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EFFECT OF CHEMICAL TREATMENT ON QUALITY OF NATURAL RUBBER

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Tetraethylenepentamine (TEP) and hydrazine hydrate are shown to react with carbonyl groups present in crumb rubber obtained from both fresh latex and field coagulum, thereby raising their initial plasticity. Hydrazine is shown to produce constant viscosity rubbers from both fresh latex and field coagulum with the value of viscosity depending on concentration of hydrazine. In fresh latex crumb, TEP is shown to react with active sites in non-rubber solids during ageing at lower temperatures (60°C/24h) and with oxidative intermediates during ageing at higher temperatures (140°C/30 min). The enhanced oxidative and thermal stability conferred by TEP are reflected in its improved vulcanizate and ageing behaviour.

INTRODUCTION

Introduction of the technical specification scheme was an important development in natural rubber processing. The quality parameters included in the specifications enabled the consumer to have a better idea of the quality of the rubber. A measure of the thermo-oxidative degradation of raw natural rubber is obtained from plasticity retention index (PRI) measurements. In many cases due to low initial plasticity (Po) or PRI the rubber may fail to meet the specifications of a particular grade.

An attempt has been made in this work to improve Po and PRI of raw rubber by chemical treatment and to evaluate the effect of these properties with performance of the vulcanizates.

EXPERIMENTAL

Tetraethylenepentamine (TEP), hydrazine hydrate ($NH_2NH_2.\ H_2O$) phosphoric acid and sulphamic acid were of laboratory grade. Crumb rubber from dry field coagulum and from fresh latex coagulum were obtained from the Pilot Crumb Rubber Factory of the Rubber Board. These samples were designated as DFC and FLC respectively.

A batch of 200 g of wet crumb rubber was soaked in solutions containing 0.25 per cent, 0.5 per cent, 0.75 per cent and 1.00 per cent of the chemicals for 10 minutes. The treated samples were dried in an air circulated laboratory oven at 70°C. Plasticity and PRI measurements were done on a Wallace Rapid Plastimeter and a Wallace-MRPRA Ageing Oven. The cure characteristics were evaluated as per ACS1 formulation (Table 1). The technical properties were evaluated in a standard tread type formulation (Table 2).

Table 1. ACS1 formulation

Natural rubber	100
Stearic acid	0.5
Zinc oxide	6.0
MBT[a]	0.5
Sulphur	3.5

a Mercaptobenzthiazole

Table 2. Formulation of a standard tread type compound

Component	Parts
Natural rubber	100
Stearic acid	2
Zinc oxide	5
HAF black(N 330)	50
Naphthenic oil	6
A/O HS[a]	1
Sulphur	2.5
MOR[b]	0.75

a. 2,2,4-trimethyl 1,2-dihydroquinoline

b. N-oxydiethylene-2-benzothiazolyl sulphenamide.

RESULTS AND DISCUSSION

Effect of chemical treatment on Po

Dry field coagulum

Effect of concentration of hydrazine hydrate (HH), TEP, phosphoric acid (PA) and sulphamic acid (SA) on initial plasticity (Po) of crumb rubber obtained from dry field coagulum (DFC), is shown in (Fig. 1). Hydrazine treatment increases plasticity and at a concentration of 0.5 per cent there is an increase of around 15 units. With further increase in concentration of hydrazine plasticity decreases. TEP treatment also increases plasticity of rubber. The increase in plasticity obtained by TEP is lower than that obtained by hydrazine. Plasticity shows an improvement even with 0.25 per cent of TEP. However, concentrations higher than this do not drastically change Po. PA and SA treatments do not affect Po.

Polyisoprene contains a number of abnormal groups such as aldehyde (Sekhar, 1960; Sekhar, 1962; Subramaniam, 1977; David, 1986) epoxide (Burfield, 1974) and lactone (Greg Jr and Marcey, 1973) along the main chain. Sekhar (1960; 1962) noted that carbonyl groups in NR could react with a number of reagents preventing increase in viscosity of rubber during storage. Reagents could either prevent or accelerate hardening depending on functionality. The increase in plasticity caused by diamines (Subramaniam, 1975) was noted earlier. Amines had been recommended to prevent storage hardening as they deactivate carbonyl groups.

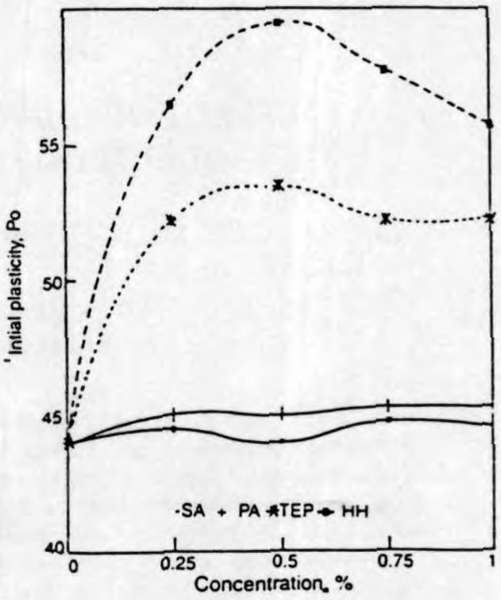

Fig. 1. Effect of concentration of HH, TEP, PA and SA on P_0 of crumb rubber (DFC)

Hydrazine was being used as a preservative (John *et al.*, 1976) for NR latex. It is capable of reacting with carbohydrates. Hence both TEP and hydrazine hydrate react with NR. The increase in plasticity with these reagents is due to their reaction with reactive groups in two adjacent rubber molecules. At higher concentrations of HH, it reacts with carbonyl groups preventing storage hardening as will be seen later but the same hydrazine molecule may not react with two adjacent rubber molecules resulting in crosslinks (Sekhar, 1960). A lower plasticity registered by TEP treatment could be due to greater flexibility of the crosslinks with TEP.

Fresh latex coagulum

The effect of TEP, HH, SA and PA on initial plasticity of crumb rubber obtained from fresh latex coagulum is shown in Fig. 2. Both PA and SA do not improve initial plasticity. Hydrazine and TEP show an increase in plasticity even with a concentration of 0.25 per cent. In the case of TEP treatment, plasticity increases steadily with concentration of TEP, while for hydrazine, although there is an increase upto 0.25 per cent, this trend is not maintained at concentrations above this.

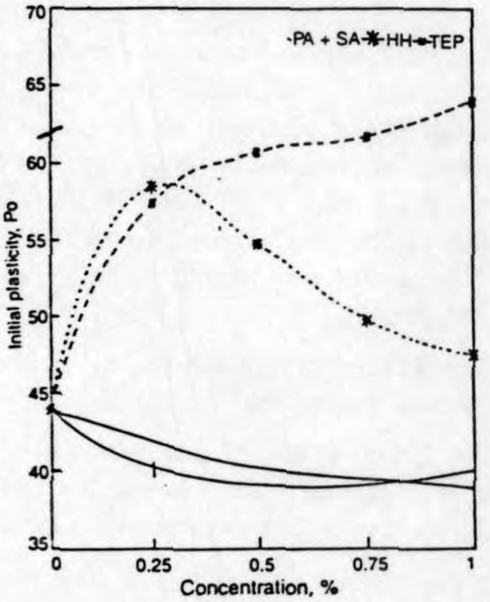

Fig.2. Effect of concentration of HH, TEP, PA and SA on P_0 of crumb rubber (FLC)

The lipids (Hasma and Subramaniam, 1986) and precipitated proteins which are retained on the dry rubber after coagulation are known to affect its properties. A very small fraction of C serum solids is shown to contribute to storage hardening and NR prepared by acid coagulation is considered to exhibit maximum storage hardening (Gregory and Tan, 1975). As TEP is more reactive than hydrazine, there is greater crosslinking reaction for TEP, resulting in a progressive increase in Po with increase in concentration than hydrazine. At higher concentrations of hydrazine there can be deactivation of carbonyl groups without forming crosslinks.Furthur work on reaction of amine with natural rubber is required to check this possibility.

Effect of chemical treatment on P_{30} and PRI

Fresh latex coagulum

The effect of concentration of hydrazine, TEP,PA and SA on P_{30} and PRI are shown in Fig. 3. TEP treated samples show very high P_{30} and PRI. Hydrazine treated samples show P_{30} similar to that of control while PA and SA show a lower P_{30} than control. A comparatively high PRI is shown by PA and SA treated samples as they have low Po, whereas hydrazine treated samples show a slightly lower PRI.

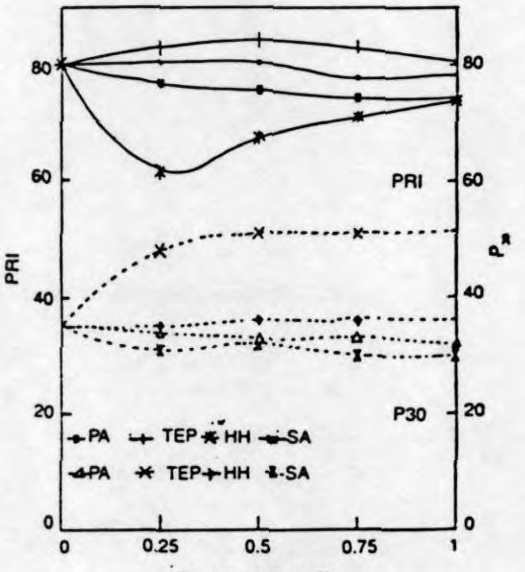

Fig.3. Effect of concentration of HH, TEP, PA and SA on P_{30} and PRI of crumb rubber (FLC)

During PRI ageing the combined effect of natural hardening, hardening by reactive oxidation products coupled with oxidative and thermal degradation are possible (Morris, 1991). It is known that during oxidation of rubber many intermediates like methacrolien, methyl vinyl ketone 4, Levulinaldehyde and 4, hydroxy -2-butanone (Morand, 1974; 1977) are formed. These can react with amines depending on their reactivity. TEP, being more reactive (Behum, 1964; Sehiessl, 1980; Frank and Reck, 1985) gives a highly crosslinked product compared to hydrazine. Hydrazine treated samples show no hardening during the accelerated hardening test as will be seen later and hence it is believed that during thermal ageing the effect due to natural hardening is absent. The net effect is the possibility of less chain scission during ageing.

Dry field coagulum

In dry field coagulation, as seen from Fig. 4 a comparatively high P_{30} and PRI are observed for phosphoric acid treated sample. Phosphoric acid is known to remove metallic impurities such as copper (Mathew and Thomas, 1975). Both TEP and hydrazine treated samples show higher P_{30} than untreated samples. Dry field coagulum, unlike fresh latex coagulum, is likely to contain metallic contaminants and hence a greater extent of chain scission reaction occurs during thermal ageing.

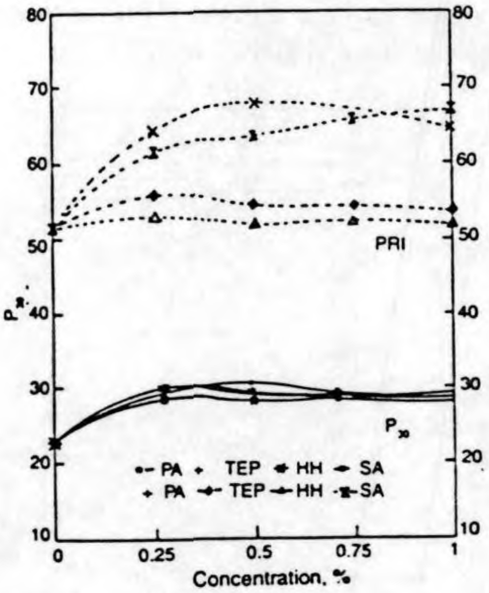

Fig.4. Effect of concentration of HH, TEP, PA and SA on P_{30} and PRI of DFC

The effects of chemical treatments on Po and P_{30} were subjected to statistical analysis and were tested for significance (Table 3). The hydrazine and TEP treatments were found to significantly influence the Po values for DFC and FLC. While the P_{30} values for DFC was also similarly influenced by both HH and TEP, only TEP treatment showed significant influence on P_{30} values of FLC.

Effect of chemical treatment on accelerated storage hardening test

The effect of TEP and hydrazine treatment on storage hardening in dry field coagulum and fresh latex coagulum are shown in Fig. 5-6.

TEP treatment causes very high hardening while hydrazine treatment shows no hardening in both DFC and FLC (Table 4), showing that all carbonyl groups on main NR chain are blocked. TEP treated samples show storage hardening even though the carbonyl groups are deactivated because it can react with active sites in rubber bound nonrubber solids (glycolipids *etc*).

Table 3. Statistical analysis data for significance of chemical treatment based on ΔPo and P_{30}

Chemical conc. %	DFC				FLC			
	0.25	0.50	0.75	1.00	0.25	0.50	0.75	1.00
Po								
HH	12.15	15.50	13.75	11.75	14.50	10.75	5.75	3.50
TEP	8.25	9.50	8.25	8.25	13.50	16.75	17.75	20.00
PA	1.00	1.00	1.25	1.25	-2.00	-3.50	4.50	-3.25
SA	0.50	0.75	0.25	0.75	-3.75	-3.50	-4.50	-3.25
(CD = 4.09)								
P_{30}								
HH	7.0	5.5	7.00	6.00	-0.5	1.75	1.00	0.5
TEP	7.0	6.5	5.5	4.75	12.5	16.0	15.75	16.25
PA	6.25	7.75	5.00	6.50	-1.0	-3.0	-5.25	-4.25
SA	5.75	5.00	5.05	5.75	-4.25	-1.75	-5.75	-5.0
(CD = 5.14)								

Table 4. Effect of chemical treatment on storage hardening (ΔP) in DFC and FLC

Conc. of chemical	DFC		FLC	
	HH	TEP	HH	TEP
Nil	10	10	24	24
0.25%	1	11	-5	18
0.50%	-1	11	-3	17
0.75%	-1	13	-3	16
1.00%	+1	15	-3	13

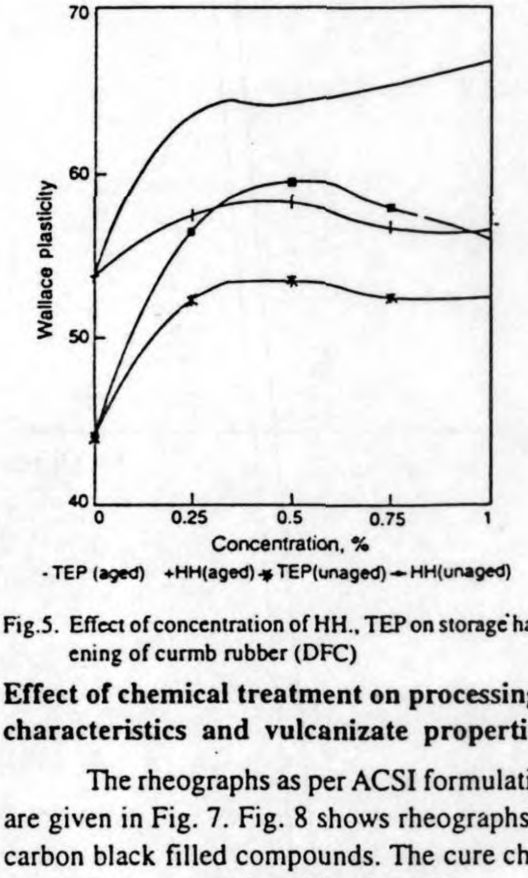

Fig.5. Effect of concentration of HH., TEP on storage hardening of curmb rubber (DFC)

Effect of chemical treatment on processing characteristics and vulcanizate properties

The rheographs as per ACSI formulation are given in Fig. 7. Fig. 8 shows rheographs of carbon black filled compounds. The cure characteristics are given in Tables 5a and b.

Table 5a. Cure characteristics of ACS1 mixes

	Control	0 .25%TEP	0. 25%HH
From Mooney viscometer (120 °C)			
Minimum Mooney	16	32	18
viscosity Scorch time, min	8	5	7.75
From Monsanto rheometer (159 °C)			
Tmax,dN.m	42	49	43
Tmin,dN.m	5	7	6
Optimum cure time, min.	10.75	8.00	10.75
Scorch time,min	1.75	1.25	2.00
Cure rate,dN m/min.	4.11	5.22	4.23

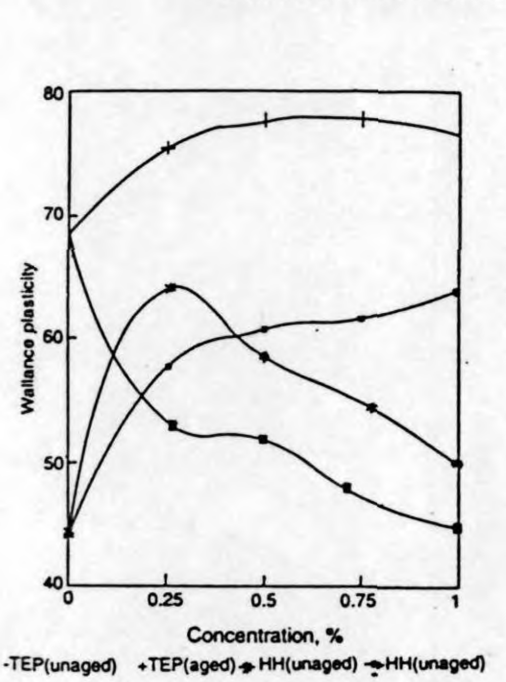

Fig.6. Effect of concentration of HH., TEP on storage hardening of crumb rubber (FLC)

Table 5b. Cure characteristics of a standard tread type compound

	Control	0 .25%TEP	0. 25%HH
From Mooney viscometer (120 °C)			
Minimum Mooney viscosity	42	50	47
Mooney scorch time, min.	9.9	8.5	9.5
From Monsanto rheometer (150 °C)			
Tmax,dN.m	61	66	63
Tmin,dN.m	9.75	10.25	10.0
Optimum cure time, min	12.50	11.00	11.50
Cure rate dNm/min	4.88	6.20	5.59

As is seen from Fig. 7 TEP treatment accelerates the cure as reflected from an earlier onset of cure and higher Tmax. TEP treated samples show a higher initial viscosity compared with other mixes. Tensile properties before and after ageing are summarised in Table 6.

The treatment with hydrazine or TEP do not adversely affect physical properties and ageing behaviour. TEP treated samples had better technical properties, compared with the control.

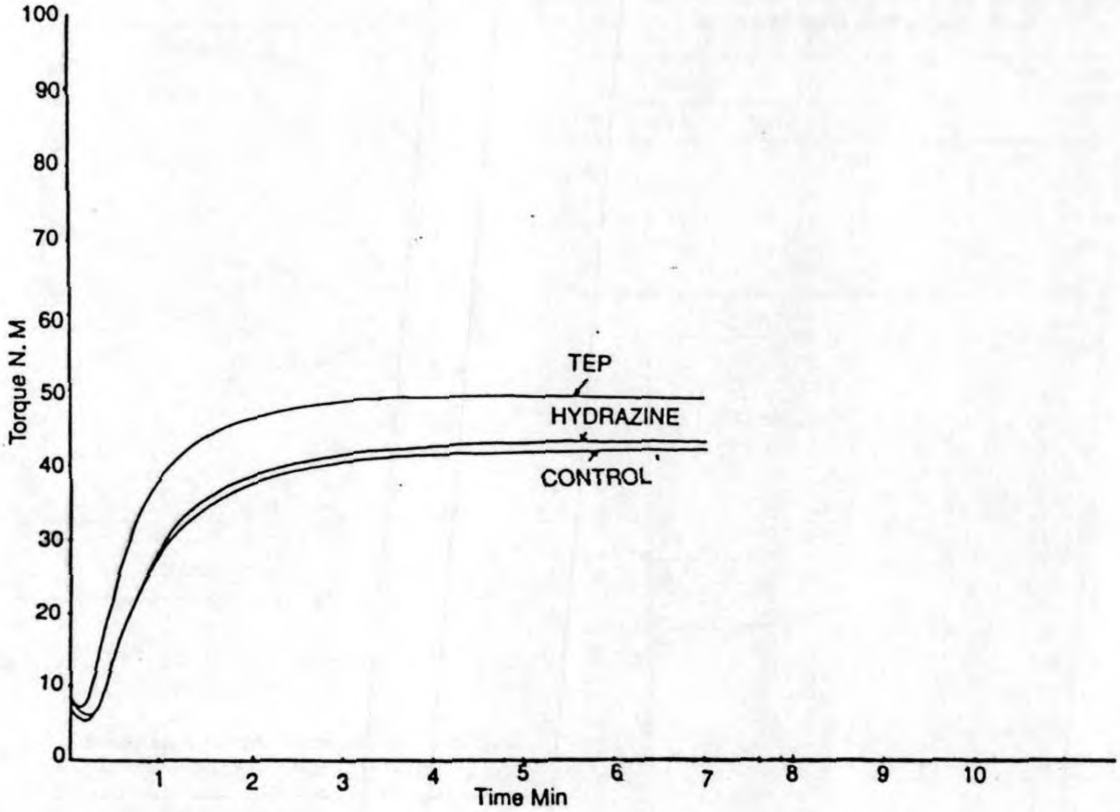

Fig.7. Rheograph of ACSI mixes at 150°C

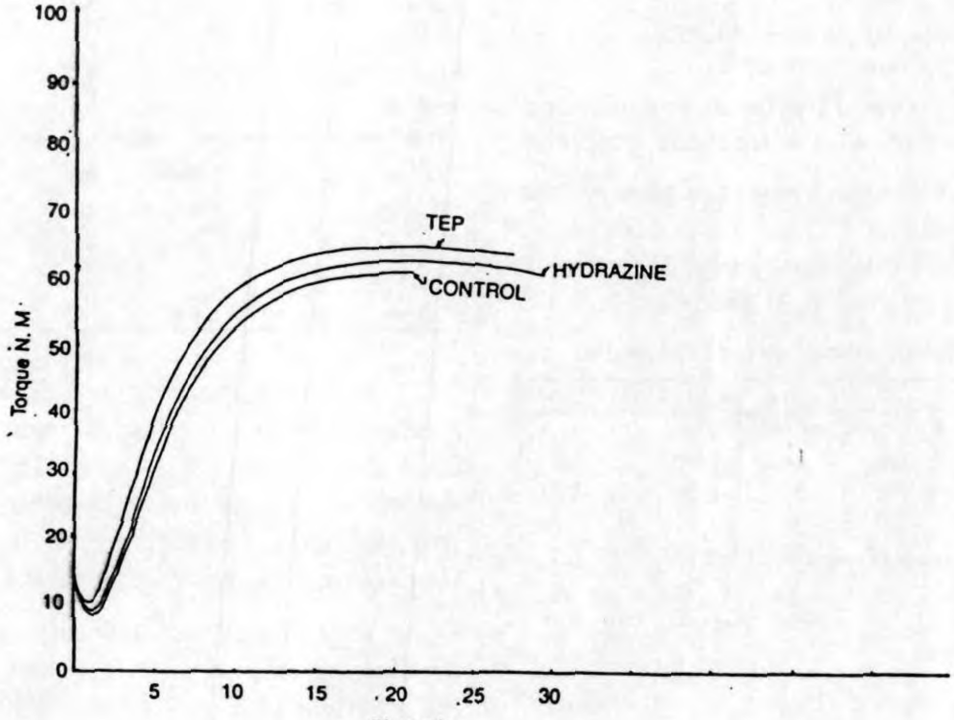

Fig.8. Rheograph of standard tread mixes at 150°C

Table 6. Effect of chemical treatment on tensile properties before and after ageing

Parameter	Control	TEP	HH
Tensile strength, MPa	20.32	25.36	21.70
Modulus, 300%,MPa	10.40	10.40	10.20
Elongation at break, %	615	680	580
Tear strength, kN/m	99	120	90
Ageing at 70°C/72 hours			
Tensile strength, MPa	23.30	25.10	23.00
Modulus, 300%, MPa	2.4	12.00	12.60
Elongation at break, %	530	590	520

CONCLUSIONS

Carbonyl groups of NR readily react with polyamines and hydrazine. Hydrazine prevents storage hardening whereas TEP has no such effect. TEP gives a higher aged plasticity and hence protection against thermal and oxidative degradation. The increase in plasticity by hydrazine depends on the concentration of hydrazine and the source of rubber.

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