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Easy Processing Epoxidised Natural Rubber

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The latest production technique in the preparation of epoxidised natural rubber (ENR) has resulted in a promising new form of ENR which can be easily processed in large internal mixers. The new samples of ENR (ENR 25 and ENR 50, i.e. *ENR containing 25 and 50 mole per cent of epoxidation, respectively) are characterised by their significantly low gel contents and high basic nature. The commercial production of this new form of ENR by Kumpulan Guthrie Sendirian Berhad (KGSB) is anticipated in 1989.*

The mill-sticking problem which was encountered when mixing ENR on small laboratory mills at high temperatures can now be avoided. The method of solving the problem involves a partial sulphur crosslinking that enhances the cohesive strength of the ENR. This improvement in the cohesive strength of ENR coupled with the incorporation of additional level of stearic acid prevents the rubber from sticking to the two-roll mill. It is to be noted that the results obtained from this study were based on small laboratory mills where high shear is created during the milling process. The results obtained may not be related to commercial operations where the magnitude of the shearing force is different from that based on small-scale operations.

Controlled epoxidation of natural rubber (NR) has been known to give a chemically modified rubber, called ENR, with improved resistance to hydrocarbon oils, lower air permeability, increased damping and good bonding properties[1–9]. The changes in physical properties from the original NR have brought about some of the unique and useful features for consideration in rubber product applications which would not otherwise be possible with NR. The high damping and good wet-grip characteristics of the rubber have been found to be useful in non-slip shoe soles, floor mats and sportballs, while the good bonding property of the rubber has been shown to give potentially useful applications in sealants and adhesives[8,9,10]. The low rolling resistance and good wet-grip of the rubber have been proven in tyre trials involving passenger car treads[6,7].

Earlier promotion of ENR[3] to consumers has been hampered by problems of high Mooney viscosity (ML1 + 4 at 100°C of about 120) and high gel contents coupled with the slightly acidic nature of the rubber (pH of aqueous extract 6.0–6.5). These preliminary samples had been shown by consumers to give mixing problems, particularly when large internal mixers are used. Longer mixing time, higher mixing energy and poor dispersion of fillers in the rubber were the main problems associated with the earlier version of ENR.

These mixing problems have necessitated an alternative technique to produce easy processing ENR. Presently, a new production technique has been found to give ENR with low Mooney viscosity and substantially reduced gel contents as well as of a highly basic nature (pH of aqueous extract of about 10).

The production process of ENR employing this new technique has been licensed to KGSB, and ENR produced by KGSB will be of two grades only, namely ENR 25 and ENR 50. The commercial production of ENR is anticipated in 1989.

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EXPERIMENTAL

Materials

ENR was prepared at the Rubber Research Institute of Malaysia (RRIM) pilot plant using the technique for easy processing ENR. The compounding ingredients used were of the recommended grades for rubber.

Procedure

Mastication of ENR 25 and ENR 50 was carried out on a 152 × 30 cm two-roll mill with a starting temperature of about 30°C. The batch size of the milling process was based on 12 kg of the raw rubber. During the mastication process, samples were taken at various time intervals for determination of the raw rubber Mooney viscosity in accordance with the *ASTM D1646* procedure.

In the case of mastication of ENR 25 and ENR 50 in an internal mixer, a Francis Shaw K2A mixer of capacity 27 litres was used. The conditions of mastication were as follows:

Starting temperature = 80°C and then water cooling

Rotor speed = 40 r.p.m.

Ram pressure = 0.69 MPa

Samples were dumped at various time intervals and refined on a 152 × 30 cm two-roll mill for 1 min.

Similar conditions as above were used for mixing ENR 25 and ENR 50 with carbon black and other ingredients based on formulations shown in *Table 1* (*Formulations 1* and *2*), but the schedule of mixing was as follows:

0 min — ENR 25 or ENR 50, zinc oxide, stearic acid and Stantoflex 13

0.5 min — ½ Carbon black and oil

1.5 min — ½ Carbon black

3.5 min — Sweep down feeding chute

4.0 min — Dump

Refining of the above masterbatches were carried out on a 152 × 30 cm two-roll mill for 1 min.

TABLE 1. FORMULATIONS USED IN THIS STUDY

Ingredient	Formulation (parts by weight) 1	2	3
ENR 25	100	—	—
ENR 50	—	100	100
ISAF carbon black (N-220)	50	50	50
Dutrex 737 MB[a]	5	5	5
Zinc oxide	5	5	5
Santoflex 13[b]	2	2	—
Permanax TQ[c]	—	—	1
Stearic acid	2	2	Variable
Sulphur	—	—	Variable

[a]Dutrex 737 MB — Aromatic processing oil
[b]Santoflex 13 — N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine
[c]Permanax TQ — Poly-(2,2,4-trimethyl-1,2-dihydroquinoline)

Samples of ENR 25 and ENR 50 masterbatches prepared from a K2A internal mixer were mill-mixed carefully and cured to optimum at 150°C using a semi-efficient vulcanisation system (sulphur 1.5 p.h.r., MOR 1.5 p.h.r. and PVI 0.2 p.h.r.). It is to be noted here that excessive milling of the compounds at high temperatures can result in mill-sticking. The physical properties of these cured samples were determined according to the testing procedures normally used at the RRIM, *i.e.*

Tensile properties to *ISO 37*

Hardness to *ISO 48 (ASTM D1415)*

Compression set to *ISO 815* using small test pieces

Tear strength, trouser, to *ISO 34*

Rebound resilience, Dunlop tripsometer, to *BS 903: Part A8.*

The study on the mill-sticking behaviour of raw ENR 50 was carried out on a 30 × 15 cm two-roll mill using a frictional ratio of 1:1.25. The mill temperature was varied by means of cooling water and steam regulation and the temperature was determined by using a surface pyrometer.

ENR 50 masterbatches with variable concentrations of sulphur and stearic acid as shown by *Formulation 3* in *Table 1* were mixed on the two-roll mill running at low temperature and cured for 5 min at temperatures ranging from 150°C–180°C. Their respective Mooney viscosities were determined.

In the preparation of ENR 50 masterbatches in a 2-litre OOC Banbury for visual observation of the subsequent milling process, the following mixing cycle was employed.

Starting rotor temperature — 100°C
Rotor speed — 80 r.p.m.

0 min — ENR 50, zinc oxide, stearic acid, Permanax TQ and sulphur
0.5 min — ½ Carbon black and oil
1.5 min — ½ Carbon black
4.5 min — Sweep down feeding chute
5.0 min — Dump

The dump temperature was varied by means of steam regulation. Refining of the masterbatches was carried out on a 50 × 20 cm two-roll mill for 1 min before the visual observation of mill-sticking. The screening test of the respective ENR 50 masterbatches for observation of mill-sticking tendency was carried out by masticating the masterbatches on a 30 × 15 cm two-roll mill with an initial roll temperature of 75°C for 15 min. The reduction in Mooney viscosity of the masterbatches during the process of mastication was also determined.

RESULTS AND DISCUSSION

Raw Rubber Properties

Typical values of basic raw rubber properties of the two available grades of ENR are summarised in *Table 2*. The new ENR grades are characterised by their significantly lower Mooney viscosity and gel contents and higher pH.

TABLE 2. TYPICAL RAW PROPERTIES OF NEW ENR

Property	ENR 25	ENR 50
Epoxidation level (mole %)	25	50
Glass transition temperature (°C)	−45.3	−22.5
Mooney viscosity (ML1+4 at 100°C)	60–80	60–80
Macrogel content (weight %)	14.9	21.5
pH	10	10

Mill-breakdown Behaviour

Mill-breakdown behaviour of raw ENR 25 and ENR 50 was studied by determining the Mooney viscosity of the rubber with respect to the mastication time. Two grades of NR, *i.e.* SMR 5 and SMR CV, were chosen for comparison. As shown in *Figure 1*, there is a drastic reduction of Mooney viscosity of ENR 25 between 0 and 5 min of mastication; beyond this the reduction is gradual and tends to level off on prolonged mastication. With SMR 5 and SMR CV, the viscosity reduction is gradual throughout the mastication.

Figure 2 shows the mill-breakdown behaviour of raw ENR 50 in comparison to SMR 5 and SMR CV. A drastic reduction of Mooney viscosity of ENR 50 occurred between 0 and 10 min of mastication. Comparing the rate of viscosity reduction from 0 to 5 min of mastication, ENR 25 showed a faster rate of reduction compared to ENR 50.

Breakdown Behaviour in Internal Mixer

Breakdown behaviour of raw ENR 25 and ENR 50 in a Francis Shaw K2A internal mixer is shown in *Figures 3* and *4*. Both ENR 25 and ENR 50 of similar initial raw rubber viscosity as SMR CV gave faster rate of viscosity reduction. Considering the breakdown behaviour between 0 and 2 min of mastication, the rate of viscosity reduction of ENR 25 was faster than that of ENR 50.

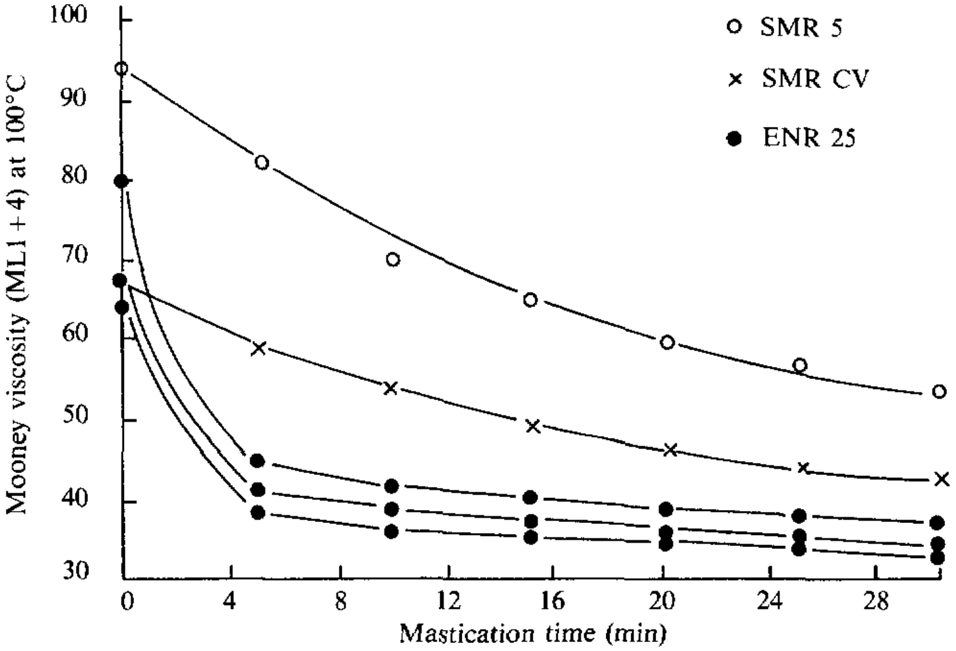

Figure 1. Mill-breakdown behaviour of raw ENR 25.

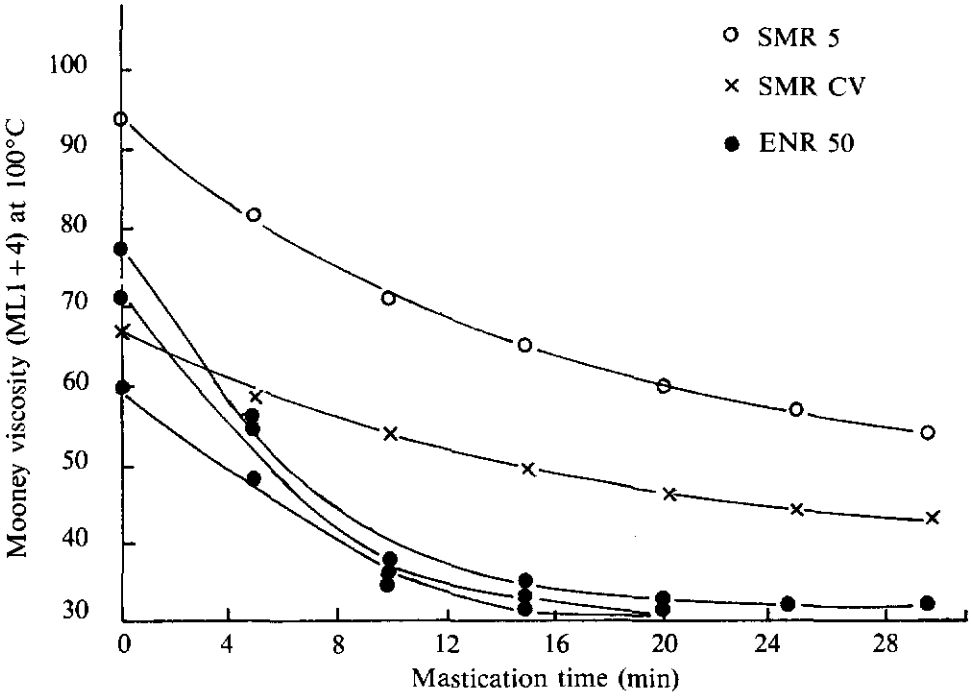

Figure 2. Mill-breakdown behaviour of raw ENR 50.

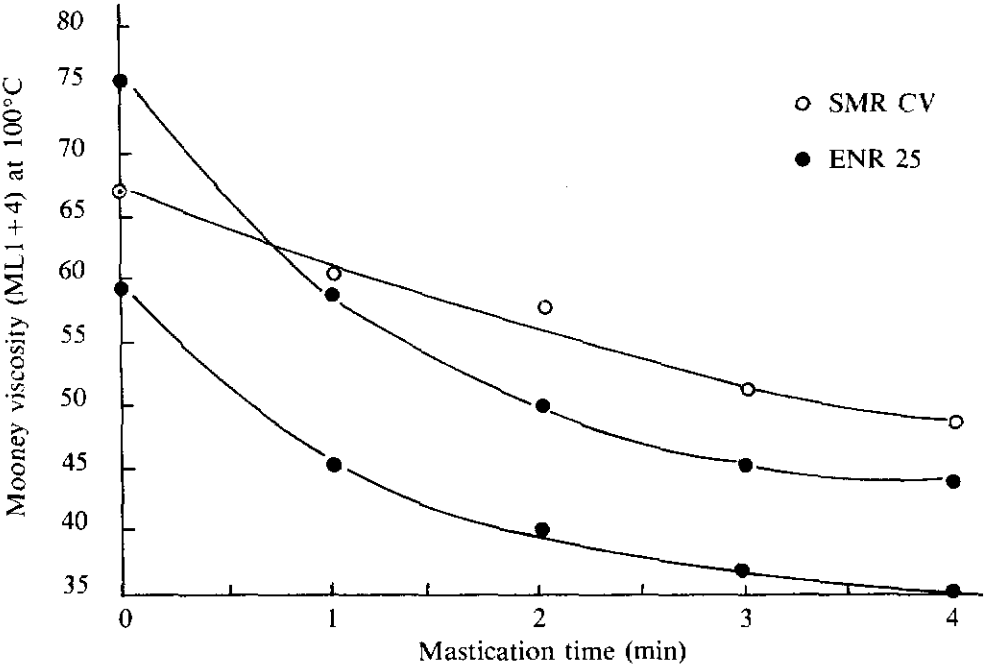

Figure 3. Mastication of raw ENR 25 in K2A mixer.

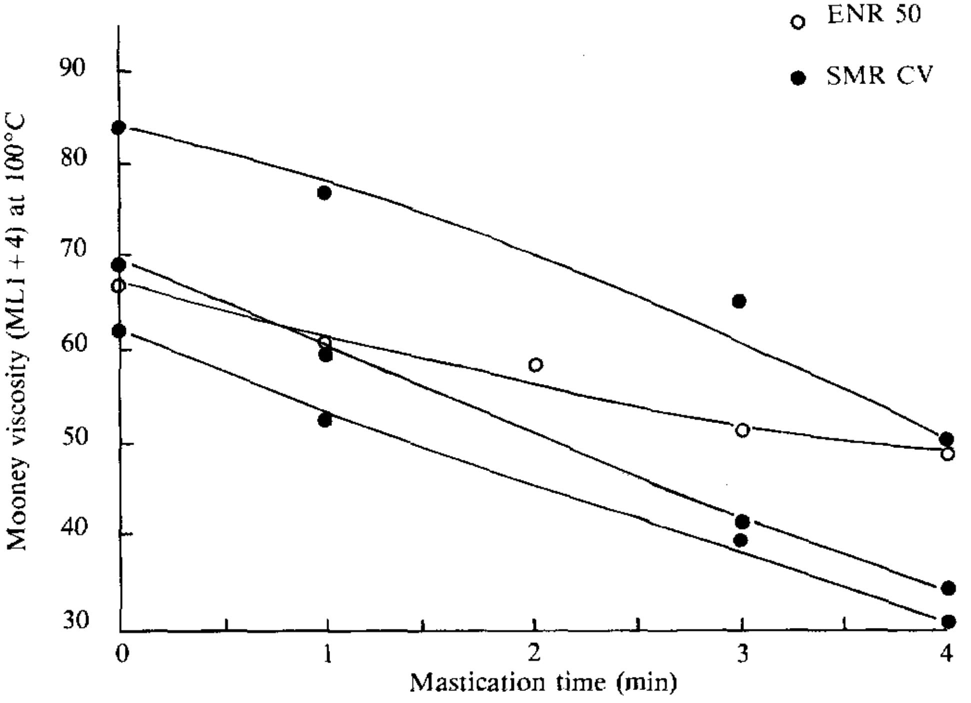

Figure 4. Mastication of raw ENR 50 in K2A mixer.

Mixing Behaviour with ISAF Carbon Black

In the majority of fabrications of rubber products, fillers are normally incorporated into elastomers for improving physical properties or for cost reduction. Thus, it is important that the ENR produced from the modified production technique can be easily mixed with fillers in internal mixers. Earlier samples[11] of ENR suffered from processing problems brought about by the high Mooney viscosity, high gel contents and slightly acidic character (pH of aqueous extract 6.0–6.5).

The relative ease of mixing ENR 25 and ENR 50 with filler was studied. In this study, ISAF carbon black was chosen and mixing was carried out in a Francis Shaw K2A mixer. The effect of raw rubber Mooney viscosity of ENR 25 and ENR 50 on the viscosity of the carbon black masterbatch prepared from the internal mixer is shown in *Figures 5* and *6*. The variation in viscosity of ENR 50 masterbatches prepared from samples of raw viscosity (V_R) 60–80 is significantly larger compared to those of ENR 25. for ENR 25 with V_R 60–80, the batch viscosity (V_B) obtained ranged from 70 to 77, while for ENR 50, the V_B range was from 60 to 90. However, this large variation in viscosity for ENR 50 masterbatches could be minimised by refining on the two-roll mill *(Figure 7)*. After 2 min of refining on the 152 × 30 cm two-roll mill, viscosity ranging from 47 to 58 could be obtained. Hence, to minimise batch variations in viscosities, it is advisable to use a longer milling time for ENR 50.

The vulcanisate properties of ENR 25 and ENR 50 mixes prepared from the K2A mixer are shown in *Tables 3* and *4*, respectively. These data suggested that the variation of the raw rubber viscosities of both ENR 25 and ENR 50 from 56 to 85 did not cause any significant variation in the vulcanisate properties.

Mill-sticking Behaviour

There are various factors affecting the mill-sticking behaviour of ENR, particularly

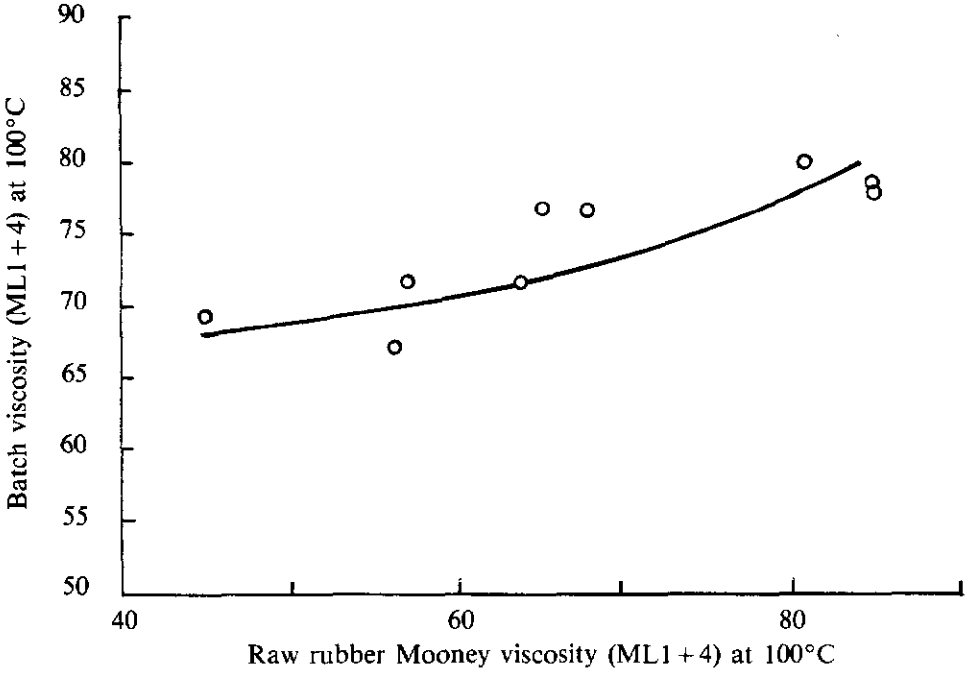

Figure 5. Effect of raw rubber Mooney viscosity on viscosity of ENR 25 batches prepared from K2A mixer. Batches prepared using Formulation 1 *of* Table 1.

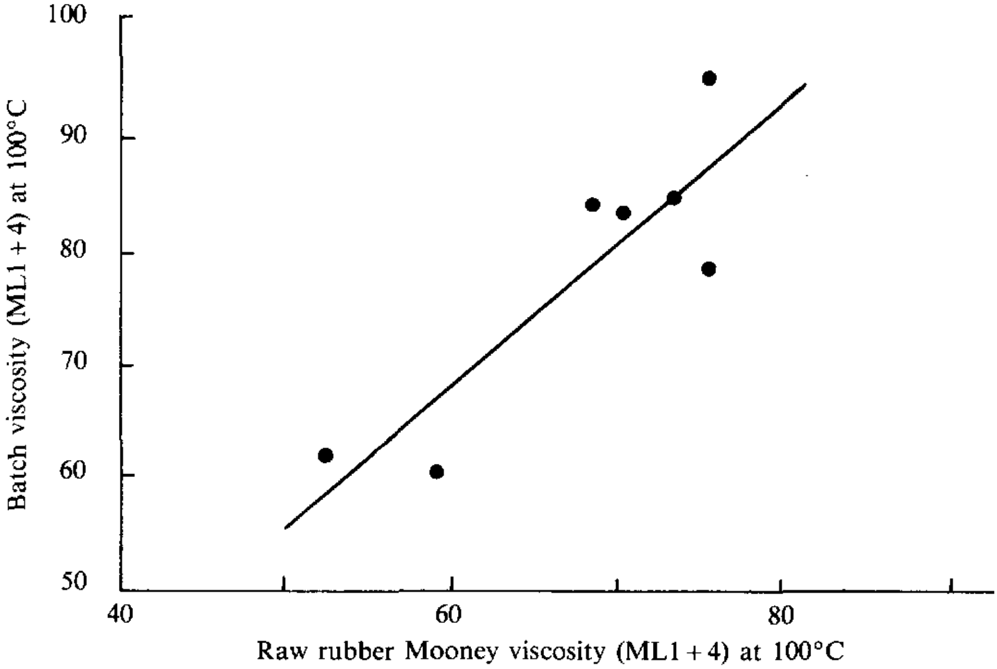

Figure 6. Effect of raw rubber Mooney viscosity on viscosity of ENR 50 batches prepared from K2A mixer. Batches prepared using Formulation 2 *of* Table 1.

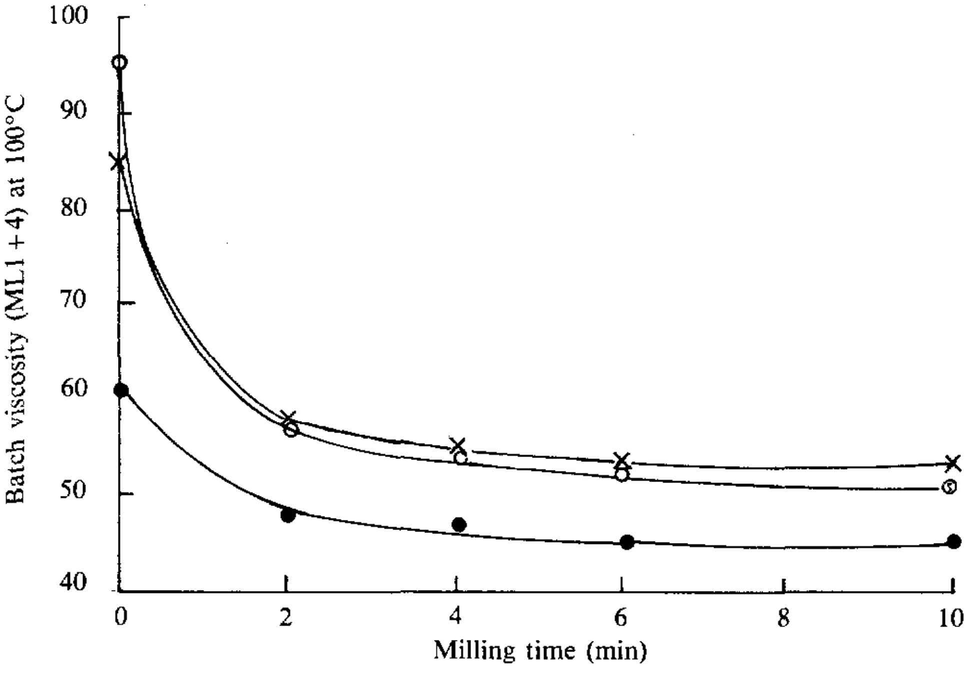

Figure 7. Effect of milling on batch viscosity of ENR 50. Batches prepared using Formulation 2 *of* Table 1.

TABLE 3. VULCANISATE PROPERTIES OF ENR 25[a]

Property	Sample 1	2	3	4	5
Raw rubber viscosity ML1 + 4 at 100°C	85	85	65	64	56
Power consumption (kwh/kg)	0.20	0.20	0.21	0.21	0.21
Dump temperature (°C)	152	156	159	153	161
Mooney scorch at 120°C (min)	31	35	38	34	31
Tensile strength (MPa)	27.2	27.2	27.2	27.0	27.0
Elongation at break (%)	510	495	505	500	495
M100 (MPa)	3.3	3.2	3.3	3.0	3.0
M300 (MPa)	14.6	14.7	15.2	14.6	15.0
Rebound resilence (%)	46	46	46	47	45
IRHD	71	69	70	70	70
Trouser tear (N/mm)	16	26	23	17	13
Compression set, 1 day/70°C (%)	27	24	25	24	24

[a] Formulation used — ENR 25 100, ISAF carbon black 50, Dutrex 737MB 5, zinc oxide 5, stearic acid 2, Santoflex 13 2, sulphur 1.5, MOR 1.5, PVI 0.2

TABLE 4. VULCANISATE PROPERTIES OF ENR 50[a]

Property	Sample 1	2	3	4	5	6
Raw rubber viscosity ML1 + 4 at 100°C	76	76	74	71	69	59
Power consumption (kwh/kg)	*0.21*	*0.18*	*0.21*	*0.17*	*0.20*	*0.20*
Dump temperature (°C)	156	149	158	150	160	156
Mooney scorch at 120°C (min)	38	33	30	32	30	31
Tensile strength (MPa)	26.2	23.9	24.6	25.3	25.1	24.6
Elongation at break (%)	485	455	480	490	470	490
M100 (MPa)	3.4	3.5	3.7	3.4	3.4	3.3
M300 (MPa)	15.2	14.9	15.4	14.9	15.2	14.8
Rebound resilence (%)	24	21	22	24	22	23
IRHD	75	78	74	77	75	75
Trouser tear (N/mm)	23	26	25	22	22	24
Compression set, 1 day/70°C (%)	29	31	33	31	32	34

[a] Formulation used — ENR 50 100, ISAF carbon black 50, Dutrex 737MB 5, zinc oxide 5, stearic acid 2, Santoflex 13 2, sulphur 1.5, MOR 1.5, PVI 0.2

ENR 50. Besides, Mooney viscosity, temperature and cohesive strength within the rubber itself[12], the gel content of the rubber is equally important. The presence of gel in the rubber enhances the cohesive strength of the rubber.

A Mooney viscosity-mill temperature relationship at which the rubber starts to stick on the roll for the new ENR 50 is shown in *Figure 8.* The data shown in this figure differ slightly from the original data[12]. The differences in the gel contents could account for such differences. The new ENR 50 as shown in the earlier data *(Figure 2)* gave a fast breakdown characteristic on the two-roll mill and this can result in a mill-sticking tendency if the temperature is not properly controlled.

Figure 8 shows that at any given Mooney viscosity, the mill-sticking tendency of ENR 50 increases with increasing mill temperature. This behaviour may be explained by the fact that by increasing the mill temperature the cohesive strength of the rubber itself decreases while the adhesive strength between the rubber and the surface of the roll increases. Thus, in avoiding the mill-sticking, the ENR 50 needs to be designed in a manner whereby the cohesive strength is greater than the adhesive strength at the given mill temperature.

One of the recommended methods to reduce the adhesive strength between rubber and metal surfaces during processing is to employ stearic acid. Stearic acid reduces the coefficient of friction between the rubber and the metal surfaces. We have observed that by incorporating stearic acid into the new ENR 50, even up to a level of 8 p.h.r., the mill-sticking of the rubber was not completely avoided. Although the adhesive strength was reduced in this case, the cohesive strength of the new ENR 50 was still insufficient to pull the rubber away from the metal surface.

In searching for an improvement in the cohesive strength of the new ENR 50, we looked into a possibility of introducing sulphur linkages since a reaction between the rubber and sulphur alone can occur rapidly and

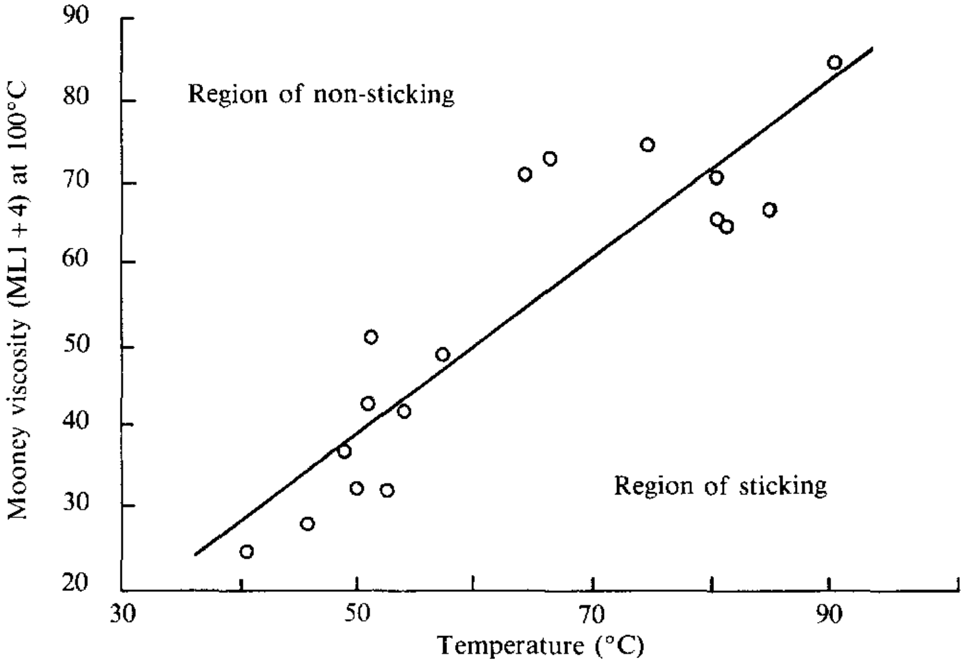

Figure 8. Mill-sticking behaviour of raw ENR 50.

efficiently[1,10]. The effects of variation in sulphur concentration on cure characteristics and torque values are shown in *Figure 9* and *Table 5*, respectively. These data illustrate the effectiveness of preparing lightly crosslinked ENR 50 by incorporating a small amount of sulphur in the absence of organic accelerator. Both the sulphur content and temperature were shown to be critical in controlling the gel of the rubber as indicated by the rise in torque values.

TABLE 5. INCREASE IN TORQUE VALUES OF ENR 50[a] MIXES AFTER 5 MIN AT VARIOUS CURE TEMPERATURES

Concentration of sulphur (p.h.r.)	Cure temperature (°C)			
	150	160	170	180
0	0	0	0	0.1
0.10	0.1	0.4	0.9	1.2
0.15	0	0.5	1.1	1.8
0.20	0.3	0.8	2.0	2.7
0.25	0.3	1.0	2.5	2.8

[a] Formulation used — ENR 50 100, ISAF carbon black 50, Dutrex 737MB 5, zinc oxide 5, stearic acid 2, Permanax TQ 1, sulphur variable

In order to incorporate this vulcanisation process in normal processing practices, sulphur needs to be introduced into the rubber during high temperature mixing in the internal mixer. The preformed gel after the internal mixing enhances the cohesive strength of the rubber and consequently prevents sticking during the subsequent milling process. In this way, the reinforcing filler can be easily incorporated and dispersed in the rubber matrix before the formation of gel.

To obtain an indication of the increase in Mooney viscosity that is unlikely to occur after

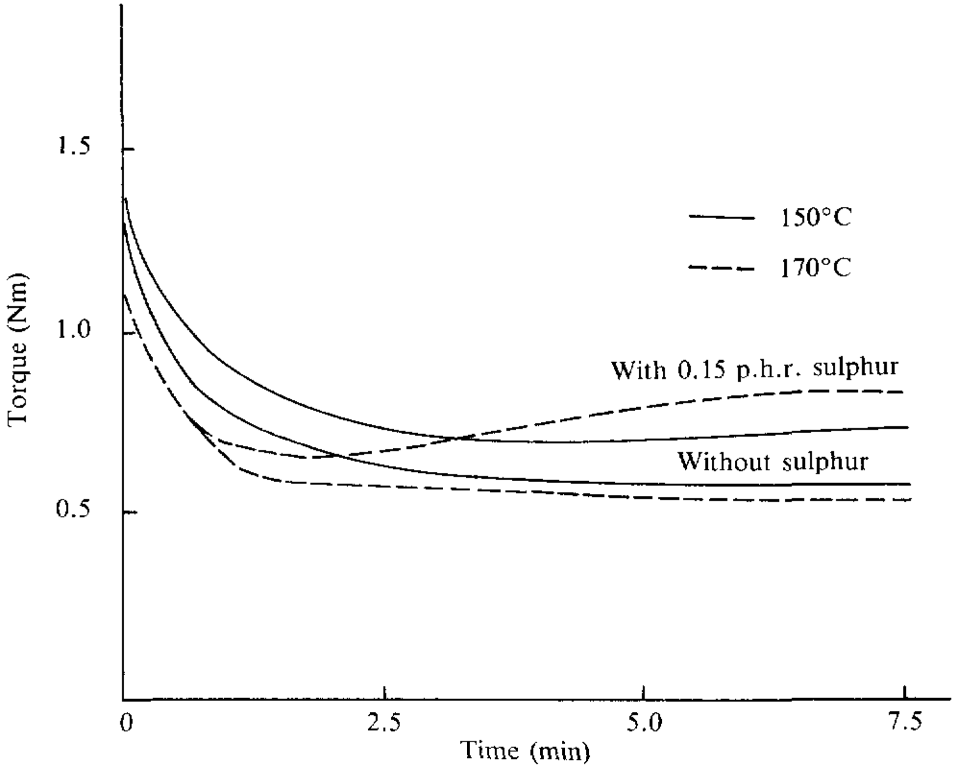

Figure 9. Cure characteristics at different temperatures. Formulation used: ENR 50 100, ISAF black 50, Dutrex 737MB 5, zinc oxide 5, stearic acid 2, Permanax TQ 1.

the process of internal mixing, samples with various concentrations of sulphur were cured for 5 min at temperatures ranging from 150°C to 180°C. *Figure 10* shows that increasing the sulphur level at a given temperature increased the Mooney viscosity. It is therefore preferable, when mixing ENR 50 in the internal mixer, to choose the lowest level of sulphur possible in order to prevent excessive increase in Mooney viscosity for easier processing in subsequent operations. A sharp increase in the Mooney viscosity also occurred when increasing the temperature from 150°C to 170°C but at 180°C the Mooney viscosity was not much different from that at 170°C.

The actual increase in Mooney viscosity after mixing ENR 50 in the internal mixer is shown in *Table 6*. In this particular experimental design, the concentrations of sulphur and stearic acid and the dump temperature were varied. Stearic acid was included in the formulation as a release aid for prevention of mill-sticking and more importantly, to minimise the usage of sulphur. With the lowest concentration of sulphur (*i.e.* 0.1 p.h.r.), the normal level of stearic acid (*i.e.* 2 p.h.r.) was shown to be insufficient to prevent mill-sticking even with a high dump temperature. With a higher level of stearic acid (*i.e.* 3 p.h.r.), the mill-sticking can be avoided. However, the preferred formulation from the data available would be the one based on 0.1 p.h.r. sulphur and 4 p.h.r. stearic acid since a wide range of dump temperature is applicable.

The effect of milling of some selected masterbatches prepared at various dump temperatures on the Mooney viscosity is shown in *Figure 11*. Although the initial batch Mooney viscosity differed significantly with dump temperature, the difference was minimised on milling for about 5 min. This fast breakdown of initially high batch Mooney viscosity provides easier

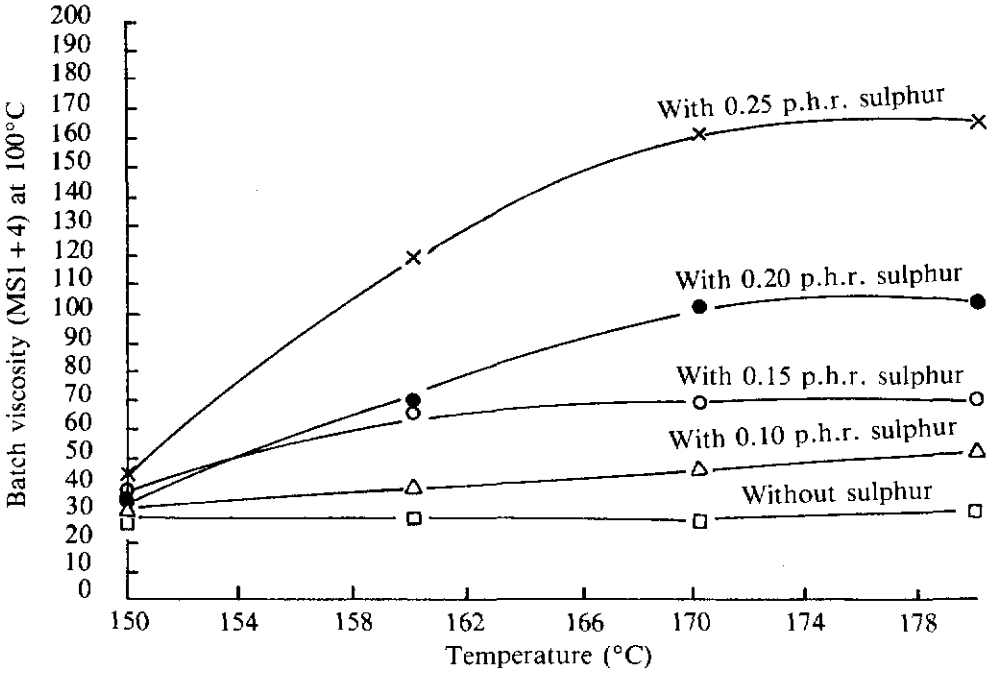

Figure 10. Effect of temperature on batch viscosity (batch viscosity taken after 5 min curing). Formulation used: ENR 50 100, ISAF black 50, Dutrex 737MB 5, zinc oxide 5, stearic acid 2, Permanax TQ 1.

TABLE 6. EFFECT OF SULPHUR, STEARIC ACID AND DUMP TEMPERATURE ON MILL STICKING BEHAVIOUR OF ENR 50[a]

Sulphur (p.h.r.)	Stearic acid *(p.h.r.)*	Dump temp. *(°C)*	Initial batch *viscosity*[b]	Final batch *viscosity*[c]	Mill-sticking *tendency*[d]
0	2	165	35.0	—	1
0.10	2	173	82.0	—	1
0.10	3	151	50.0	—	1
0.10	3	171	73.0	35.5	2
0.10	4	155	47.5	34.0	2
0.10	4	173	75.0	36.5	2
0.10	4	180	86.0	36.5	2
0.10	5	150	52.0	28.0	2
0.15	2	185	95.0	—	1
0.15	4	158	59.0	32.0	2
0.15	4	171	75.0	32.0	2
0.15	4	178	77.0	34.5	2
0.20	2	168	119.0	—	1
0.20	4	161	78.5	38.5	2
0.20	4	172	115.0	36.0	2
0.20	5	158	74.0	31.5	2

[a] Formulation used was based on *Formulation 3* of *Table 1*.

[b] *Batch viscosity (MS 1+4) at 100°C after mixing in the internal mixer.*

[c] Batch viscosity (MS 1+4) at 100°C after 15 min of milling on the two-roll mill with initial temperature of 75°C.

[d] 1. Adhered to the rolls.
2. No mill-sticking observed.

processing in the subsequent operations such as addition of curatives and accelerators.

Figure 12 shows the relationship between Mooney viscosities based on a large rotor and those based on a small rotor. These data are provided for the purpose of conversion as the processability parameter is normally quoted in terms of measurements based on a large rotor.

CONCLUSIONS

Both ENR 25 and ENR 50 produced from the new production technique have been demonstrated to give very satisfactory processing behaviour in large internal mixers. The mill-sticking problem associated with ENR 50 during high temperature mixing can now be avoided by incorporating a small amount of sulphur and a slightly higher level of stearic acid. However, this investigation was carried on small laboratory mills and the results may not be related to commercial operations.

ACKNOWLEDGEMENTS

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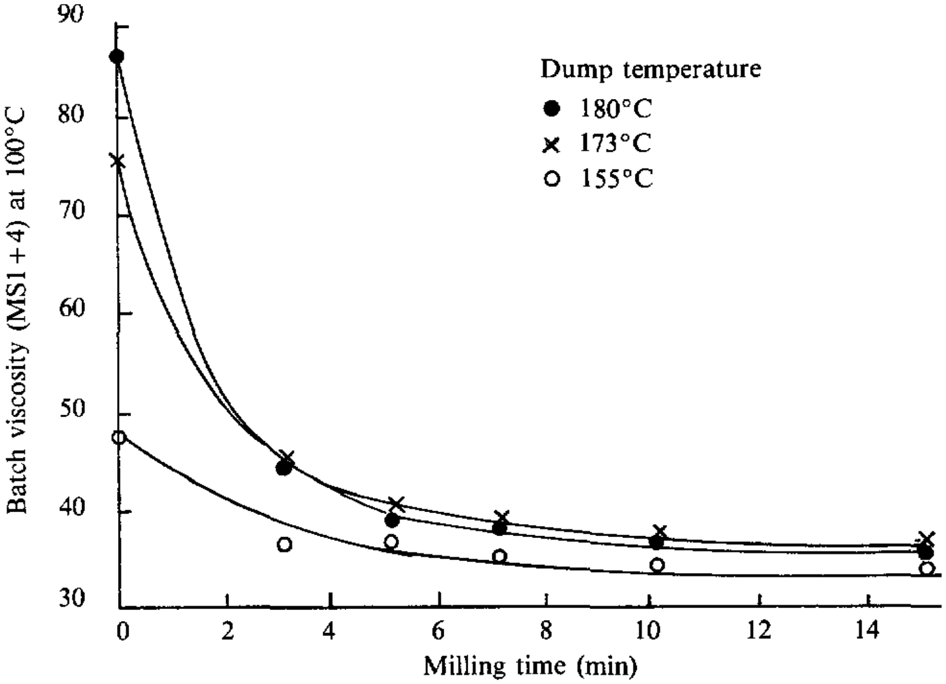

Figure 11. Effect of milling on batch viscosity (batches were obtained at various dump temperatures). Formulation used: ENR 50 100, ISAF black 50, Dutrex 737MB 5, zinc oxide 5, stearic acid 4, Permanax TQ 1, sulphur 0.1.

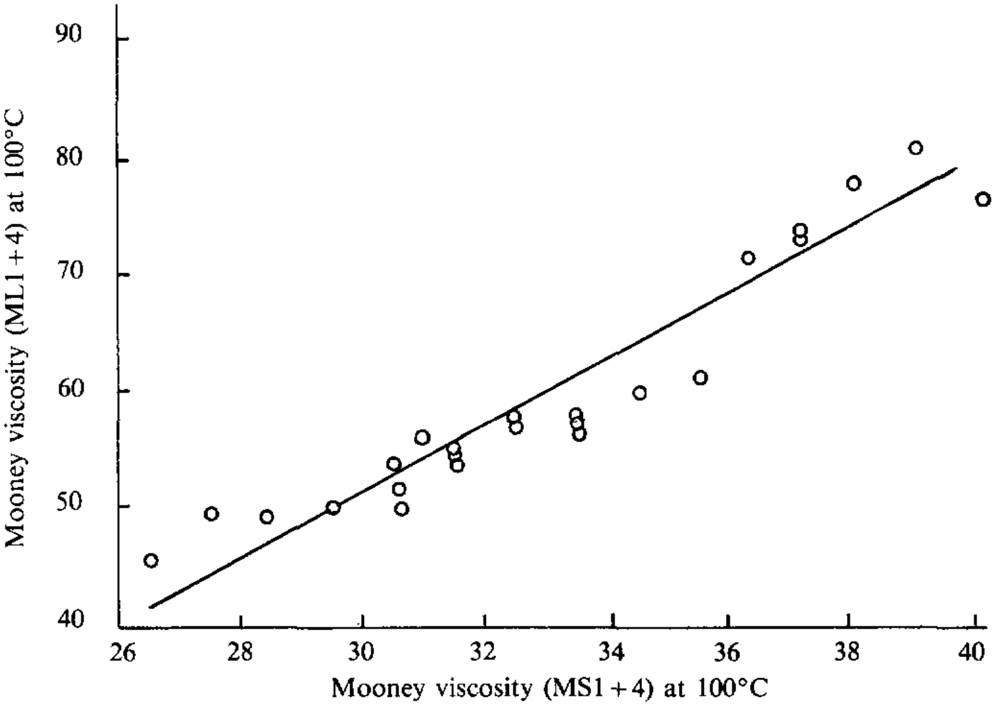

Figure 12. Relationship between (MS1 + 4) and (ML1 + 4).

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