Natural rubber latex · Prevulcanization · Storage · After-treatment

Centrifuged latex concentrate was freshly prepared and stored up to 18 months. The effect of storage of the latex and its subsequent prevulcanization on tensile properties of the film was evaluated. The effect of storage after-treatment, and ageing characteristics of prevulcanized latex films were also investigated. Properties and ageing resistance of the prevulcanized latex films were affected by storage of latex. Storage or after-treatment of the films substantially improved the tensile properties.

Einfluß der Lagerbedingungen von Naturkautschuk-Latexkonzentrat auf die Eigenschaften von vorvulkanisierten Latexfilmen

Naturkautschuklatex · Vorvulkanisation · Lagerzeit · Nachbehandlung

Zentrifugierter Latex wurde frisch hergestellt und bis zu 18 Monate gelagert. Der Einfluß von Latex-Lagerzeit und dessen nachfolgende Vorvulkanisation auf die Zugfestigkeitseigenschaften eines Films wurde bestimmt. Der Einfluß von Lagerung, Nachbehandlung und Alterungscharakteristik der vorvulkanisierten Latexfilme wurden ebenfalls untersucht. Eigenschaften und Widerstand gegen Alterung der vorvulkanisierten Latexfilme sind durch Latex-Lagerung beeinflußt. Lagerung oder Nachbehandlung der Filme verbessern die Eigenschaften beträchtlich.

Effect of Storage of Natural Rubber Latex Concentrate on Properties of Prevulcanized Latex Film

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Prevulcanization of latex was first introduced by *Schidrowitz* [1]. Prevulcanized latex is now widely used for the manufacture of several latex products, especially dipped rubber products. The popularity of prevulcanized latex arises from the ease of forming vulcanized film on drying the latex. Prevulcanization of natural rubber (NR) latex can be effected by reaction with sulphur [2–4], sulphur donors [5], peroxides [6] or radiation [7]. However, only the dithiocarbamate accelerated sulphur cure systems have achieved wide commercial acceptance for the production of prevulcanized NR latex [8].

During storage, latex undergoes changes associated with bacterial and hydrolytic actions. Changes will also be effected by many factors such as handling, seasonal effect and storage conditions. The present study reports the effect of storage of centrifuged NR latex on properties of prevulcanized latex (PVL) film. The effect of after-treatment, storage and ageing characteristics of the films were also investigated.

Materials

High ammonia (HA) preserved 60 % centrifuged latex conforming to the specifications of the Bureau of Indian Standards (BIS), IS:5430-1981, was freshly prepared and stored for periods of up to 18 months. Sulphur, zinc oxide and zinc diethyldithiocarbamate were of commercial grade and were used as 50 % dispersions in water, prepared by ball milling. Other chemicals were of laboratory grade and were used as solutions in water.

Prevulcanization

Latex samples were withdrawn periodically and compounded according to recipe of *Tab. 1*. The compounded latex was heated in a water bath set at 70 °C for 2 h under stirring, cooled and kept at room temperature.

Film preparation

The prevulcanized latex (PVL) was strained through a muslin cloth on the next day and films were cast in shallow glass dishes to a thickness of ~ 1 mm.

After-treatment of PVL films

The films were removed from the glass dishes after 48 h and subjected to different treatments as follows.

1. Leaching in water for 24 h and drying at room temperature.
2. Heating in air at 100 °C for 30 min.
3. Treatment 1 followed by 2.

Tab. 1. Formulation of latex compound

Ingredients	Parts by weight (aqueous)
Centrifuged latex (60 %)	167.0
Potassium hydroxide solution (10 %)	2.5
Potassium laurate solution (20 %)	1.3
Sulphur dispersion (50 %)	2.0
Zinc diethyldithiocarbamate dispersion (50 %)	1.0
Zinc oxide dispersion (50 %)	0.4

Tensile testing

Tensile test pieces were punched out from the films using a dumbbell die (C-type). Tensile tests were performed on a Zwick Universal Testing Machine model 1474. The tests were carried out according to ASTM D 412 (1994).

Determination of volume fraction of rubber

The volume fraction of rubber (Vr) in the swollen vulcanizate was determined from equilibrium swelling in toluene at 30 °C following the method suggested by *Ellis* and *Welding* [9].

Ageing studies

Tensile test pieces punched out from the after-treated PVL film (treatment 3) were aged in an air oven at 70 °C for 14 days. Tensile properties of the aged samples were determined after conditioning the specimens for 16 h at room temperature.

Properties of PVL films without after-treatment

Table 2 shows the effect of storage of latex concentrate up to 4 months on tensile properties of PVL films without after-treatment. It can be seen that the PVL film prepared from fresh latex is having low tensile properties. When the storage period of latex was two months the PVL film showed better tensile properties. On increasing the storage period to four months the tensile properties remained more or less constant. This shows that the strength of PVL film is affected by the storage period of latex and the optimum storage period is around 2 months.

During prevulcanization, each individual latex particle is vulcanized and immediately on the formation of the film primary bands may not form between the rubber particles. The structure of the rubber film obtained by drying vulcanized latex is, therefore, discontinuous and the forces which unite the latex particles can only be secondary forces or van der Waals forces [1]. The tensile strength of such a film is governed mainly by the magnitude of these secondary forces and thus depends, in a very large measure, on the extent to which the particles in the film can approach one another. The adsorption layer of proteins and phospholipids present on the surface of the rubber particles in latex [1] also plays an important role during the formation of film from vulcanized latex. When the latex is fresh, the adsorption layer is thick and compact and more firmly attached to rubber particles so that merging together of rubber particle is rather hindered, thus exhibiting low tensile properties. When the latex is aged, structural changes occur on the adsorption layer of the rubber particles [10] and the predominantly protein-phospholipid layer is largely replaced with a fatty acid soap layer. The merging together of rubber particles is made easier, thus increasing the tensile properties of film.

Tab. 2. Properties of PVL film with and without after-treatment from latex stored for different periods

Storage period of latex (months)	After-treatment of PVL film	Modulus at 100 % elongation (MPa)	Tensile strength (MPa)	Elongation at break (%)
0	Nil	0.60	11.5	810
2		0.70	17.3	898
4		0.71	17.7	921
0	2	0.76	26.4	939
2		0.76	25.8	935
4		0.79	25.9	943
0	1	0.78	28.9	927
2		0.81	30.0	930
4		0.82	31.4	940
0	3	0.79	29.5	938
2		0.79	29.8	940
4		0.80	30.6	932

Effect of after-treatment of films

The effect of after-treatment of PVL films is also shown in *Tab. 2*. It substantially improved the tensile properties of the films irrespective of the storage period of latex used for prevulcanization. Treatment 1 (leaching) was found to be better than 2 (heat treatment). In the case of a purely prevulcanized film there is only limited interdiffusion of the rubber molecules between individual internally crosslinked rubber particles as the mobility of the molecular chain ends becomes restricted. This results in a film in which the original particles are held together principally by chain entanglement. During heating more crosslinks are formed. During leaching most of the soluble hydrophilic materials are washed away [11] thus facilitating better cohesion of the rubber particles, allowing greater degree of entanglement between molecules anchored in different particles and enhanced tensile properties.

Tab. 3. Effect of after-treatment of PVL film on volume fraction of rubber

After-treatment of PVL film	Volume fraction of rubber (Vr)
Nil	0.1628
1	0.1632
2	0.1743
3	0.1674

Table 3 shows the effect of after-treatment of PVL film on volume fraction of rubber (Vr). It is revealed that by treatment 2 (heating) more crosslinks were introduced. By treatment 1 (leaching) the degree of crosslinking remained almost the same, but in treatment 3 (leaching followed by heating) a slight increase in Vr was obtained which is lower than that obtained in treatment 2. All these treatments improved the tensile properties of the films. Although maximum Vr values were realised by treatment 2, 1 and 3 gave better properties to the films than treatment 2. This shows that in prevulcanized latex film, tensile properties are not governed solely by the degree of crosslinking, but the degree of cohesion of the particles also has some influence.

Effect of storage of PVL film at room temperature

Figure 1 shows the effect of storing prevulcanized latex film prepared from latex stored for different periods on tensile strength. It is seen that when the film was stored at room temperature its tensile strength increased and attained a maximum value, irrespective of the storage period of latex used for prevulcaniza-

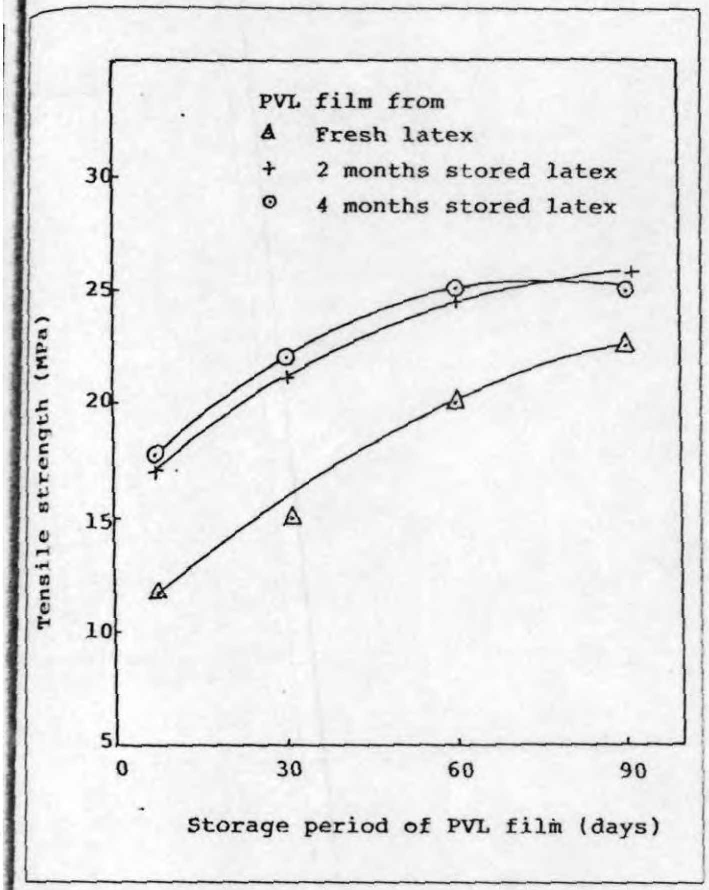

Fig. 1. Effect of storage of PVL film on tensile strength

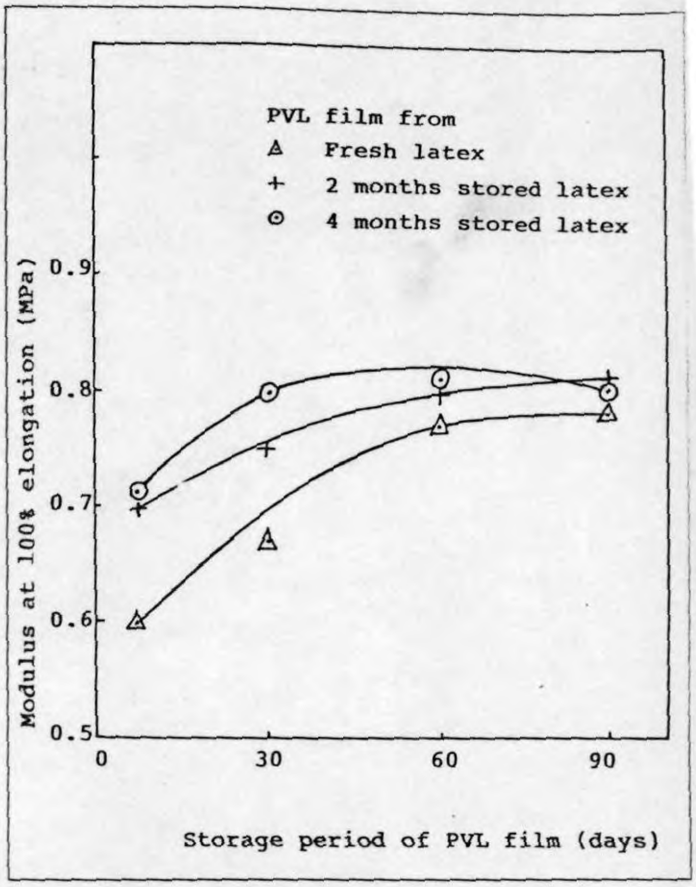

Fig. 2. Effect of storage of PVL film on modulus

tion. However, the maximum tensile strength obtained by PVL film from fresh latex was low compared to that from stored latex. As the storage period of latex increased to two months, a similar increase was also attained. A further increase in the storage period did not cause an appreciable change. This shows that properties of untreated film improves on keeping at room temperature. The improvement does not change after 2 months storage of latex.

Modulus at 100 % elongation and elongation at break (*Figs. 2 and 3*, respectively) show a similar trend, but in case of elongation at break the PVL film showed only marginal increase on storage with aged latex.

On storing the films at room temperature, further gradual coalescence occurs [12] which improves film properties. Coalescence is also influenced by the adsorption layer on rubber particles. When the latex is aged structural changes occur due to the presence of enzymes, bacteria and preservatives. During a 2 months storage period major changes occurring in latex are stabilized

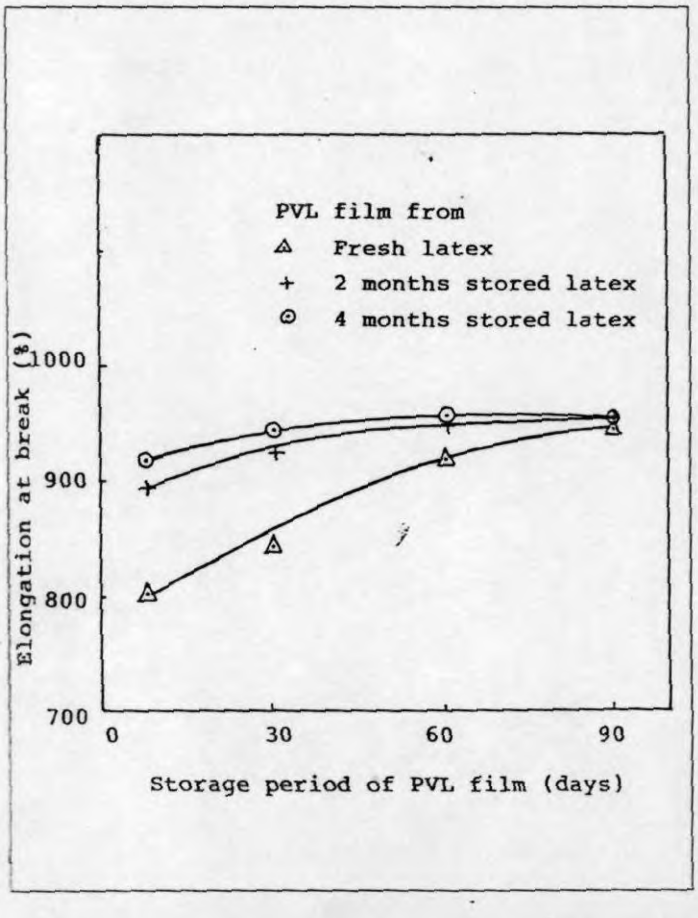

Fig. 3. Effect of storage of PVL film on elongation at break

and further storage does not cause significant changes.

Effect of ageing

The tensile properties of after-treated PVL films before and after ageing are shown in *Tab. 4*. It is seen that before ageing properties such as tensile strength, modulus at 100 % elongation and elongation at break of the films are more or less unaffected by storage of latex up to 6 months. But when the latex was stored for 1 year and above, properties decrease. On ageing the properties decreased as the storage period of the latex increased. The decrease was faster when the storage period was 1 year and more.

The presence of materials which exert an antioxidant effect in latex has been recognized for many years [13]. Choline compounds present in latex are vulcanization accelerators and also show antioxidant properties in rubber. The higher the concentration of undegraded phospholipids in latex the higher the rate of cure [14]. During long term storage the natural accelerators and antioxidants present in latex are getting converted into other products and/or are used up which cause a reduction in technological properties and ageing resistance of the vulcanizates.

Conclusions

Storage periods of latex concentrate affect the tensile properties of prevulcanized latex films prepared from it. PVL film prepared from fresh latex showed low tensile properties. When prevulcanization was conducted using stored latex the film properties improved. After-treatment of the films substantially improved tensile properties irrespective of the storage of latex. PVL films from fresh and stored latex exhibited comparable properties after the treatments. However, on storage of latex to beyond 1 year, a decrease in properties was observed. Out of the treatments studied, leaching in water gave better properties to the films than heat treatment. Storage of films at room temperature also improved the tensile properties. The ageing resistance of the films decreased as the storage period of latex increased. The rate of decrease was more when the storage period was beyond 1 year.

References

[1] D.C. Blackley, High Polymer Latices, vol 1. Maclaren & Sons, Ltd, London (1966), p. 383, p. 399, p. 218.

[2] D.C. Blackley, Proc. Rubb. Tech. Conf; Malaysia (1988) 3.

[3] A.D.T. Gorton, Proc. Int. Rubb. Tech. Conf, Penang, Malaysia (1988) 85.

[4] E.H. Low, Proc. Rubb. Res. Inst. Malaysia Planters Conference, Kuala Lumpur (1977) 307.

[5] M.W. Philpott, J. Rubb. Res. Inst. Malaysia **22** (1969) 441.

[6] Ma'zam Md.Said, T.D. Pendle and D.C. Blackley, J. Nat. Rubb. Res. **5** (1990) 27.

[7] S. Kartowardoyo and F.L. Sundardi, J. Appl. Polym. Sci. **27** (1977) 3077.

[8] C.T. Loo and N.P. Wong, Proc. Int. Conf. on Developments in the Plastics and Rubber Product Industries, Kuala Lumpur, Malaysia (1987) 265.

[9] B. E[illegible]s and G.N. Welding, Rubb. Chem. Technol. **37** (1964) 571.

[10] E.G. Cockbain and M.W. Philpott, The Chem[illegible]try and Physics of Rubber-like Substances. E[illegible] L. Bateman. Maclaren & Sons LTD, London (1963), p. 81.

[11] K.F. Gazeley, A.D.T. Gorton and T.D. Pendle, Natural Rubber Science and Technology. Ed. A.D. Roberts. Oxford University Press, Oxford (1988), p. 131.

[12] E.B. Bradford and J.W. Vanderhoff, J. Macromol. Sci.-Phys., **B6** (1972) 671.

[13] R.J. Noble, Latex in Industry. Ed. 2. Rubber Age. New York (1953), p. 74.

[14] B.L. Archer, D. Barnard, E.G. Cockbain, P.B. Dickenson and A.I. Macmullen, The Chemistry and Physics of Rubber-like Substances. Ed. L. Bateman. Maclaren & Sons Ltd, London (1963), p. 56.

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Tab. 4. Effect of ageing the after-treated PVL film at 70 °C for 14 days, prepared from latex stored for different periods

Storage period of latex (months)	Modulus at 100 % elongation (MPa)		Tensile strength (MPa)		Elongation at break (%)	
	Before ageing	After ageing	Before ageing	After ageing	Before ageing	After ageing
0	0.79	0.75	29.5	24.6	938	848
2	0.79	0.74	29.8	23.1	940	841
4	0.80	0.72	30.6	23.0	932	836
6	0.80	0.72	29.6	22.0	928	833
12	0.70	0.66	26.6	16.5	898	759
18	0.64	0.55	21.0	8.0	886	741