Advantages of radiation in latex vulcanisation

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Radiation vulcanised natural rubber latex (RVNRL) has definite technical advantages over conventional sulphur cured latex in making value added medical and pharmaceutical products. Extractable proteins in NR latex are degraded to a very low level of 21.9 ug/g during irradiation. RVNRL is less cyto toxic and nitrosamine problems are totally absent. Though it costs a little more, its technical advantages outweigh the cost addition.

Introduction

A new material is now available to latex technologists, Radiation vulcanized natural rubber latex (RVNRL). The usual process in latex industry, especially in the dipped goods sector, is to shape the article by dipping, followed by vulcanization. Schidrowiz (1) discovered in the early years of 20th century that latex itself could be vulcanized without any colloidal destabilisation. Such vulcanized latex is known as prevulcanized latex, as vulcanization is carried out prior to shaping. It is very advantageous to vulcanize a small volume of latex, rather than vulcanizing the thin films deposited on innumerable formers (2). Latex goods manufactured by dipping process include different types of gloves, condoms, catheters and toy balloons.

During the previous century latex prevulcanization process has undergone considerable developments. Even though the process of radiation vulcanization was reported about 40 years back, (3, 4), this technique was not of any interest to the industry due to the high cost of irradiation and the low quality of the products obtained out of it (5). The driving force behind the revival of the technique was support of the International Atomic Energy Agency and the Regional Co-operative Agreement (RCA) of the UN in the Asia and Pacific Region (6).

Radiation vulcanization of natural rubber latex

Crosslinking of the rubber molecules in latex particles is brought about by gamma radiations from a Cobalt 60 source in radiation vulcanised natural rubber latex (RVNRL). The dose requirement of radiation vulcanization is very high, about 250-350 kGy. If latex is irradiated directly this is reduced to an acceptable level of 15 kGy, by using normal butyl acrylate (nBA) as sensitizer. It is generally added as 50% emulsion (7). However, when nBA is added, latex exhibits some tendency to destabilise. This can be overcome by prior addition of potassium hydroxide (8). During irradiation the solid content of the latex is kept at 57-58%.

It is believed that nBA migrates to the rubber particles. The aquated electrons generated by the radiolysis of water molecules within the latex produce negatively charged polymeric nBA radicals. These radicals get grafted onto the rubber hydrocarbon molecules. Simultaneously, polymerisation and crosslinking take place via the carbon-carbon linkage (9). Homopolymerisation occurs on nBA to a certain extent and the polymeric chains entangle the crosslinked rubber particles to provide additional strength

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John S. Powath, ~~Rubber Asia~~, Dhanam Publications, to the vulcanisate (10). Typical formulation currently used for RVNRL processing is given in Table 1.

Table 1.

Latex compound for radiation vulcanization

Ingredients	Parts by dry weight
60% Natural latex	100
50% nBA emulsion	5
10% KOH solution	0.3
1% Ammonia water	To 58% total solids.

For RVNRL processing only high quality high ammonia preserved centrifuged latex is used. The specification of centrifuged latex currently used in India for RVNRL processing is given in table 2. Use of high-quality centrifuged latex ensures good processability and shelf-life for RVNRL. Low ammonia latex containing zinc oxide and TMTD is not generally used as TMTD interferes with the crosslinking reaction by functioning as a radical scavenger (11).

RVNRL films generally exhibit poor heat resistance. For imparting good ageing resistance to dry RVNRL film, antioxidants are added.

Tris-nonylated phenyl phosphite (TNPP) is generally added at 2 phr level and retention of physical properties is almost 100% after heat ageing (12).

Table 2:

Properties of centrifuged latex used for processing RVNRL in India.

Dry rubber content (min.)	60.0%
Non rubber solids (max.)	1.5%
Alkalinity as ammonia (min.)	0.8%
Mechanical stability time (min.)	1000 sec.
VFA no. (max.)	0.02
KOH no. (max.)	0.5
Coagulum content (max.)	0.01%
Sludge content (max.)	0.01%
Copper content (max.)	4 ppm.
Manganese content (max.)	trace
Magnesium content (max.)	10 ppm.
Colour and odour	Not objectionable.

Properties of RVNRL

Initially RVNRL was prepared at about 50% dry rubber content. However, process conditions have been standardised to make available RVNRL of 57-58% DRC. Typical properties of RVNRL are given in table 3.

Table 3:

Physical Properties of RVNRL

Dry rubber content	57.10%
Total solids content	58.82%
Non rubber solids content	1.72%
Alkalinity as ammonia	0.70%
Volatile fatty acid no.	0.02%
Potassium hydroxide no.	1.40%
Mechanical stability time (at 55% TS)	1140 sec
Coagulum	0.005%
Viscosity (at 58% TS)	62 cps
pH	10.10

KOH number is a measure of the total acidic materials in latex. Generally, high KOH number indicates low stability. KOH number of RVNRL is generally high, possibly due to the hydrolysis occurring to a portion of nBA, liberating acrylic acid. Even with high KOH number, the stability of RVNRL is found to be high due to the presence of fixed alkali added before irradiation. Low viscosity of RVNRL at low solid content enables the formation of thin deposits on the formers during dipping. This makes RVNRL suitable for the production of condoms and gloves.

Residual nBA imparts a characteristic odour to RVNRL after irradiation. However, nBA is highly volatile. It escapes from RVNRL on keeping. If RVNRL is used immediately after irradiation, nBA is partly removed by the leaching of the dipped article. The residual nBA escapes during the drying of the dipped film and the final product is absolutely free of odour. R & D work is, however, in progress to avoid the smell of residual nBA in RVNRL.

Coagulant dipping of RVNRL

During RVNRL processing 5 phr of nBA, an organic liquid, is added as 50% emulsion to function as sensitizer. It is likely that the rheological behaviour of RVNRL in dipping may be different from that of conventional sulphur prevulcanized natural latex of similar solid content. However, the dipping characteristics of RVNRL is found to be very similar to that of conventional latex (13). The film formation is very good in uniform thickness on ceramic and glass moulds in straight, as well as coagulant dipping. The coagulants examined are aqueous solutions of formic and acetic acids and calcium nitrate and chloride. Table 4 gives the thickness of RVNRL films using different coagulants at a dwell time of 1 min. when dipping is carried out at 50% solids content (13).

Table 4:

Effect of the type of coagulant on thickness of dry RVNRL films

Coagulant	Thickness of film (mm)
Straight dipping	0.02
10% Calcium chloride	0.18
10% Calcium nitrate	0.14
10% Formic acid	0.14
10% Acetic acid	0.12

Heat sensitive dipping

For producing thick articles like latex tubings or teats, a heat sensitive dipping system has been developed for RVNRL (14). Articles of 2-3 mm thickness can be produced in a singl dip. The films have to be properl leached to attain good tensile properties. Considering the thickness of the films, it is preferable to give wet gel leaching.

Tensile properties of RVNRL films

Dipped RVNRL films show excellent physical properties after proper leaching. RVNRL films containing 2 phr TNPP as antioxidant show very good ageing behaviour. Table 5 shows the tensile properties of RVNRL films before and after ageing at 70° C for 168 hrs. It can be seen that tensile properties of RVNRL films are very comparable to that of sulphur prevulcanized latex films. Films prepared by heat-sensitive dipping have lesser tensile properties compared to coagulant dipped films. However, films prepared by heat-sensitive dipping meet the specifications for common dipped products.

Table 5:

Tensile properties of RVNRL films

Property	Before ageing	After ageing
Modulus at-		
100% (MPa)	1.08	0.97
300% (MPa)	1.54	1.42
500% (MPa)	2.50	2.08
Tensile strength (MPa)	30.28	29.12
Elongation at break (%)	965	890

Processing factors such as wet gel leaching or dry film washing and post-drying also influence the tensile properties of dry RVNRL films (15). Tensile strength increases sharply on drying, due to better fusion of rubber particles and increased chain entanglements of the rubber molecules. Tensile strength also increases on leaching the latex film. This is due to removal of water soluble non-rubber substances from the rubber particles. (16)

Comparison of RVNRL and sulphur prevulcanised latex

Several authors have reported the results of comparative evaluation of the physical properties of RVNRL with sulphur vulcanised natural rubber latex (SVNRL). Table 6 gives such a comparison (17).

It can be seen that physical properties of RVNRL films are readily comparable to the properties of sulphur prevulcanised latex films.

Table 6:

Physical properties of gloves prepared from RVNRL and SVNRL.

Property	RVNRL	SVNRL
Modulus (Mpa)		
M 100	1.08	1.14
M 300	1.54	1.68
M 500	2.50	2.74
Tensile Strength (MPa)		
Before ageing	29.42	31.20
After ageing*	32.00	
Elongation at break (%)	965	845
Permanent set (%)	4	2

*Aged at 70° C for 168 hours

Cytotoxic behaviour of RVNRL film

There is no dithiocarbomate in RVNRL film. This is a distinct advantage over conventional sulphur vulcanizates because zinc dithiocarbomate residues cause cell damage. Quantitative cell cytotoxicity evaluation by a colony suppression assay method (18, 19) indicated that the cytotoxicity of RVNRL films is much lower than those of conventional sulphur vulcanized films. The cytotoxic potential of a material is expressed as the extract concentration which suppresses colony formation to 50% of the control (IC50). Table 7 gives the IC50 values for commercial surgical gloves and urinary catheters made from natural latex and RVNRL films (18).

Table 7:

Results of cytotoxicity testing of commercial surgical gloves, urinary catheters and RVNRL films.

Material	IC50
Surgical gloves	
S1	4.7
S2	3.1
S3	1.5
S4	26.7
Urinary catheters	
C1	14.8
C2	12.9
C3	85.0
C4	45.2
RVNRL film*	
RO	74
R 0.5	84
R 1	95
R 4	>100
R 24	>100

*Sample RO is not leached. Others are leached for 0.5, 1, 4 and 24 hours respectively in 1% sodium hydroxide solution at room temperature.

Articles made from sulphur vulcanised natural latex have low IC 50 values i.e. higher cytotoxicity than RVNRL film. Cytotoxicity of RVNRL films decreases with increasing leaching period. Thus RVNRL films are safer than sulphur prevulcanized latex.

Extractable protein content in RVNRL film

Extractable proteins in latex products cause allergic reactions in sensitized people. Health care workers are identified as a high risk group. An unleached film of RVNRL shows a high level of extractable protein. This is because irradiation facilitates the dissolution of proteins on NR latex particles by breaking the polypeptide chains (20). The effect of latex irradiation on allergenic reactions of soluble proteins was investigated by passive cutaneous anaphylaxis (PCA) test (21). The PCA test demonstrated weaker allergenicity for RVNRL films than sulphur-cured latex films. It has been reported that more than 90% of the total extractable proteins in RVNRL products can be reduced by prolonging the leaching period and/or increasing the temperature of the leaching bath. The results reported by Zin and Othman (22) on the effect of leaching time are given in table 8 and the effect of temperature of leaching bath in table 9.

Table 8:

Effect of leaching on extractable protein content of RVNRL films irradiated at 12 kGy.

Leaching time (min)	Extractable protein (ug/g)
5	53
10	47
15	35
30	25

Table 9:

Effect of leaching time and temperature on extractable protein content of RVNRL films

Leaching time (min)	Leaching temperature (deg.C)	Extractable protein (ug/g)
5	30	61
	60	48
	90	28
10	30	51
	60	37
	90	21

The data presented suggests that online leaching of RVNRL films in hot water can reduce extractable protein content to low levels, comparable to that of chlorinated gloves.

Recently, it has been found that the extractable protein content in examination gloves (powder free) processed out of RVNRL has been reduced to a very low value of 21.9 ug/g (23).

Advantages of RVNRL

The following are the major advantages of RVNRL over conventional sulphur prevulcanized latex.

1. Absence of nitrosamines

RVNRL does not contain any vulcanization accelerators based on dithiocarbomates or thiurams that can liberate volatile nitrosamines. Many of the volatile nitrosamines are proved to be carcinogenic.

2. Very low cytotoxicity

Leached RVNRL films are almost pure crosslinked rubber, containing only small amounts of antioxidants. Hence RVNRL films exhibit very low cytotoxicity.

3. Low emission of sulphur dioxide and less formation of ashes on burning.

In conventional vulcanization, 0.5-3.0 phr sulphur is added (depending on the cure systems). Sulphur vulcanizates liberate substantial quantities of sulphur dioxide and leave ashes on burning. RVNRL films contain no sulphur or chemicals and hence produce very little sulphur dioxide and ashes on burning.

4. Transparency and softness (low modulus)

RVNRL films are generally soft due to their lower modulus and high transparency.

5. Biodegradability on weathering

Sulphur vulcanisates contain residues of accelerators which have some bactericidal activity and hence offer some resistance to biological degradation. Since RVNRL is free of any residual chemical, it easily undergoes biodegradation.

6. Less extractable protein content

During irradiation, proteins are degraded and become more water soluble. They are removed during leaching. Leaching RVNRL films contain less extractable proteins and cause less allergic reaction.

7. No problem with chemical stability or zinc oxide thickening.

Zinc oxide is generally added as activator to vulcanization in sulphur systems. It dissolves in the aqueous phase to cause thickening of latex. In RVNRL no zinc oxide is used and it is free from problems.

8. No problem with zinc contamination in the effluent.

Dissolved zinc is considered to be a pollutant in waste water. In a latex product manufacturing unit using RVNRL, the waste water is free of dissolved zinc.

Storage stability of RVNRL

A reasonably long shelf life is essential for any prevulcanized latex. On monitoring the properties of RVNRL for a period of one year, gradual thickening is observed after a period of 5-6 months. Physical properties of films prepared from 3-6 months old RVNRL are good.

Economic aspects

Fixed capital investment for erecting the radiation plant being high, RVNRL will be a little costlier than conventional latex. This cost of RVNRL processing may come to about Rs. 12/- per kg. dry rubber, but there is saving; the processor need not add any vulcanising chemicals. This saving along with technical advantages outweigh the additional cost. RVNRL can be utilized with advantage in production of value added articles in the medical field.

Application of RVNRL

I. Examination Gloves

Use of RVNRL for examination gloves was reported in 1989 from Indonesia (24). Studies on its use for examination glove manufacture has been undertaken in India also (25). The physical properties of the gloves prepared from RVNRL are given in table 10. For comparison the current ASTM specifications for examination gloves are also given.

It is seen that gloves made from RVNRL conform to the specifications for examination gloves. The colour is white and appearance is good. The widespread use of examination gloves is likely to pose environmental problems in disposal of used gloves. Release of sulphur dioxide and carbon monoxide on burning RVNRL gloves is much less compared to conventional sulphur vulcanized gloves. RVNRL gloves are easily biodegradable due to absence of dithiocarbomates or other accelerator residues. They have low modulus, and will not cause discomfort to the user during prolonged use. The level of extractable protein is less and type IV allergic problems are absent in RVNRL gloves. They are most environment friendly.

Table 10:

Physical properties of RVNRL gloves and specifications for examination gloves (ASTM D 3578-99)

Property	RVNRL glove	Requirements as per ASTM D 3578-99
Tensile strength (MPa) min		
Before ageing	28.5	14
After ageing*	26.9	14
Elongation at break (%) min.		
Before ageing	930	700
After ageing*	800	500

* Aged at 70 deg. C for 168 hours.

II. Condoms

Both laboratory scale and factory level production of condoms using RVNRL have been reported from Indonesia (24). The physical properties of the condoms produced from RVNRL and the current Indian standard specifications are given in table 11. The condoms are white in colour and have good appearance. Coloured condoms can also be made by appropriate mixing of colour. The advantages of condoms prepared from RVNRL are low modulus, high elongation at break and high burst volume.

Table 11:

Physical properties of condoms made from RVNRL and the Indian standard specifications for condoms

Property	Condom from RVNRL	IS 3701-1985
Thickness (mm)	0.066	0.07 (max)
Tensile strength (MPa)	22.06	20 (min)
Elongation at break (%)	970	650 (min)
Burst volume (litre)	42	Not specified

III. Catheters

Catheter has very close contact with soft body tissues when used. Catheters made from RVNRL have very smooth surface, low extractable proteins and very low cytotoxicity. Other physical properties are comparable to sulphur vulcanized catheters. Thus catheters made from RVNRL are very safe and impart least discomfort to users.

IV. Other medical and pharmaceutical products

Products made from RVNRL can be used with advantage in the medical field because of its very low cytotoxicity. The use of optical endoscopic balloon made from RVNRL was reported in 1989 (26). RVNRL balloon transmits 98% of laser, compared to 65% for sulphur vulcanised films. The high transparency and low thickness facilitate accurate endoscopic examinations. The accuracy of the examination is improved by the balloon method in blood vessel, urinary bladder and digestive track such as stomach and bile duct.

A drainage bag (26) used to collect discharged fluids in post-operative measure restricts mobility of the patient due to its bulkiness. The drainage bag made of RVNRL is compact and causes less irritation to the attached skin because of its low toxicity. The high transparency of the bag facilitates easy observation of discharged fluids without detaching the bag from the tube.

Other potential areas of application, again because of low cytotoxicity, are medical tubings, feeding bottle nipples etc. By adopting heat-sensitive dipping process, feeding bottle nipples and medical tubings of required thickness can be prepared in a single dip.

V. Toy balloons

Low modulus, high transparency, low cytotoxicity, absence of carcinogenic nitrosamines and easy biodegradability make RVNRL a suitable material for toy balloon manufacture. Balloons made from RVNRL can be inflated easily because of low modulus. The appearance is excellent.

Conclusion

RVNRL has definite technical advantages over conventional sulphur-cured latex in making value-added products used in medical and pharmaceutical fields. Proteins in natural latex are degraded to a great extent during irradiation and removed during leaching. RVNRL is less cytotoxic; type IV allergic and nitrosamine problems are totally absent. Hence it can be safely used in making products that come into contact with body and food. RVNRL films are very transparent and hence high quality balloons can be made. Low modulus and absence of allergic reactions make it suitable for the production of examination gloves, catheters, condoms etc. Since RVNRL is slightly costly its use in the more value added medical and pharmaceutical products will be more advantageous.

References

1. P. Sehindrowitz. British Patent No. 193 451 Feb. 26, 1923.
2. A.D.T. Gorton. NR Technol. 10.9 (1979)
3. Y. Minoura and M.Asao, J. Appl. Polym. Sci. 5, 233 (1961)
4. Y. Minoura and M. Asao. J. Appl. Polym. Sci. 5, 401 (1961)
5. K. Makkuchi. RVNRL Consultant Meeting Vienna. Nov. 22-23, 1995.
6. K. Makkuchi and V. Markovic. IAEA Bull. 33(1), 25 (1991)
7. K. Makkuuchi K., T. Sushima, J. Soc. Rubber Ind. Japan. 61, 478 (1988).
8. C. Zhonhai, K. Makuuchi, Proc. Int. Sym. Radiation Vulcanisation of Natural Rubber Latex. JAERI-M 89, 228. p-326 (1989).
9. S. Sabhawal, T.N. Das, C.V. Chaudhari, Y.K. Bharadwaj and A.B. Majali. Radiat. Phys. Chem. 51, 309 (1998).
10. K. Makuuchi and T. T. Sushima Proc. Int. Rubber Conf. Kuala Lumpur. p-502 (1985)
11. S.P. Pansa, R. Devendra, A.W. Shukri and K. Makuuchi, unpublished data.
12. A.M.D. Rosa, L.V. Abad, L.P.S. Ana Relieve, C.O. Tranqilan - Arinalla, C.L. Pascual. Proc. Second Int. Sym. RVNRL. 1996. Kuala Lumpur. p-15.
13. M.S. Sebastian, V. George, I J Britto, K.C. Vijayakumar, J. Jacob, Rubber India, 51 (6), 7(1999).
14. V. George, I.J. Britto, M.S. Sebastian and E.V. Thomas - Under publication.
15. A.W. Shukri, S.B. Siti, B. Sulaiman, K. Makuuchi, R. Devendra, C.P. Pansa. Proc. Int Sym. Radiation Vulcanisation of Natural Rubber Latex. JAERI. M 89 - 228. p-189 (1989).
16. L.C. Teik and W.N. Poh. Developments in Plastics and Rubber Industries. Plastics and Rubber Institute of Malaysia. Kuala Lumpur. p-265 (1989)
17. RVNRL Plant, Rubber Board, India. Unpublished Data.
18. A. Nakamura, T. Ikarashi, M. Kanimi. Proc. Int. Sym. Radiation Vulcanization of Natural Rubber Latex. JAERI. M 89-228, p-79 (1989)
19. T. Tsuchiya, Y.Ikarashi, K. Toyoda, T. Uchima, T. Miyahara, M. Takashashi, A. Nakamura, Radiat. Phys, Chem. 39, 541 (1992)
20. K. Makuuchi, T. Sushima, J. Soc. Rubber Ind. Japan. 61, 710 (1988)
21. K. Makuuchi, F. Yoshii, K. Hyakutaka, T. Kume. J. Soc. Rubber Ind. Japan. 68, 263 (1995)
22. W.M.W. Zin, N. Othman. Proc. Second Int. Sym. RVNRL. 1996 Kuala Lumpur. p-115.
23. RVNRL Plant, Rubber Board, India. Unpublished Data.
24. F. Sundardi, M. Utama, S. Iskandar, Herwinarni. Proc. Int. Sym. Radiation Vulcanization of Natural Rubber Latex. JAERI. M. 89-228. p-132 (1989).
25. E.V. Thomas - Paper presented at the First Research Coordination Meeting on Improvement of Physical Properties of RVNRL. Bangkok. 1998.
26. Shimaura. Proc. Int. Sym. Radiation Vulcanization of Natural Rubber Latex. JAERI. M. 89-228. p-88 (1989).