

STABILITY AND VULCANIZATION CHARACTERISTICS OF ENZYME DEPROTEINIZED NATURAL RUBBER LATEX

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The colloidal stability of enzyme deproteinized natural rubber latex (EDPNRL) was investigated in comparison with the conventional high ammonia (HA) latex. The colloidal stability of EDPNRL was improved by the addition of potassium hydroxide or a combination of potassium hydroxide and ammonium laurate during compounding. The vulcanization characteristics of EDPNRL were compared with HA latex in a conventional sulphur system using zinc diethyldithiocarbamate (ZDC) as primary accelerator and ZDC in combination with other accelerators namely zinc di-n-butyldithiocarbamate (ZDBC), zinc dibenzylthiocarbamate (ZDBEDC) and activated dithiocarbamate (Setsit-5). The compounds of EDPNRL with ZDC, ZDBC and their combinations were fast curing. The mechanical properties and ageing resistance were within the limits specified for dipped goods.

Key words: Accelerators, Chemical stability, Colloidal stability, Enzyme deproteinized natural rubber latex, Mechanical properties, Vulcanization characteristics.

INTRODUCTION

The use of natural rubber latex products has been facing serious challenges owing to the allergic effects of some of the extractable proteins (EP) present in it (Pendle, 1994). Several techniques are being adopted for manufacturing products with very low EP content. Low protein latex is one of the important requirements for this. NR latex contains 2 to 3 per cent proteins. Only a part of the soluble proteins are removed by centrifuging the latex. The proteins inherently associated with the surface of the rubber particles cannot be removed by this process (Blackley, 1997). Several methods such as multiple centrifugation and enzyme treatment have been adopted for removing the rubber particle bound proteins. Enzyme

treatment involves a combination of digestion with a proteolytic enzyme, displacement of adsorbed proteins using a surfactant and the subsequent purification of the treated latex by centrifugation or creaming. Treatment with a proteolytic enzyme (Anilozyme-P) was reported to produce latex with low protein content in a single centrifuging process (George *et al.*, 2001). The physiochemical properties and the vulcanization characteristics of the enzyme deproteinized natural rubber latex (EDPNRL) are likely to be influenced by the extent of protein removal.

In this study, the colloidal stability of EDPNRL was compared with HA latex. EDPNRL was used in the manufacture of dipped products through modified com-

pounding techniques. The effect of using different combinations of accelerators on the vulcanization and technological properties of EDPNRL were also investigated.

MATERIALS AND METHODS

EDPNRL was prepared from field latex in the Pilot Latex Processing Centre, Rubber Board, India, as per the method reported earlier (George *et al.*, 2001). Preserved field latex containing one per cent ammonia, stored for 20 days, was used. The latex was treated with 1 phr of Anilozyme-P (prepared as 5% aqueous solution) and stored for 48 h. Subsequently it was treated with ammonium laurate (0.1% on latex), stored for further 24 h and diluted to 25% DRC. It was then subjected to centrifuging in a De Laval centrifuging machine. Centrifuged latex (HA) was also prepared to serve as control.

The accelerators, namely, zinc diethyldithiocarbamate (ZDC), zinc di-n-butyl dithiocarbamate (ZDBC), zinc dibenzyl dithiocarbamate (ZDBEDC) and activated dithiocarbamate (Setsit-5) manufactured by R.T. Vanderbilt Co., USA, were used. Other compounding ingredients were of commercial grade obtained from indigenous sources.

Physicochemical characteristics of EDPNRL

The physicochemical characteristics of EDPNRL such as mechanical stability time and Brookfield viscosity were determined as per BIS method. Zinc oxide viscosity (ZOV), zinc oxide stability time (ZST) and zinc oxide heat stability time (ZHST) were also determined. For the measurement of zinc oxide viscosity, the latex was treated with 1 phr of ZnO (40% dispersion) and the viscosity of the compounded latex was measured

after 5 and 60 min using Brookfield viscometer. For determining ZST, the latex was treated with 1 phr of ZnO (40% dispersion), kept for 1 h and mechanical stability time of the latex compound was measured using MST apparatus. For the measurement of ZHST, the latex was treated with 1 phr of zinc oxide (40% dispersion), kept for 1 h and the time for complete coagulation when heated in a waterbath at 90°C was noted.

Before compounding, the latex was treated with 0.05% potassium hydroxide and 0.05% ammonium laurate. The properties such as viscosity, zinc oxide viscosity, zinc oxide stability time and zinc oxide heat stability time were determined.

Cure characteristics of EDPNRL

EDPNRL compounds (A, B, C, D, E, F and G) containing different accelerators were prepared as per details given in Table 1. Setsit-5 was added as 50 per cent solution in water and the other ingredients as 50 per cent dispersions prepared by ball milling. Latex compounds (H, I, J, K, L, M and N) were prepared from HA latex as shown in Table 2.

Films were cast from the latex compounds and dried for 24 h at 30°C. Different layers of dried films were placed one above the other to give a total thickness of 2.5 mm and rheometer test specimens were prepared from the piled up sheet. The cure graph was plotted using a Monsanto Rheometer R 100 at 120°C as per ASTM (D 2084-83).

Crosslink density of the cast latex films from each compound was determined after vulcanizing the dried films at 120°C for different durations *viz.*, 15, 30, 45 and 60 min. Each sample weighing 0.2 – 0.3 g was al-

Table 1. Formulation of EDPNRL compounds

Ingredient	Parts by weight (wet)						
	A	B	C	D	E	F	G
EDPNRL, 60%	167	167	167	167	167	167	167
Potassium hydroxide, 20% solution	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Sulphur, 50% dispersion	2.0	2.0	2.0	2.0	2.0	2.0	2.0
ZDC, 50% dispersion	2.0	-	-	-	1.0	1.0	1.0
ZDBC, 50% dispersion	-	2.0	-	-	1.0	-	-
ZDBEDC, 50% dispersion	-	-	2.0	-	-	1.0	-
Setsit-5, 50% solution	-	-	-	2.0	-	-	1.0
Zinc oxide, 50% dispersion	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Table 2. Formulation of HA latex compounds

Ingredient	Parts by weight (wet)						
	H	I	J	K	L	M	N
Centrifuged latex, 60%	167	167	167	167	167	167	167
Sulphur, 50% dispersion	2.0	2.0	2.0	2.0	2.0	2.0	2.0
ZDC, 50% dispersion	2.0	-	-	-	1.0	1.0	1.0
ZDBC, 50% dispersion	-	2.0	-	-	1.0	-	-
ZDBEDC, 50% dispersion	-	-	2.0	-	-	1.0	-
Setsit-5, 50% solution	-	-	-	2.0	-	-	1.0
Zinc oxide, 50% dispersion	1.0	1.0	1.0	1.0	1.0	1.0	1.0

lowed to swell in toluene at 30°C for 48h. The swollen sample was weighed, the solvent removed in vacuum and the sample weighed again. Values of V_v , the volume fraction of rubber in the swollen vulcanizate, which is a measure of the total number of crosslinks, were determined using the method suggested by Ellis and Welding (1964).

In order to assess the tensile properties, the dried cast latex films were vulcanized at 120°C for 30 min in an air oven. Tensile properties of the films were determined as per ASTM D-412, using a Universal Testing Machine (Instron Model 4411). Films were subjected to ageing at 70°C for 10 days in a multicellular ageing oven and the tensile properties determined according to ASTM D 573-99.

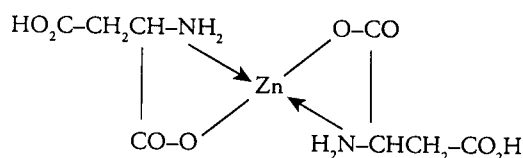
RESULTS AND DISCUSSION

The ZST and ZHST of EDPNRL were much lower than those of normal HA latex (Table 3). The increased sensitivity of EDPNRL towards zinc oxide may probably be a consequence of increased aqueous phase anion content (and hence increased ammonium ion content) due to enzymatic degradation of proteins to amino acids and polypeptides (Blackley, 1997). A second factor is that the latex may be partially destabilized by the enzymatic degradation and perhaps partial desorption of surface bound proteinaceous stabilizers. Similar results have been reported by Lepetit (1947) for natural rubber latex, which has been digested with trypsin, a proteolytic enzyme preparation. It has been proved that the heat sensitivity induced by protein degradation in the pres-

Table 3. Stability characteristics of EDPNRL and HA latex

Latex	Mechanical stability time(s)	Brookfield viscosity (mPa s)	Property			
			ZOV 5 min (mPa s)	ZOV 60 min (mPa s)	ZST (s)	ZHST (s)
60% centrifuged latex	>1000	70	72	75	14	130
60% EDPNRL	>1000	70	70	75	188	696
60% EDPNRL + 0.05 phr KOH + 0.025 phr ammonium laurate	>1000	48	50	50	40	160

ence of zinc oxide is not caused by the formation of amino acids and polypeptides in which the ratio of free amino to carboxyl groups is 1:1. It is the presence of amino acids and polypeptides having a stoichiometric excess of free carboxyl groups over free amino groups which cause enzymatically degraded ammonia preserved natural rubber latex to become more heat sensitive in the presence of zinc oxide. Although such amino acids and polypeptides form strong chelate complexes with zinc ions of the type shown below, only a small proportion of the added zinc is so bound, and a proportion of the carboxylic acid groups remain available to interact with ammonia to form ammonium soaps. The requisite conditions for the development of heat sensitivity in the presence of sparingly soluble zinc compounds are thus fulfilled.



• The effect of addition of potassium hydroxide and ammonium laurate on the chemical stability of EDPNRL is given in

Table 3. It is observed that the colloidal stability could be improved by this treatment. The addition of potassium hydroxide into the latex reduces heat sensitivity and retards zinc oxide thickening. Though the amount of added alkali is very small, the concentration of hydroxide ions in the aqueous phase increases significantly. The hydroxide ions react with ammonium ions to form ammonia and water, the system to some extent being buffered against pH changes. Thus the added hydroxide has several effects such as increase in the concentration of free ammonia, reduction in the concentration of free ammonium ions and suppression of solubility of zinc hydroxide. The addition of a small amount of ammonium laurate increases colloidal stability of the system by strong adsorption of laurate ions at the rubber / water interface (Blackley, 1997).

The rheometric cure curve gives two basic properties of the cure system, the cure rate and the maximum torque. The value of $t_{cr} = t_{50} - t_1$ (where t_{50} = time to reach 50% of maximum torque and t_1 = scorch time) and maximum torque as obtained from rheometric traces for all the compounds studied are given in Table 4. A low value of t_{cr} indicates high cure rate.

With EDPNR latex, the formulations

Table 4. Cure characteristics of EDPNRL and HA latex compounds

Accelerator	$t_{cr} = (t_{50} - t_1)$ min		Maximum torque (T_{max}) dN.m	
	EDPNRL	HA Latex	EDPNRL	HA Latex
ZDC	0.45	0.59	4.25	4.56
ZDBC	0.44	0.55	4.32	4.13
ZDBEDC	1.09	1.16	4.01	4.08
Setsit-5	2.03	2.29	3.44	4.01
ZDC + ZDBC	0.40	0.55	4.42	4.26
ZDC + ZDBEDC	0.52	0.62	4.13	4.41
ZDC + Setsit-5	0.95	1.01	3.85	4.20

containing ZDC, ZDBC and ZDC + ZDBC gave lower values of t_{cr} viz., 0.45, 0.44 and 0.40 min respectively indicating high cure rate. However, in formulations containing ZDC + ZDBEDC and ZDC + Setsit-5, the value of t_{cr} increased to 0.52 and 0.95 respectively. The lower cure rate for these combinations may be due to the low cure rate of ZDBEDC and Setsit-5, for which t_{cr} values are found to be 1.09 and 2.03 respectively. The low cure rate for Setsit-5 accelerator is due to the absence of zinc ions (Vanderbilt, 1987). Consequently, during storage, little precure will occur provided ZnO or other Zn bearing materials are absent in the compound. The presence of zinc dithiocarbamate in a compound initiates precure because zinc ions are liberated from the accelerator to the latex which increases the cure rate of Setsit-5. The use of this liquid accelerator thus facilitates direct control of precure of the compound. With HA latex also, ZDC + ZDBC combination was faster curing whereas ZDC + ZDBEDC and ZDC + Setsit-5 combinations were slower curing than ZDC.

A comparison of the cure rate of EDPNRL and HA latex compounds shows that EDPNRL compounds had higher cure rate than HA latex compounds. It has been reported by Gorton (1975) that absence of

non-rubbers in NR latex may decrease the cure rate as they play a unique role as activators for vulcanization. The higher cure rate observed with EDPNRL compounds may be

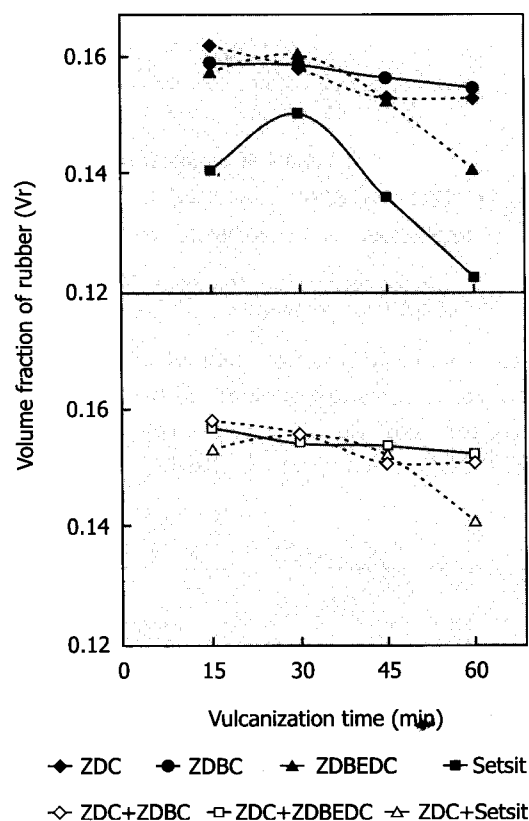


Fig. 1. Effect of vulcanization time on crosslink density of EDPNRL vulcanizate

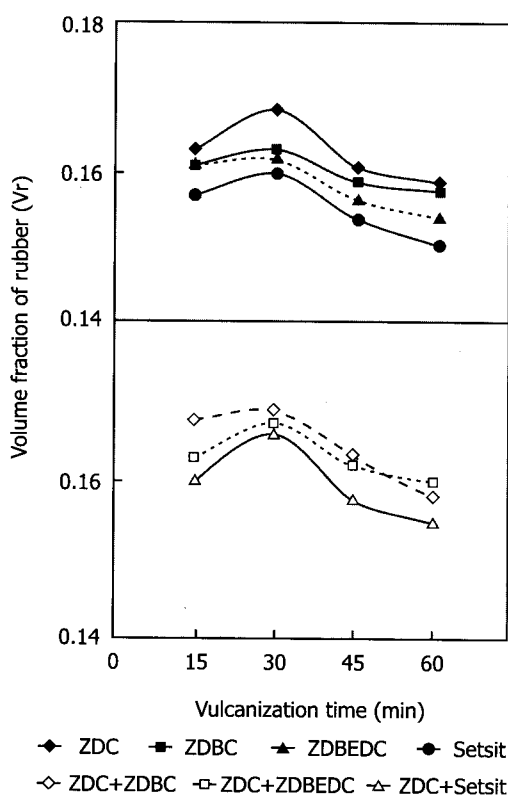


Fig. 2. Effect of vulcanization time on crosslink density of HA latex vulcanizate

due to the activating effect of any residual enzyme materials present in the latex. A higher ash content was reported for EDPNRL (George *et al.*, 2001). There was

no significant change in the modulus values recorded for compounds with different combinations of accelerators in both types of latices.

Plots of vulcanization time against V_r of EDPNRL compounds are given in Fig. 1 and those of HA latex compounds in Fig. 2 respectively. With EDPNRL, systems with ZDBEDC, Setsit-5 and ZDC + Setsit-5 gave maximum V_r values at 30 min whereas for the other systems, maximum V_r values were obtained at 15 min with HA latex compounds. Maximum V_r values were obtained at 30 min for all the accelerator systems. This shows that EDPNRL compounds are slightly faster curing than HA latex compounds. This can also be attributed to the presence of residual enzyme in the latex.

The physical properties of NR latex films prepared from EDPNRL and HA latex compounds are given in Tables 5 and 6 respectively. EDPNRL compounds with ZDC and ZDBC gave higher tensile strength than those with ZDBEDC and Setsit-5. However, these when used in combination with ZDC improved the tensile strength in all cases. With HA latex, the tensile strength of Setsit-5 containing compounds was the lowest but in combination

Table 5. Physical properties of vulcanized films from EDPNRL

Compound	Accelerator	Before ageing			After ageing at 70°C for 10 days		
		500% modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	500% modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
A	ZDC	1.86	23.50	1091	1.90	20.92	1076
B	ZDBC	1.98	22.40	1076	2.02	18.02	1052
C	ZDBEDC	1.69	20.07	1111	1.66	18.51	1049
D	Setsit-5	1.57	18.78	1118	1.51	15.72	1180
E	ZDC + ZDBC	2.04	24.34	1085	2.16	20.45	1062
F	ZDC + ZDBEDC	1.87	24.02	1100	1.94	19.50	1045
G	ZDC + Setsit-5	1.71	19.69	1104	1.81	16.73	1068

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