Bulletin of the Rubber Research Institute of Sri Lanka, (1999) 39, 33-39

RADIATION VULCANISED NATURAL RUBBER LATEX (RVNRL) – A MATERIAL WITH LESS OR NO PROTEIN ALLERGENS?

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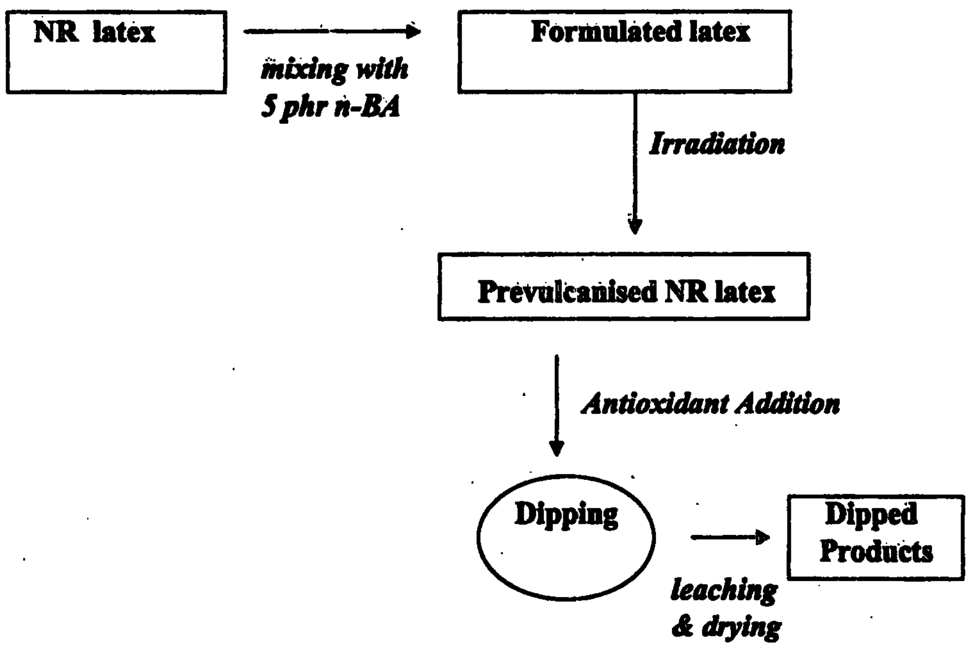
INTRODUCTION

Since the discovery of the process of sulphur vulcanisation in 1839 by Goodyear, Natural Rubber (NR), either in centrifuged latex form or in dry rubber form has been crosslinked by sulphur to make a variety of products ranging from automobile tyres to medical gloves. Various other techniques for crosslinking of NR have been investigated , but none of them is commercially viable due to various reasons. The use of high energy radiation for crosslinking of NR has been investigated since 1950's. However, until recently, the process was less attractive commercially due to many reasons such as;

- High cost of irradiation
- Poor physical properties
- Ambiguous advantages of the products

Over the last decade or so, this situation has changed to a greater extent. Significant progress has been made both in cost reduction and in quality improvement through extensive research programmes.

At the inception of the RVNRL technology the main obstacle for the commercial implementation was the high cost of irradiation. The radiation dose (D_v) required for obtaining the maximum tensile strength (Tb) was found to be more than 250KGy, and this is too high to be used in the industry. Later it was found that the use of certain chemicals as radiation sensitisers reduces the required dose for crosslinking of NR dramatically. The very first sensitisers proposed were halogenated hydrocarbons such as carbon tetrachloride & chloroform. The use of 5phr of carbon tetrachloride reduces the Dv to 50KGy. Since CCl_4 is a toxic chemical both to the humans as well as to the environment the use of various other chemicals as sensitisers for the radiation process has been evaluated. Extensive research on the subject has revealed that many polyfunctional monomers such as neopentylglycol diacrylate (A-NPG) and 1,6-hexane diacrylate (A-HD), and monofunctional acrylates such as 2-ethylhexyl acrylate (2EHA) and n-butyl acrylate (n-BA) can be used as sensitisers for the process. However, though the sensitising efficiency of diacrylates are as good as those of halogenated hydrocarbons these diacrylates are reported to cause strong skin irritations. In the case of 2EHA the removal of unreacted monomer is difficult due to its low vapour pressure. Inevitably the products are less attractive due to the bad smell. Several attempts to remove residual 2EHA have so far been failed. Therefore n-BA has been selected as the best sensitiser for the radiation crosslinking of NR. One problem with using n-BA is that increases the viscosity of NR latex and sometimes it even causes the coagulation of latex. However, this problem can be overcome with the use of a little amount of KOH. The process of radiation vulcanization of NR latex using n-BA as the sensitizer can be outlined as follows.



Physical properties Of RVNRL films

It has been shown that the tensile properties of RVNRL would vary depending on the radiation dose employed. It would also depend on the type of sensitiser used and the postcure treatments such as leaching and drying. The Fig. 1 illustrates the variation of tensile strength of RVNRL films with the dose and the type of sensitiser (Makuuchi & Tsushima, 1988).

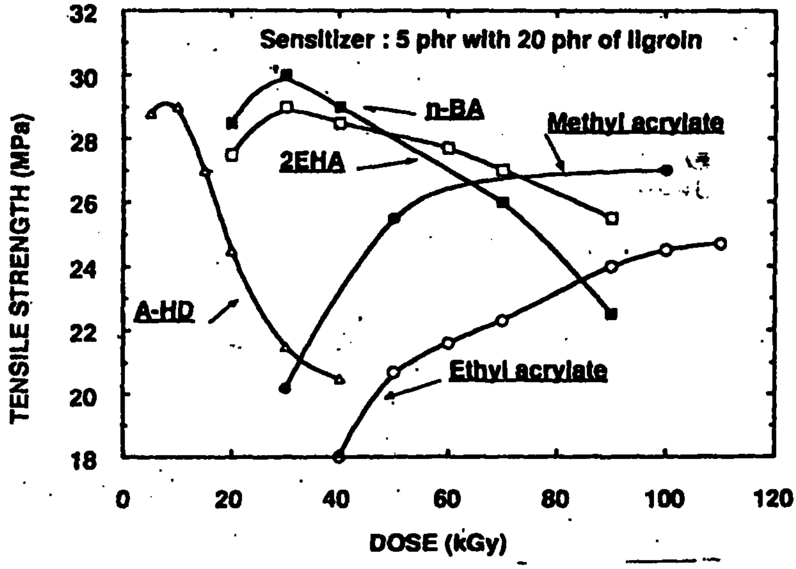


Fig. 1. Variation of tensile strength of RVNRL films with radiation dose and type of sensitiser (Makuuchi & Tsushima, 1988).

Advantages of RVNRL over conventional vulcanisates

It has been proven that the RVNRL has the following advantages over the conventional sulphur vulcanisates;

- absence of nitrosamines
- very low cytotoxicity
- less protein allergy response
- high biodegradability
- transparency and softness
- low emission of SO_2 and less formation of ashes when burned

Of the above advantages, the less protein allergy response can be considered as the most important advantage with regard to the current issue on latex protein allergy. In this paper the results which have been published of the radiation effects on the proteins in NR latex will be reviewed.

Extractable proteins in irradiated latex products :

Makuuchi *et al.* (1995) have compared the water soluble components isolated from non-irradiated and 20 KGy irradiated NR latex by centrifugation, filteration & freeze drying. They have found that the water-soluble components increased from 0.7% to 1.7% by irradiation and this observation has been attributed to the radiolysis of non-rubber components in latex *i.e.* Table 1.

Table 1. *Weight percentage of water soluble components extracted from NR latex (Makuuchi et al., 1995)*

Sample	Weight percentage
non-irradiated	0.7
20 KGy irradiated	1.7

Nitrogen content in above rubber films have been determined using the Kjeldahl method and results have been reported as in Table 2.

Table 2. *Nitrogen contents of NR latex films (Makuuchi et al., 1995)*

Sample	Nitrogen Content (%)
non-irradiated,non leached	0.26
non-irradiated,leached	0.19
20 KGy irradiated,non-leached	0.53
20 KGy irradiated, leached	0.06

They have also measured the molecular weight distribution of water soluble components of each sample by using the GPC and their results have been reported as given in Fig. 2.

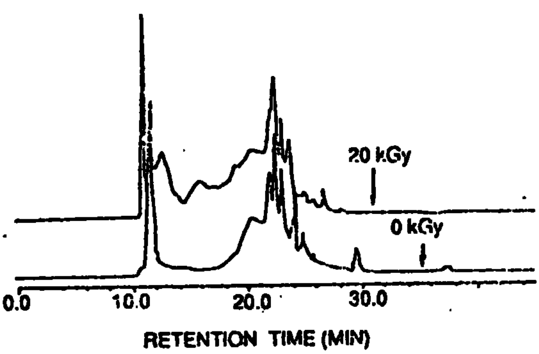


Fig. 2. Molecular weight distribution of water soluble components of NR latex (Makuuchi *et al.*, 1995)

The molecular weight distribution of peptides in water soluble components have also been analysed by SDS-PAGE analysis and the results are as shown in Fig. 3. These results indicate some radiolysis of proteins. They have concluded that the water solubility of rubber proteins increases through radiolysis.

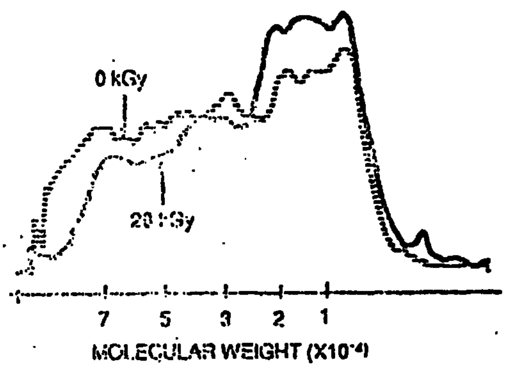


Fig. 3. Molecular weight distribution of peptides in the water soluble components in NR latex (Makuuchi *et al.*, 1995)

Bez (1996) has reported the effects of radiation on the extractable protein content in NR latex in a paper titled "Status of RVNRL in German Latex Industry and its Introduction to the European Market". Their results are given in Table 3.

Table 3. *Extractable proteins in RVNRL gloves (Bez, 1996)*

Phase	Extractable proteins μg/g
After dipping	1000
After wet gel leaching	850
After 24 h leaching	16

He has also conducted some clinical tests, *i.e.* prick test, using some 18 patients who have been diagnosed to have immediate Type 1 Allergy to NR latex proteins. Out of 18 patients sensitive to NR latex proteins only six were found to have a positive response RVNRL proteins.

Binh & Hang (1996) have investigated for a suitable leaching medium for RVNRL with a view to obtain a no protein/less protein product. They claim that the best treatment media for RVNRL films are either diluted alkaline solutions, because this media could make the protein structure to limit a remarkable amount of soluble proteins released and leach a part of soluble proteins from RVNRL films, or neutral surfactant solution which could dissolve and reduce soluble protein content in the product.

Wan Manshol *et al.* (1996) have investigated the effects of various factors such as radiation dose, different leaching treatments, leaching time, and leaching temperature etc. upon the soluble protein content of RVNRL products. The effects of radiation dose upon the soluble protein content of the products are given in Table 4.

Table 4. *Effects of radiation dose upon soluble protein content of RVNRL films (Wan Manshol et al., 1996)*

Dose, KGy	Soluble protein content,mg/ml	
	5 mins leached	10 mins leached
5.3	0.022	0.016
6.0	0.029	0.021
9.3	0.043	0.034
12.0	0.053	0.047
13.0	0.058	0.053
15.0	0.064	0.057
19.0	0.075	0.062
25.2	0.078	0.072

Their results on the effects of leaching time and the leaching temperature on the soluble protein content are given in the Table 5.

Table 5. *Effects of leaching time and temperature on soluble protein content (Wan Manshol et al., 1996)*

Leaching time, mins	Leaching temp., C	Soluble protein content, mg/ml
5	30	0.061
	60	0.048
	90	0.028
10	30	0.051
	60	0.037
	90	0.021

Based on the above results they claim that the soluble protein content of RVNRL is high and therefore, through the establishment of proper leaching techniques RVNRL products of low protein content could be made.

However, all the above studies have been done on the total protein content of the products and it has not been made clear whether the amount of allergic proteins are also removed or even reduced during the process of irradiation and consequent postcure treatments. A few publications appear in the literature on the identification and quantification of the protein allergens in NR latex based products. Geertsma *et al* have reported that some, but not all proteins are destroyed during irradiation. An important protein (14 kD), which is known to be one of the major latex allergens, is still present and seems hardly to be affected by the radiation process.

Vargiise *et al* (1997) have reported that as the radiation dose increases, the soluble protein content in the serum phase increases whereas that in the rubber phase decreases. They have shown by using SDS-PAGE analysis that 27 kD protein together with 14kD protein which are normally considered as the allergens appear in the radiation vulcanised latex up to a radiation dose of 160 kGy and at 320 kGy they completely disappears. However, as one can very well imagine the use of such a high dose is not commercially viable.

They have also shown that that the irradiation of field latex followed by centrifugation removes almost all the proteins and if the latex is diluted to 20% DRC before centrifugation a protein free latex can be produced

REFERENCES

Bez, W (1996). Proc. 2nd Intern. Symp. Radiat. Vulc. Nat. Rubb. Latex, 121

Binh, D, Hang, N D (1996). Proc. 2nd Intern. Symp. Radiat. Vulc. Nat. Rubb. Latex, 108.

Geertsma, R E, Orzechowski, T J H, Jonker, M, Dorpema, J W and Van Asten, J A.A M. Report No. 605148007, National Institute of Public Health and the Environment, Bilthoven, The Netherlands.

Makuuchi, K and Tsushima, K (1988). *J. Soc. Rubb. Ind. Japan* 61, 478.

Makuuchi, K, Yoshii, F, Hyakutake, K, Kume, T and Suzuki, K (1995). *J. Soc. Rubb. Ind. Japan,* **68**, 263

Vargiise, S, Katsumara, Y, Yoshi, F and Mucuuchi, K (1997). Proc. Intern. Rubb. Conf., 127.

Wan Manshol W. Zin, N. Othman (1996). Proc. 2nd Intern. Symp. Radiat. Vulc. Nat. Rubb. Latex, 115.