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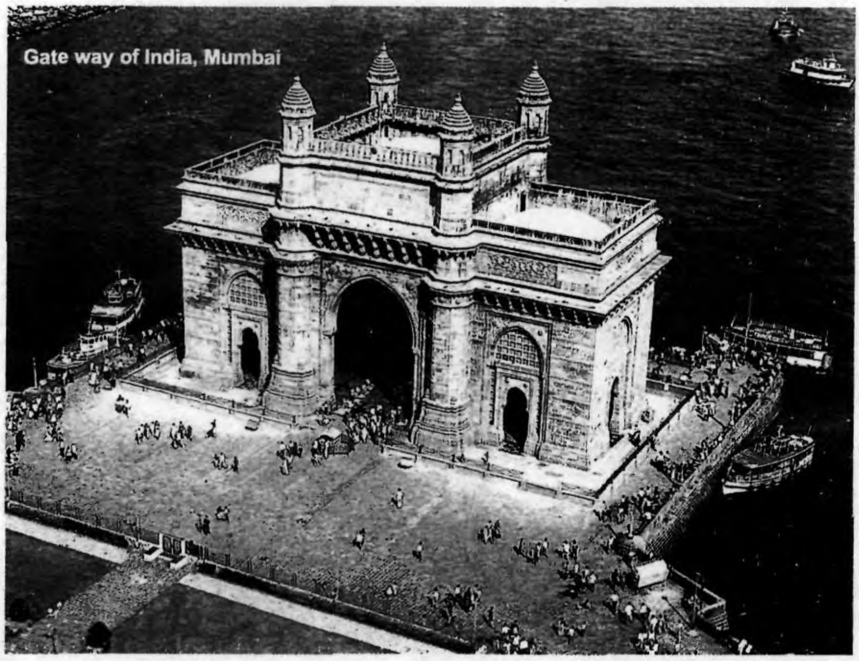

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Improvement in tensile properties of radiation vulcanised natural rubber latex prepared at low dose rate by post vulcanisation treatments (EA-023)

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Introduction

Natural rubber latex vulcanised with the aid of gamma radiation can be used to produce latex products free from chemical toxicity[1] and carcinogenic nitrosamines[2]. The irradiation conditions, properties of NR latex[3,4], green strength of NR[5] and post vulcanisation treatments affect efficiency of radiation vulcanisation and the tensile strength properties of the resulting latex film. The parameters of extreme importance are the presence of required amount of radiation accelerator and dose rate at which the vulcanisation is carried out. One of the most efficient radiation vulcanisation accelerators is n-Butyl acrylate[6] (n-BA) which is highly prone to hydrolysis during the vulcanisation process which in turn reduces the efficiency of the radiation vulcanisation process. The kinetic studies on polymerisation of n-BA have reported that a dose rate of 5-8 kGy/h is required to achieve n-BA polymerisation rate much greater than the rate of hydrolysis of n-BA in latex during the vulcanisation process. A lower radiation dose rate will lead to longer vulcanisation time, more hydrolysis of n-BA and subsequent lower efficiency of the process leading to inferior tensile properties of the vulcanised latex film. The continuously declining γ– ray source strength and the dose rate necessitates the frequent replacement of costly radiation source to maintain the optimum dose rate required for the production of high strength radiation vulcanized natural rubber latex (RVNRL). Therefore there is a need to explore the effect of various process parameters and post vulcanisation treatments on the tensile behaviour of RVNRL prepared at low radiation dose rate.

The present paper attempts to improve the tensile properties of RVNRL films prepared at a low dose rate of around 1.26 kGy/h, using latex of higher green strength and by adoption of suitable post vulcanisation treatments.

Experimental

Preserved field latex collected from Pilot Latex processing Center (PLPC) of RRII was used. Centrifuged latex was prepared at PLPC using L-D Lavel latex centrifuging machine, operating at 7000 rpm. Latex of varying particle size is obtained by using skim screws of 9.5, 10.5 and 11 cm. The particle size distribution of the three cenex samples were determined using Malvern Zetasizer Nano series (Nano S) particle size analyzer. Radiation vulcanisation was effected by gamma rays from a Cobalt 60 source using Gamma Chamber- 5000. Latex was exposed to gamma radiation of 1.26

kGy/h for 11.9 hours (total of 15 kGy). Latex was compounded with 0.3 phr potassium hydroxide as stabiliser and 5 phr n-BA as sensitizer. Mechanical stability time was measured using Mechanical Stability Tester.

The quality of RVNRL was evaluated by measuring the latex quality parameters and strength of RVNRL films obtained by casting technique. Tensile properties were determined using Hounsfield Universal Testing machine. The dried films were heated at 100°C for a short period to improve the mechanical properties. Leaching of the RVNRL films were carried out by immersing in calcium nitrate solution of varying concentrations ranging from 2.5 to 10 % for one hour.

Sulphur pre-vulcanisation of the cenex samples were carried out by heating the compounded latex at 50°C for 5 hours and the strength properties were measured from the films obtained by casting technique.

Results and discussion

Particle size and green strength

It is possible to get centrifuged latex fraction containing comparatively only bigger particles with lower proportion of smaller particles. A shorter screw length encourages a greater difference in density between skim and cream and hence the cream tends to have increased rubber content and the proportion by volume of skim also increases. Latex of varying particle size is obtained by using skim screw of 9.5, 10.5 and 11 cm. Thus cenex using a short screw of 9.5 cm has a higher DRC than those prepared using screws of 10.5 and 11 cm length as seen from Table 1.

Table 1 : Initial latex property

Parameter	Latex samples		
	Cenex 1	Cenex 2	Cenex 3
Dry rubber content, %	64.30	63.08	62.38
Non-rubber solids, %	1.26	1.30	1.34
Mechanical stability time, sec	1053	749	740
Volatile fatty acid number	0.01	0.01	0.01

The particle sizes of the different fractions are shown in Figure 1. Cenex 1 contains comparatively higher particle size as compared to Cenex 2 and 3. The variation in particle size between 2 and 3 are less as seen from the figure. It is known that molecules present in bigger particles are highly branched and that in smaller particles are linear. So rubber molecules in latex concentrate is highly branched and molecules in skim latex comparatively linear with a higher proportion of non-rubber ingredients[7].

Raw rubber properties and green strength

Raw rubber properties of the 3 cenex samples are shown in Table 2.

Table 2 : Raw rubber properties

Parameter	Cenex 1	Cenex 2	Cenex 3
Nitrogen content, %	0.35	0.45	0.41
Ash content, %	0.05	0.07	0.07
Initial plasticity, P_o	34	38	37
Plasticity retention index, PRI	21	24	22
Acetone extract, %	1.72	2.02	1.96

Cenex 2 and 3 contain higher proportions of nitrogen and acetone extractable than cenex 1. The initial plasticity values are also higher for cenex 2 and 3 and this can be due to cross linking reactions involving proteinaceous materials. As proteins also act as antioxidant, latex containing higher proportions of protein shows higher PRI. Hence it is expected that based on particle size, cenex 1 has higher molecular weight/branching compared to cenex 2 and 3. The green strength is also expected to be higher. The green strength of the three cenex samples is shown in Table 3.

Table 3 : Green strength of the cenex samples

Latex sample	Tensile strength, MPa	300 % modulus, MPa	500 % modulus, MPa	Elongation at break, %
Cenex 1	2.43	0.38	0.41	1786
Cenex 2	1.98	0.42	0.45	1637
Cenex 3	1.74	0.41	0.43	1605

As seen comparatively higher tensile strength and elongation is shown by cenex 1. A higher modulus shown by cenex 2 and 3 can be due to cross linking reactions involving the proteins. Green strength is reported to increase with nitrogen content and then tend to decrease with further increase in nitrogen content[8].

Samples were irradiated after 22 days of collection of latex. The quality parameters of field latex after irradiation are given in Table 4.

Table 4 : Latex property after irradiation

Parameter	Latex samples		
	Cenex 1	Cenex 2	Cenex 3
Dry rubber content, %	56.15	56.63	55.65
Non-rubber solids, %	2.14	2.20	2.21
Mechanical stability time, sec	2485	2511	2592

DRC and NRS of the cenex samples increase after irradiation. It is known that during exposure to gamma irradiation free radicals are formed from the rubber molecules which cross link through C=C bonds. During irradiation it is also possible that grafting of polymerized n-butyl acrylate molecules on to NR molecules also take place. It is due to this grafting reaction that there is an increase in DRC and TSC after irradiation. The increase in MST observed is mainly due to the irradiation process [9].

Effect of green strength on RVNRL films

Strength properties of RVNRL films prepared from latex with 22 days storage after collection are shown in Table 5.

Table 5 : Tensile properties of RVNRL films (22 days after collection)

Latex sample	Tensile strength, MPa	500 % modulus, MPa	700 % modulus, MPa	Elongation at break, %
Cenex 1	23.50	1.68	2.75	1478
Cenex 2	21.01	1.64	2.80	1389
Cenex 3	20.82	1.80	2.88	1376

A comparatively higher tensile strength is obtained for cenex 1 which is having higher green strength. There are earlier reports that cenex of high green strength produces RVNRL of high tensile strength[10]. On exposure of latex to gamma radiations cross-links occur between molecules by free radical formation which results in enhanced tensile strength. Radiation cross linking of NR chains can be enhanced by addition of n-butyl acrylate (n-BA).

Effect of leaching in calcium nitrate solution on RVNRL films

Effect of leaching in calcium nitrate solution on quality of RVNRL films are shown in Figures 2a and 2b. From the figures it was observed that there is an increase in tensile strength during leaching. As the concentration of calcium nitrate solution increases, the tensile strength does not increase but there is a slight increase in modulus. The tensile strength of NR films depends on the degree of cross-linking and includes chemical and physical cross-links. Inter particle cross-linking can improve properties of RVNRL. . This cannot be attempted during irradiation as this can lead to coagulation of latex. When films are immersed in salt solution it is possible that calcium ions participate in an inter particle cross-linking process and consequently there is an increase in tensile strength.

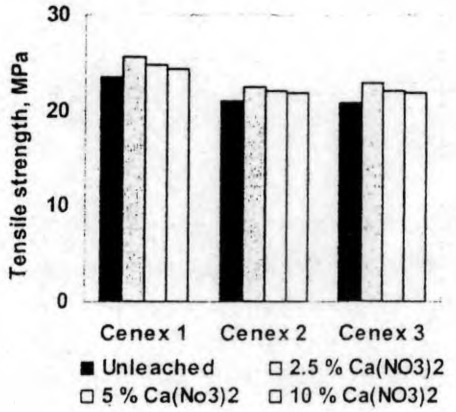

Figure 2a : Effect of leaching in $Ca(NO_3)_2$ solution on tensile strength

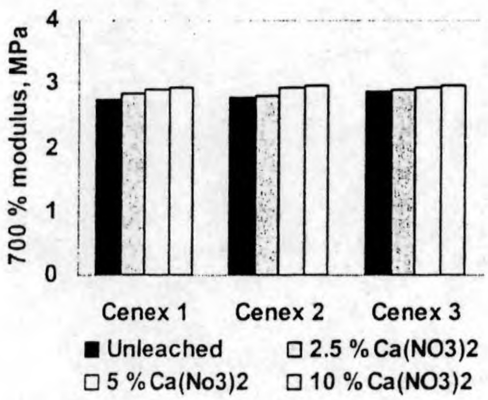

Figure 2b : Effect of leaching in $Ca(NO_3)_2$ solution on 700 % modulus

Effect of heating for short duration at higher temperature

RVNRL films prepared in the conventional way and after immersion in 2.5 % $Ca(NO_3)_2$ solution were heated at 100°C for 3 hrs. Strength properties obtained are given in Figures 3a and 3b. In all cases tensile strength of the films increased after heating. During heating there is enhanced fusion of rubber particles and increased chain entanglement of the rubber molecules[11].

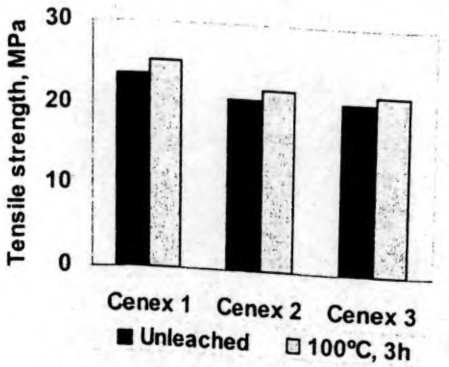

Figure 3a : Effect of heating RVNRL films on tensile strength

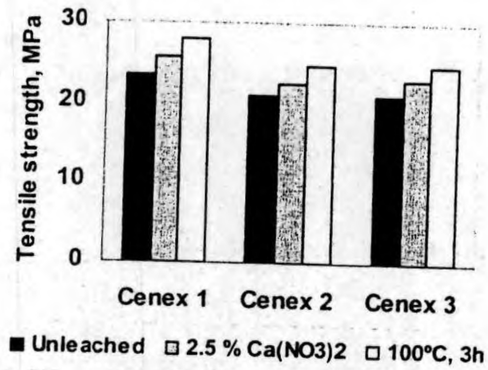

Figure 3b : Effect of $Ca(NO3)_2$ leaching and heating of RVNRL films on tensile strength

Ageing of RVNRL films

Percentage retention on tensile properties of RVNRL films (after leaching and heating) and sulphur pre-vulcanised latex films subjected to hot air ageing at 100°C for 12 hrs are given in Table 6. Values given in the brackets were the initial tensile strength obtained for the films. Comparatively good retention in tensile strength was observed for the RVNRL films and the values were slightly higher than that obtained for the sulphur pre-vulcanised latex films.

Table 6 : Percentage retention of tensile strength

Latex sample	RVNRL	Sulphur pre-vulcanised
Cenex 1	91 (28.00)	90 (27.10)
Cenex 2	92 (24.70)	90 (26.90)
Cenex 3	92 (24.66)	89 (26.33)

Conclusions

It is possible to obtain RVNRL of good tensile strength at a comparatively low dose rate of 1.26 kGy/h by selecting concentrated latex of higher green strength obtained by using skim screw of suitable length during centrifugation, leaching of the casted films in calcium nitrate solution and heating of the films at 100°C for short duration. The ageing resistance of the RVNRL films in terms of tensile strength are comparable to that of sulphur pre-vulcanised NR films.

References

1. Nakamura, Y. Ikarashi, T. Tsuchiya and M. Kaniwa, *Proc. Int. Sym. Radiation vulcanisation of natural rubber latex, JAERI-M*, 89-228, 79 (1989).
2. K.F. Gazeley and T.D. Pendle, *Proc. Int. Sym. Radiation vulcanisation of natural rubber latex, JAERI-M*, 89-228, 189 (1989).
3. W. Manshol, W. Zin and R.I.H. Hashim, *Proc. Sec. Int. Sym. on RVNRL*, 55 (1996).
4. N.C. Dafader, E. Haque, F. Akhtar, M.U. Ahmad and M. Utama, *Macromol, Rept., A33, Suppl.* **2**, 73 (1996).
5. Y. Tanaka, S. Kawahara and J. Tangpakdee, *KGK Kautschuk Gummi Kunststoffe*, **50**, 6 (1997).
6. K. Makuuchi, F. Yoshii, I. Ishigaki, K. Tsushima, M. Mori and T. Saito, *Radiat. Phys. Chem.*, **35**, 154 (1990).
7. S. Kawahara, Y. Isono, J. T. Sakdapipanich, Y. Tanaka, *Rubber Chemistry and Technology*, **75**, 739 (2002).
8. K.Makuuchi, "An Introduction to radiation vulcanization of natural rubber latex", Ed., T.R.I. Global Co. Ltd., Thailand, Chapter 5, NR latex for RVNRL, 70 (2003).
9. V.I. Lukhovitskii, *High Energy Chem.*, **17**, 81 (1983).
10. K. Makuuchi, F. Yoshii, K. Hyakutake, *Proc. of 5th Sym. on Radiation Processing*, 116 (1993).
11. K.Makuuchi, "An Introduction to radiation vulcanization of natural rubber latex", Ed., T.R.I. Global Co. Ltd., Thailand, Chapter 7, Physical properties of RVNRL, 88 (2003).