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BREAKDOWN BEHAVIOUR AND TECHNOLOGICAL PROPERTIES OF NATURAL RUBBER FROM SELECTED *HEVEA BRASILIENSIS* CLONES

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The breakdown properties of sheet rubber from twelve exotic clones and RRII 105 did not show significant differences. Compounds prepared from ACS 1 as well as HAF filled mixes showed comparable cure characteristics and technological properties. Similar retention of strength and modulus when subjected to thermal ageing were observed for samples of both the mix types using rubber from all the clones studied.

Key words: Breakdown behaviour, Clones, *Hevea brasiliensis*, Sheet rubber, Technological properties.

INTRODUCTION

The breeding programme for *Hevea brasiliensis* aims mostly at improvements in biological characters such as growth, yield and resistance to biotic and abiotic stresses. However, a high yielding clone with vigorous growth need not always produce latex (rubber) of desirable physical properties. Hence, latex qualities also require attention in breeding. A major source of variability within and among natural rubber (NR) grades probably is the clone from which the latex is derived (Fuller, 1988). Properties of latices from different clones have been studied (Subramaniam, 1976; Saraswathyamma *et al.*, 1990). However, there are very few reports on the physical properties of rubbers from different clones. Environmental and soil factors may influence both the quantity and composition of latex (Ebi and Kolawole, 1992). Clonal variations may influence the non-rubber constituents, which in turn affect the properties of latex and bulk rubbers.

RRII 105 is the most popular *H. brasiliensis* clone developed by the Rubber Research Institute of India and is widely cultivated in the country. Significant clonal and seasonal variation in plasticity, Mooney viscosity and gel content in the latex of 12 exotic clones and RRII 105 has been reported earlier (George *et al.*, 2004).

Uniformity and consistency in the processability of elastomers are essential for providing solutions to the rubber industry's increasing demands for higher productivity, quality and energy conservation. Earlier studies on the processability of natural rubber (NR) have been based on parameters such as Mooney viscosity and plasticity (Bristow, 1982; Lim and Ong, 1986). Breakdown of rubber occurs in most of the processing operations. Consistency in the breakdown behaviour of NR is an important factor in its processing. The plasticity retention in-

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dex (PRI) test (BIS, 1990) was introduced as an indicator of the oxidation resistance of rubber i.e. as a measure of the rate of breakdown due to the oxidative scission of the molecular chains. However, the breakdown in the PRI test occurs under different conditions from that happen during mastication and hence the measurement of PRI is insufficient for the prediction of breakdown rate during processing (Bristow and Sears, 1984). The processability of different elastomers has been studied earlier using a Brabender Plasticorder (Blake, 1962; Bartha *et al.*, 1983; Onufer, 1966; Thomas *et al.*, 1998). A breakdown index derived from the mastication of NR in a laboratory rheometer, takes into account the mechanical work exerted and correlates with the breakdown behaviour in an internal mixer as well as in capillary extrusion (Lim and Ong, 1986).

In the present work, a rheometer has been used to study the breakdown behaviour of sheet rubber. Technological properties of rubber compounds based on ACS 1 and HAF filled formulations were also evaluated.

MATERIALS AND METHODS

The clones selected for the study, namely RRII 105, PB 217, PB 235, PB 255, PB 260, PB 280, PB 310, PB 311, PB 312, PB 314, KRS 25, KRS 128 and KRS 163, were planted in the RRII Farm, Kottayam, Kerala, during 1989 in randomized block design with five replications and seven trees per plot. All the trees were opened for tapping during 1996 and tapped ½ S d/3 without stimulation. Latex samples were collected from three replications of each clone at specific intervals to represent three seasons, namely, January to April (S1), May to August (S2) and September to December (S3). For analysis, the samples were bulked to form one composite for each clone in a season. Latex from each clone was then processed into sheet rubber.

Mastication characteristics were assessed in terms of breakdown index and associated parameters using a Haake Rheocord 90 (Bartha *et al.*, 1983). This instrument imparts a very complex shearing motion to the polymer and the design of the mixing head of the equipment is similar to that of an internal mixer. Therefore, the behaviour of the rubber in actual processing can be simulated. Mastication was carried out at 40 RPM for 10 min with an initial temperature of 40°C. Figure 1 gives a typical Haake Rheogram from which various parameters were measured. The measurements made included torque at the fifth minute (TQ_5) and tenth minute (TQ_{10}), the rate of breakdown measured from the drop in torque $TQ_5 - TQ_{10}$ with time [BI], totalized torque at the fifth minute ($[TTQ]_1$), and at the tenth minute ($[TTQ]_2$) and the difference in temperature at the tenth minute (DT).

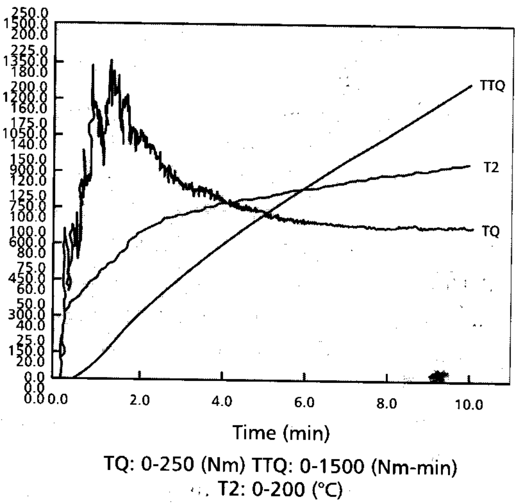

Fig. 1. Breakdown properties of sheet rubber

To assess whether the clonal variation observed earlier (George *et al.*, 2004) has any effect on the rate of vulcanization and on the properties of vulcanizates, a gum and HAF filled compounds were prepared using rubber from the 13 clones. The compounding ingredients used were of commercial grades. Cure characteristics of the compounds were determined using a Monsanto Rheometer R 100 at 150°C. Test samples were moulded using an electrically heated hydraulic press to their respective optimum cure time. Physical properties of the vulcanizates namely, stress-strain properties (ASTM D 412-80 Zwick UTM, model 1474), tear strength (ASTM D 624-00 Zwick UTM, model 1474), hardness (ASTM D 2240-04, Shore A), compression set (ASTM D 395-03, Method B), abrasion resistance (DIN 53516), heat build-up (ASTM D 623-99, Goodrich flexometer) and ageing resistance (ASTM D 573-04) were tested.

RESULTS AND DISCUSSION

Breakdown behaviour

The breakdown properties of the samples prepared from the 13 clones are presented in Table 1. The torque at the fifth minute (TQ_5) was low for the samples from clones PB 260, PB 312 and KRS 163 which produce rubber of medium viscosity i.e. V_R 60 to 70 units (George *et al.*, 2004). Higher torque values were obtained for the clones which produce medium to hard and hard rubber whose viscosity ranges are 70 to 80 and more than 80 units respectively. Significant differences do not exist between the clones (as observed from the low CV values). As mastication proceeds, torque reaches a maximum value and then descends. It almost stabilizes at the end of the tenth minute and this torque is taken as the stabilized torque. The stabilized torque is a measure of the viscosity of the masticated rubber. The stabilized torque was lower for the clones, which produce rubber of medium viscosity range. But the differences are not significant between the clones. The rate of breakdown (BI) at the tenth minute was also lower

Table 1. **Breakdown parameters**

Clone	Parameter					
	TQ_5 (Nm)	TQ_{10}(Nm)	BI	$[TTQ]_1$(Nm/min)	$[TTQ]_2$(Nm/min)	DT(°C)
RRII 105	95	81	2.8	586	1016	66
PB 217	87	76	2.2	576	987	64
PB 235	87	76	2.2	567	972	63
PB 255	96	81	3.0	583	1010	64
PB 260	84	74	2.0	574	972	62
PB 280	92	78	2.8	598	1006	67
PB 310	88	76	2.4	610	1020	66
PB 311	91	75	3.2	573	986	62
PB 312	81	72	1.8	540	915	60
PB 314	93	79	2.8	547	973	64
KRS 25	93	85	2.4	590	1035	70
KRS 128	92	80	2.4	610	1036	67
KRS 163	83	73	2.0	549	937	60
Mean	89.38	77.54	2.46	577.15	989.62	64.23
SD	4.75	3.69	0.43	22.52	36.25	2.92
CV	5.31	4.76	17.48	3.90	3.66	4.55

for the clones, which have low stabilized torque. There was no significant difference in the mastication behaviour for the different clones.

The totalized torque, TTQ, is a measure of the work done during mastication. The TTQ measured at the fifth and tenth minutes were lower for the clones, which produce rubber with medium Mooney viscosity. No significant differences were observed among the clones. The heat generated during mastication is an indication of the state of degradation of the rubber. A highly degraded rubber will generate less heat during mastication (Thomas *et al.*, 1998) The difference in temperature observed during mastication at the tenth minute is also lower for the clones, which produce medium viscosity rubber, but the difference in DT between the clones is not significant.

Table 2. **Formulation of compounds (phr)**

Ingredient	ACS 1	HAF filled
Natural rubber	100.0	100.0
Zinc oxide	6.0	5.0
Stearic acid	0.5	2.0
HAF black (N300)	-	40.0
Naphthenic oil	-	4.0
CBS	-	0.6
MBT	0.5	-
Sulphur	3.5	2.5

Cure characteristics and technological properties

ACS 1 and HAF filled compounds were prepared as per the formulation given in Table 2. Consistency in cure behaviour is important in determining the ease with which a product can be fabricated. A rheometric test is preferred to characterize the cure behaviour (Marsden, 1979 & Esah, 1990). Results of the measurements using the ACS 1 formulation for the rubber from the different clones are shown in Table 3. Four clones RRII 105, PB 217, PB 255 and KRS 128 which produce hard rubbers with viscosity more than 80, showed higher Mooney viscosity values for their compounds. Optimum cure, scorch time and cure rate index were comparable for all the clones studied.

Technological properties observed for the ACS 1 formulation are shown in Table

Table 3. **Cure characteristics of ACS 1 compounds**

Clone	Scorch time (ts_2, min.)	Optimum cure time (t_{90}, min.)	Cure rate index	Rheometric torque (Nm)	Mooney scorch time at 120°C (min.)	Mooney viscosity at 100°C (ML (1+4))
RRII 105	3.0	17.0	7.14	33.5	16.56	23.1
PB 217	2.5	16.0	7.41	36.5	14.49	23.2
PB 235	2.5	17.0	6.89	33.0	16.65	21.8
PB 255	2.5	16.5	7.14	31.5	14.52	24.3
PB 260	3.0	17.0	7.14	32.0	16.09	18.7
PB 280	2.5	16.5	7.14	31.5	16.44	21.8
PB 310	2.5	16.0	7.41	33.0	14.22	21.3
PB 311	2.5	16.5	7.14	33.5	14.73	20.8
PB 312	2.5	16.0	7.41	36.5	14.39	19.3
PB 314	3.0	16.0	7.69	34.5	15.50	20.0
KRS 25	2.5	16.0	7.41	35.5	14.44	21.4
KRS 128	3.0	18.0	6.67	34.5	15.59	22.4
KRS 163	2.5	18.0	6.45	35.0	14.72	20.4

4. Hardness and tensile properties were similar for the compounds formulated using rubber from all the clones. The tensile strength and modulus of ACS 1 mixes before and after ageing at 70°C for 14 days are shown in Figures 2 and 3 respectively. The extent of retention after ageing was almost identical. The compound with rubber from the clone RRII 105 has shown an intermediate behaviour for all the properties studied.

The cure characteristics of HAF black filled compounds are presented in Table 5. Optimum cure time, cure rate index and Mooney scorch time were comparable for all the clones studied. Technological properties of HAF filled compounds are given in Tables 6 and 7. Only marginal differences in technological properties were observed between the compounds with rubber from the different clones. Figures 4 and 5 represent the tensile strength and modulus of the carbon black filled compounds before and after ageing at 70°C for 14 days. The extent of retention after ageing was almost identical.

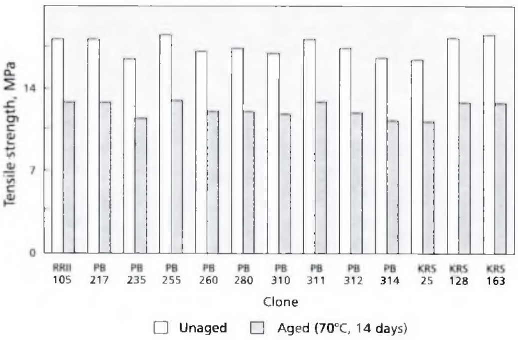

Fig. 2. Effect of ageing on tensile strength of ACS 1 vulcanizates

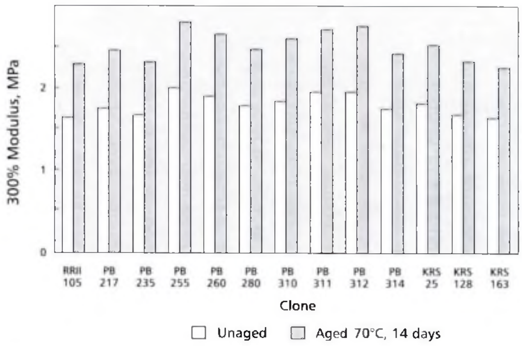

Fig. 3. Effect of ageing on 300% modulus of ACS 1 vulcanizates

Table 4. **Technological properties of ACS 1 compounds**

Clone	Hardness (Shore A)	Tensile strength (MPa)	300 % Modulus (MPa)	Elongation at break (%)	Tear strength (N/mm)
RRII 105	32	18.17	1.62	624	24.04
PB 217	30	18.16	1.74	619	25.93
PB 235	30	16.49	1.65	608	23.44
PB 255	32	18.56	1.99	613	22.78
PB 260	31	17.19	1.89	596	24.46
PB 280	31	17.51	1.78	603	22.88
PB 310	30	16.94	1.84	611	22.52
PB 311	32	18.24	1.94	610	23.77
PB 312	31	17.41	1.95	599	25.96
PB 314	30	16.59	1.74	584	22.25
KRS 25	30	16.46	1.81	581	25.00
KRS 128	32	18.37	1.67	621	24.20
KRS 163	32	18.64	1.63	616	23.21

Table 5. **Cure characteristics of HAF filled compounds**

Clone	Scorch time (ts_2, min.)	Optimum cure time (t_{90}, min.)	Cure rate index	Rheometric torque (Nm)	Mooney scorch time at 120°C (min.)
RRII 105	3.5	9.5	16.66	62.0	23.07
PB 217	3.0	8.5	18.18	62.5	23.80
PB 235	3.5	9.5	16.66	64.0	21.99
PB 255	3.5	9.5	16.66	63.0	21.41
PB 260	3.0	9.5	16.00	65.0	21.79
PB 280	3.5	9.5	16.66	64.0	22.12
PB 310	3.0	9.5	15.38	64.0	19.85
PB 311	3.0	9.5	15.38	65.0	20.00
PB 312	3.0	8.5	18.18	63.0	21.79
PB 314	3.0	9.0	16.66	65.5	19.85
KRS 25	2.5	8.5	16.66	64.5	22.02
KRS 128	3.0	8.5	18.18	62.0	22.04
KRS 163	3.5	9.0	16.66	62.0	20.85

Table 6. **Technological properties of HAF filled compounds**

Clone	Hardness (Shore A)	Compression set (%)	DIN abrasion Loss (mm^3)	Heat build-up (ΔT °C)
RRII 105	59	24.85	62.05	16.0
PB 217	57	26.77	69.13	15.0
PB 235	57	25.68	69.95	14.5
PB 255	58	26.13	79.96	17.0
PB 260	58	24.81	65.79	16.0
PB 280	58	24.73	74.91	15.0
PB 310	57	28.29	80.84	19.0
PB 311	59	25.61	73.75	18.0
PB 312	58	27.03	70.65	18.0
PB 314	57	24.29	73.65	17.0
KRS 25	57	29.21	60.22	14.5
KRS 128	59	28.45	77.54	15.0
KRS 163	59	28.51	76.34	16.5

Table 7. **Stress-strain properties and tear strength of HAF filled compounds**

Clone	Tensile strength (MPa)	300 % Modulus (MPa)	Elongation at break (%)	Tear strength (N/mm)
RRII 105	26.43	12.68	467	105
PB 217	26.17	12.14	490	106
PB 235	26.04	12.06	495	104
PB 255	25.96	13.21	476	106
PB 260	26.17	12.49	505	108
PB 280	26.53	14.22	454	104
PB 310	26.49	12.53	538	104
PB 311	25.32	14.31	460	107
PB 312	26.33	13.50	490	104
PB 314	26.93	12.64	541	109
KRS 25	26.42	12.38	517	103
KRS 128	26.37	12.77	532	109
KRS 163	26.19	12.57	529	104

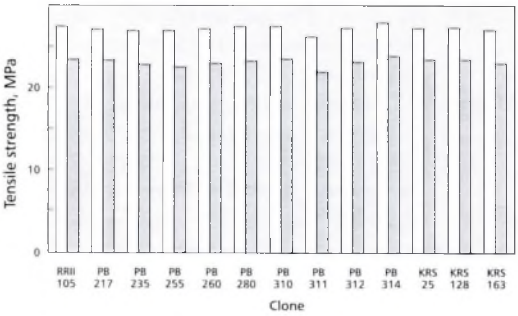

Fig. 4. Effect of ageing on tensile strength of HAF filled vulcanizates

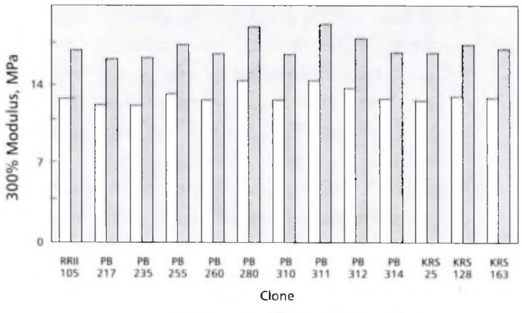

Fig. 5. Effect of ageing on 300% modulus of HAF filled vulcanizates

CONCLUSION

This study indicated that the clonal differences in the source of rubber do not significantly influence the breakdown behaviour of sheet rubbers in an internal mixer. The cure characteristics and technological properties of ACS 1 and HAF filled compounds of the rubbers from the different clones were comparable. Ageing properties also showed a similar trend.

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