

Room Temperature Prevulcanization of Natural Rubber Latex Using Xanthate

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ABSTRACT: Room temperature prevulcanization of natural rubber latex using a combination of xanthate and a dithiocarbamate accelerator system was investigated. The mechanical properties of the room temperature prevulcanized latex compound was compared with that of a dithiocarbamate system and a commercial prevulcanized latex. Films were prepared from the room temperature prevulcanized latex, commercial prevulcanized latex, and prevulcanized latex prepared by heating latex compound at 55°C. The mechanical properties were compared. The results show

that xanthate in combination with dithiocarbamate can bring about prevulcanization at room temperature. The latex film prepared from the room temperature prevulcanized latex compound gives better clarity and tensile properties than conventional and commercial samples. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1164–1174, 2004

Key words: compounding; crosslinking; dispersions; viscosity; vulcanization

INTRODUCTION

The term prevulcanization is used by the industry to describe the process of vulcanization in the latex stage.¹ The terms prevulcanized latex and vulcanized latex are interchangeable. When latex is vulcanized, it retains its original fluidity and general appearance.² Vulcanization takes place in the individual latex particles without altering their state of dispersion.³ Such a latex has obvious advantages as it eliminates the need for compounding and requires less energy for drying. The overhead and other associated costs involved in the use of room temperature prevulcanized latex are consequently lower. The latex is widely used in many applications, such as dipped goods, adhesives, etc. It is especially suitable for the products made by dipping because of the convenience of vulcanizing latex in bulk in relation to the trouble and expense of curing the equivalent amount of rubber in the form of a thin deposit over innumerable formers.⁴

This article presents the details of the studies conducted on

- Sulfur prevulcanization of natural rubber (NR) latex under room temperature conditions by using xanthate and dithiocarbamate and by using

dithiocarbamate alone by heating the latex compound at 55°C.

- The crosslink efficiency, tensile properties, and colloidal stability of xanthate-cured system and dithiocarbamate-cured system.
- Prepared casted films from xanthate room temperature prevulcanized system, dithiocarbamate heating system, and commercially available prevulcanized latex from Malaysia.
- The casted film of prevulcanized latex under heating system, room temperature curing system and commercially available sample, characterized by IR spectroscopy.

EXPERIMENTAL

Materials used

High ammonia centrifuged NR latex conforming to the BIS 5430-1981 specification given in Table I was collected from the Pilot Latex Processing Centre (Rubber board, Kottayam, India) and used for the preparation of prevulcanized latex. Prevulcanized latex from a commercial sample (Malaysia) and zinc diethyl dithiocarbamate, sulfur, zinc oxide, etc., commercial grade, were used.

The equipment used in this study were a prevulcanizer, a liquid bath known as Insef ultra cryostat circulator, supplied by M/s Inlab Instruments (Cochin, India), Brookfield viscometer LVT model supplied by M/s Brookfield Engineering Laboratories Inc. (Strongton, MA, USA), Universal tensile tester UTM

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TABLE I
Properties of Centrifuged Natural Rubber Latex Used for the Production of Pre vulcanized Latex

Properties	Value	Requirements (BIS 5430-1981)	Test methods (IS 9316, 1987)
Dry rubber content (% by mass)	60	60 ^a	IS 3708 (Part 1) 1985
Nonrubber solids (% by mass)	1.5	2 ^b	IS 9316 (Part 4) 1988
Sludge content (% by mass)	0.5	0.1 ^b	IS 3708 (Part 2) 1985
Ammonia content (% by mass)	0.8	0.6 ^a	IS 3708 (Part 4) 1985
Potassium hydroxide number	0.5	1 ^b	IS 3708 (Part 5) 1985
Mechanical stability time (s)	1000	475 ^a	IS 3708 (Part 6) 1985
Volatile fatty acid number	0.02	0.15 ^b	IS 3708 (Part 7) 1986
Coagulum content (% by mass)	0.03	0.05 ^b	IS 9316 (Part 3) 1987
Copper content (ppm)	1	8 ^b	IS 9316 (Part 8) 1987
Manganese content (ppm)	Traces	8 ^b	IS 9316 (Part 9) 1987

^a Minimum.

^b Maximum.

Model 4411 (M/s Instron, Buckinghamshire, UK), mechanical stability apparatus (M/s Klaxon Signals, Birmingham, UK), digital pH meter (M/s Systronics, Mumbai), and infrared spectrophotometer (Shimadzu, 8101M, Japan).

Experimental procedure

The properties of centrifuged latex, given in Table I, were determined as per IS 3708-1985 and 9316-1987. Potassium xanthate was prepared in the laboratory as per the procedure reported earlier.⁵

Chloroform number test for determining crosslinking in latex compound was done as follows. A sample of the latex was coagulated by mixing with an equal volume of chloroform. After 2–3 min, the coagulum was examined and graded depending upon the form of coagulum and chloroform number given as (1) unvulcanized state, (2) light vulcanized, (3) moderately vulcanized, and (4) fully vulcanized. Equilibrium swelling values were determined by immersing a thin film of the rubber in toluene for 36 h at room temperature and measuring the increase in weight. The equilibrium swelling ratio was calculated as

$$\text{Swell Index}(Q) = \frac{W_2 - W_1}{W_1}$$

where W_1 is the initial weight and W_2 is the swollen weight. The variation of swelling ratio with crosslink density for conventionally vulcanized NR in toluene may be broadly described as follows: Unvulcanized rubber, >15; light vulcanized, 7–15; moderately vulcanized, 5–7; and fully vulcanized, <5.

The formulations for prevulcanization are given in Table II. After adding the ingredients, compounds B, C, and D were stirred for 1 h. After stirring, the compounds were transferred to bottles and allowed to stand at room temperature ($28 \pm 2^\circ\text{C}$). At various

periods, the latex compounds were stirred and samples were drawn for testing. The films were prepared by drying latex compounds at room temperature on glass plates. After drying, the films were removed, dusted with talc, and leached in water for 24 h. After leaching, the films were dried at room temperature at least for another 48 h.

IR spectra of the thin latex film samples were recorded by using a Shimadzu Model 8101M Fourier transform infrared spectrophotometer.⁶

Brookfield viscosity determinations were carried out at 25°C by using a Brookfield viscometer (ASTM D 2526-229) and the results were expressed in mPa s (Brookfield). The tensile properties of prevulcanized NR latex vulcanizate were measured from the cast film. Film test pieces were taken from each sample and tested for tensile properties, as per ASTM D 3138.

Properties of room temperature prevulcanized latex compounds (B, C, and D) such as total solids, mechanical stability time, Brookfield viscosity, chloroform number, swell index, pH, and tensile properties are given in Tables III, IV, and V.

Compound A was prepared as per formulations given in Table II. Fine ball-milled dispersions of the vulcanization ingredients were added into centrifuged latex.

TABLE II
Formulation of Prevulcanized NR Latex Compound

Ingredients	Parts by wet weight			
	A	B	C	D
60% Natural rubber latex	167	167	167	167
10% Potassium hydroxide solution	2.5	2.5	2.5	2.0
10% Potassium oleate solution	0.75	0.75	2.0	—
50% Sulphur dispersion	2.4	2.4	4	2
50% ZDC dispersion	1.6	1.6	2	1
50% Potassium xanthate dispersion	—	1.6	2	1
50% ZnO dispersion	0.5	0.5	0.5	0.5

TABLE III
Properties of Prevulcanized Latex Compound A

Properties	Vulcanization time (h)				
	2	4	6	8	10
Total solids content	59	59	59	59	59
pH at 28°C	10.2	10.2	10.2	10.2	10.2
MST at 55% TSC (s)	565	586	604	751	912
Viscosity (mPa s)	50	50	50	45	40
Chloroform number	2	2	3	3	4
Swelling ratio	5.58	5.38	5.21	5.01	4.22
Tensile properties before aging (film casted at 70°C 1 h, air oven)					
Tensile strength (MPa)	26.17	27.75	28.15	29.15	29.70
Modulus 100% (MPa)	0.65	0.68	0.70	0.81	0.85
Modulus 300% (MPa)	1.05	1.07	1.10	1.26	1.36
Modulus 500% (MPa)	2.59	2.73	3.17	4.71	4.08
Modulus 700% (MPa)	6.45	8.26	8.38	8.95	11.33
Elongation at break (%)	1030	990	950	920	920
Tensile properties after aging at 70°C 10 days (air oven)					
Tensile strength (MPa)	25.5	26.4	26.8	27.4	28.0
Modulus 100% (MPa)	0.89	0.99	1.24	1.77	1.95
Modulus 300% (MPa)	2.91	3.14	3.24	3.54	3.71
Modulus 500% (MPa)	3.45	3.75	3.85	4.01	4.74
Modulus 700% (MPa)	5.47	5.8	5.9	7.1	8.99
Elongation at break (%)	970	1000	930	920	910

Its prevulcanization was affected by heating the compound at 55°C in the prevulcanizer. Constant stirring of the latex was maintained throughout the

course of prevulcanization. Rapid cooling of prevulcanized latex samples was carried out to arrest further prevulcanization.

TABLE IV
Properties of Prevulcanized Latex Compound B

Properties	Vulcanization time (days)				
	1	2	3	4	5
Total solids content	58.50	58.50	58.50	58.54	58.50
pH at 28°C	10.8	10.8	10.8	10.8	10.8
MST at 55% TSC (sec)	900	900	850	850	820
Viscosity (mPa s)	85	80	95	90	95
Chloroform number	2	2	2	3	3
Swelling ratio	6.42	6.05	5.57	5.00	4.56
Tensile properties before aging [film casted at room temperature (28 ± 2°C) 48 h]					
Tensile strength (MPa)	20.00	22.15	23.56	24.80	25.20
Modulus 100% (MPa)	0.56	0.71	0.78	1.47	1.78
Modulus 300% (MPa)	0.76	1.21	1.71	2.80	2.75
Modulus 500% (MPa)	1.52	1.95	2.00	3.15	3.00
Modulus 700% (MPa)	4.25	5.80	6.24	6.01	5.41
Elongation at break (%)	1060	1020	990	970	900
Tensile properties after aging at 70°C 10 days (air oven)					
Tensile strength (MPa)	24.35	27.84	26.84	27.14	26.50
Modulus 100% (MPa)	0.76	0.94	0.90	1.24	1.05
Modulus 300% (MPa)	0.95	2.10	2.27	2.54	1.99
Modulus 500% (MPa)	2.66	2.78	2.56	2.95	3.75
Modulus 700% (MPa)	8.16	8.51	8.50	7.88	7.91
Elongation at break (%)	935	950	975	940	930

TABLE V
Properties of Prevulcanized Latex Compound C

Properties	Vulcanization time (days)				
	1	2	3	4	5
Total solids content	58	58	58	58	58
pH at 28 °C	10.5	10.5	10.5	10.5	10.5
MST @ 55% TSC (sec)	540	540	540	550	550
Viscosity (mPa.s)	90	95	100	100	100
Chloroform Number	2	2	2	2	3
Swelling ratio	6.54	6.14	5.20	5.01	4.75
Tensile properties before aging [film casted at room temperature (28 ± 2°C) 48 h]					
Tensile strength (MPa)	21.25	25.74	25.84	28.51	30.85
Modulus 100% (MPa)	0.53	0.59	0.48	0.57	0.71
Modulus 300% (MPa)	0.78	0.92	0.75	0.91	0.98
Modulus 500% (MPa)	0.91	1.67	1.60	2.07	2.57
Modulus 700% (MPa)	5.67	4.47	4.30	5.71	6.10
Elongation at break (%)	1020	990	1030	990	970
Tensile properties after aging at 70°C 10 days (air oven)					
Tensile strength (MPa)	26.48	27.81	27.46	27.05	28.50
Modulus 100% (MPa)	0.64	0.59	0.74	0.78	0.81
Modulus 300% (MPa)	0.91	1.91	0.99	0.95	1.05
Modulus 500% (MPa)	1.92	2.34	2.27	2.11	2.77
Modulus 700% (MPa)	6.48	9.13	7.47	6.04	6.85
Elongation at break (%)	970	900	980	970	960

To study the effect of prevulcanization time on di-thiocarbamate heating systems, samples were collected at different periods of 2, 4, 6, 8, and 10 h.

Colloidal stability and physical properties of prevulcanized lattices were determined and the results are given in Table VI.

TABLE VI
Properties of prevulcanized latex compound D

Properties	Vulcanization time (days)				
	1	2	3	4	5
Total solids content	55	55	55	55	55
pH at 28°C	10.9	10.9	10.9	10.9	10.9
MST at 55% TSC (s)	560	540	500	500	440
Viscosity (mPa s)	50	50	60	80	100
Chloroform number	2	2	2	2	3
Swelling ratio	6.90	6.53	5.34	5.14	4.95
Tensile properties before aging [film casted at room temperature (28 ± 2°C) 48 h]					
Tensile strength (MPa)	16.34	18.36	22.42	23.68	25.41
Modulus 100% (MPa)	0.48	0.49	0.67	0.69	0.85
Modulus 300% (MPa)	0.95	0.98	1.10	1.12	1.15
Modulus 500% (MPa)	1.35	1.94	3.94	3.99	4.41
Modulus 700% (MPa)	4.46	4.85	7.17	7.74	8.86
Elongation at break (%)	1210	1190	970	950	920
Tensile properties after aging at 70°C 10 days (air oven)					
Tensile strength (MPa)	20.22	22.15	24.85	25.10	26.57
Modulus 100% (MPa)	0.99	0.67	0.71	0.78	0.95
Modulus 300% (MPa)	1.83	1.71	1.95	1.99	2.11
Modulus 500% (MPa)	3.40	3.56	4.10	4.20	4.77
Modulus 700% (MPa)	7.50	5.84	8.50	8.04	8.96
Elongation at break (%)	1080	1050	920	940	950

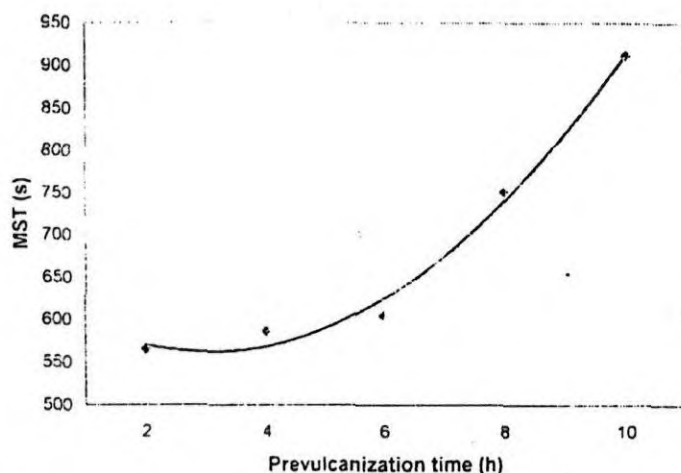


Figure 1 Variation of vulcanization of MST with time of prevulcanization.

RESULTS AND DISCUSSION

Figure 1 shows the change in mechanical stability time (MST) with time of prevulcanized sample A. Prevulcanization is done at different periods (viz., 2, 4, 6, 8, and 10 h). It is seen that, as prevulcanization time increases, the MST increases considerably up to 10 h. The colloidal stability of prevulcanized latex depends on many factors (viz., the properties of NR latex, amount of potassium hydroxide and carboxylate soap, dosage of vulcanizing ingredients, and prevulcanization conditions such as time and temperature).⁷ The increase in MST as vulcanization time increases may be due to the fact that, during heating, the presence of

alkali may accelerate the hydrolysis of proteins and phospholipids adsorbed on the surface of the rubber particles, thereby producing higher fatty acid soap.⁸

In Figure 2, the effect of vulcanization time on tensile properties and swelling ratio of sample A is shown. As prevulcanization time increases, tensile strength and modulus increases and elongation at break decreases. When prevulcanization time increases, crosslinking increases, which leads to an increase in modulus and that will result in a decrease in elongation.⁹ The swelling ratio of prevulcanized latex films also decreases with increasing prevulcanization time. According to Blackley et al., change in tensile

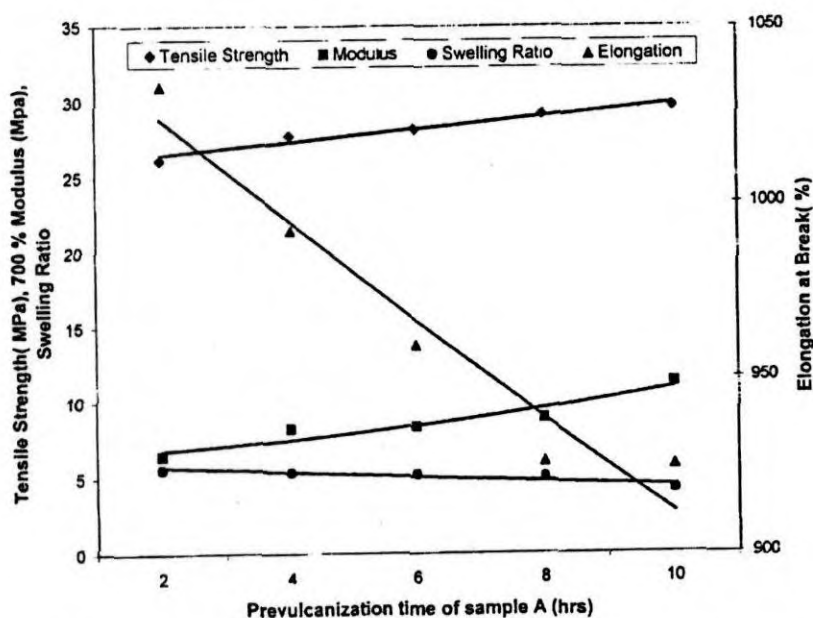


Figure 2 Variation of tensile properties and swelling ratio with time of prevulcanization.

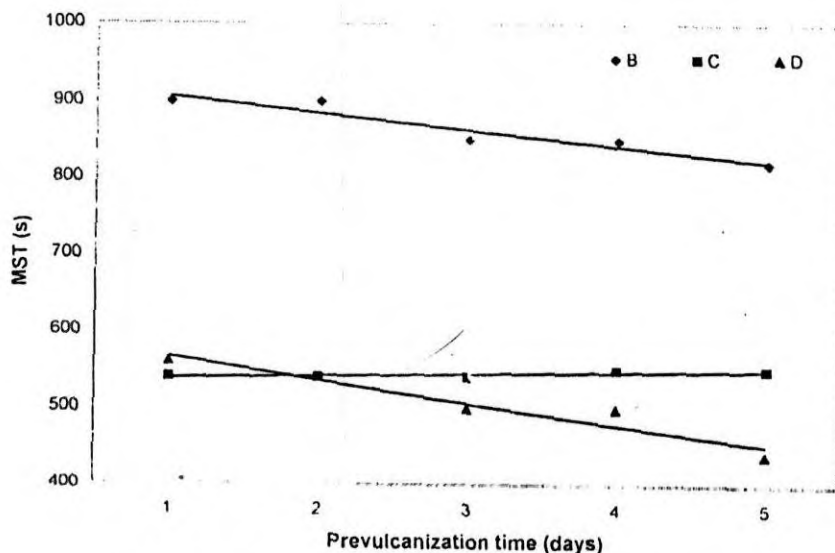


Figure 3 Variation of MST with time of prevulcanization.

strength, elongation at break, modulus, and swelling ratio are due to the crosslinking of rubber particles.¹⁰

Figure 3 shows the variation of mst of prevulcanized samples b, c, and d.

The colloidal stability of prevulcanized latex is determined by two opposing factors. The presence of residual vulcanizing ingredients such as zinc oxide may reduce the stability of latex because of zinc oxide thickening. In the case of samples B and D, a

slight drop in MST may be due to the low dosage of alkalis and carboxylate soaps. Addition of alkalis and carboxylate soaps can increase the stability of latex by increasing the negative charge on the surface of the particles and by surface adsorption, respectively.¹¹ In the case of sample C, a slight increase in MST may be due to the fact that during prevulcanization the presence of alkali accelerates the hydrolysis of proteins and phospholipids adsorbed on the surface of the rubber particles, thereby producing higher fatty acid soaps. The dos-

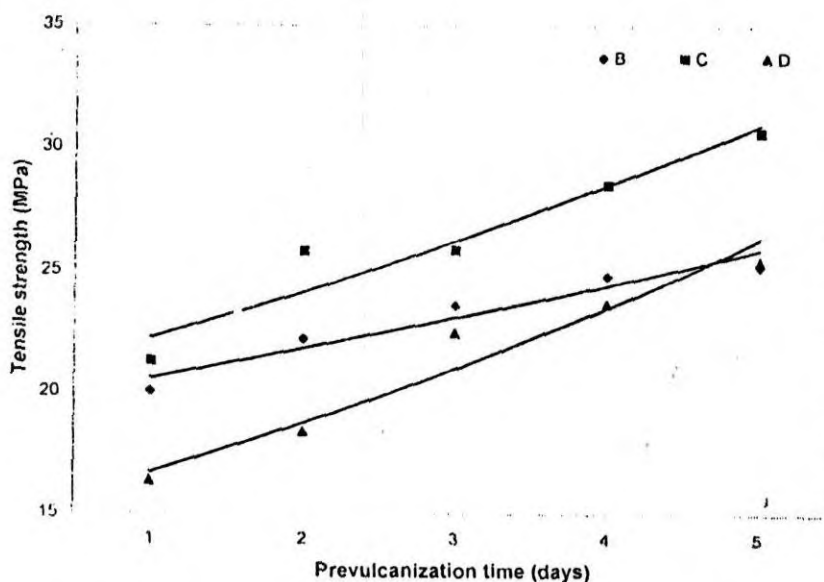


Figure 4 Variation of tensile strength with time of prevulcanization.

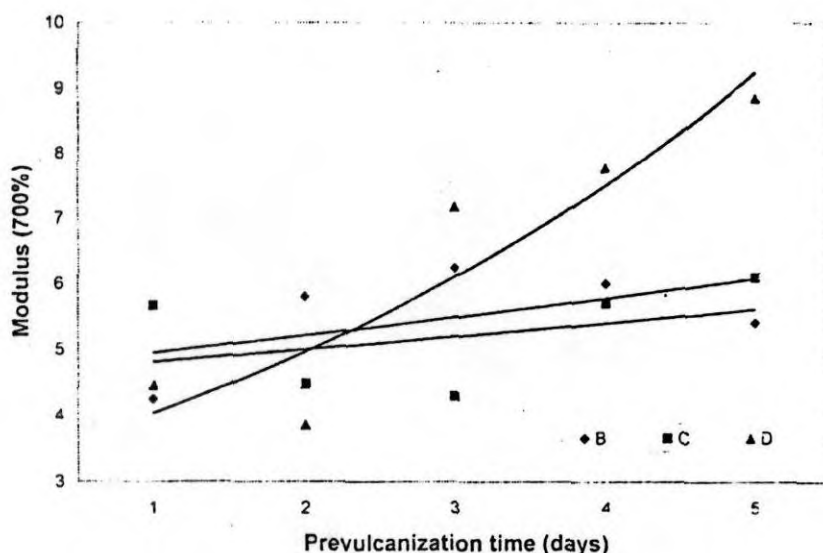


Figure 5 Variation of modulus 700% with time of prevulcanization.

age of alkali and carboxylate soap in the case of sample C is greater than in B and D.

Figure 4 shows the tensile strength values of samples B, C, and D during prevulcanization. The increase in tensile strength may be due to the increase in crosslinking during prevulcanization. Blackley and Merrill reported that the tensile strength of the film from prevulcanized NR latex compounds depends on the ability of the particles to coalesce and integrate, when the film dries, as well as on the concentration of the crosslink in the rubber.¹²

Figure 5 shows the effect of prevulcanization time

on 700% modulus of compounds B, C, and D. It is seen that 700% modulus increases with prevulcanization time from 1 to 5 days. Blackley reported that, on prevulcanization of NR latex, the modulus increases with crosslinking. The change in modulus during prevulcanization may be due to crosslinking of rubber particles.¹³

Figure 6 shows that the elongation at break decreases with an increase in prevulcanization time for all samples B, C, and D. This may be due to the crosslinking occurring during prevulcanization. Elongation at break decreases by increasing prevulcanization time.¹⁴

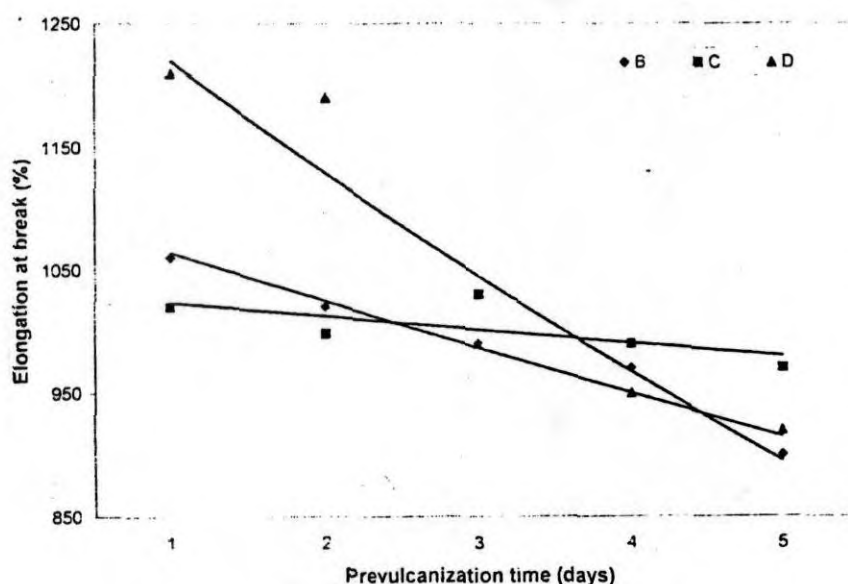


Figure 6 Variation of elongation at break with time of prevulcanization.

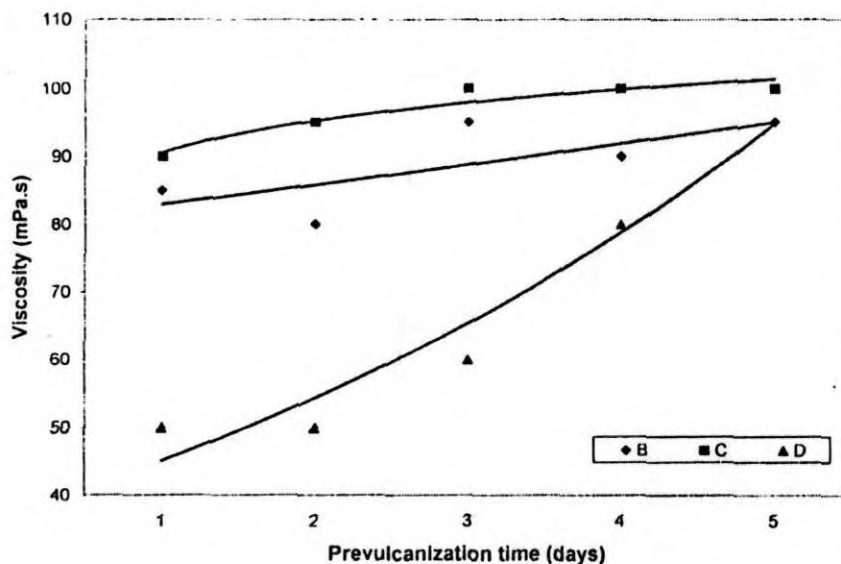


Figure 7 Variation of viscosity with time of prevulcanization.

Figure 7 shows the variation in viscosity of prevulcanized latex during prevulcanization from 1 to 5 days. In samples B and C, it is seen that the viscosity is almost constant, and for sample D, it increases slightly up to 100 from 50 mPa s. The variation in viscosity may be due to the absence of potassium oleate in compound D.

Figure 8 shows the effect of prevulcanization time on the swelling ratio of latex films. As prevulcanization time increases, swelling ratio decreases in compounds B, C, and D. It shows that crosslinking takes place during prevulcanization.

Figures 9, 10, and 11 show the infrared spectra of films prepared from conventional sulfur prevulcanized NR latex under heating systems, xanthate/dithiocarbamate room temperature prevulcanized system, and a commercial prevulcanized latex compound, respectively. All the spectra show a peak at about 1376 cm^{-1} , which corresponds to C=S stretching. Another peak at about 797 cm^{-1} corresponds to C-S stretching. These peaks represent the vulcanized state of NR chains. Trial products (viz., balloons, industrial gloves, and rubber bands) were made from the above compounds and the results

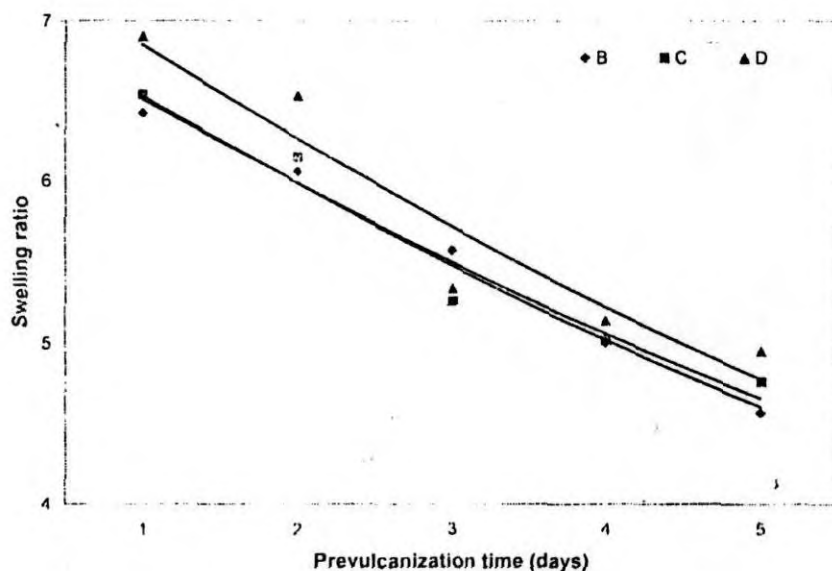


Figure 8 Variation of swelling ratio with time of prevulcanization.

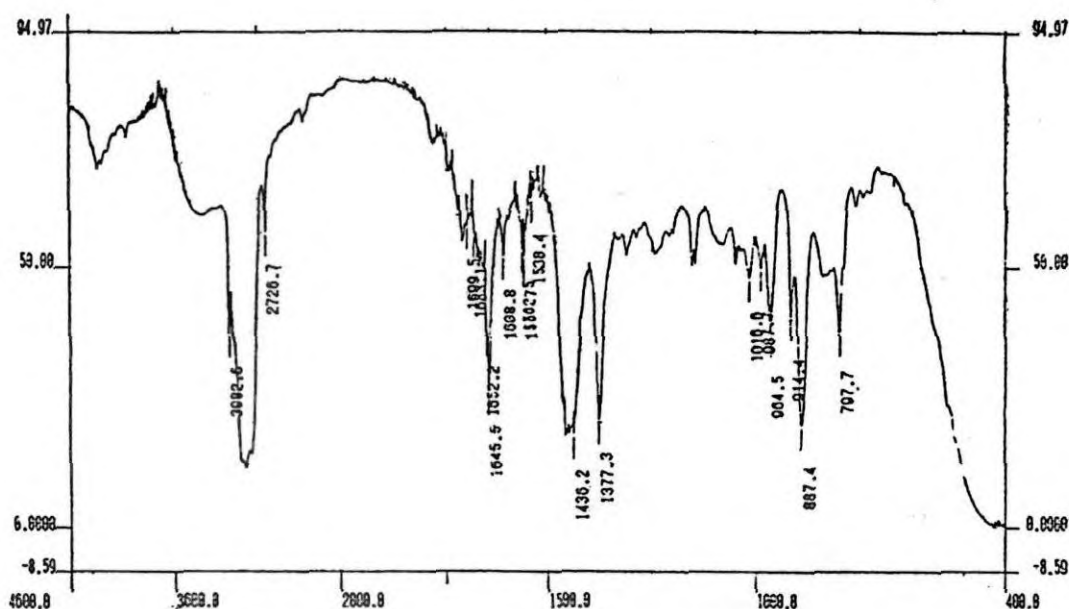


Figure 9 IR spectrum of conventional sulfur prevulcanized latex film under heating system.

show that the products from the xanthate/dithiocarbamate accelerator system give the best color and clarity and better physical properties.

Tables III-VII show the properties of prevulcanized latex compounds A, B, C, and D and commercial prevulcanized compounds. The mechanical properties of compounds B, C, and D are found

to be comparable to that of the commercial prevulcanized compound. The aging resistance values of samples A, B, C, and D are given in Tables III-VI. The aging resistance is found to be better for the xanthate/dithiocarbamate prevulcanized latex than the other two systems. The total solids content and viscosity are found to be higher for the pre-

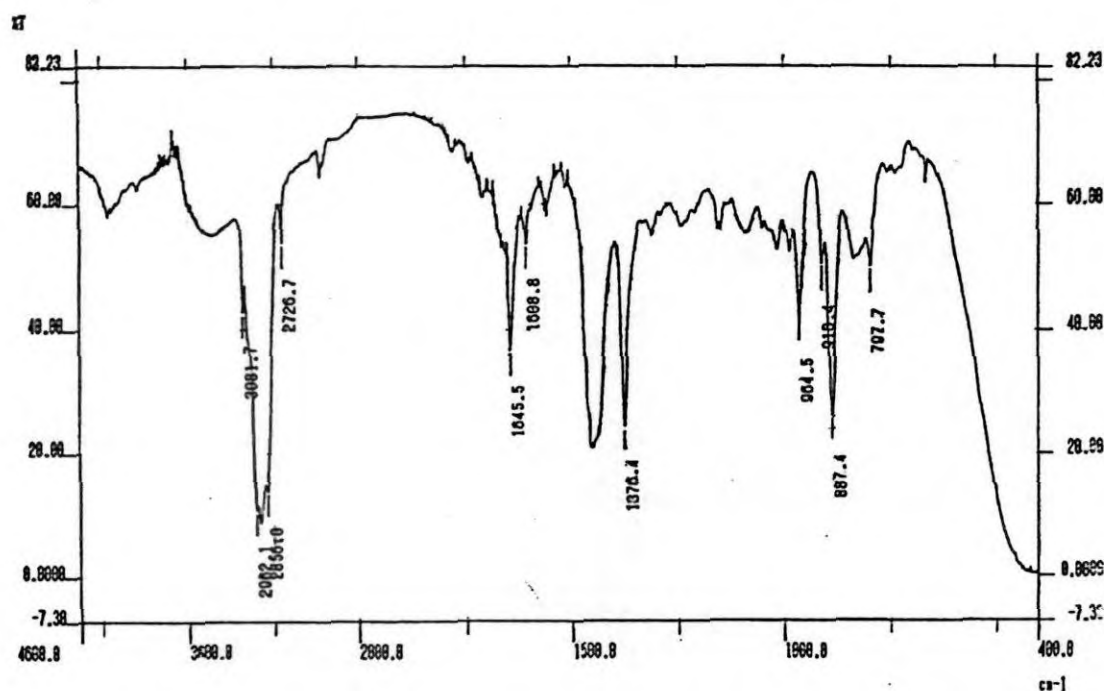


Figure 10 IR Spectrum of prevulcanized latex film under room temperature curing system.

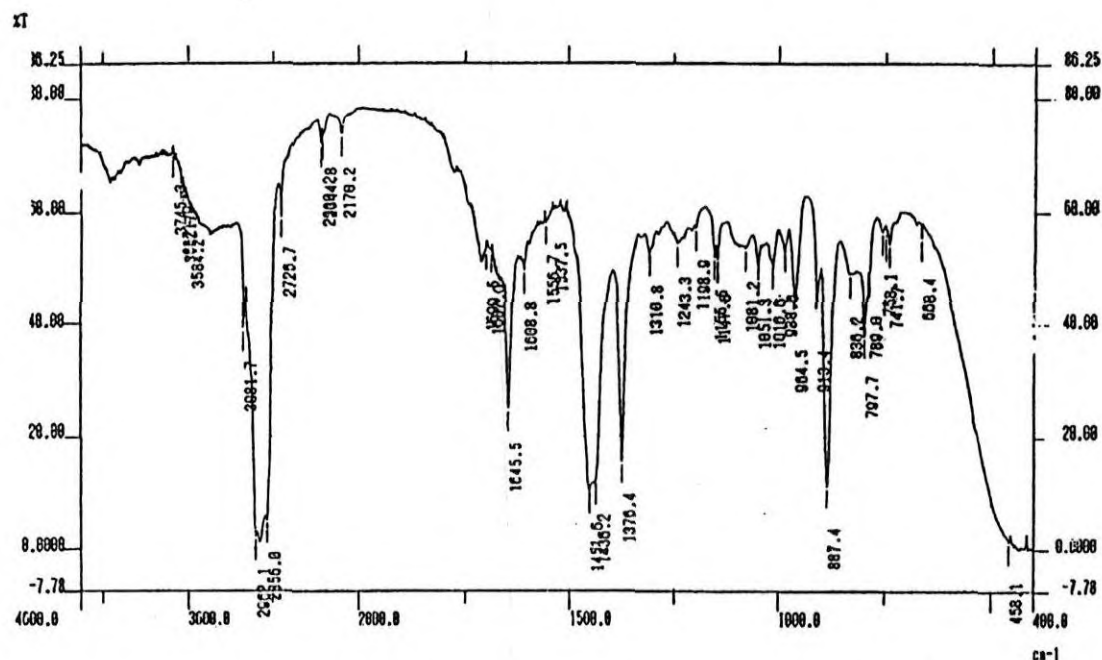


Figure 11 IR Spectrum of commercial prevulcanized latex film.

vulcanized compounds B, C, and D than for the commercial sample from Malaysia. p11 and chloroform number are found to be almost the

same. The MST is found to be better for the xanthate/dithiocarbamate prevulcanized compound.

TABLE VII
Properties of Commercial Prevulcanized
Latex from Malaysia

Properties	
Total solids content	42
pH at 28°C	9.8
MST at 42% TSC (s)	480
Viscosity (mPa s)	15
Chloroform number	3
Swelling ratio	5.29
Tensile properties before aging (film casted at 70°C 1 h, air oven)	
Tensile strength (MPa)	21.52
Modulus 100% (MPa)	0.57
Modulus 300% (MPa)	0.98
Modulus 500% (MPa)	1.65
Modulus 700% (MPa)	4.40
Elongation at break (%)	1090
Tensile properties after aging at 70°C 10 days (air oven)	
Tensile strength (MPa)	22.48
Modulus 100% (MPa)	0.66
Modulus 300% (MPa)	1.27
Modulus 500% (MPa)	2.46
Modulus 700% (MPa)	7.15
Elongation at break (%)	980

CONCLUSION

Room temperature prevulcanization of centrifuged latex was done by using a xanthate/dithiocarbamate accelerator combination and also with a conventional sulfur prevulcanization under heating system compared to the colloidal and tensile properties of the above prevulcanized lattices with a commercial prevulcanized latex. The results showed that xanthate in combination with dithiocarbamate can bring about prevulcanization at room temperature. The latex film prepared from the room temperature prevulcanized latex compound gives better clarity compared to the conventional and commercial samples. The tensile properties of the xanthate prevulcanized films are comparable to that of the conventional films and higher than that of commercial film. The colloidal stability of the room temperature prevulcanized latex is comparable to that of conventional and commercial samples.

Products (viz., balloons, industrial gloves, rubber bands, etc.) were produced from all three types of compounds at Janatha Rubbers Ltd. (Cochin, India). The xanthate/dithiocarbamate room temperature prevulcanized latex products showed better clarity, color, and technological properties.

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