Studies on the Radiation Vulcanisation of Low Protein Natural Rubber Latex

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Abstract

The presence of extractable protein (EP) in latex products can cause allergic problems in sensitized people. Low protein latex has been developed as a means of reducing EP. Radiation vulcanisation of natural rubber latex can avoid type IV allergy and the possible generation of carcinogenic nitrosamines in latex products. This paper reports the results of radiation vulcanisation characteristics of low protein natural rubber latex, using gamma radiation. Radiation vulcanised low protein latex films exhibit good tensile properties and very low EP.

1. INTRODUCTION

There are several reports about the allergic reactions of natural latex products, caused by the proteins present in them (1-4). Recently a new method, based on a nonenzymic chemical treatment has been developed for the production of low protein latex (5), which shows very low levels of extractable protein (EP) in dipped films produced by conventional sulphur vulcanisation. Vulcanisation with gamma radiation can produce latex products free from chemical toxicity (6) and carcinogenic nitrosamines (7). It was thought that radiation vulcanisation of low protein latex can provide latex products free from chemical toxicity and very low in EP.

However, EP is only a small fraction of the total proteins in latex products (8,9) and gamma radiation can disintegrate the proteins and make them water extractable (10,11). Further, the radiation dose (Dv) for vulcanisation decreases with increasing protein content in the rubber phase(12). Hence it seemed worth studying the radiation vulcanisation characteristics of low protein latex.

This paper reports the viscosity changes due to irradiation, the effect of dose and dose rate on viscosity of irradiated latex, tensile properties and EP of films prepared from irradiated low protein latex.

2. EXPERIMENTAL

The low protein latex used in this study is prepared by a nonenzymic method. This method is subject to a patent application and hence will not be discussed here. Radiation vulcanisation was effected by gamma rays from a Cobalt-60 source using Gamma Chamber-5000. Latex is compounded with 0.3 phr potassium hydroxide as stabiliser and 5 phr normal butyl acrylate (nBA) as sensitizer. Irradiation dose is varied by changing the duration of irradiation. Dose rate is varied by use of attenuators. Viscosity measurements are carried out using a Brookfield Viscometer at 60 rpm using spindle number 2.

Leached films prepared by casting are used for tensile property determinations. Tensile properties are determined by using Hounsfield Universal Testing Machine. Samples for EP estimation are prepared by casting, dried at 70 °C for 3 hrs, then leached in water at 30 °C for 4 hrs and the wet films are dried in air. EP is determined by the modified Lowry method (13).

3. RESULTS AND DISCUSSION

Viscosity Measurements.

The data on viscosity of compounded latex in Table-1 show only marginal increase in viscosity due to irradiation in the case of double centrifuged and low protein latices, while once centrifuged latex shows considerable increase. It is believed that irradiation of latex decomposes some of the non rubber substances, either soluble or adsorbed, thus releasing more particles in to the aqueous phase, resulting in an increase in viscosity. Vulcanised latex from double centrifuged and low protein latices, prepared at low dose rates, after one week storage show only a marginal increase in viscosity. Increasing the dose and dose rate in the vulcanisation of low protein latex results in slight increase in viscosity (Table-2 and 3), however this increase is less than that of once centrifuged and double centrifuged latices. The results indicate that the stabilizer system in low protein latex does not interfere much with gamma radiation and the storage stability of vulcanised low protein latex is good.

Table 1 : VISCOSITY CHANGE OF LATEX COMPOUND BY IRRADIATION. (DOSE 15 kGy)

Type of Latex	Viscosity(cps)		
	Before Irradiation	Immediately after Irradiation	One week after Irradiation
Once Centrifuged Latex	22.5	65.0	65.0
Double Centrifuged Latex	27.5	35.0	45.0
Low Protein Latex	25.0	32.5	35.0

Table 2 : EFFECT OF DOSE RATE OF IRRADIATION ON VISCOSITY OF COMPOUNDED LOW PROTEIN LATEX. (DOSE 15 kGy)

Dose Rate (kGy/hr)	Viscosity(cps)		
	Before Irradiation	Immediately after Irradiation	One week after Irradiation
1.333	25.0	32.5	35.0
2.578	25.0	27.5	32.5
4.258	25.0	25.0	35.0
6.108	25.0	25.0	35.0

Table 3 : EFFECT OF DOSE OF IRRADIATION ON VISCOSITY OF COMPOUNDED LOW PROTEIN LATEX. (DOSE RATE 1.333 kGy/HR)

Dose (kGy)	Viscosity (cps)		
	Before Irradiation	Immediately after Irradiation	One week after Irradiation
15	25.0	32.5	35.0
20	25.0	30.0	32.5
25	25.0	30.0	37.5

Extractable Protein Content

Table 4 : EFFECT OF THE TYPE OF LATEX IRRADIATED ON EP. (DOSE 15 kGy)

Type of Latex	EP content in vulcanised film (mg/kg)	
	Before Leaching	After Leaching
Once centrifuged latex	1045.1	31.0
Double centrifuged latex	0571.2	25.4
Low protein latex	0092.5	03.7

EP content of dry RVNRL films irradiated at 15 kGy are estimated before and after leaching. The results obtained for the films from different types of latices are given in Table-4 Before leaching EP content in low protein latex film is only 8.8% of that shown by once centrifuged latex. This low value indicates that soluble proteins were effectively removed during the production of low protein latex. After leaching this film shows EP content of 3.7 mg/kg, which is lower than the EP content reported for sulphur vulcanised low protein latex from Malaysia (14). EP values on leached films prepared from radiation vulcanised films of once centrifuged and double centrifuged latices are comparable to that of sulphur vulcanised low protein latex films of Malaysia. This is due to the degradation of proteins by gamma radiations (12).

Table 5 : EFFECT OF DOSE RATE ON EP. CONTENT IN VULCANISED FILMS MADE FROM LOW PROTEIN LATEX (DOSE 15 kGy)

Dose Rate (kGy/hr)	EP content in vulcanised film (mg/kg)	
	Before Leaching	After Leaching
1.333	092.5	03.7
2.758	163.4	08.6
4.258	614.6	25.3
6.102	495.8	10.4

Table 6 : EFFECT OF DOSE ON EP. CONTENT IN VULCANISED FILMS MADE FROM LOW PROTEIN LATEX

Dose (kGy)	EP content in vulcanised film (mg/kg)	
	Before Leaching	After Leaching
15	092.5	3.7
20	133.8	4.1
25	094.4	5.2

Table-5 gives the results of dose rate on EP content in radiation vulcanised low protein latex. It is seen that EP content in unleached and leached films increases with increasing dose rate. A similar behaviour is observed when higher doses are applied for vulcanisation (Table-6). The increase in EP is due to higher degradation occuring to the adsorbed proteins, at high doses and dose rates, making them extractable. With single centrifuged latex, a similar effect of dose on EP has been previously reported (15,16).

Tensile Properties

The data on tensile properties of radiation vulcanised films given in Table-7 show a fall in tensile properties on going from once centrifuged latex to double centrifuged latex. This is in agreement with earlier reports (17,18). It is supposed that proteins which combine natural rubber molecules through hydrogen bonds, are further removed in the second stage of centrifuging, thus contributing to lower tensile strength of double centrifuged latex films. Even though low protein latex is still lower in protein content than double centrifuged latex (5), the tensile properties are comparable to that of once centrifuged latex. This is probably because the surface active agents added to low protein latex as stabilisers fulfill the role played by proteins from the point of view of colloidal stability. There are previous reports that the non rubber substances in latex do not have much effect on the radiation vulcanisation of natural latex (19). The effect of dose rate on the tensile properties of low protein latex are studied and the results are given in Table-8. It is seen that tensile strength and modulus decrease and elongation at break increases with increasing dose rate. When latex is irradiated the formation and breaking of crosslinks occur simultaneously, but at different rates. At low dose rate, the rate of rupture of crosslinks is very low, but increases at higher dose rates. This results in a fall in tensile properties. A similar results on the reduction of tensile strength in radiation vulcanisation of HA latex has been reported (20).

Table 7 : PHYSICAL PROPERTIES OF VULCANISED FILMS. (DOSE 15 kGy, DOSE RATE 1.333 kGy/HR)

Material	Tensile strength (MPa)	Elongation at Break (%)	Modulus(MPa)		
			M100	M300	M500
Once Centrifuged latex	22.94	1276	0.616	1.09	1.479
Double Centrifuged latex	19.89	1244	0.533	1.034	1.706
Low Protein latex	23.30	1016	0.720	1.327	2.416

Table 8 : EFFECT OF DOSE RATE ON PHYSICAL PROPERTIES OF VULCANISED LOW PROTEIN LATEX FILM. (DOSE 15 kGy)

Dose Rate (kGy/hr)	Tensile strength (MPa)	Elongation at Break (%)	Modulus (Mpa)		
			M100	M300	M500
1.333	23.30	1016	0.720	1.327	2.416
2.758	21.22	1038	0.668	1.311	2.196
4.258	20.86	1087	0.652	1.239	2.133
6.102	20.70	1163	0.639	1.133	1.766

Table 9 : EFFECT OF DOSE ON PHYSICAL PROPERTIES OF VULCANISED LOW PROTEIN LATEX FILM. (DOSE RATE 1.333 kGy/HR)

Dose (kGy)	Tensile Strength (MPa)	Elongation at Break (%)	Modulus (MPa)		
			M100	M300	M500
15	23.30	1016	0.720	1.327	2.416
20	19.40	1015	0.828	1.233	2.325
25	16.02	0964	0.588	1.230	2.102

Similar behaviour in tensile properties is observed when higher doses are applied for vulcanisation (Table 9). Again the fall in physical properties are attributed to increased rate of crosslink rupture.

4. CONCLUSIONS.

- Radiation vulcanised low protein latex show only small increase in viscosity during storage.
- Radiation vulcanisation of low protein latex, followed by leaching in water, reduces extractable proteins to very low levels, without compromising physical properties.
- On increasing the dose rate of irradiation, fall in tensile properties are observed.

5. REFERENCES

1. NUTTER, A.F. (1979) *Brit. J. Dermatol.* **101**, 597.
2. TURJAN MAA. K, AND REUNALA. T, (1988). *Dermatologic Clinics* **6**, 47.
3. WRANGSJO. K, WAHLBERG, J.E. AND AXELSSON, I.G.K. (1988). *Contact Dermatitis* **19**, 264.
4. LEVY, D.A (1995). *Latex Protein Allergy: the Latest Position. Int. Conf.* Paris. p-1
5. SEBASTIAN. M.S. under publication.
6. NAKAMURA. A. IKARASHI.Y, TSUCHIYA. T, AND KANIWA. M (1989) *Proc. Int. Sym. Radiation Vulcanisation of Natural Rubber Latex.* JAERI-M 89-228. p-79.
7. GAZELEY. K.F. AND PENDLE. T.D. (1989) *Proc. Int. Sym. Radiation Vulcanisatiuon of Natural Rubber Latex.* JAERI M 89-228. p-189.
8. HASMA. H (1994) *Proc. IRTC 93 Wkshop on Latex Proteins.* Kuala Lumpur. p-27.
9. YIP. E, POON. N.K, LANG. M.K. and TURJANMAM. K. (1995) *Latex Protein allergy : The Latest Position. Int. Conf.* Paris. p-33.
10. AKHTAR.F, YOSHII.F AND MAKUUCHI. K. (1996). *Proc. Second Int. Sym. RVNRL.* Kuala Lumpur. p-133.
11. GEERTSMA. R.E, ORZECHOWSKI. T.J.H, JONKER. M, DORPEMA. J.W. AND VANAASTEN. J.A.A.M. (1996). Report No. 605148007. *National Institute of Public Health and the Environment, Bilthoven.* The Nederlands.
12. MAKUUCHI. K. (1997) *Radiation Vulcanisation of Natural Rubber Latex. RCA Regional Training Course.* Indonesia.
13. FARIDAH YUSOF AND YEANG. H.Y.(1992) *J.nat. Rub. Res.* **7**, 206.
14. GHAZALY. H.M, (1994) Proc. IRTC 93 *Wkshop on Latex Proteins.* Kuala Lumpur. p - 81.

15. ZIN.W.M.W and OTHMAN. N. (1996). *Proc. Second Int. Sym. on RVNRL.* Kuala Lumpur. p - 115.
16. AKHTAR. F. YOSHII.F and MAKUUCHI K. (1996) *Proc. Second Int. Sym. on RVNRL.* Kuala Lumpur. p - 133.
17. MOHID.N, MAKUUCHI.K, YOSHII.Fand ISHIGAKI.I (1989) *Proc. Int. Sym. Radiation Vulcanisation of Natural Rubber Latex.* JAERI - M89 - 228. p - 157.
18. HAQUE, M.E., DAFADER, N.C., AKHTAR. F and AHMAD. M.U (1996). *Radiat. Phys. Chem.* **48**, 505.
19. THOMAS, E.V., (1989) *Proc. Int. Sym. Radiation vulcanisation of Natural Rubber Latex.* JAERI - M 89 - 229. p- 178.
20. THOMAS, E.V., (1998) Paper presented at *The Coordinated Research Programme Meeting on RVNRL*, Bangkok.