 4 - (\text{torque after 90s relaxation})$$

Relaxation rate has a marked dependence on the initial stress, as shown by the plot of  $a$  vs ML5 + 4 (*Figure 2*). Within the precision of the data, which as has been noted previously<sup>6</sup> is not very high, there is no suggestion that sheet and crumb rubbers have inherently different relaxation rates. An apparently more precise measure of relaxation is furnished by the parameters  $D_1$  and  $D_2$ , but here too discrimination between sheet and crumb materials was not observed (*Figure 3*). The different

TABLE 2. RAW RUBBER ANALYSIS AND SMR PROPERTIES

Tests on 'SMR blend'	SMR CV					RSS CV				
	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261
Nitrogen (%)	0.49	0.43	0.54	0.45	0.43	0.56	0.46	0.56	0.46	0.47
Ash (%)	0.14	0.16	0.18	0.16	0.18	0.20	0.16	0.27	0.21	0.16
Dirt (%)	0.028	0.023	0.029	0.029	0.031	0.012	0.010	0.019	0.020	0.009
P <sub>0</sub> (mean of 6)	27.7	31.0	52.1	27.8	37.8	31.6	35.5	53.6	30.5	41.3
PR1	91	90	81	83	88	89	81	75	78	85
ML1 + 4 at 100°C	52.5	56.5	84	52	67.5	57	62	87	56	72.5
ASHT $\Delta P_0$	+3	+2	+4.5	+2	+4	+6	+6.5	+5	+3	+6.5
Hydroxylamine (p.p.m.)	135	95	100	130	115	95	111	71	135	115
Gel <sup>a</sup> wt (%)	10.0	2.4	16.9	Nil	12.7	19.2	15.6	17.6	10.6	18.8
Swelling, w/w	28	—	24	—	34	26	30	29	30	31
ACS 1 cure system, 160°C										
Scorch time, t <sub>2</sub> (min)	2.8	2.3	2.5	2.1	2.8	1.7	1.9	1.8	2.2	2.2
Cure time, t' <sub>c</sub> (90) (min)	13.3	11.3	12.8	11.6	13.0	9.5	9.6	9.2	10.1	10.9
M <sub>HR</sub> -M <sub>L</sub> (torque units <sup>b</sup> )	27.5	30.7	28.0	26.7	28.1	30.6	33.2	32.7	30.4	30.2
ACS 1 cure system, 140°C										
MR100 <sup>c</sup> (MPa)	0.440	0.503	0.460	0.422	0.457	0.540	0.548	0.598	0.514	0.517
MOD (kg/cm <sup>2</sup> )	4.82	5.45	4.95	4.78	4.90	5.93	5.91	6.22	5.54	5.43

<sup>a</sup>In 100°C-120°C petroleum spirit<sup>b</sup>1 torque unit = 0.11Nm<sup>c</sup>Relaxed modulus at 100% extension, 40 min at 140°C. BS 1673:4

TABLE 3. ANALYSIS OF THE DATA OF TABLE 2

Test	RSS CV		SMR CV		$\Delta$ (RSS CV - SMR CV)					Mean	SD
	Mean	SD	Mean	SD	RRIM 600	RRIM 623	RRIM 628	RRIM 700	PR 261		
Nitrogen (%)	0.50	0.05	0.47	0.05	+0.07	+0.03	+0.02	+0.01	+0.04	+0.03	0.02
Ash (%)	0.20	0.05	0.16	0.02	+0.06	0	+0.059	+0.05	-0.02	0.04	0.05
Dirt (%)	0.014	0.005	0.028	0.003	-0.016	0.013	-0.010	-0.009	-0.022	-0.014	0.005
$P_0$	—	—	—	—	+3.9	+4.5	+1.5	+2.7	+3.5	+3.2	1.2
PRI	81.6	5.6	86.6	4.4	-2	9	-6	-5	-3	-5.0	2.7
ML1+4 at 100°C	—	—	—	—	+4.5	+5.5	+3	+4	+5	+4.4	1.0
ASHT $\Delta P_0$	5.4	1.5	3.1	1.1	+3	+4.5	+0.5	+1	+2.5	+2.3	1.6
Hydroxylamine (p.p.m.)	105	24	115	18	-40	+16	-29	+5	0	10	24
ACS 1 cure system, 160°C											
Scorch time, $t_{s2}$ (min)	2.0	0.2	2.5	0.3	-1.1	-0.4	-0.7	+0.1	-0.6	-0.5	0.4
Cure time, $t'_c$ (90) (min)	9.9	0.7	12.4	0.9	-3.8	1.7	-3.6	-1.5	-2.1	-2.5	1.1
$M_{HR}-M_L$ (torque units)	31.4	1.4	28.2	1.5	+3.1	+2.5	+4.7	+3.7	+2.1	+3.2	1.1
ACS 1 cure system, 140°C											
MOD (kg/cm <sup>2</sup> )	5.81	0.32	4.98	0.27	+1.11	+0.46	+1.27	+0.76	+0.53	+0.83	0.35

TABLE 4. RAW RUBBER MOONEY VISCOSECITY TESTS

Test	SMR CV					RSS CV				
	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261
ML5+4 at 100°C										
ML <sub>max</sub>	75	81.5	112.5	71.5	92.5	83	87.5	116	75	101
ML4'	52.5	58.5	85	52.5	70.5	57	63.5	88	58	77
ML <sub>max</sub> - ML4'	22.5	23	27.5	19	22	26	24	28	17	24
ML <sub>max</sub> / ML4'	1.43	1.39	1.32	1.36	1.31	1.46	1.38	1.32	1.29	1.31
ML4' / P <sub>0</sub>	1.90	1.89	1.63	1.89	1.87	1.80	1.79	1.64	1.90	1.86
ML5+4 at 100°C, relaxation parameters										
a <sub>r</sub>	0.329	0.313	0.244	0.341	0.261	0.283	0.297	nl	0.337	0.230
ML <sub>R</sub> 20	17	20.5	41.5	16.5	28.5	18.5	22.5	45	19	33
ML <sub>R</sub> 90	10.5	13	29	10	19.5	12.5	14.5	31	11.5	23.5
D <sub>1</sub>	35.5	38	43.5	36	42	38.5	41	43	39	44
D <sub>2</sub>	42	45.5	56	42.5	51	44.5	49	57	46.5	53.5
a <sub>r</sub> ML4'	17.3	18.3	20.7	17.9	18.4	16.1	18.9	—	19.5	17.7
ML5+4 at 110°C										
ML <sub>max</sub>	68	76	107.5	67	88	76	80	106	77	92
ML4'	52	58	85.5	53.5	70	57	64.5	90	59	75.5
ML <sub>max</sub> - ML4'	16	18	22	13.5	18	19	15.5	16	18	16.5
ML <sub>max</sub> / ML4'	1.31	1.31	1.26	1.25	1.26	1.33	1.24	1.18	1.31	1.22
ML5+4 at 90°C										
ML <sub>max</sub>	80.5	88.5	137	78	100.5	87.5	92.5	138	86.5	113
ML4'	55.5	59.5	86.5	55	71	60.5	66	89.5	60	75.5
ML <sub>max</sub> - ML4'	25	29	50.5	23	29.5	27	26.5	48.5	26.5	37.5
ML <sub>max</sub> / ML4'	1.45	1.49	1.58	1.42	1.42	1.45	1.40	1.54	1.44	1.50
ML5+4 at 80°C										
ML <sub>max</sub>	90	103.5	191.5	89.5	134.5	111.5	118	191.5	101	141
ML4'	61	65	101	57	79	63.5	70	101.5	62.5	84
ML <sub>max</sub> - ML4'	29	38.5	90.5	32.5	55.5	48	48	90	38.5	57
ML <sub>max</sub> / ML4'	1.48	1.59	1.90	1.57	1.70	1.76	1.69	1.89	1.62	1.68

nl = Log-log plot not linear

TABLE 5. ANALYSIS OF THE DATA OF TABLE 4

Test	RSS CV		SMR CV		$\Delta$ (RSS CV - SMR CV)					Mean	SD
	Mean	SD	Mean	SD	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261		
ML5+4 at 100°C											
$ML_{\max} - ML4'$	23.8	4.1	22.8	3.1	+3.5	+1	+0.5	-2	+2	1.0	2.0
$ML_{\max} / ML4'$	1.35	0.07	1.36	0.05	+0.03	-0.01	0	-0.07	0	-0.01	0.04
$MP4' / P_0$	—	—	—	—	-0.10	-0.10	+0.01	+0.01	-0.01	-0.04	0.06
$a_r^a$	0.287	0.044	0.311	0.035	-0.046	-0.016	—	-0.004	-0.031	-0.024	0.018
$D_1$	41.1	2.4	39.0	3.6	+3	+3	-0.5	+3	+2	+2.1	1.5
$D_2$	50.1	5.2	47.4	6.0	+2.5	+3.5	+1	+4	+2.5	+2.7	1.2
$a_r ML4'^a$	18.1	1.5	18.0	0.5	-1.2	+0.6	—	+1.6	-0.7	+0.1	1.3
ML5+4 at 110°C											
$ML_{\max} - ML4'$	17.0	1.5	17.5	3.1	+3	-2.5	-6	+4.5	-1.5	-0.5	4.3
$ML_{\max} / ML4'$	1.26	0.06	1.28	0.03	+0.02	-0.07	-0.08	+0.06	-0.04	-0.02	0.06
ML5+4 at 90°C											
$ML_{\max} - ML4'$	—	—	—	—	+2	-2.5	+2	+3.5	+8	—	—
$ML_{\max} / ML4'$	—	—	—	—	0	-0.09	-0.04	+0.02	+0.08	—	—
ML5+4 at 80°C											
$ML_{\max} - ML4'$	—	—	—	—	+19	+9.5	-0.5	+6	+1.5	—	—
$ML_{\max} / ML4'$	—	—	—	—	+0.28	+0.10	-0.01	+0.05	-0.02	—	—

<sup>a</sup>Mean values excluding clone RRIM 628

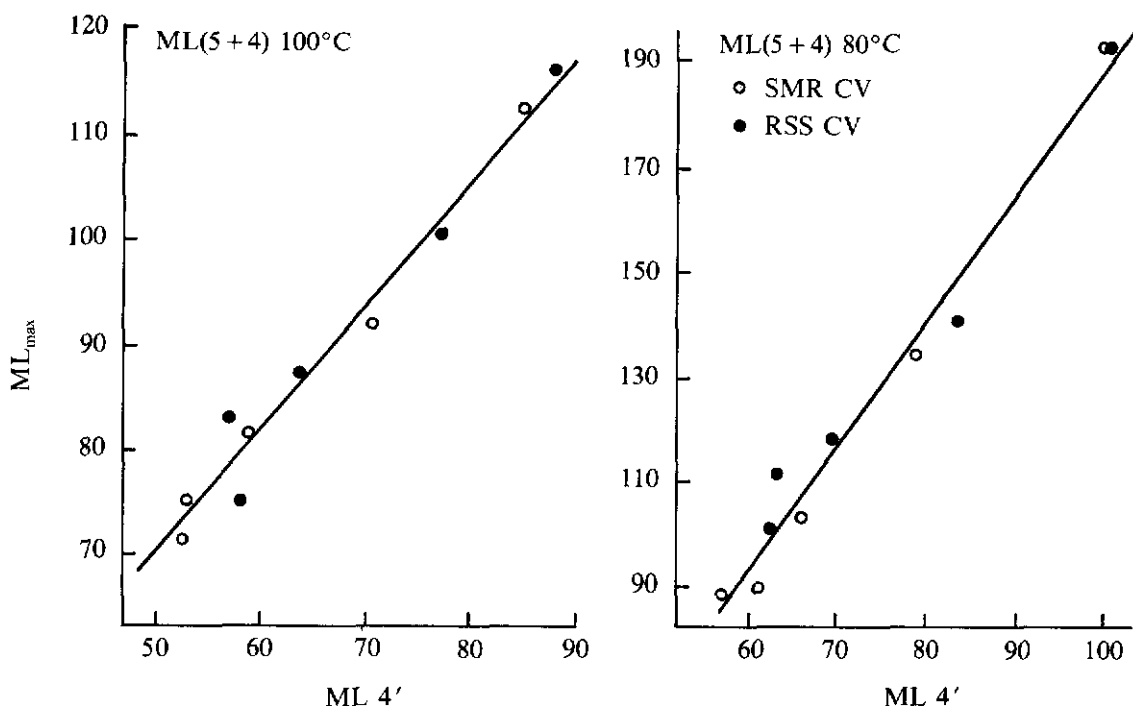


Figure 1. Correlation between  $ML_{max}$  and  $ML5+4$  at  $80^{\circ}C$  and  $100^{\circ}C$ .

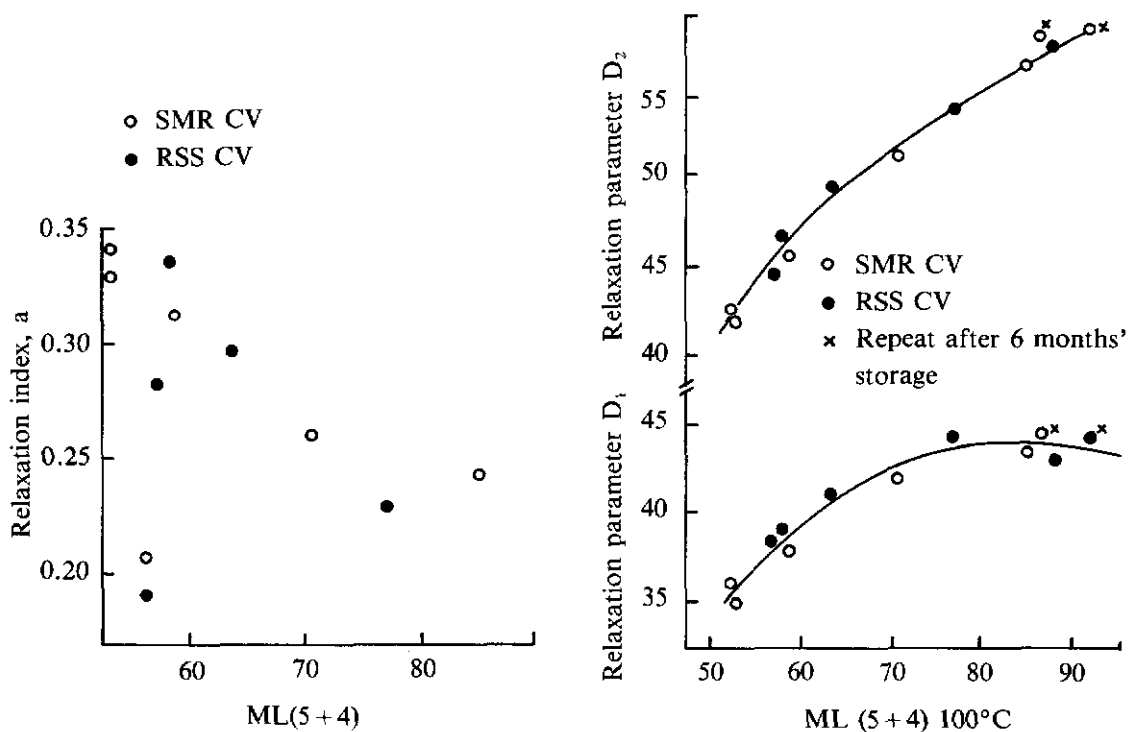


Figure 2. Dependence of the relaxation index  $a$  on  $ML\ 5+4$ .

Figure 3. Dependence of the relaxation parameters  $D_1$  and  $D_2$  on  $ML\ 5+4$ .



TABLE 6. CAPILLARY FLOW DATA, EXTRUSION AT 100°C

Item	$\gamma^a$	SMR CV					RSS CV				
		RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261
Wall shear stress $\tau_w$ (MPa)	0.9	0.088	—	0.131	0.092	0.122	0.099	—	0.157	0.107	0.139
	2.9	0.110	—	0.162	0.111	0.145	0.120	—	0.182	0.120	0.157
	9.4	0.141	—	0.191	0.134	0.157	0.146	—	0.202	0.142	0.179
	15.6	0.151	—	0.213	—	—	0.162	—	0.209	—	—
	26.6	0.158	—	0.308 <sup>b</sup>	0.149	—	0.169	—	0.328 <sup>b</sup>	0.169	—
	47.2	0.187	—	—	0.171	—	0.189	—	—	0.185	—
	79.1	0.211	—	—	0.202 <sup>b</sup>	—	0.217	—	—	0.220 <sup>b</sup>	—
	147.5	0.303 <sup>b</sup>	—	—	0.253 <sup>b</sup>	—	0.308 <sup>b</sup>	—	—	0.293 <sup>b</sup>	—
	265.5	—	—	—	0.301 <sup>b</sup>	—	—	—	—	0.350 <sup>b</sup>	—
	472.0	—	—	—	0.362 <sup>b</sup>	—	—	—	—	0.404 <sup>b</sup>	—
	885.0	—	—	—	0.438 <sup>b</sup>	—	—	—	—	0.452 <sup>b</sup>	—
End correction, $e$	0.9	19	—	16	13	14	14	—	11	9	13
	2.9	19	—	19	16	20	18	—	14	18	19
	9.4	23	—	23	22	31	25	—	21	23	27
	15.6	27	—	27	—	—	26	—	30	—	—
	26.6	33	—	19	30	—	34	—	16	28	—
	47.2	34	—	—	29	—	40	—	—	34	—
	79.1	38	—	—	29	—	43	—	—	35	—
	147.5	31	—	—	33	—	35	—	—	33	—
	265.5	—	—	—	41	—	—	—	—	37	—
	472.0	—	—	—	49	—	—	—	—	38	—
	885.0	—	—	—	41	—	—	—	—	44	—

TABLE 6. CAPILLARY FLOW DATA, EXTRUSION AT 100°C (CONT'D.)

Item	$\dot{\gamma}^a$	SMR CV					RSS CV				
		RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261
Extrudate swell area (%) L/D = 5	0.9	74	—	68	82	76	65	—	61	78	71
	2.9	108	—	84	90	101	82	—	71	101	102
	9.4	165	—	145	165	167	148	—	127	148	177
	15.6	183	—	176	—	—	174	—	175	—	—
	26.6	267	—	254	275	—	238	—	230	272	—
	47.2	351	—	—	298	—	328	—	—	311	—
	79.1	422	—	—	385	—	406	—	—	385	—
	147.5	525	—	—	473	—	483	—	—	479	—
	265.5	—	—	—	594	—	—	—	—	571	—
	472.0	—	—	—	640	—	—	—	—	682	—
	885.0	—	—	—	705	—	—	—	—	—	—
Extrudate swell area (%) L/D = 40	0.9	37	—	52	48	40	34	—	55	45	39
	2.9	54	—	64	50	56	51	—	58	54	61
	9.4	86	—	106	79	118	88	—	99	73	99
	15.6	107	—	149	—	—	105	—	137	—	—
	26.6	153	—	198	118	—	146	—	183	131	—
	47.2	217	—	—	174	—	224	—	—	201	—
	79.1	282	—	—	225	—	256	—	—	261	—
	147.5	300	—	—	261	—	281	—	—	273	—
	265.5	—	—	—	287	—	—	—	—	293	—
	472.0	—	—	—	347	—	—	—	—	321	—
	885.0	—	—	—	370	—	—	—	—	429	—
Flow index, n	—	0.189	—	0.166	0.144	0.107	0.169	—	0.100	0.135	0.107

<sup>a</sup>Newtonian shear rate ( $s^{-1}$ )<sup>b</sup>Omitted from calculation of flow index

TABLE 7. ANALYSIS OF THE DATA OF TABLE 6

Item	$\gamma^a$	RSS CV		SMR CV		$\Delta$ (RSS CV - SMR CV)						
		Mean	SD	Mean	SD	RRIM 600	RRIM 623	RRIM 628	RRIM 701	PR 261	Mean	SD
$\tau_w$ (MPa)	0.9	na	na	na	na	+0.011	—	+0.026	+0.015	+0.017	+0.017	0.006
	2.9	na	na	na	na	+0.010	—	+0.020	+0.009	+0.012	+0.013	0.005
	9.4	na	na	na	na	+0.005	—	+0.011	+0.008	+0.022	+0.012	0.007
	15.6	na	na	na	na	+0.011	—	-0.004	+0.020	—	+0.004	—
	26.6	na	na	na	na	+0.011	—	—	+0.020	—	+0.016	—
End correction, c	0.9	11.8	2.2	15.5	2.6	-5	—	-5	-4	-1	-3.8	1.9
	2.9	17.3	2.2	18.5	1.7	-1	—	-5	+2	-1	-1.3	2.9
	9.4	24.0	2.6	24.8	4.2	+2	—	-2	+1	-4	-0.8	2.8
	15.6	28.0	—	27.0	—	-1	—	+3	—	—	+1.0	—
	26.6	26.0	9.2	27.3	7.4	+1	—	-3	-2	—	-1.3	2.1
Extrudate swell area (%) L/D = 5	0.9	69	7	75	6	-9	—	-7	-4	-5	-6.3	2.2
	2.9	89	15	96	11	-26	—	-13	+11	+1	6.8	16.2
	9.4	150	21	161	10	-17	—	-18	-17	+10	-10.5	13.7
	15.6	175	—	180	—	-9	—	-1	—	—	-5.0	—
	26.6	247	22	265	11	-29	—	-24	-3	—	-18.7	13.8
Extrudate swell area (%) L/D = 40	0.9	43	9	44	7	-3	—	+3	-3	-1	-1.0	2.8
	2.9	56	4	56	6	-3	—	-6	+4	+5	0	5.4
	9.4	90	12	97	18	+2	—	7	-6	-19	-7.5	8.7
	15.6	121	—	128	—	-2	—	-12	—	—	-7.0	—
	26.6	153	27	156	46	-7	—	-15	+13	—	-3.0	14.4
Flow index, n	—	0.128	0.031	0.152	0.035	-0.020	—	-0.066	-0.009	0	-0.024	0.029

<sup>a</sup>Newtonian shear rate ( $s^{-1}$ )

na = Comparison would not be appropriate.

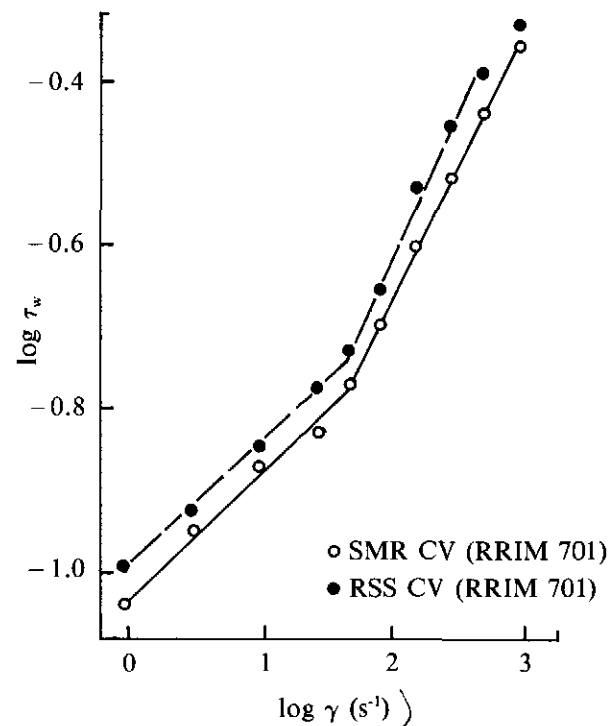
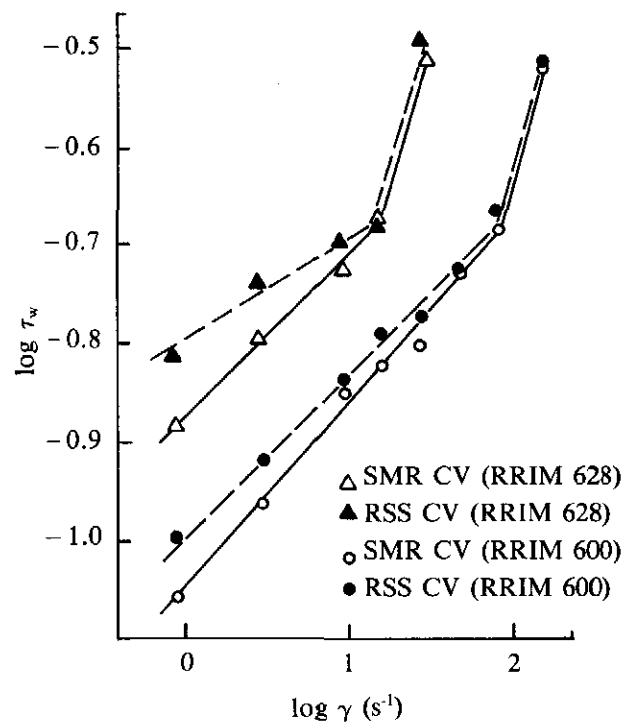


Figure 4. Dependence of wall shear stress on shear rate.

dependence of  $D_1$  and  $D_2$  on ML5 + 4, shown by both sheet and crumb rubbers, probably arises from the presence of more than one relaxation process. A similar contention has been used to interpret the relaxation behaviour found with black-filled rubbers<sup>9</sup>.

Capillary flow data are given in *Tables 6 and 7*. For a given clone, shear stress values for the RSS CV sample are rather greater than those for SMR CV, an observation consistent with the Mooney viscosity values. The data are plotted in 'power law' form in *Figure 4*. For

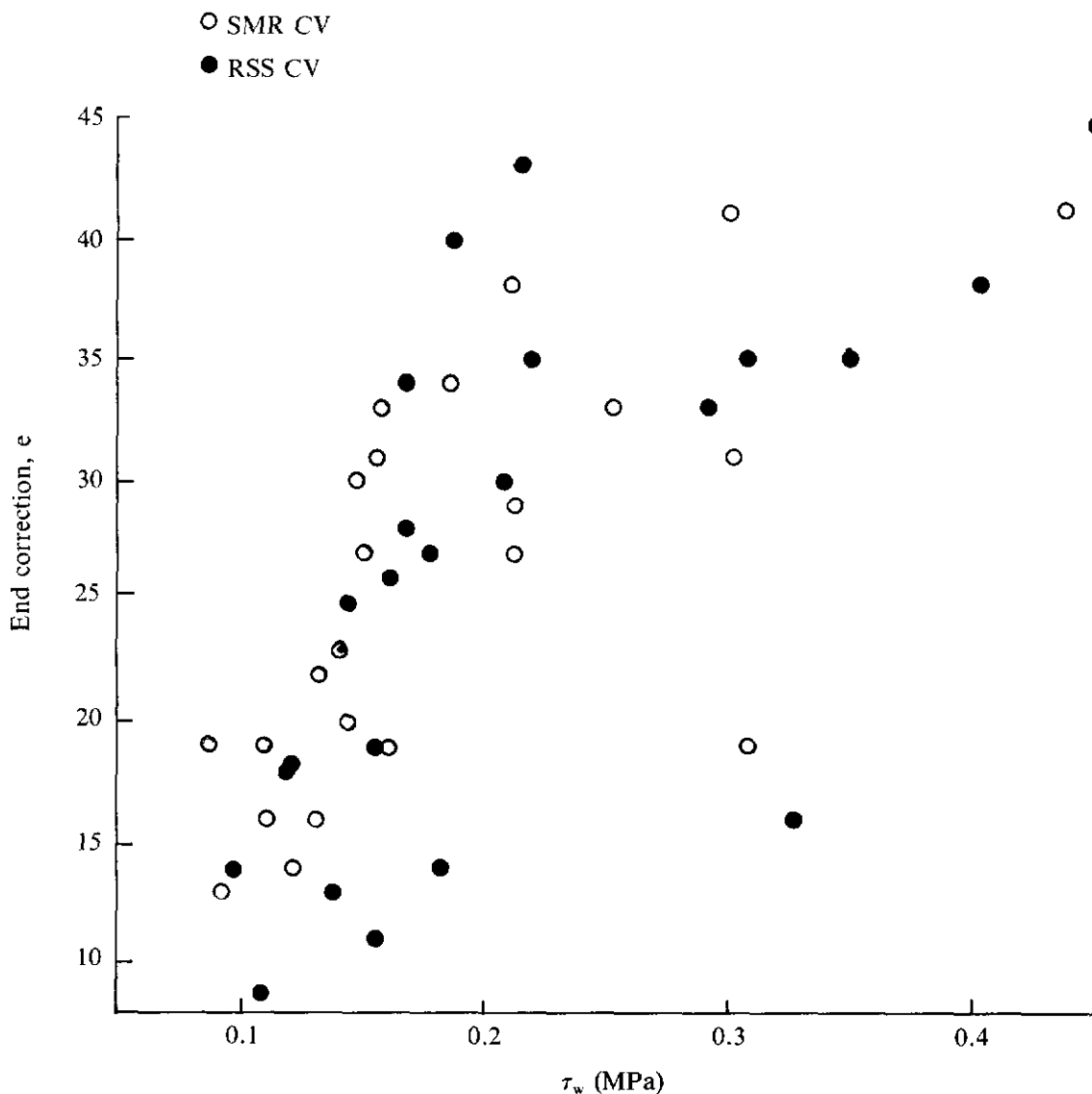


Figure 5. Dependence of end correction on shear stress for all samples.

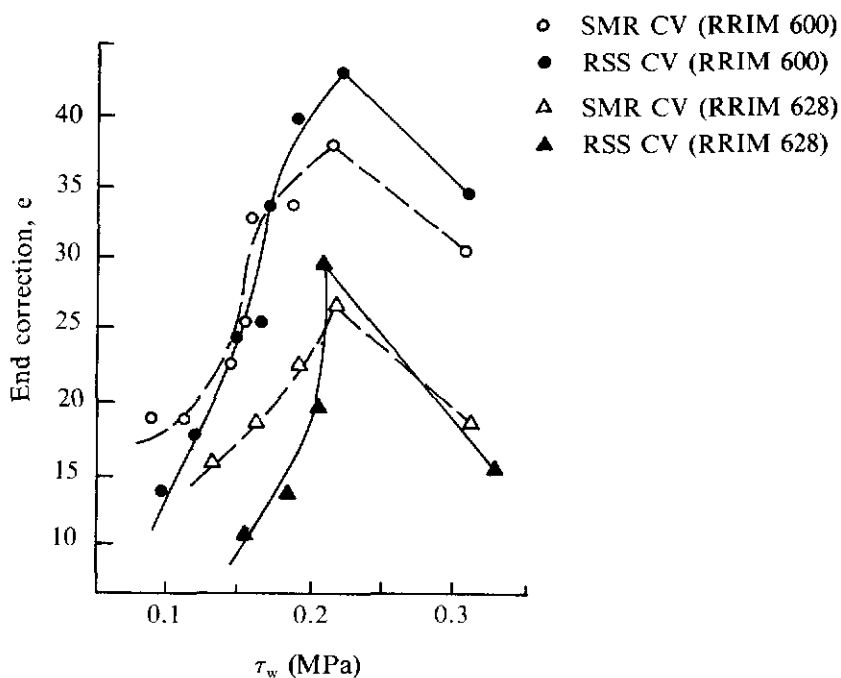


Figure 6. Dependence of end correction on shear stress for clones RRIM 600 and RRIM 628.

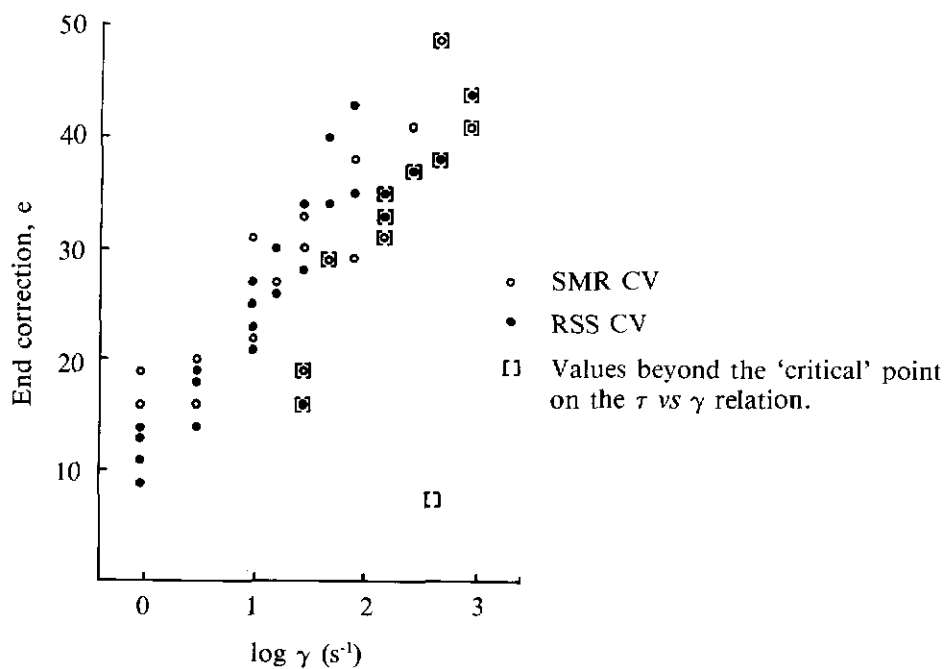


Figure 7. Dependence of end correction on shear rate for all samples.

shear stresses up to *ca.* 0.2MPa the data conform fairly well to simple power law expressions with values for the flow index,  $n$ , comparably low for sheet and crumb rubbers for all but one of the samples tested. The exception is RSS CV (RRIM 628) which displays an even lower value of  $n$ . Above *ca.* 0.2MPa, shear stress rises much more rapidly with shear rate, a phenomenon which can be ascribed to strain-induced crystallisation<sup>10</sup>. Similar effects have been described for synthetic polyisoprene<sup>11</sup>. The critical stress value of *ca.* 0.2MPa is not very dependent on the clone and, more importantly in the context of this paper, is independent of the sheet or crumb nature of the rubber.

For an elastic polymer such as NR, values of the end correction,  $e$ , are predictably large, though, despite the greater 'nerve' or elasticity often said to characterise sheet rubber, such a

difference is not evident in these data. Presumably the effects usually noted with RSS 1 stem from its viscosity, which is almost invariably high, rather than from any inherently superior elasticity. The end correction increases with both shear stress and shear rate, though as shown in *Figures 5, 6 and 7*, the dependence on shear rate is far less influenced by sample or clone. Once again, there is no obvious difference between sheet and crumb rubber in this respect. A further feature of note is the decrease in  $e$  for values of  $\tau_w$  greater than 0.2MPa.

The data for extrudate swell for a given sample conform to the expected pattern, in that swell is greater for a short capillary and increases with shear rate, and hence also with shear stress. A more general correlation between swell and shear stress for the several samples is, however, not evident, particularly at higher shear rates. This is probably due at

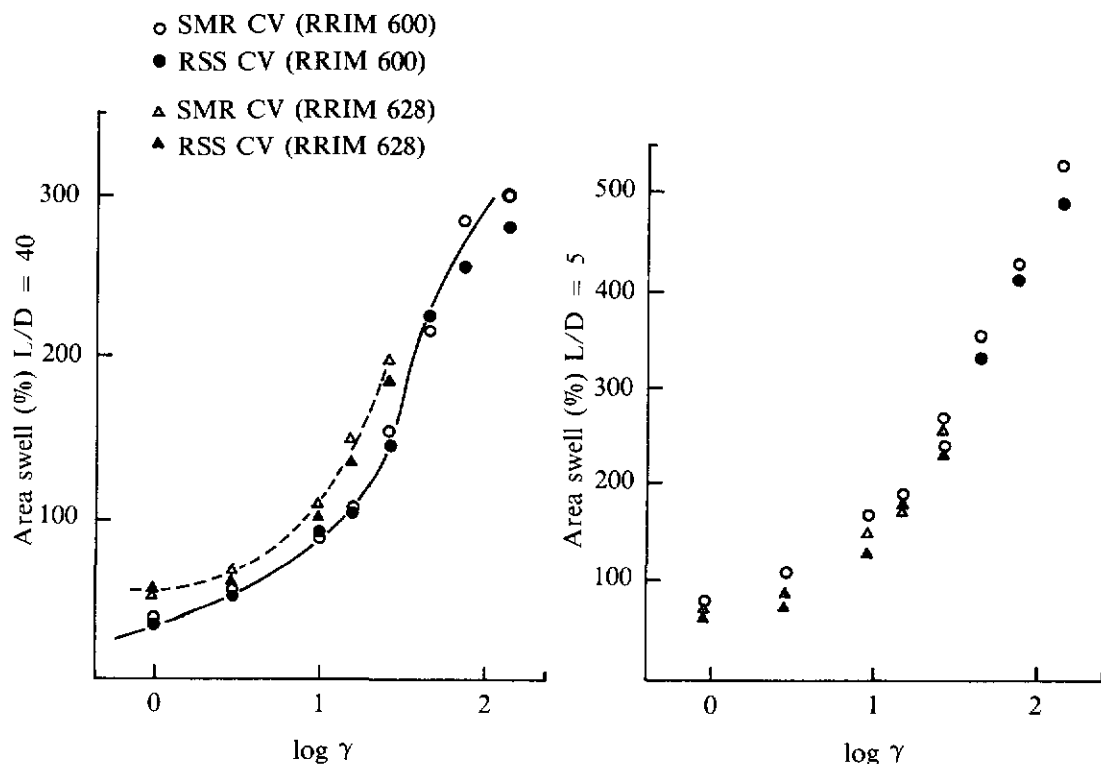


Figure 8. Dependence of extrudate swell on shear rate.

least partially to imprecision in the estimation of swell for a distorted extrudate. Ong *et al.*<sup>12</sup> have reported on the varied forms that this distortion can take.

In the present context, the most significant feature of the extrudate swell data is the near parity in the values for sheet and crumb rubbers derived from a given clone. This is seen in both *Tables 6* and *7* and further demonstrated in *Figure 8*. Finally, it is noted that, while both the end correction, *e*, and extrudate swell are associated with rubber elasticity, any correlation between these parameters does not extend to extrusion at stresses beyond the critical stress where *e* falls but swell continues to increase.

#### CONCLUSIONS

Complementary samples of RSS CV and crumb SMR CV covering the Mooney viscosity range *ca.* 50–85 have been prepared from five lots of monoclonal latex. Standard SMR tests on these rubbers showed small but consistent differences between the sheet and crumb materials. However, with the exception of cure rate, these were considered to be insufficient to be reflected as differences in technical quality between RSS and crumb rubber. In a range of Mooney and capillary flow tests, similar rheological behaviour for sheet and crumb rubbers was observed.

#### ACKNOWLEDGEMENTS

The authors thank staff of the Rubber Research Institute of Malaysia, especially Dr Ong Eng

Long and Mr Ong Chong Oon, for the preparation of SMR CV and RSS CV samples.

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