

Effect of the Vulcanization Time and Storage on the Stability and Physical Properties of Sulfur-Prevulcanized Natural Rubber Latex

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ABSTRACT: Prevulcanized natural rubber latex was prepared by the heating of the latex compound at 55°C for different periods of time (2, 4, 6, 8, and 10 h). The changes in the colloidal stability and physical properties were evaluated during the course of prevulcanization. The prevulcanized latex compounds were stored for 300 days, and the properties were monitored at different storage intervals (0, 20, 40, 60, 120, 180, 240, and 300 days). During prevulcanization, the mechanical stability time increased, and the vis-

cosity remained almost constant. The tensile strength increased during storage for a period of 20 days. The degree of crosslinking, modulus, elongation at break, and chloroform number were varied with the time of storage. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1804–1811, 2005

Key words: crosslinking; latices; rubber; swelling; vulcanization

INTRODUCTION

Prevulcanized natural rubber latex is defined as a latex in which the rubber particles are chemically crosslinked so that, upon the drying of the latex, a vulcanized film is obtained without further heating.¹ The production of sulfur-prevulcanized latex involves heating a raw latex compound containing ingredients such as sulfur and an accelerator until the required degree of crosslinking is obtained. Then, it is cooled and allowed to mature for a few days.

Prevulcanized latex compounds are convenient materials for the manufacturers of latex goods, especially dipped goods. They are also used in adhesives, textiles, carpet backing, and cast rubber products. Other advantages are shorter drying times and products of high clarity, particularly if the prevulcanized latex is clarified before use.²

The chemical and physical properties of sulfur-prevulcanized natural rubber latex may undergo changes during the storage of the latex because of the presence of surface-active agents and residual vulcanizing ingredients.³ Knowledge of the storage characteristics of sulfur-prevulcanized latex is essential for the manufacture of latex products with consistent quality.

Studies have been reported on the influence of storage on the properties of natural rubber latex concentrates.⁴ However, a systematic study of the effect of storage on the stability of sulfur-prevulcanized natural rubber latex has not yet been reported. The rate of prevulcanization varies with different vulcanization systems, and the extent of prevulcanization has a pronounced influence on the final vulcanizate properties. The effect of temperature on the rate of prevulcanization and its effect on the final vulcanizate properties have been reported.⁵

This article reports the effect of storage on the colloidal stability and physical properties of typical sulfur-prevulcanized latex compounds with different degrees of prevulcanization. The following factors have been investigated:

- Changes in the colloidal stability as measured by the mechanical stability time and viscosity.
- Changes in the crosslink density as measured by the swelling ratio and chloroform number.
- Changes in the tensile properties of unaged and aged cast films.

EXPERIMENTAL

High-ammonia centrifuged natural rubber latex conforming to BIS 5430-1981 (Table I) was collected from the Rubber Board's Pilot Latex Processing Centre

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

Property	Value	Requirement (BIS 5430-1981)	Test method
Dry rubber content (mass %)	60	60 ^a	IS 3708 (part 1) 1985
Non rubber solids (mass %)	1.5	2 ^b	IS 9316 (part 4) 1988
Sludge content (mass %)	0.05	0.1 ^b	IS 3708 (part 2) 1985
Ammonia content (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
Coagulam content (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.

(Kottayam, India) and used for the preparation of prevulcanized latex.

The equipment used in this study included a prevulcanizer, a liquid bath known as an Insef ultracryostat circulator (Inlab Instruments, Cochin City, India), a Brookfield LVT viscometer (Brookfield Engineering Laboratories, Stroughton City, MA), a model 4411 universal testing machine (Instron, Buckingham-Shire, England), a mechanical stability tester (Klaxon Signals, Birmingham, England), and a digital pH meter (Systronics, India).

The properties of the centrifuged latex, given in Table I, were determined according to IS 9316-1987. The latex was compounded according to the formulation given in Table II. Fine ball-milled dispersions of the vulcanization ingredients were added to the centrifuged latex. Prevulcanization was performed by the heating of the latex compound at 55°C in a prevulcanizer for different time intervals with constant stirring. During heating, samples were collected at different intervals (2, 4, 6, 8, and 10 h). Rapid cooling of the prevulcanized latex samples was carried out to arrest further prevulcanization. The colloidal stability and physical properties of these samples were determined and are given in Table III.

The chloroform number test was performed through the coagulation of a sample of the latex via mixing with an equal volume of chloroform. After 2-3 min, the coagulum was examined and graded according to the texture of the coagulum. The chloroform number was expressed as follows: (1) unvulcanized, (2) lightly vulcanized, (3) moderately vulcanized, and (4) fully vulcanized.

Equilibrium swelling values were determined by the immersion of a thin film of the rubber in toluene for 48 h and the measurement of the increase in the weight. The equilibrium swelling ratio was usually calculated as follows:

$$\text{Swelling index} = \frac{W_2 - W_1}{W_1}$$

where W_1 is the initial weight and W_2 is the swollen weight.

The variation of the swelling ratio with the crosslink density for conventionally vulcanized natural rubber in toluene may be broadly described as follows: unvulcanized (>15), lightly vulcanized (7-15), moderately vulcanized (5-7), and fully vulcanized (<5).

Brookfield viscosity determinations were carried out at 25°C with a Brookfield viscometer (ASTM D 2526-229). All viscosity values are expressed in mPa s.

The samples collected at different intervals during prevulcanization are designated as A (2 h), B (4 h), C (6 h), D (8 h), and E (10 h).

Films were cast with samples A-E. Test pieces were taken from each sample film and tested for tensile properties according to ASTM D 3138.

Prevulcanized latices were stored at room temperature (30°C) for 300 days for studying their storage characteristics. The properties of the prevulcanized latex compounds, such as the total solid content, mechanical stability time, Brookfield viscosity, chloroform number, swelling index, and pH, were determined at intervals of 0, 20, 40, 60, 120, 180, 240, and 300 days. The tensile properties of the cast films were also

TABLE II
Formulation of the Natural Rubber Latex Compound

Ingredient	Parts by weight	
	Dry weight	Wet weight
60% centrifuged latex (high-ammonia type)	100	167
10% potassium hydroxide solution	0.25	2.5
10% potassium oleate solution	0.075	0.75
50% sulfur dispersion	1.2	2.4
50% ZDC dispersion	0.8	1.6
50% ZnO dispersion	0.25	0.5

TABLE III
Effect of the Variation of the Vulcanization Time on the Colloidal Stability and Physical Properties of the Latex Compound

Compound	Time of heating at 55 °C	Chloroform number	Toluene swelling (g/g)	MST at 55% total solid content (s)	Viscosity (mPa s)	Tensile properties of cast film (70°C, 1 h)					Elongation at break (%)
						Tensile strength (MPa)	100% modulus (MPa)	300% modulus (MPa)	500% modulus (MPa)	700% modulus (MPa)	
A	2	2	5.59	565	50	26.2	0.65	1.06	2.60	6.5	1033
B	4	2	5.39	586	50	27.8	0.69	1.07	2.73	8.3	992
C	6	3	5.22	604	50	28.2	0.70	1.11	3.17	8.4	959
D	8	3	5.01	751	45	29.2	0.82	1.27	4.07	9.0	926
E	10	4	4.22	912	40	29.7	0.85	1.36	4.09	11.3	925

determined at these intervals. The results are given later in Table IV and Figures 1-7.

RESULTS AND DISCUSSION

The mechanical stability time (MST) values of prevulcanized latices A-E are given in Table III. As the prevulcanization time increases, MST increases considerably up to 10 h. The colloidal stability of the prevulcanized latex depends on many factors, such as the properties of the natural rubber latex, the amounts of potassium hydroxide and carboxylate soap added, the dosage of other vulcanizing ingredients, and prevulcanization conditions such as the time and temperature.^{6,7}

The colloidal stability of prevulcanized latex is affected 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. At the same time, the addition of alkalis and carboxylate soaps can increase the stability by increasing the negative charge on the surface of the particles and by increasing surface adsorption. During heating, the presence of alkalis may accelerate the hydrolysis of proteins and phospholipids adsorbed on the surface of the rubber particles, thereby producing higher fatty acid soap, which increases MST. Similar results were reported by Yang.⁸

Table III shows that as the vulcanization time increases, the tensile strength and modulus increase and the elongation at break decreases. The changes in the tensile strength, elongation at break, and modulus are due to the crosslinking of rubber particles during prevulcanization.^{9,10}

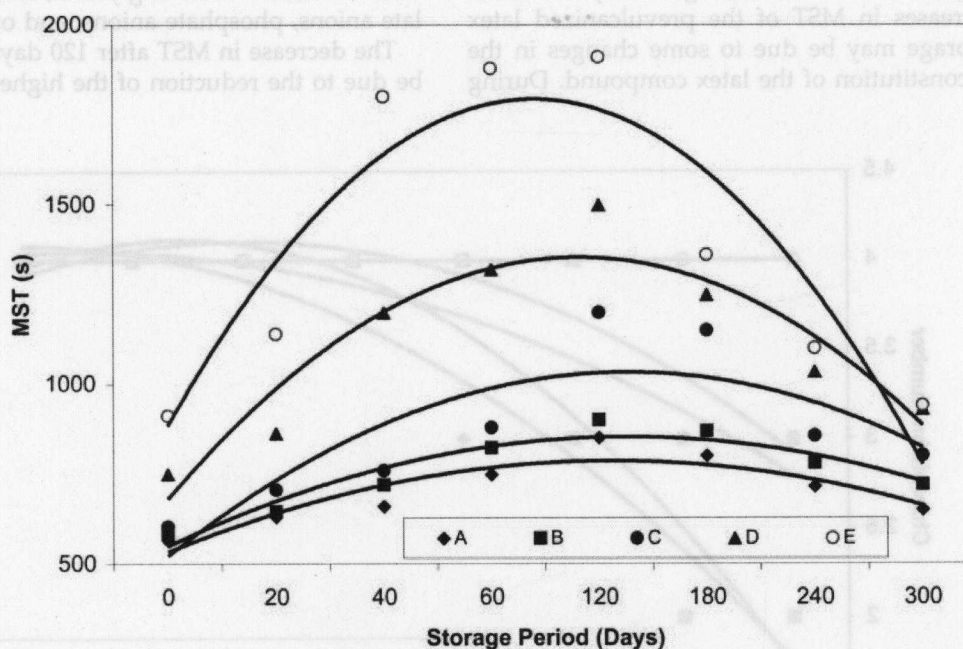


Figure 1 Variation of MST of the prevulcanized latex compounds during storage.

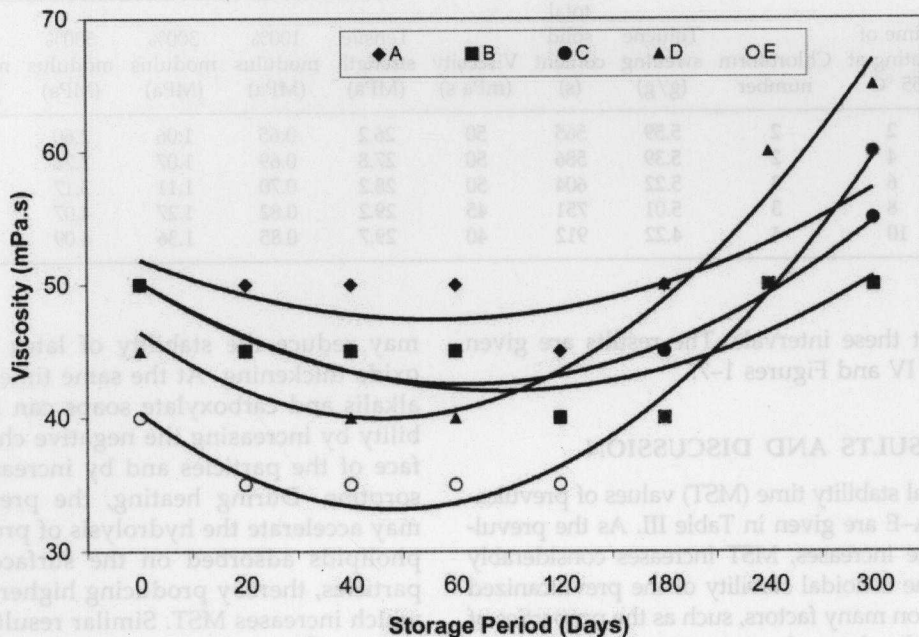


Figure 2 Variation of the viscosity of the pre-vulcanized latex compounds during storage.

Figure 1 shows the mechanical stability time of pre-vulcanized compounds A-E at different periods of storage (0, 20, 40, 60, 120, 180, 240, and 300 days). The MST values of all the samples increase during storage for 120 days, and thereafter MST gradually decreases.

The increases in MST of the pre-vulcanized latex during storage may be due to some changes in the chemical constitution of the latex compound. During

storage, the hydrolysis of protein adsorbed onto the surface of the rubber particles may continue, leading to the formation of polypeptides and amino acids. The hydrolysis of lipids may lead to the formation of various substances such as glycerol, long-chain carboxylate anions, phosphate anions, and organic bases.^{7,11}

The decrease in MST after 120 days of storage may be due to the reduction of the higher fatty acid soap

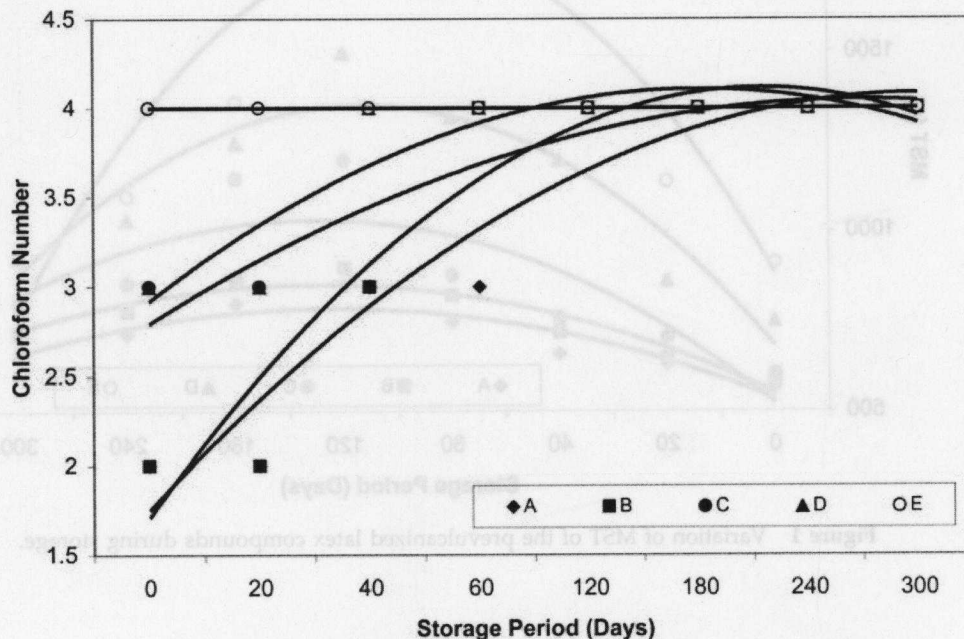


Figure 3 Variation of the chloroform number of the pre-vulcanized latex compounds during storage.

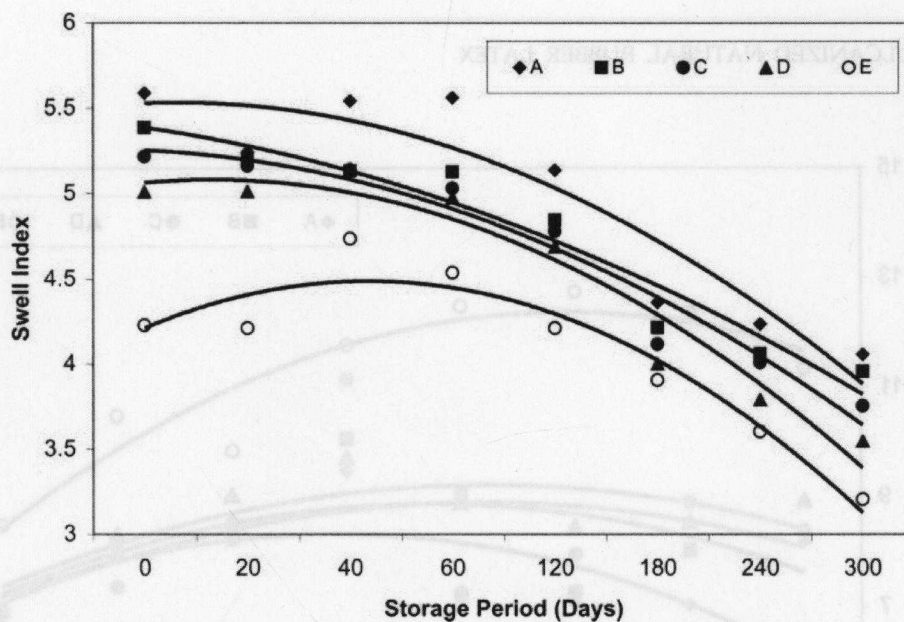


Figure 4 Variation of the swelling index of the prevulcanized latex compounds during storage.

and the increase in the viscosity of the latex compounds.¹²

Figure 2 shows the effect of storage on the viscosity of the prevulcanized latex. The viscosity of the samples gradually decreases up to 120 days and thereafter increases slightly. The decrease in the viscosity of the latex indicates improved colloidal stability.^{10,11}

Figure 3 shows the effect of storage on the chloroform number. During storage, the chloroform number

increases for compounds A–D. Below 10 h, prevulcanization is not completed, and some extent of vulcanization takes place during storage for latex samples A–D. However, the chloroform number of compound E remains constant during storage. This shows that the prevulcanization of the latex is complete when the vulcanization time is 10 h.

Figure 4 shows the effect of storage on the swelling index of the prevulcanized latex films. As the prevul-

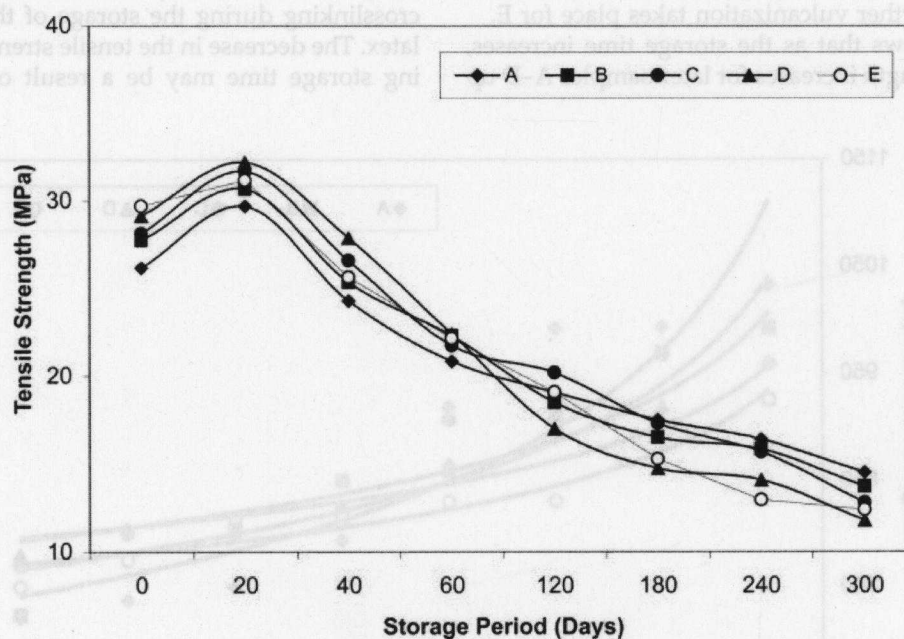


Figure 5 Variation of the tensile strength of the prevulcanized latex compounds during storage.

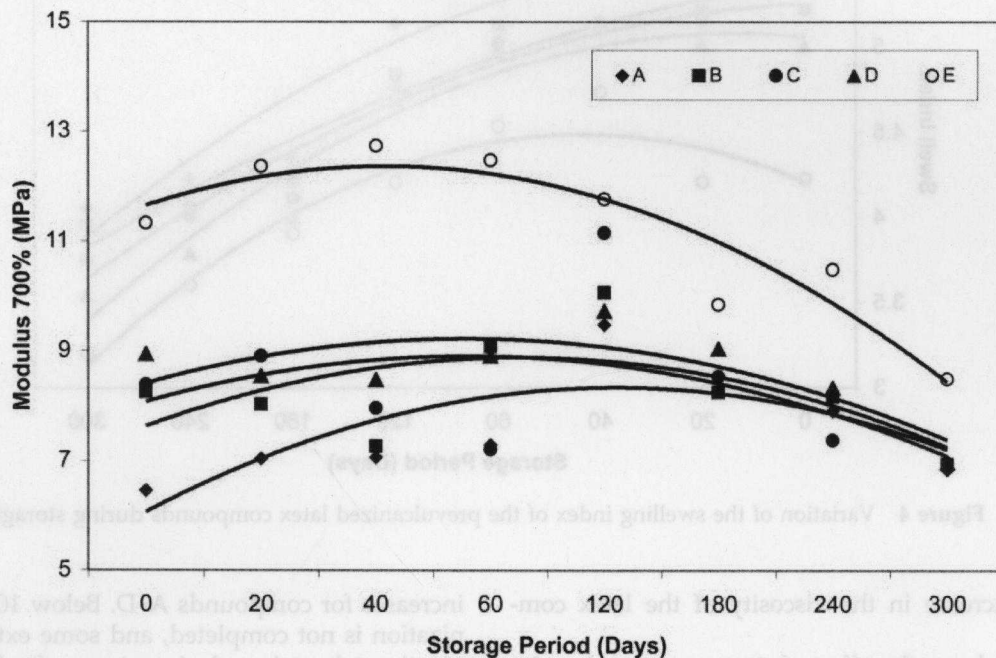


Figure 6 Variation of the 700% modulus of the pre-vulcanized latex compounds during storage.

canization time increases, the swelling index decreases. During storage, the swelling index of latex samples A-D decreases, and that of E remains almost constant. This shows that some extent of vulcanization takes place during the storage of latex samples A-D, whereas no further vulcanization takes place for E.

Figure 5 shows that as the storage time increases, the tensile strength increases for latex samples A-D up

to 20 days and thereafter decreases. However, for latex sample E, the tensile strength decreases from 29.7 to 12.41.

The initial increase in the tensile strength for latex compounds A-D may be due to the increase in crosslinking during the storage of the pre-vulcanized latex. The decrease in the tensile strength with increasing storage time may be a result of the decreasing

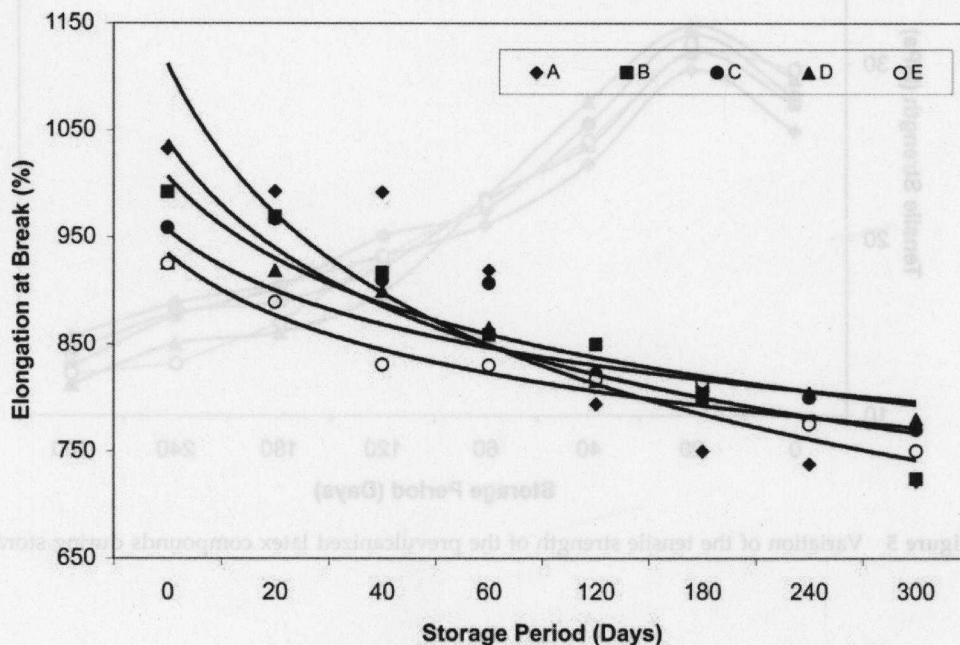


Figure 7 Variation of the elongation at break of the pre-vulcanized latex compounds during storage.

TABLE IV
Changes in the Properties of Prevulcanized Latex During Storage

Property	Period of storage (days)							
	0	20	40	60	120	180	240	300
Sample A								
Total solid content (%)	59	59	59	59	59	59	59	59
pH at 28°C	10.2	10.2	10.2	10.2	10.2	10.2	10	10
Tensile properties after aging (70°C for 10 days)								
Tensile strength (MPa)	25.3	26.9	23.5	20.1	19.5	16.2	13.5	10.2
700% modulus (MPa)	6.1	6.8	6.9	7.1	8.5	6.2	5.8	5.2
Elongation at break (%)	950	925	900	888	825	750	775	800
Sample B								
Total solid content (%)	59	59	59	59	59	59	59	59
pH at 28°C	10.2	10.2	10.2	10.2	10.2	10.2	10.0	10.0
Tensile properties after aging (70°C for 10 days)								
Tensile strength (MPa)	27.5	28.6	26.5	24.4	19.5	16.3	13.5	11.5
700% modulus (MPa)	9.6	9.4	8.6	9.8	10.5	8.4	8.2	7.2
Elongation at break (%)	950	900	875	850	800	815	825	780
Sample C								
Total solid content (%)	59	59	59	59	59	59	59	59
pH at 28°C	10.2	10.2	10.2	10.2	10.2	10.1	9.8	9.8
Tensile properties after aging (70°C for 10 days)								
Tensile strength (MPa)	27.01	31.5	25.75	24.74	21.21	18.13	15.41	12.1
700% modulus (MPa)	8.55	9.75	8.75	7.80	12.58	9.45	7.12	6.59
Elongation at break (%)	940	900	890	845	825	850	800	825
Sample D								
Total solid content (%)	59	59	59	59	59	59	59	59
pH at 28°C	10.2	10.2	10.2	10.2	10.2	10.0	9.8	9.8
Tensile properties after aging (70°C for 10 days)								
Tensile strength (MPa)	28.6	30.5	28.9	24.5	19.04	15.28	12.01	10.54
700% modulus (MPa)	9.25	9.55	9.05	9.35	9.48	8.25	6.78	7.25
Elongation at break (%)	950	915	980	985	800	750	830	775
Sample E								
Total solid content (%)	59	59	59	59	59	59	59	59
pH at 28°C	10.2	10.2	10.2	10.2	10.2	10.0	9.8	9.8
Tensile properties after aging								
Tensile strength (%)	28.55	28.21	24.75	21.75	20.12	16.41	12.31	10.08
700% modulus (MPa)	11.21	11.75	9.75	10.95	11.5	8.55	7.984	7.214
Elongation at break (%)	900	830	800	850	800	715	810	770

ability of latex particles to coalesce and integrate fully as the concentration of the crosslinks in the particles increases.¹³ Blackley and Merrill¹⁴ reported that the tensile strength of films from prevulcanized natural rubber latex compounds depends on the ability of the particles to coalesce and integrate when the film dries and on the concentration of the crosslinks in the rubber.

Figures 6 and 7 show the effects of the variation of the 700% modulus and percentage of the elongation at break during the storage of the prevulcanized latex. The 700% modulus increases during storage up to 120 days and thereafter slightly decreases. Blackley⁹ reported that upon the prevulcanization of natural rubber latex, the modulus increases with crosslinking during storage. The change in the modulus during storage may be due to the additional crosslinking of rubber particles during storage.

Figure 7 shows that the elongation at break decreases for all samples, A–E. This may be due to crosslinking during storage. However, the decrease is higher for samples A and B. Blackley⁹ reported that the elongation at break decreases somewhat during the storage of prevulcanized latex.

Table IV shows the effects of the aging and storage, pH, total solid content, and tensile properties of the prevulcanized latex. The pH is almost constant during storage, but a slight decrease can be observed after 120 days, possibly because a slight loss of ammonia. The total solid content remains constant during the entire period of storage of 300 days.

CONCLUSIONS

During storage, MST of the prevulcanized latex increases, reaches a maximum around 120 days of stor-

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age, and then decreases up to 300 days. There is not much change in the crosslink density for samples prevulcanized for 6 h or more, as measured by the chloroform number and swelling rate. The tensile strength increases during storage up to 20 days and then decreases.

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Figure 7 shows the effects of the aging and storage period of prevulcanized latex. The pH is almost constant during storage, but a slight decrease can be observed after 120 days, possibly because a slight loss of ammonia. The total solid content remains constant during the entire period of storage of 300 days.

Table IV shows the effects of the aging and storage period on the tensile properties of the prevulcanized latex. The pH is almost constant during storage, but a slight decrease can be observed after 120 days, possibly because a slight loss of ammonia. The total solid content remains constant during the entire period of storage of 300 days.

CONCLUSIONS

During storage, MST of the prevulcanized latex increases, reaches a maximum around 120 days of stor-

ability of latex particles to coalesce and integrate fully as the concentration of the crosslinks in the particles increases. Blackley and Merrill¹⁴ reported that the tensile strength of films from prevulcanized natural rubber latex compounds depends on the ability of the particles to coalesce and integrate when the film dries and on the concentration of the crosslinks in the rubber particles.

Figures 6 and 7 show the effects of the variation of the 700% modulus and percentage of the elongation at break during the storage of the prevulcanized latex. The 700% modulus increases during storage up to 120 days and thereafter slightly decreases. Blackley¹⁴ reported that upon the prevulcanization of natural rubber latex, the modulus increases with crosslinking during storage. The change in the modulus during storage may be due to the additional crosslinking of rubber particles during storage.