# RADIATION VULCANIZATION OF NATURAL RUBBER LATEX: EFFECT OF SPLIT ADDITION OF INITIATOR AND ANTIOXIDANT

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Radiation vulcanization of natural rubber latex is a free radical assisted crosslinking reaction induced by Y-radiation. It is carried out using a <sup>60</sup>Co source at room temperature using n-butyl acrylate as sensitizer. The optimum radiation dose for obtaining maximum properties for RVNRL film is optimized as 15 k.Gy. The residual n-BA in the latex causes several problems in the products derived out of the latex. The split-dose addition of n-BA was proposed to overcome this difficulty. The order of addition of antioxidants also has some effect on radiation crosslinking reaction as antioxidants are free radical scavengers. Accordingly, the effect of different modes of addition of antioxidants on mechanical properties of the vulcanizates was studied. Among the different methods attempted, addition of antioxidant at mid time (M.I) and after irradiation (A.I) gave better mechanical properties and thermal stability.

Key words: Antioxidant, Natural rubber latex, Radiation vulcanization, Tensile strength

### INTRODUCTION

Research on new materials technology is attracting the interest of researchers all over the world. Efforts are being made to build up materials that can confer advantageous properties. Radiation technology has emerged as one of the foremost techniques for the processing of polymer materials. It has been an area of enormous interest in the last few decades. The technique is not being used in industries due to the high cost of irradiation and low quality of the products (Makuuchi *et al.*, 1984). Recently, significant progress has been made in cost reduction and quality improvement. In radiation

vulcanization of natural rubber latex (RVNRL), the crosslinking of rubber particles is brought about by  $\Upsilon$ - radiation from a  $^{60}$ Co source (Makuuchi, 2003).

Some of the natural rubber latex products made using sulphur vulcanization are currently being substituted by RVNRL. The residual chemicals in sulphur vulcanized products cause detrimental effects both to environment and human body. The dipped rubber goods are quite often used in contact with human body. In order to reduce the nitrosamine level, RVNRL is an ideal material in which vulcanization is effected using high energy Y-radiation (Minoura et al., 1961). Thus RVNRL provides an alternative

process for the vulcanization of natural rubber latex. Studies reported that radiation prevulcanized natural rubber latex is suitable for manufacturing latex products. Radiation vulcanized natural rubber latex products have many advantages over sulphur vulcanized (SVNRL) products. The advantages are the absence of carcinogenic nitrosoamines, low cytotoxicity, better transparency and softness (Minoura *et al.*, 1961). These are achieved by the absence of accelerators in sulphur vulcanization that occurs in conventional sulphur cure system.

At the early stages, radiation vulcanization was carried out without sensitizing agent. Hence, higher radiation dose was required for crosslinks between the rubber molecules. Later on, several kinds of sensitizers were used to reduce the radiation dose required for vulcanization. Halogenated hydrocarbons such as carbon tetrachloride and chloroform were used as sensitizers for radiation crosslinking (Ambroz et al., 2007; Kartowardoyo et al., 1977). Monofunctional and polyfunctional monomers were also used by some investigators (Makuuchi et al., 1984). Some researchers obtained the optimum vulcanization dose of 15k.Gy using 5phr nbutyl acrylate as a sensitizer and claimed to reduce the vulcanization dose to 10k.Gy by using hydrogen peroxide together with n-BA and CCl<sub>4</sub> (Zhonghai et al., 1996).

However, some parts of the added n-BA tend to remain in the RVNR latex. The residual n-BA causes health hazards and environmental pollution. Complete consumption of n-BA by irradiation is not practical because irradiation beyond the optimum level results in lower physical properties.

Polymers are prone to oxidation due to environmental influences, such as heat, oxygen, ozone, mechanical shearing, ultraviolet, etc. (Ambroy, 2007). The carbon radicals of the polymer chains, formed during the degradation, can produce a series of damage to the polymer.

At the time of irradiation, the rubber hydrocarbon undergoes oxidation to peroxy entities. To avoid self-oxidation of rubber molecules, antioxidants are recommended in latex. Radiation crosslinking being a free radical assisted crosslinking reaction, the presence of antioxidant being radical scavengers may reduce the efficiency of crosslinking. To avoid this situation, antioxidant is added usually after the irradiation process. However, the latex after irradiation may be in a partially oxidised state in the absence of an antioxidant. Hence a study was undertaken to develop a protocol for the addition of antioxidant during the irradiation process of natural rubber latex.

In this work, the mode of addition of n-BA and antioxidant on the mechanical properties of RVNRL film was investigated. Incorporation of antioxidant at three different stages was carried out (1) at the beginning of irradiation (B.I), (2) mid time (M.I) and (3) after the irradiation (A.I).

### MATERIALS AND METHODS

### Natural rubber latex

The centrifuged natural rubber latex used conformed to Indian Standards (IS) specification (5430- 2017). Samples were irradiated with Y-rays from a <sup>60</sup>Co source using a gamma chamber (model 5000) supplied by the Board of Radiation and Isotope Technology, Bhabha Atomic Research Centre, Mumbai. The samples were irradiated at a dose rate of 0.62 k.Gy/h, at atmospheric conditions.

The sensitizer used for this study was nbutyl acrylate (n-BA). The stabiliser used was potassium hydroxide. A phenolic antioxidant namely Aquanox LP (butylated reaction product of para cresol and dicyclopentadiene) was used as antioxidant.

### Optimisation of radiation dose

The sensitizer, stabiliser and the water are first made into an emulsion and added into 60 per cent centrifuged latex with gentle stirring for two hours. The total solid content of the latex was kept at 50 per cent. The irradiation was carried out at different dose rates *viz*. 10, 15, 20, 25 and 30 k.Gy, respectively. The irradiated latex is then tested and the properties were evaluated. Formulation for the preparation of RVNRL was presented in Table 1.

Table 1. Formulation of radiation vulcanized latex

Ingredients	Parts by weight		
	Dry	Wet	
60 % Centrifuged latex	100	167	
10 % Potassium hydroxide (KOH)	0.2	2.0	
n-butyl acrylate (n-BA)	5.0	5.0	

### Split dose addition of n-BA during irradiation

The mode of addition of n-BA was shown in Table 2. The irradiation was carried out at 15 k.Gy. The antioxidant was added after irradiation and kept over overnight. The antioxidant employed was Aquanox LP (butylated reaction product of para cresol and dicyclopentadiene). After irradiation, the prevulcanized latex is tested and evaluated the properties.

Table 2. Split dose addition of n-BA

Dose, k.Gy	Sensitizer (dry weight)
0-8 (First half)	2.5
8-15 (Second half)	2.5
Control C	5

### Effect of antioxidant

Since radiation vulcanization is a free radiation induced crosslinking reaction, the

presence of antioxidants, which are free radical scavengers, might have some role in the crosslinking reactions. Hence, studies were conducted with the incorporation of antioxidants in three separate stages *viz.* at the beginning of irradiation (B.I), at mid time addition (M.I) and after the irradiation (A.I). It is to be noted that the B.I and A.I were carried out with full recommended amount of antioxidant (1 phr) whereas only half the amount of antioxidant (0.5 phr) was added at the mid time (M.I) and the remaining antioxidant (0.5 phr) was added after the irradiation. Sample without antioxidant was taken as control (C).

#### Determination of n-BA in RVNRL

Analysis of n-BA was carried out by gas chromatography. Five grams of the RVNRL was transferred to a 50 ml volumetric flask with hexane. The sample was diluted to 50 ml with hexane and shaken for 3-4 h to completely extract the residual n-BA. Then 1 µl hexane solution was injected into GC. Measurement was carried out after irradiation.

### Preparation of RVNRL films

The RVNRL latex was casted by pouring the filtered latex on a levelled glass plate of suitable dimensions. After spreading, the glass plate containing latex is kept overnight for drying. The dried films were collected from the glass plate after dusting with talc powder. The dusting helps to prevent the self-adhesion and also to avoid accumulation of dirt particles on film surface. The film was leached in one per cent ammonia solution for 24h, dried at room temperature till transparent and again dried at 70°C for 2h in a hot air oven. The dried films are used for mechanical testing and stored in desiccators.

Accelerated ageing was carried out in an air oven at 70°C for seven days according to ASTM D573-04 (2010).

# Testing of vulcanizates Measurement of cross-link density of rubber

The cross-link density *i.e.* degree of cross-link in irradiated latex was measured by swelling methods. Volume fraction of rubber (V<sub>r</sub>) was calculated using the Ellis and Welding equation and crosslink density was calculated on the basis of Flory and Rehner equation as follows (Flory *et al.*, 1943):

$$V_r = \frac{D/\rho_r}{D/\rho_r + A_o/\rho_s} \qquad \dots 1$$

Where D and  $\rho_p$  are the weight and density of dry rubber (for vulcanised rubber,  $\rho_p = 0.9203 \ gcm^{-3}$  and  $A_a$  and  $\rho_s$  are the weight and density of solvent (for toluene,  $\rho_s = 0.865 \ gcm^{-3}$ , V = crosslink density,  $M_c$  is the molecular weight between the cross-links,  $V_s$  is the molar volume of the solvent.

### Chloroform number

This is probably the most widely used procedure for assessing the vulcanization level of prevulcanized latices (Table 3). The procedure involves mixing equal parts of compounded latex and chloroform. 10 ml of each material is mixed and stirred with a glass rod until coagulation is complete. The coagulum is allowed to stand for two to three

minutes and after it is numerically rated from 1 to 4 by pressing between thumb and finger.

### Mechanical properties

The tensile properties of the test specimens were tested using dumbbell shaped specimens according to the ASTM D-412 on an universal testing machine Instron 3343 at a crosshead speed of 500 mm per minute. The test value is the average of five test specimen and all mechanical tests were carried out at ambient temperature.

The percentage retention in tensile strength was calculated as follows

# Fourier Transform Infrared (Attenuated Total Reflectance) Spectroscopy (FT-IR)

FT-IR spectral analysis of thin film was obtained from a Bruker FT-IR ATR spectrophotometer (Bruker Tensor 27, Germany) using a Zn-Se crystal in the wavenumber range of 600-4000cm<sup>-1</sup> (ASTM D 2702- 05) 2011.

### Conversion of substrate

The percentage conversion of substrate and selectivity of products were calculated from GC data using the formulae,

$$\left.\begin{array}{l} \text{Percentage} \\ \text{conversion} \\ \text{of substrate} \end{array}\right\} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of}}{\text{(substrate} + \text{product)}}} = \frac{5}{\frac{\text{Area of substrate} \times 100}{\text{Total area of product}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}}{\text{Substrate}}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total area of product}}}{\text{Substrate}} = \frac{100 - \text{Area of substrate} \times 100}{\frac{\text{Total$$

Table 3.	Grading as	per	chlo	ro	form	test

Chloroform number	Nature of coagulum
Number 1	The coagulum is a tacky mass and break in a stringy manner when stretched (un-vulcanized)
Number 2	The coagulum is a weak lump which breaks short when stretched (lightly vulcanized)
Number 3	The coagulum is in the form of non-tacky agglomerates (vulcanized)
Number 4	The coagulum is in the form of small dry crumps (over vulcanized)

# RESULTS AND DISCUSSION Optimisation of radiation dose

In order to optimize the radiation dose, suitably formulated latex was irradiated and the crosslink density was recorded (Fig. 1). Swell-index which is a direct measure of the crosslink density, decreases up to 15 k.Gy and thereafter it remains constant with total dose. The decrease in swell- index is due to increase in crosslinking between rubber molecules in presence of n-BA (Haque *et al.*, 1996).

Thus swell-index can be used as a proxy measure of crosslinks. The extent to which the sample swells is inversely proportional to the degree of vulcanization. In this experiment 15 k.Gy is the optimum dose required for crosslinking of rubber.

The level of prevulcanization can be assessed by chloroform number. Chloroform number test is probably the most rapid procedure for determining crosslink density in the latex mixes. The nature of the coagulum is examined and graded depending upon the form of coagulum after irradiation is shown in Table 4. As the chloroform number increases the crosslinking of rubber hydrocarbon in the discrete rubber particles dispersed in the aqueous phase of the latex also increases.

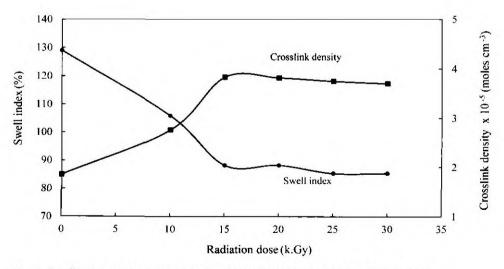


Fig. 1. Swell index and crosslink density of RVNRL films at various radiation doses

Radiation	Chloroform	Nature of the coagulum
dose, k.Gy	number	
0	1	The coagulum is a tacky mass and break in a stringy manner when stretched· Unvulcanized state
10	2	The coagulum is a weak lump which breaks short when stretched Lightly vulcanized state
15	3	The coagulum is in the form of non- tacky agglomerates Vulcanized state
20	3	The coagulum is in the form of non- tacky agglomerates Vulcanized state
25	3	The coagulum is in the form of non- tacky agglomerates Vulcanized state
30	3	The coagulum is in the form of non- tacky agglomerates Vulcanized state

The effect of radiation dose on chloroform number is described in Table 4.

### Effect of irradiation dose on crosslink density

When the natural rubber is irradiated by

high energy  $\gamma$ - radiation, hydrogen atoms of the trunk chain, mainly of methylene groups adjacent to double bonds, are ejected and radical sites are formed and these radical sites are combined to form C-C crosslinks.

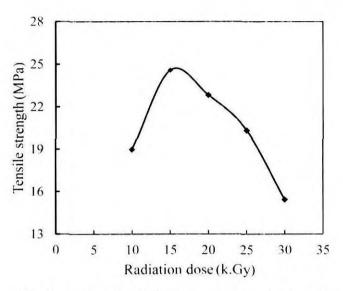


Fig. 2. Tensile strength of RVNRL films at various radiation doses

The crosslink density increases with the increasing radiation dose is showin in Figure 1.

Theoretically, the radiation dose governs crosslink density of final vulcanizates. The number of hydrated electrons generated within latex particles during irradiation determines the amount of crosslinks formed. In addition to crosslinking reactions, hydrated electrons can also undergo certain side reactions. At low dose rate, generation of hydrated electrons is also low leading to minimum side reactions *i.e*, more crosslinks are formed. It is established that the optimum dose required for getting maximum crosslink density in 15 k.Gy (Haque *et al.*, 1996).

### Mechanical properties

Figure 2 shows the variation of tensile strength with radiation dose. At low radiation doses, tensile strength increases and then decreases after reaching the maximum. The maximum value of tensile

was at 15 k.Gy. It was also reported that after vulcanization, rubber particles undergo integration during drying of the films (Roslim *et al.*, 2018). The fall in tensile strength at high radiation dose might be due to lower level of fusion of highly cross linked rubber particles which does not form a coherent film during drying.

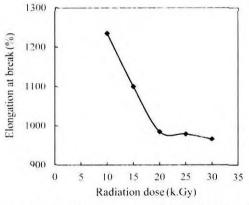


Fig. 3. Elongation at break of RVNRL films at various radiation doses

Table 5. Crosslink density and chloroform number of RVNRL

Samples	Crosslink density x 10 <sup>-5</sup> moles cm <sup>-3</sup>	
Control (C)	3.93	15
A (split dose addition	) 4.01	0-8-15

Figure 3 shows that increase in dose is accompanied by a reduction in elongation at break. This is due to the increased crosslinks which restrict the relative movement of molecular chains. Figure 4 shows that modulus at 300 per cent elongation increases with increasing dose rate. The increase in modulus shows close resembles to the changes in crosslink density at higher dose rates (Haque et al., 2005). In short, on increasing the time of irradiation, the modulus is increased appreciably with reduction in elongation at break, while tensile strength showed sudden fall after reaching the optimum level. Thus the optimum radiation dose for obtaining maximum tensile strength (24.58) for RVNRL film is 15 k.Gy.

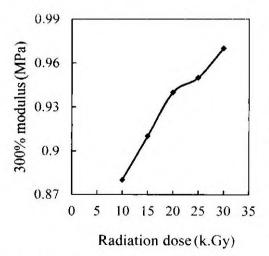


Fig. 4. Modulus of RVNRL films at various radiation doses

### Split dose addition of n-butyl acrylate

Radiation vulcanization is expected to be initiated by creating active sites on rubber hydrocarbon by an initiator say n-butyl acrylate (n-BA). These active sites link together to form crosslinks between the polymer chains. However during irradiation a portion of n-BA undergo polymerization which results in the formation of polybutyl acrylate. Moreover, excess use of n-BA cause residual monomer in the vulcanized latex. This causes unpleasant smell and is also hazardous to the consumers of the latex products. Hence the concentration of n-BA needs to controlled during the radiation process. In order to ensure the complete consumption of n-BA, it was proposed to add n-BA to the latex in two split doses. Here half amount of n-BA was added in the beginning of the radiation process and remaining half at the mid time of irradiation.

### Effect of crosslink density

Table 5 shows that crosslink density of samples A and C. Sample C contains full amount of n-BA added at the beginning of the radiation process whereas sample A contains half amount of n-BA was added in the beginning and second half at the mid time of irradiation process. Comparison between samples C and A shows that sample A showed slight increase in crosslink density than sample C. This implies that split addition of n-BA enhance the crosslinking reactions.

### Mechanical properties

The effect of mechanical properties of mixes with different mode of addition of n-BA is summarized in Table 6. Apparently,  $\rm M_{300}$  and  $\rm M_{500}$  values are increased in sample A. The increase in modulus values of the film might be due to the increased crosslink density of the film. In sample A, n-

BA introduce more free radicals that will abstract hydrogen radicals from the rubber hydrocarbon which will introduce more crosslinks. Elongation at break value was decreased by the split addition of n-BA. It is evident that with the increase of crosslinks will yield to decrease of elongation at break. There was no significant change in tensile strength for samples C and A. This means that addition of half amount n-BA during irradiation is an effective method to reduce the residual n-BA without lowering the tensile strength (Chuniel *et al.*, 1996).

# Determination of residual n-BA in RVNR latex by GC-MS

It is expected that ammonia in NR latex will catalyze the hydrolysis of n-BA. As a result of hydrolysis acrylic acid and butanol are formed. Figures 5 and 6 shows the GC-MS spectra of samples C and A. The

concentration of residual n-BA decreased in sample A when compared to control. This means that when half amount of n-BA was added, complete polymerization occurs. Thirty per cent of n-BA still remained in sample A after irradiation process. But in control C, 45 per cent of n-BA is present. After two weeks, no n-BA smell exists in RVNR latex. No n-BA was detected in the latex by GC.

### **EFFECT OF ANTIOXIDANT**

### Crosslink density and mechanical properties

Unsaturated polymers and their products need to be prepared with antioxidants in order to protect them from oxidative degradation during service. The order of addition of antioxidant in a free radical induced crosslinking process like  $\gamma$ -irradiation is important. Antioxidants being

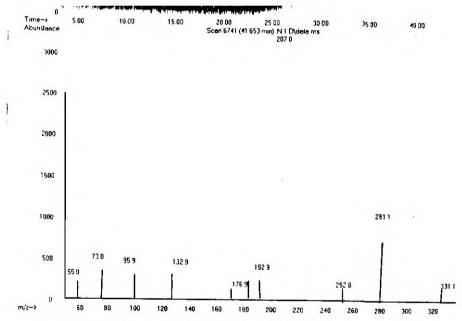


Fig. 5. Mass spectrum of half addition of n-BA

Table 6. Mechanical properties of RVNRL films

Sample	Tensile strength (MPa)	Elongation at break (%)	300 % modulus (MPa)	500 % modulus (MPa)
Control (C)	24.58	1100	0.92	3.28
A (split dose addition)	23.41	1089	1.02	3.56

Table 7. Ageing properties

Samples	At 70°C for seven days			
Samples	C	B.I	M.I	A.I
Tensile strength (MPa)	4.39	9.88	21.56	22.34
Retention in tensile strength (%)	19.36	67.99	90.32	96.25

free radical scavengers may absorb free radicals produced as a result of  $\gamma$ -irradiation which may affect the rate of crosslinking reactions.

In order to ensure this the addition of antioxidant was conducted in three ways such as before irradiation (B.I), split addition (M.I), after irradiation (A.I) and also without antioxidant (control, C). The split addition was conducted by the addition of 50 per cent

of the antioxidant in the beginning of irradiation and the remaining 50 per cent after the irradiation process.

The swelling studies (Fig. 7) showed that B.I has minimum crosslink density and mechanical properties. Addition of antioxidant before irradiation (B.I) deactivates the radicals released by radiation induced decomposition of n-BA and thus reduces the mechanical properties. This

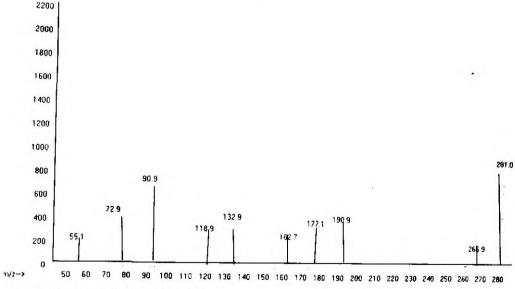


Fig. 6. Mass spectrum of control

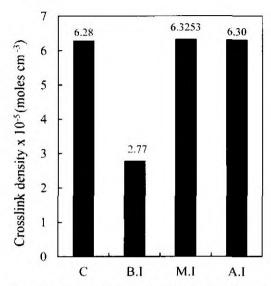


Fig. 7. Variation of crosslink density with different modes of addition of antioxidant

means that antioxidant retards the crosslinking reactions by consuming radicals. Thus there is a competition for the formation of free radicals between the scavenging reaction of antioxidant and the radiation crosslinking reactions. Thereby, both the efficiency of vulcanization and ageing resistance significantly reduced. This is supported by FT-IR spectrum.

The crosslink density and mechanical properties of M.I and A.I are comparable. This means that there is no remarkable difference in properties (Fig. 8).

Ageing is the process of deterioration of desirable properties during storage or on service. The shelf-life of the compounds is determined by ageing the samples and measuring the mechanical properties thereafter. The mechanical properties of RVNRL film with three systems after ageing at 70°C for 7 days are shown in Table 7.

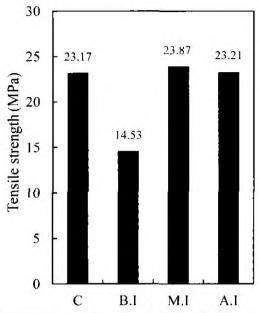


Fig. 8. Variation of tensile strength with different modes of addition of antioxidant

The result shows that the control (C) degrades fast compared to others. The poor ageing properties of control (without antioxidant) may be due to the loss of natural antioxidants during leaching and also due to the absence of dithiocarbamate accelerators which are also powerful antioxidants (Makuuchi et al., 2003).

In the case of B.I, the decrease in tensile strength during ageing can be attributed to the chain scission and the reduction in properties is related to the crosslink density of vulcanizates. As the polymer chains breaks, the two ageing mechanisms, the chain scission and crosslinking reactions, begin to occur. They competed each other in thermal ageing process. In the presence of antioxidant as after irradiation or split addition, the thermal ageing resistance is enhanced. The obvious influence of antioxidant is evident from the variation

Table 8. Extractable protein content in RVNRL films at various radiation doses

Radiation dose	Extractable protein (µg g		
(k.Gy)	Unleached	Leached	
10	503	69	
15	428	41	
20	474	40	

tensile properties compared to control. It can be inferred that these compounds were protected by inhibiting the radicals by the antioxidant.

The percentage retention in properties of films after ageing is shown in Table 7. It can be seen that the percentage retention in tensile strength is higher in A.I followed by M.I due to the better protection by the antioxidant.

### FT-IR (before and after ageing)

FT-IR spectroscopy was successfully used to analyse the role of antioxidant on physical properties of the latex films. FT-IR spectra of three systems say before irradiation (B.I) mid addition (M.I) and after irradiation (A.I) are shown in Figures 9-12. The spectra were measured in the frequency range 700-3500 cm<sup>-1</sup>. Figures (a)

and (b) represent FT-IR spectra before and after ageing at 70°C for 7 days respectively. The peaks under considerations are 1022, 1124 cm<sup>-1</sup> (C-C stretch), 1260 cm<sup>-1</sup> (C-O stretch) and 1635 cm<sup>-1</sup> (C=C stretch) and 1745 cm<sup>-1</sup> (C=O stretch).

FT-IR spectrum of (B.I) sample-a (before ageing) shows that intensity of absorption bands at 1026 and 1124 cm<sup>-1</sup> (C-C stretch) are reduced by the addition of antioxidants. This may be due to scavenging of free radicals. The reduction in crosslinking can cause reduction in physical properties.

FT-IR spectra (before (a) and after (b) ageing) of samples (control (C), M.I and A.I) are given in Figures 10, 11 and 12, respectively. The absorption bands at 1023, 1141 cm<sup>-1</sup> (C-C stretch) are comparable and there is no change in the structure of hydrocarbon chain. The FT-IR spectra (after ageing) show that control sample has undergone thermal degradation due to the absence of antioxidant. The transmittance of C=C bond (835 and 1660 cm<sup>-1</sup>) and the secondary methyl group (1440 cm<sup>-1</sup>) decreased whereas those of carbonyl group (1715 cm<sup>-1</sup>) and hydroxyl group (3300 cm<sup>-1</sup>)

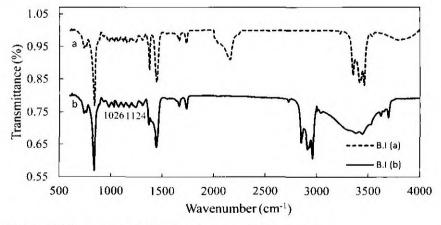


Fig. 9. FT-IR spectrum of B.I (before ageing and after ageing)

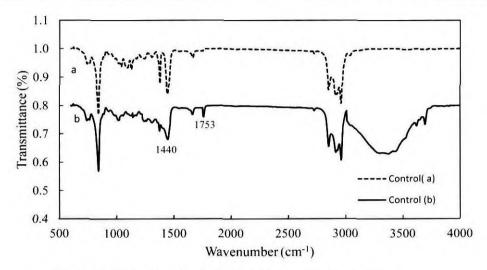


Fig. 10. FT-IR spectrum of control (before ageing and after ageing)

increased. The presence of aldehyde, ketone, carboxylic acid and ester groups are confirmed in the sample upon thermal degradation. After ageing, the vulcanizates (A.I and M.I) showed no change in the FTIR spectra. Therefore, it concluded that the time of addition of antioxidant can be either at the end of radiation process or split dose (at

mid time and after completion) addition is recommended.

## Extractable protein (EP) contents in RVNRL films

The soluble proteins which cause allergic reactions were investigated by modified Lowry method (Lowry et al.,

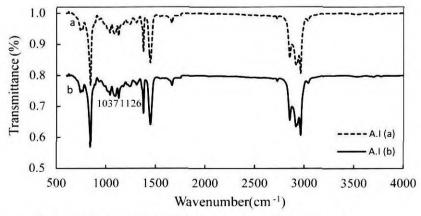


Fig. 11. FT-IR spectrum of A.I (before ageing and after ageing)

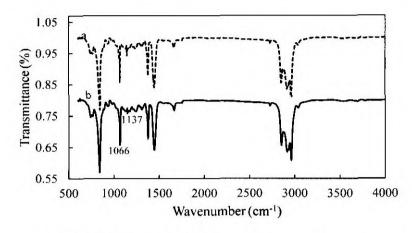


Fig. 12. FT-IR spectrum of M.I (before ageing and after ageing)

1951). This test demonstrated less allergenicity for RVNRL films than sulphur cured latex films.

The effect of irradiation dose on extractable protein content in unleached and leached latex films are presented in Table 8. Unleached film shows high EP content. This is because irradiation facilitates the dissolution of proteins on natural rubber latex particles by breaking the polypeptide chains (Varghese et al., 1999). The residual EP is progressively extracted by continued leaching. It has been reported that more than 90 per cent of the total EP in RVNRL can be removed by extraction with one per cent ammonia solution. The total EP content in the unleached film is very high when compared to leached films (Parra et al., 2005).

Slight variations are observed in the total EP content among leached films subjected various radiation doses. This observation suggests that irrespective of the total dose, the proteins in the latex were degraded to a large extent and thereafter washed away by the leaching medium.

### CONCLUSION

Radiation vulcanization of natural rubber latex was carried out using a 60Co source at room temperature using n-BA as sensitizer. The optimum radiation dose for obtaining maximum mechanical properties for RVNRL film is 15 k.Gy. Effective reduction in the residual n-BA was achieved by split addition method. The increase in modulus values of the film is due to the increased crosslink density of the film. This implies that split addition of n-BA during irradiation is an effective method to reduce the residual n-BA without lowering the tensile strength. The effect of three different modes of addition of antioxidant (B.I, M.I and A.I) on RVNRL indicated that addition of antioxidant before irradiation (B.I) delayed the cure process by scavenging the radicals thereby the efficiency of vulcanization declined. Among the different methods, M.I. and A.I were gave the best protection during ageing. It can be concluded that the antioxidant has to be added either after irradiation or as a split dose (at mid time and on completion) addition is recommended.

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