

Effect of Production Procedures on Properties of PA 80 Rubber

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The occurrence of abnormal properties in some samples of PA 80 rubber has been investigated. Certain production practices have been shown to cause these abnormalities. The mechanisms proposed to explain the abnormalities include a 'second vulcanisation' reaction not observed previously. Methods of overcoming these problems to ensure more acceptable rubbers are described.

Preparation of crepe rubber containing a proportion of vulcanised rubber has already been described (RUBBER RESEARCH INSTITUTE OF MALAYA, 1955) and the product has been named 'Superior Processing Rubber' (or SP Rubber). This rubber is prepared from a latex blend of which 20% by weight is vulcanised. Commercial production of SP crepe commenced in 1955, followed by production of smoked sheet and air dried SP rubbers. SP brown crepe introduced in 1959 gave the consumer a lower grade rubber with superior processing properties. The need for a SP masterbatch soon became apparent, leading to the preparation of Processing Aid 80 (SEKHAR AND DRAKE, 1958; BAKER, 1960; RUBBER RESEARCH INSTITUTE OF MALAYA, 1960). This rubber is prepared from a latex blend comprising 80% vulcanised and 20% unvulcanised latex. PA 80 can be used by the consumer in blends with the desired grade of natural or synthetic rubber to give the required superior processing properties. An oil-extended form of PA 80 rubber is available and is termed PA 57 rubber (O'CONNELL *et al.*, 1965). The technological advantages of SP, PA 80 and PA 57 rubbers have been described (BAKER AND FODEN, 1959; BAKER AND STOKES, 1961; NATURAL RUBBER PRODUCERS' RESEARCH ASSOCIATION, 1965); SP rubber and PA 80 have, in particular, been established as unique technological aids in processing natural and synthetic rubber, especially in applications involving extrusion and calendering of rubber

compounds. In both cases superior processing is observed; for example, a compounded rubber stock containing PA 80 extrudes faster

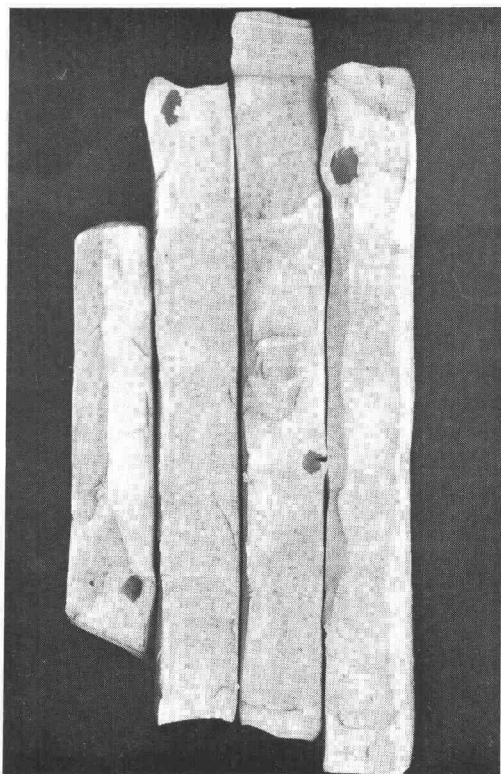


Figure 1. Sample of rubber stock containing undispersed lumps of PA 80.

with better shape retention or less collapse and a better surface finish than a compound without PA 80. Examples of finished products using SP rubbers are extruded seals and surgical items where close dimensional tolerances are required.

As SP and PA rubbers contain vulcanised material, they are stiffer (*i.e.*, their Mooney viscosity is higher) than ordinary raw rubber. This is especially true of PA 80 because of the 80% content of vulcanised rubber. In order to obtain a good blend of PA 80 with raw rubbers, it is usually necessary to pre-masticate on a mill or in an internal mixer, to reduce its viscosity to a level closer to that of ordinary rubber. Failure to pre-masticate will give a heterogeneous blend sometimes with discrete

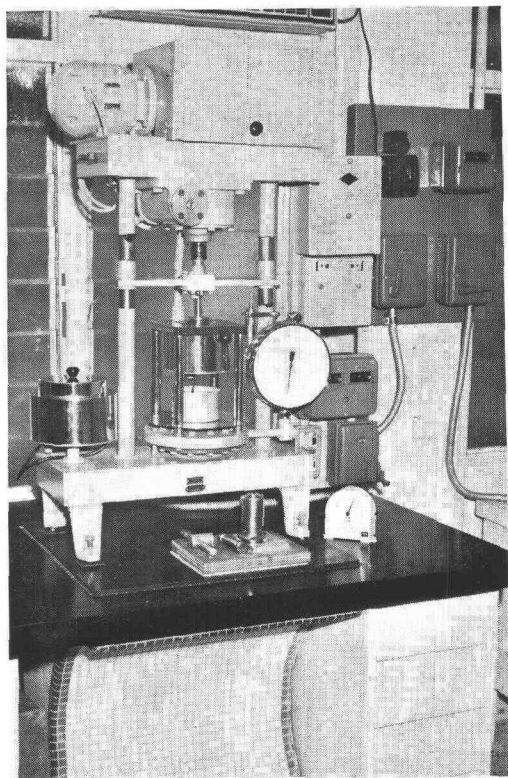


Figure 2. The Macklow-Smith R33 Extrusion Plastometer used to test for extrusion swell and extrudate characteristics.

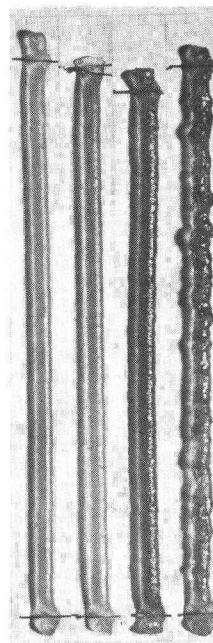


Figure 3. Examples of excellent (far left), moderate, poor, and very bad extrudates from stocks containing PA 80 rubber.

visible particles of undispersed PA 80. If this mix is extruded, a poor surface finish is obtained.

Recently, an increasing number of complaints had been received from consumers in the manufacturing sector about the poor dispersibility of PA 80. In some cases, this was due to lack of experience with the new material and failure to pre-masticate it sufficiently. However, regular batches of this rubber gave dispersion trouble which could not be solved merely by increasing the pre-mastication. An example of this is shown in *Figure 1* where PA 80 has been used in the preparation of a white rubber stock. The lumps of undispersed PA 80 are clearly seen. In rare instances, a batch of PA 80 has resisted mastication in an internal mixer and has come out as a powder. It is important to realise that these batches had already met the existing specification limits and were apparently normal.

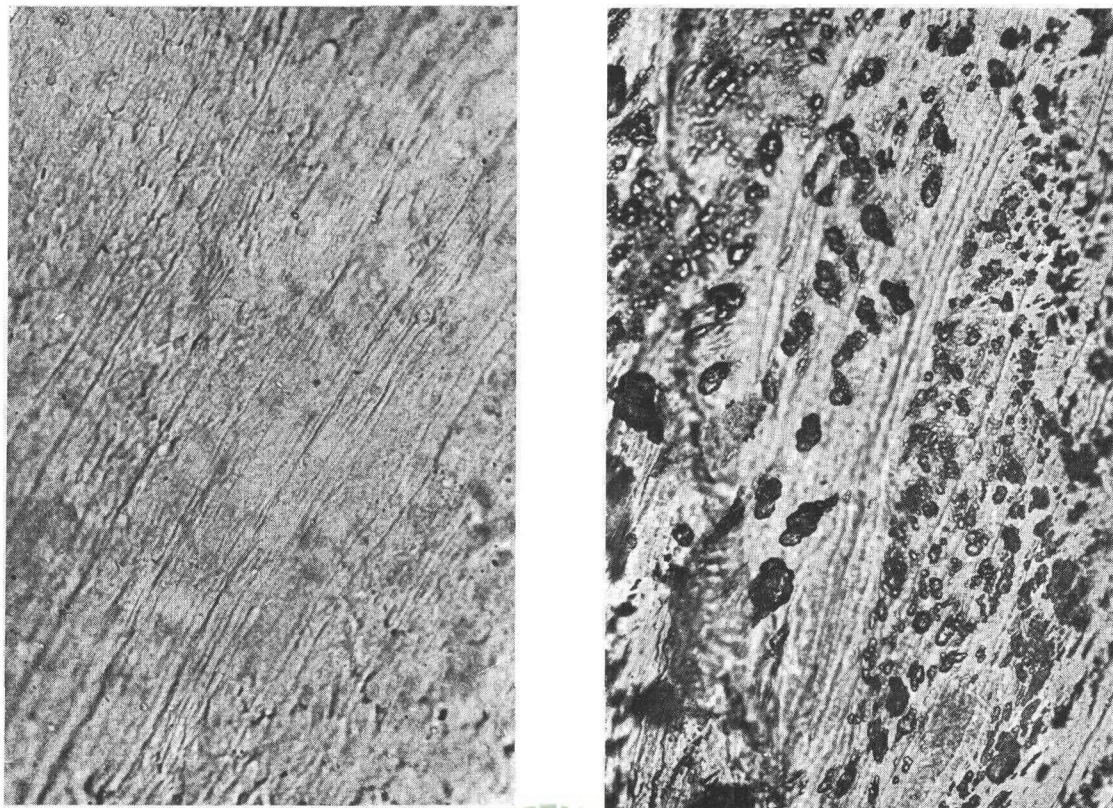


Figure 4. Optical micrographs of cross-sections of stocks containing PA 80 samples of good (left) and bad dispersion characteristics.

In such cases, the stock must be rejected as unusable, and a complaint about the quality of PA 80 and claims for compensation made. Repeated complaints will cause a manufacturer to discard the use of SP rubbers generally, and the reputation of producers will suffer.

This study was undertaken to investigate the occurrence, causes and control of dispersibility problems in PA 80. Preliminary information containing practical advice to producers of SP rubber has been published (RUBBER RESEARCH INSTITUTE OF MALAYA, 1967).

METHODS

Recommended procedures for the preparation of SP and PA rubbers (RUBBER RESEARCH INSTITUTE OF MALAYA, 1960) are:

- (1) The components of the vulcanising system are ball-milled with a dispersing agent to give a fine water-based dispersion.
- (2) The field latex of known rubber content is ammoniated to about 0.3% and charged into the reaction tank to give the required weight of rubber.
- (3) The correct quantity of vulcanising dispersion is added with stirring. The compounded latex is then heated by live steam injection with gentle stirring to a temperature of 80°C, and maintained at this temperature for about 2 hours.
- (4) When the vulcanisation reaction is completed, the latex is allowed to cool. Vulcanisation is regarded as complete when a

TABLE 1. TEST RESULTS FOR ALL PA 80 SAMPLES SUBMITTED TO R.R.I.M. SPECIFICATIONS SECTION IN 1966

Source	Estate A	Estate B	Estate C	Estate D	Estate E
Mooney viscosity—small rotor					
Range	54–212	55–225	54–82	50–65	49–104
Mean	76	63	64	57	60
Total number of samples	292	108	117	49	159
No. of samples with Mooney viscosity greater than 100	36	1	0	0	1
No. of samples with Mooney viscosity 80 to 100	6	1	1	0	0
Extrusion die swell, %					
Range	5.4–10.1	5.5–10.1	4.5–9.8	6.0–9.3	5.0–9.9
Mean	8.2	8.5	6.9	7.2	6.7
Mean scorch, min	8.7	9.7	8.4	8.7	8.5
Total sulphur, %					
Range	1.03–1.78	1.15–1.86	1.10–1.89	1.40–1.73	1.06–1.82
Mean	1.45	1.45	1.52	1.60	1.51
Free sulphur, %					
Range	1.05–0.82	0.30–0.83	0.17–0.49	0.40–0.64	0.17–0.55
Mean	0.46	0.58	0.33	0.53	0.28
Proportion of free to total sulphur, %	31.9	40.2	21.4	32.9	18.4

TABLE 2. PROPERTIES OF PA 80 SAMPLES

PA 80 sample number	Mooney viscosity	Die swell on extrusion %	Mooney scorch, min	Extrudate	
				Appearance	Number
10	75	3.8	10.5	Excellent	24
11	78	3.2	9.8	Poor	25
12	65	4.5	9.1	Very bad	26
13	106	4.6	8.3	"	27
14	87	4.2	8.8	"	28

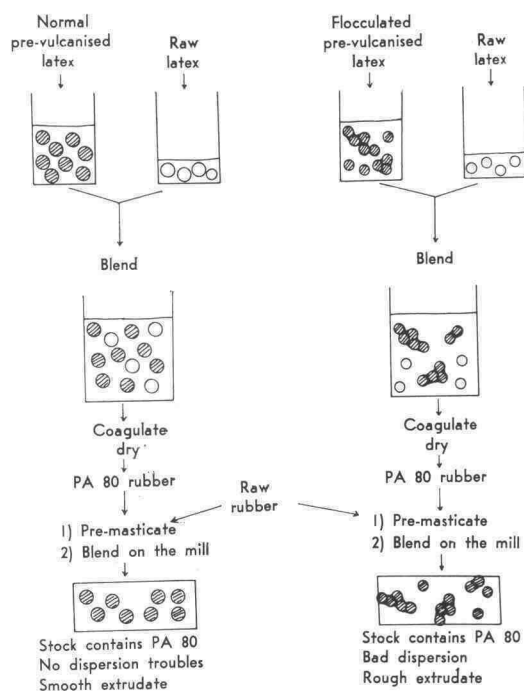


Figure 5. Diagrammatic representation of the formation of PA 80 with bad dispersion characteristics using flocculated pre-vulcanised latex.

small latex sample coagulated with acid has a powdery appearance.

(5) The pre-vulcanised latex is diluted to 20% total solids content, and the appropriate amount added to the raw latex with stirring.

(6) The latex blend is coagulated with 5% sulphuric acid, and the coagulum washed, machined and dried.

(7) The dry rubber is then pressed and packed as 70 or 100 lb bales.

The vulcanisation system has the following components in proportions based on 100 parts by weight of rubber:

	parts by weight dry
Sulphur	2.00
Zinc oxide	0.75
Zinc diethyl-	
dithiocarbamate	0.20
Mercaptobenzthiazole	0.40

In the preparation of the vulcanising dispersion, a suitable dispersing agent must be added.

The above procedures formed the basis of the preparation of experimental samples of PA 80 rubber. Variations in the procedure were introduced in certain instances as indicated elsewhere in this paper.

The samples of PA 80 were tested according to the standard methods used by the Specifications Section of the Rubber Research Institute of Malaya for testing commercial production. British Standard 903.1956, and A.S.T.M. D927-55T and D1077-55T methods were adopted for additional tests.

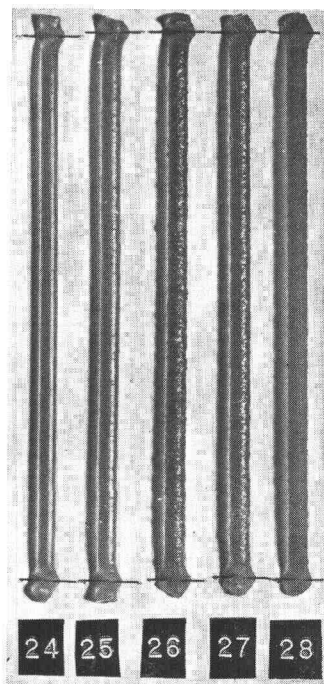


Figure 6. Extrudates from stocks containing samples of PA 80 prepared from flocculated pre-vulcanised latex.

TABLE 3. EFFECT OF STORAGE CONDITIONS ON PROPERTIES OF PA 80

Sample	Ageing	Mooney viscosity	Extrusion swell %	Mooney scorch @ 120°C, min	Free sulphur %	Total sulphur %	Free/total sulphur %	Extrudate	
								Appearance	Number*
PA 80/1	Unaged	59	8.9	8.5	0.27	1.59	17.1	Excellent	382
PA 80/11	"	61	11.0	7.1	0.42	1.81	23.3	"	407
PA 80/commercial	"	57	11.0	7.9	0.69	1.42	48.7	"	433
PA 80/1	24 days†	66	14.2	7.8	0.29	1.51	19.4	Moderate	408
PA 80/11	"	79	12.2	7.8	0.37	1.87	20.1	"	431
PA 80/commercial	"	67	11.8	8.3	0.74	1.48	50.2	"	420
PA 80/1	66 days†	78	11.6	7.4	0.27	1.55	17.3	Moderate	453
PA 80/11	"	96	11.7	8.3	0.44	1.78	24.6	"	475
PA 80/commercial	"	73	12.8	10.0	0.29	1.55	18.6	"	449
PA 80/1	91 days†	77	10.2	8.0	0.26	1.60	16.0	Moderate	484
PA 80/11	"	99	10.5	6.9	0.80	2.46	32.3	Poor	486
PA 80/commercial	"	79	11.1	8.6	0.58	1.53	37.7	Moderate	483
PA 80/1	180 days†	87	11.2	10.0	0.23	1.60	14.4	Moderate	504
PA 80/11	"	99	12.4	9.1	0.16	1.73	9.5	"	506
PA 80/commercial	"	86	12.3	11.0	0.53	1.40	38.2	"	502
PA 80/1	24 days‡	84	12.5	8.5	0.29	1.53	18.9	Poor	411
PA 80/11	"	82	11.9	8.1	0.41	1.83	22.7	"	432
PA 80/commercial	"	84	12.4	8.3	0.72	1.47	49.1	"	421
PA 80/1	66 days‡	63	13.8	8.5	0.26	1.47	17.7	Very bad	452
PA 80/11	"	70	13.9	8.3	0.40	1.79	22.4	"	476
PA 80/commercial	"	65	17.9	8.8	0.57	1.46	40.2	"	448
PA 80/1	91 days‡	68	14.0	9.1	0.26	1.52	17.1	Very bad	494
PA 80/11	"	72	12.0	8.1	0.39	1.94	20.0	"	496
PA 80/commercial	"	70	16.6	9.2	0.36	1.14	31.5	"	492
PA 80/1	180 days‡	62	13.9	10.2	0.07	1.51	5.0	Very bad	514
PA 80/11	"	70	16.4	9.7	0.16	1.47	11.2	"	516
PA 80/commercial	"	63	15.9	10.8	0.21	1.23	16.8	"	512

† At 40°C

‡ At 60°C

* See Figure 7

TABLE 4. BEHAVIOUR OF A COMMERCIAL SAMPLE OF PA 80 AFTER STORAGE AT 70 AND 100°C

Storage conditions	Mooney viscosity	Extrusion swell %	Scorch min	Total sulphur %	Free sulphur %	Proportion of free to total sulphur, %	Extrudate	
							Dispersibility	Number*
Unaged	57	11.0	7.9	1.42	0.69	47.7	Excellent	433
4 days at 70°C	75	11.2	9.3	1.41	0.77	54.8	"	388
7 days at 70°C	77	11.6	8.8	1.37	0.58	42.5	"	389
15 days at 70°C	82	11.8	9.0	1.33	0.47	35.3	Moderate	394
1 day at 100°C	69	14.2	9.0	1.44	0.75	52.0	Poor	390
2 days at 100°C	60	20.6	9.8	1.38	0.69	50.0	"	391
5 days at 100°C	48	12.8	9.8	1.34	0.13	9.5	Very bad	392
7 days at 100°C	44	9.3	11.0	1.37	0.05	3.9	"	393

* See Figure 8

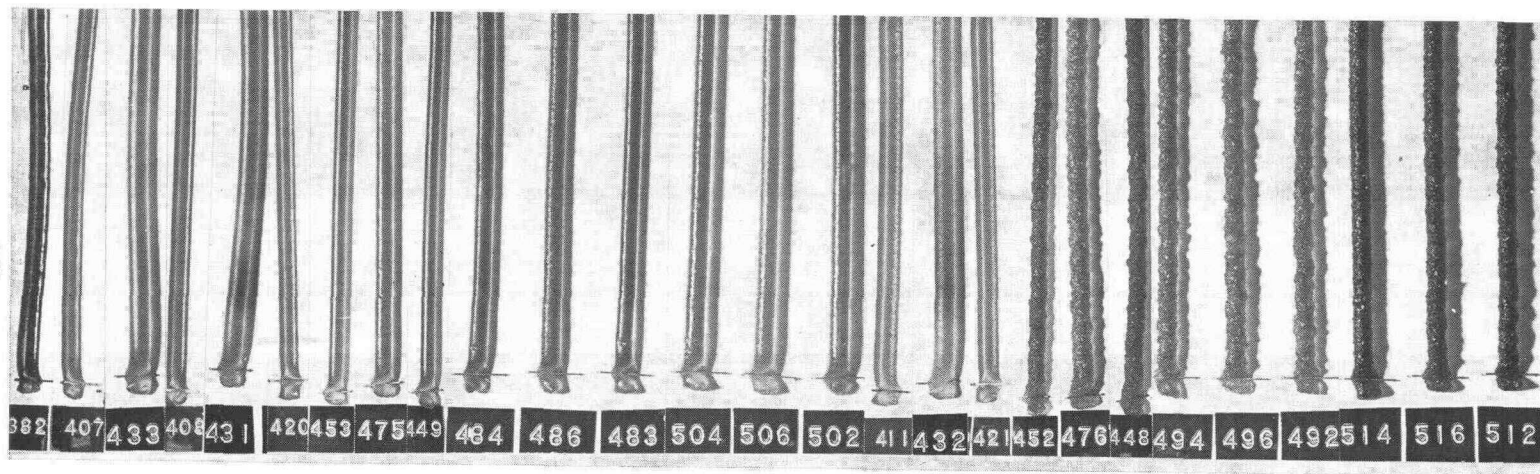


Figure 7. Extrudates from stocks containing PA 80 samples aged at 40° and 60°C.

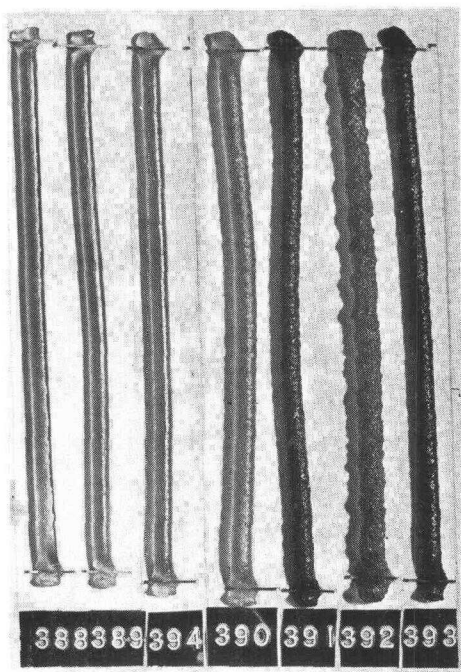


Figure 8. Extrudates from stocks containing PA 80 samples aged at 70° and 100°C.

Scorch and extrusion swell were measured using the following compound:

	Parts by weight
PA 80	25
RSS 1	75
HAF black (Philblack 0)	50
Zinc oxide	5
Stearic acid	4
Sulphur	2.5
Pine tar	3
Cyclohexyl-benzthiazyl sulphenamide (CBS)	0.6

The extrusion swell was measured as described (SEKHAR AND NIELSEN, 1961).

A new method for the determination of extrusion swell using the Macklow-Smith R33 Extrusion Plastometer (Figure 2) was used in later experiments (TEO, 1966). The maximum upper limit in this method is 12.7% as compared to 10.4% in the original test method. A die swell of about 20% is obtained if no PA 80 is used.

A simple test for dispersibility was used. A 6" × 12" laboratory mill on a friction setting of 1 : 1.2, with rolls at 100°C and nip at 0.02 inch, was used to masticate 112.5 g of RSS1 rubber for four passes and 3 minutes banding. A charge of 37.5 g of PA 80 was given four passes and banded for 2 minutes. The two masticated rubbers were blended by placing together, passing ten times through the mill and sheeting out. A 20 g sample of the sheet was weighed and placed in the Macklow-Smith Plastometer. After an initial period of 4 minutes at 100°C, the sample was extruded through a 0.1 inch circular die into dilute Teepol solution. The extrudate was extracted, dried and mounted on white board.

Dispersibility was then assessed by visual examination of the surface of the extrudate and rated as: 1. excellent; 2. moderate; 3. poor; and 4. very bad. Illustrations of these conditions are given in Figure 3.

In general, ratings of 1 and 2 were considered commercially acceptable, while 3 and 4 were counted as rejections.

Although this test appears to be subjective, it adequately shows up differences in dispersibility between good and bad samples.

Prior experimentation showed that the dispersibility test as described here clearly distinguished between samples of PA 80 which required slightly extra pre-mastication to give satisfactory blending and samples which gave inherently poor dispersibility, however much pre-masticated.

RESULTS AND DISCUSSIONS

Occurrence of Abnormal PA 80

Table 1 contains data for all samples of PA 80 passed by the Institute's Specifications Section during 1966, on the basis of specification limits then existing.

Examination of the data indicates that extrusion die swell and scorch figures fall within reasonable limits, while extreme variation is noticed for the Mooney viscosity (then not subject to specification limits). The viscosity varies from 49 minimum to 225 maximum with an overall mean value of 64. Although only 6% of the total samples had Mooney

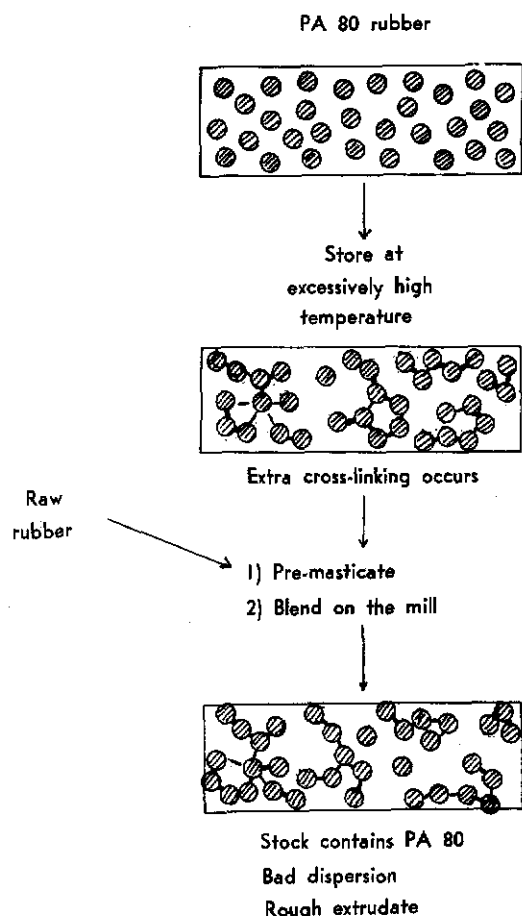


Figure 9. Diagrammatic representation of the effect of severe high temperature ageing on the dispersibility of PA 80 rubber.

viscosities of greater than 80, there were 14% of such samples in Estate A.

A further point to note is the comparatively high proportion of free to total sulphur, indicating an inefficient vulcanisation reaction. There appears to be no correlation between the amount and proportion of free to total sulphur, and the scorch and die swell behaviour.

An investigation into the complaints from buyers and consumers showed clearly that those samples of PA 80 rubber with high Mooney viscosity were extremely difficult or impossible to disperse satisfactorily in raw rubber. It was evident that dispersibility became unacceptable when the Mooney viscosity was between 80 and 100. No established complaints about dispersibility were received when the viscosity was less than 80.

Optical examination of rubber stock containing badly dispersed PA 80 revealed small pieces of this rubber imbedded in the softer matrix. Microscopic studies of sectioned and stained samples of rubber stock containing good and bad PA 80 are shown in Figure 4. The dark patches that are visible correspond to undispersed PA 80. Where blending is satisfactory, the particles of PA 80 are too small and well distributed to be seen.

Causes of Abnormal PA 80

1. *State of the pre-vulcanised latex.* Possible causes of dispersibility trouble using PA 80 were considered. It was shown that bad dispersion was associated with unhomogeneously distributed vulcanised rubber particles.

TABLE 5. EFFECT OF MIXING CONDITIONS ON THE PROPERTIES OF PA 80

Mixing conditions	Coagulation temperature °C	Mooney viscosity	Extrusion swell %	Proportion of free to total sulphur %	Dispersibility
Blend at 80°C, cool immediately and coagulate	30	69	7.6	14.0	Good
Blend at 80°C, for $\frac{1}{2}$ h, with slow cooling and coagulate	77	86	7.5	16.0	Moderate
Blend at 80°C, for 1 h, with slow cooling and coagulate	75	133	7.2	18.0	Poor
Blend at 80°C, for 2 h, with slow cooling and coagulate	68	149	7.2	17.0	Very bad

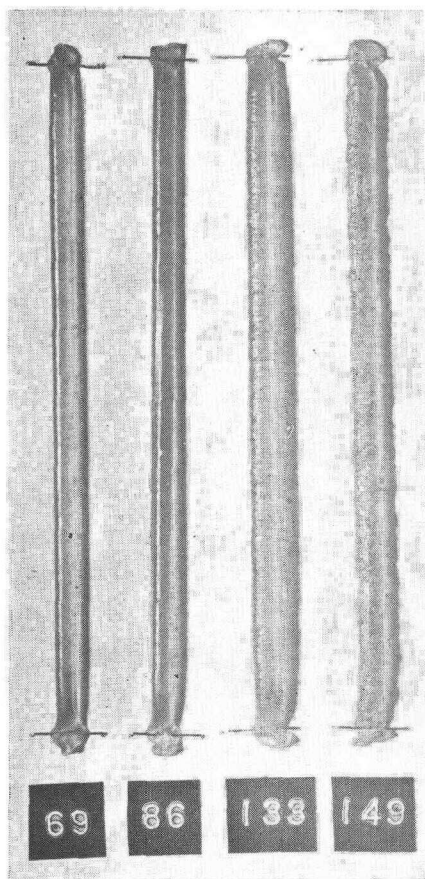


Figure 10. Extrudates from stocks containing PA 80 samples prepared using different conditions of blending pre-vulcanised and raw latices. (Values of Raw Mooney are shown in Arabic numerals under each extrudate sample).

This may be due to either *all* the PA 80 itself being hard to disperse, or to unhomogeneity *within* the PA 80 which would be carried through into the rubber stock. The latter case will be discussed first.

Unhomogeneity within PA 80 can be caused by failure to blend the pre-vulcanised latex with the raw latex. If the pre-vulcanised latex is in its normal colloidal state, normal blending procedures can ensure the attainment of homogeneity. However, if the pre-vulcanised latex is destabilised to a flocculated state or contains solid lumps of coagulum, mixing with the raw

latex cannot give proper dispersion of the vulcanised particles. This is illustrated in Figure 5 and in the following experiment.

Samples of pre-vulcanised latex were prepared using diluted high ammonia latex concentrate. One sample (latex A), on heating, badly flocculated to a semi-solid, while the other was protected by non-ionic surface active agents and retained its fluidity and stability. Both latices were vulcanised at 80°C for 2 hours. Samples of PA 80 were prepared using both the fluid latex (B) and the flocculated latex (A):

PA 80/10 from strained latex B;

PA 80/11 from latices B and A using 2 : 1 ratio by weight;

PA 80/12 from latices B and A using 1 : 1 ratio by weight;

PA 80/13 from latices B and A using 1 : 2 ratio by weight; and

PA 80/14 from latex A.

The properties of these rubbers and specimens of the extrudates from the dispersion test are given in Table 2 and Figure 6 respectively.

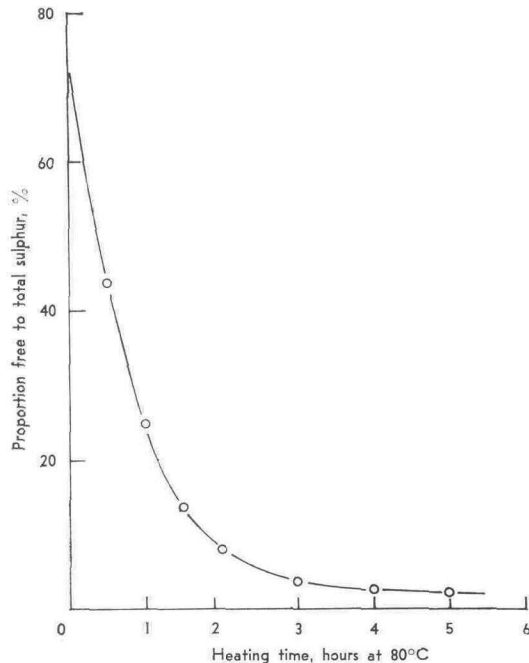


Figure 11. Graph illustrating rate of pre-vulcanisation of latex at 80°C.

TABLE 6. EFFECT OF TIME OF PRE-VULCANISATION OF LATEX ON PROPERTIES OF PA 80

Sample number	Time of pre-vulcanisation at 80°C, h	Blending conditions		Mooney viscosity	Scorch min	Extrusion swell %	Total sulphur %	Free sulphur %	Proportion of total to free sulphur %	Extrudate	
		Time h	Coagulation temp. °C							Appearance	Number
1/1	1	0	80	86	7.8	7.1	1.53	0.60	38.4	Excellent	205
2	1	0.5	75	135	7.0	6.3	1.56	0.44	28.3	Very bad	206
3	1	1	70	140	7.3	5.4	1.76	0.38	21.7	„	207
4	1	2	65	156	7.2	6.0	1.49	0.32	21.3	„	208
3/1	3	0	80	71	7.8	5.6	1.72	0.30	17.5	Excellent	209
2	3	0.5	76	73	7.8	5.9	1.60	0.25	15.4	„	210
3	3	1	73	75	8.4	5.8	1.69	0.32	19.0	„	211
4	3	2	66	77	8.2	5.9	1.63	0.21	12.3	„	212
4/1	4	0	80	72	8.3	5.9	1.51	0.32	21.0	Excellent	201
2	4	0.5	76	76	7.3	5.8	1.55	0.29	18.5	„	202
3	4	1	73	68	7.8	5.5	1.53	0.29	18.7	„	203
4	4	2	63	80	8.1	4.5	1.58	0.16	9.9	„	204
5/1	5	0	80	80	7.9	4.4	1.11	0.23	20.8	Excellent	197
2	5	0.5	73	74	7.2	3.5	1.09	0.23	21.5	„	198
3	5	1	72	71	7.9	4.7	0.96	0.28	29.4	„	199
4	5	2	64	74	8.0	3.8	1.10	0.16	14.1	„	200

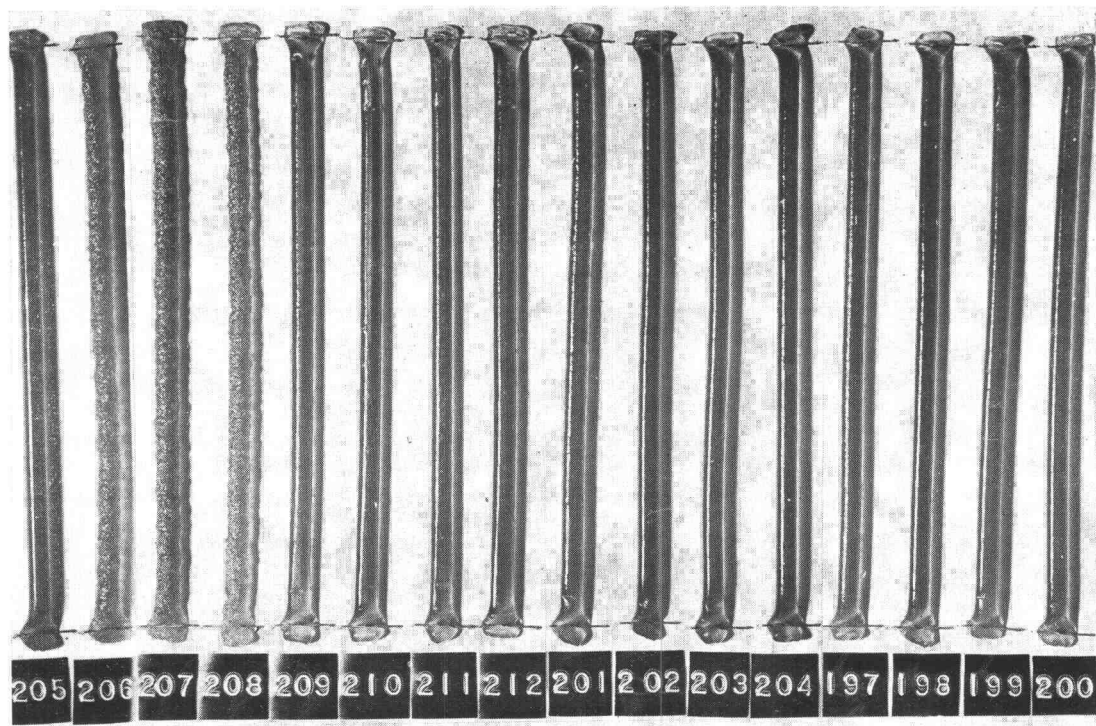


Figure 12. Extrudates from stocks containing PA 80 prepared using different times of pre-vulcanisation and mixing conditions of pre-vulcanised and raw latices.

The results confirm the view that any flocculation or coagulation of the pre-vulcanised latex prior to the incorporation of the unvulcanised latex component will be the cause of dispersibility problems in the resultant PA 80. Adequate straining of the pre-vulcanised latex must be carried out therefore to obviate this effect.

In the estate factory however, the latex very rarely destabilises, and filtration of the vulcanised latex through a fine mesh is normal practice. It should also be noted that the Mooney viscosity of these experimental samples is not abnormally high, except in one case (Sample 13, Table 2) which appears anomalous.

In conclusion, while the use of unstable pre-vulcanised latex giving rise to unhomogeneous material can be the cause of dispersion trouble,

this is a rare occurrence and does not explain the origin of the PA 80 complaints.

2. *Excessive heating of PA 80 rubber.* It is known that excessive overheating during drying or exposure of dried rubber to prolonged high temperatures during shipping or storing can spoil PA 80. Commercial producers use air drying units such as the Woods tunnel described elsewhere (RUBBER RESEARCH INSTITUTE OF MALAYA, 1963). It has been established that estates producing batches of high Mooney PA 80 did not vary from the approved drying conditions for these batches, and the abnormality cannot be explained by the drying.

Overheating during storing and transporting may sometimes occur. The effect of storing PA 80 at various temperatures has been examined and is discussed below:

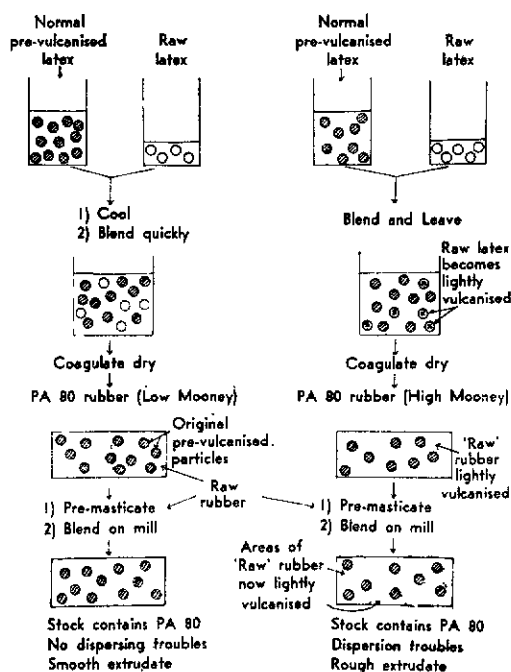


Figure 13. Diagrammatic representation of secondary vulcanisation that can occur within the blended latices and its effect on the dispersibility of PA 80.

(a) *Storage at 40° and 60°C.* The properties and dispersibility of various PA 80 samples were examined after periods of storage as wrapped compressed bales in a hot air chamber. The results are given in Table 3 and Figure 7. Samples 1 and 2 were prepared in the laboratory to give different levels of vulcanisation, as indicated by the free and total sulphur contents and the remaining sample was from commercial production.

As expected, the higher the storage temperature and the longer the time, the less satisfactory is the dispersibility of the sample. However, PA 80 stored at 40°C is satisfactory for at least six months. At this temperature, the Mooney viscosity is seen to rise slowly with time. The rate of rise is faster when the PA 80 has a higher free to total sulphur proportion.

At 60°C, the storage time which is permissible for good dispersing PA 80 is shortened,

and the Mooney viscosity is lowered with time undoubtedly due to degradation.

(b) *Storage at 70° and 100°C.* At these very extreme temperatures, the PA 80 is seriously affected. The behaviour of a commercial sample of PA 80 is summarised in Table 4 and Figure 8. It is seen that after fifteen days at 70°C, the rubber is beginning to show dispersibility troubles while at 100°, one day is sufficient to spoil it.

Storage at these temperatures will cause extra chemical cross-linking or re-arrangement within the PA 80. The extra cross-linking will begin in the original pre-vulcanised particles and spread from there. Where these particles are very close, then linking in particles is possible, which may produce a structure not greatly different from that shown in Figure 5.

The unhomogeneity produced by this re-arrangement means that the SP rubber cannot be satisfactorily dispersed in raw rubber. This postulate is illustrated in Figure 9. The reactions would also occur at the lower storage temperatures but will obviously take much longer.

Storage at high temperatures can result in a slight increase in the Mooney viscosity of the rubber, but does not produce the excessively high viscosities already referred to.

The data indicate that PA 80 must be protected from excessive temperatures during storage and transportation. Storage at normal temperatures is satisfactory provided reasonable precautions are observed. Prolonged storage of commercial production PA 80 for more than two and a half years under tropical conditions at the Experiment Station of the Rubber Research Institute of Malaya has not affected its dispersibility when used in a local factory.

3. *Effect of the conditions under which the latices are mixed.* Vulcanised latex is blended with raw latex followed by coagulation, milling and drying. The effect of the conditions of blending the latices has been examined.

A batch of latex was vulcanised for 2 hours at 80°C. Portions of this were blended with raw latex under various conditions, and the mixture was then processed to give PA 80. The effect of the conditions of mixing on the

TABLE 7. DEPENDENCE OF RATE OF LATEX PRE-VULCANISATION ON THE pH OF LATEX

pH of latex	Heating time at 80°C, h	Cooling time, h	Free sulphur %	Total sulphur %	Proportion of free to total sulphur, %
10.0	0.0	—	1.19	2.48	48.0
	0.5	—	0.86	2.49	35.0
	1.0	—	0.47	2.41	20.0
	1.5	—	0.42	2.53	17.0
	2.0	—	0.25	2.54	10.0
	—	0.5	0.28	2.49	11.0
	—	1.0	0.26	2.47	11.0
	—	1.5	0.25	2.52	10.0
	—	2.0	0.27	2.54	11.0
	—	—	—	—	—
7.0	0.0	—	0.85	1.78	48.0
	0.5	—	0.52	1.86	28.0
	1.0	—	0.32	1.81	18.0
	1.5	—	0.24	1.86	13.0
	2.0	—	0.16	1.93	8.0
	—	0.5	0.12	1.90	7.0
	—	1.0	0.11	1.89	6.0
	—	1.5	0.12	1.96	6.0
	—	2.0	0.12	1.75	7.0
	—	—	—	—	—
5.0	0.0	—	1.28	2.25	57.0
	0.5	—	1.11	2.15	52.0
	1.0	—	1.11	2.17	51.0
	1.5	—	1.14	2.14	53.0
	2.0	—	0.95	2.05	46.0
	—	0.5	0.87	2.48	35.0
	—	1.0	0.94	2.20	43.0
	—	1.5	0.97	2.15	45.0
	—	2.0	0.96	2.12	45.0
	—	—	—	—	—

properties of the rubber are illustrated in Table 5 and Figure 10.

If the mixture of pre-vulcanised and raw latices is maintained at a high temperature for too long, the resultant PA 80 has a high Mooney viscosity and poor dispersibility. However, fast mixing and cooling produces a satisfactory rubber.

It can be further demonstrated that the effect of the mixing conditions is related to the degree of vulcanisation and hence the time of heating of the pre-vulcanised latex. Firstly, the rate of latex vulcanisation under laboratory conditions was determined by measuring free sulphur concentrations after various times of heating (Figure 11). The usual period of vulcanisation (2 hours at 80°C) gives appreciable

free sulphur content and hence the time of heating should be increased to complete the reaction. The effect of blending conditions as described in Table 5 was next examined with pre-vulcanised latices prepared using different times of vulcanisation at 80°C. Full details and results are given in Table 6 and Figure 12.

The data indicate that short times of pre-vulcanisation can give rise to high Mooney viscosity under certain blending conditions. However, if the degree of vulcanisation is increased by reacting for longer times (e.g., 3 hours or more) blending even under the most adverse conditions does not give rise to a PA 80 with bad dispersibility characteristics.

These effects would appear to be associated with the ability of the pre-vulcanised latex to

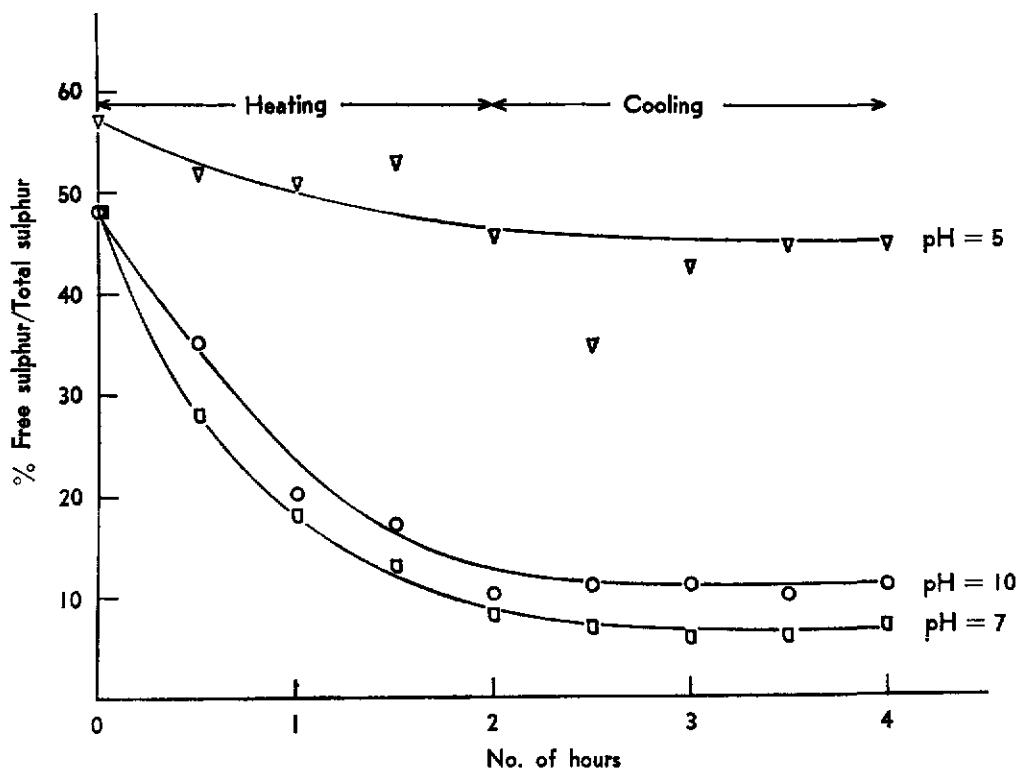


Figure 14. Graph showing the change in the proportion of free to total sulphur in pre-vulcanised latex with time at 80°C at various pH levels.

undergo a secondary vulcanisation reaction when the raw latex is added. By mixing in the raw latex with the partly cured pre-vulcanised latex, it acquires a small degree of sulphur cross-linking. On coagulation, a product is obtained which, although passing the existing PA 80 extrusion specification tests, in fact is more like a completely vulcanised or 'PA 100' rubber which is harder than PA 80. On mastication the rubber is resistant to shearing, and forms small pieces or lumps, which are revealed in the dispersibility test. This is represented diagrammatically in Figure 13.

It may be asked why the vulcanisation does not continue under normal storage conditions in the PA 80 rubber. It appears that sulphuric acid plays a further role in addition to that of coagulation, de-activating the vulcanisation accelerator system and thus effectively termi-

nating further chemical cross-linking in the dry rubber (except under special high temperature storage conditions as stated above). The de-activation is probably achieved in association with the chemical decomposition of zinc diethyl-dithiocarbamate. The influence of the pH conditions on rate of vulcanisation is demonstrated in Table 7. Samples of latex were compounded with the requisite vulcanisation components and stabilised with non-ionic surface active agent (Ethomeen 18/60). By the addition of formalin and formic acid, the pH was adjusted as shown. The latices were then heated at 80°C for 2 hours and cooled for 2 hours, taking samples at various stages for determination of total and free sulphur. The change of the proportion of free to total sulphur is seen in Figure 14.

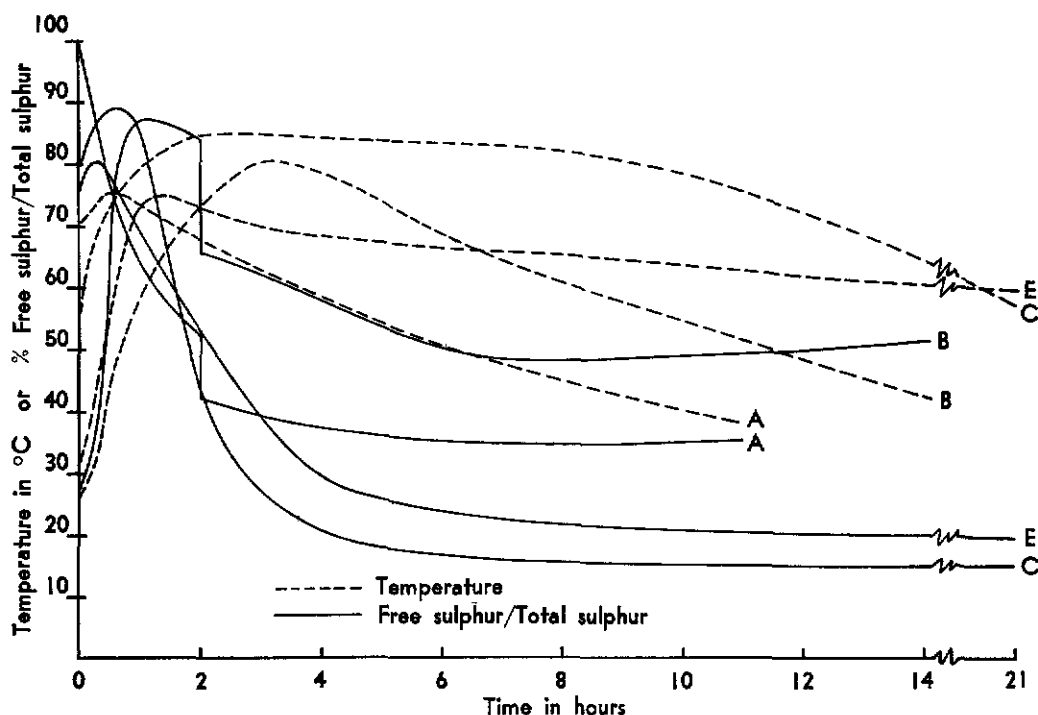
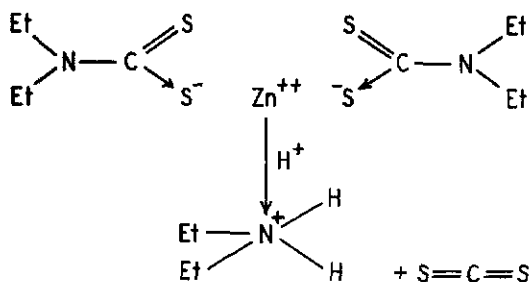


Figure 15. Graph showing the variation of temperature and proportion of free to total sulphur with time in commercial production for four estate factories.

The almost complete absence of vulcanisation in the latex heated at pH 5 indicates the de-activation of the accelerator system. This may be due to acidic decomposition of the dithiocarbamate, as proposed (THORN AND LUDWIG, 1962).



The products of this reaction—diethylamine and carbon disulphide would not be accelerators.

The thiazole will largely be unaffected by the

acid pH. It is known that sulphur/thiazole vulcanisation systems are considerably slower than sulphur/thiazole/dithiocarbamate systems, so the former are not normally used.

Great care must be exercised over the blending of the pre-vulcanised and raw latices. Use of a short time of vulcanisation and lack of proper cooling before blending can give rise to high Mooney viscosity PA 80 rubber with poor dispersion characteristics.

Practical Significance

Process conditions by which PA 80 is prepared have been described. Although it passes the existing extrusion swell specifications tests, the rubber cannot be processed satisfactorily in the consumer's factory and gives rise to complaints. The results described here are important to producers, in avoiding procedures which result in abnormal PA 80 rubber. Abnormalities can be avoided by:

- (i) ensuring that the pre-vulcanised latex is cooled sufficiently before the raw latex is added, and also by allowing a minimum time between proper blending and coagulation;
- (ii) increasing the time of vulcanisation, to enable reduction of free sulphur present to a minimum, avoiding thereby any 'secondary vulcanisation' on blending.

Of the two, the second method is more reliable. Estate production has, in the past, been vulnerable to such 'secondary vulcanisation' because of the generally high free sulphur content in the PA 80 (*Table 1*). Examples of heating cycles and changes in free sulphur level on four of the producing estates are given in *Figure 15*. The practice of Estate C in prolonging the heating time gives a low proportion of free to total sulphur and reduces the risk of secondary vulcanisation. This should be compared to Estate A which has a short heating cycle and is potentially more liable to produce PA 80 with a high Mooney value (*Table 1*).

The producers have been advised of the new recommendations (RUBBER RESEARCH INSTITUTE OF MALAYA, 1967). As a result of this investigation, a new specification limit for PA 80 has been introduced—that of a maximum Mooney viscosity of 80, in addition to the other specification limits.

CONCLUSION

The occurrence and causes of PA 80 rubber which showed poor dispersibility in the consumer's factory have been investigated. The most important cause is 'secondary vulcanisation' during the mixing of pre-vulcanised and raw latices. Methods of avoiding this reaction have been described.

Other causes include the use of flocculated pre-vulcanised latex in preparation of the rubber and the storage of the PA 80 at excessively high temperatures.

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