Rubber Science, **33**(1): 74-85, 2020 *RESEARCH ARTICLE*

RADIATION INDUCED PEROXIDE VULCANIZATION OF NATURAL RUBBER LATEX

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Received: 24 March 2020 Accepted: 13 April 2020

Varghese, N., Varghese, S., Nambiathodi, V. and Kurian, T. (2020). Radiation induced peroxide vulcanization of natural rubber latex. *Rubber Science*, **33**(1): 74-85.

The mechanical properties especially the after-ageing properties of both radiation vulcanized natural rubber latex (RVNRL) and peroxide vulcanized natural rubber latex (PVNRL) are inferior when compared to sulphur prevulcanized natural rubber latex (SVNRL). Accordingly, a new method *viz.* radiation induced peroxide vulcanization (RIPV) was proposed to improve the properties of latex vulcanized by radiation process. This paper deals with the effect of radiation induced vulcanization by peroxide on the mechanical properties of NR latex film. Here, n-butyl acrylate (n-BA) was used as sensitizer and t-butyl hydroperoxide (t-BHPO) as co-vulcanizing agent during irradiation. It was found that the addition of t-BHPO is a more practical method to reduce the vulcanization dose required for natural rubber latex. The FT-IR spectra showed that RIPV contained more C-C crosslinks than RVNRL and PVNRL. Since the RIPV was performed in room temperature, the thermal oxidation of polymer chain was less compared to PVNRL and accordingly the samples retained their strength even after thermal ageing. Solvent diffusion studies showed that mole per cent uptake of RIPV was the lowest indicating comparatively tight crosslinks.

Key words: Ageing studies, FT-IR, Mechanical properties, Radiation vulcanization

INTRODUCTION

Natural rubber latex (NRL) is the material of choice for the manufacture of products such as gloves, condoms *etc.* owing to its high strength, elasticity, comfort in use, good barrier properties and 'green image' (Chaudhari *et al.*, 2005). The virgin natural rubber (NR) is a sticky and non-elastic material. The crosslinking of NR molecules *via* vulcanization process causes changes in the physical properties whereby NR becomes heat stable and elastic. Natural rubber gains unique properties by crosslinking reactions which can be achieved through different routes, namely sulphur, peroxide and radiation vulcanizations. Among these vulcanization techniques, sulphur vulcanization provides products with superior tensile strength compared to radiation/peroxide vulcanization. Sulphur vulcanization is still adopted in the curing of rubber products used in food and medical industry. The accelerators used in sulphur cure system may cause formation of nitrosamines in products. This poses a potential danger to human health and safety (Craciun *et al.*, 2016).

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In order to control the level of nitrosamines, alternative vulcanization methods such as radiation vulcanization is used. The radiation vulcanization is carried out using high energy γ-radiation. Research studies reported that prevulcanized latex can be produced by radiation vulcanization which was suitable for the manufacturing of latex products. Radiation vulcanized natural rubber latex (RVNRL) products have many advantages over sulphur vulcanized (SVNRL) products. The advantages are the absence of carcinogenic nitrosoamines, low cytotoxicity, high transparency and softness. These properties are achieved due to the absence of residual sulphur, zinc oxide and dithiocarbamates that occur in sulphur vulcanizates (Ibrahim *et al.*, 2016; Pairu *et al.*, 2017).

In the early days, radiation vulcanization was carried out without sensitizing agent. Accordingly, higher radiation dose was needed in order to achieve sufficient level of crosslinking 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 (Devendra and Makuuchi, 1990). Monofunctional and polyfunctional monomers were also used by some investigators for this purpose (Makuuchi *et al.*, 1984; Makuuchi *et al.*, 1988). An optimum vulcanization dose of 15 k.Gy using n-butyl acrylate as sensitizer was reported by Makuuchi *et al.* (1989).

In peroxide vulcanization of natural rubber latex (PVNRL), the organic peroxide decomposes to produce reactive free radicals. The resulting free radicals will abstract hydrogen radical from the polymer backbone, encouraging formation of free radicals on the rubber molecular chains (Makuuchi *et al.*, 2001; Kruzelak *et al.*, 2017).

However, the tensile strength of both RVNRL and PVNRL is very low when compared to SVNRL. Radiation induced peroxide vulcanization (RIPV) is proposed as a new method to improve the properties of RVNRL. This paper will discuss the effect of radiation induced peroxide vulcanization on the mechanical properties of NR latex films.

MATERIALS AND METHODS

Natural rubber latex

Centrifuged natural rubber latex conforming to Indian Standards (IS) specification (5430- 2017) was used for radiation vulcanization. Samples were irradiated with γ-rays from a ^{60}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 $k.Gyh^{-1}$, at atmospheric conditions.

The sensitizer and co-vulcanizing agents used are n-butyl acrylate and tert-butyl hydroperoxide, respectively. The stabiliser used was potassium hydroxide. A phenolic antioxidant namely Aquanox LP (butylated reaction product of para cresol and dicyclopentadiene) was used as antioxidant.

Radiation vulcanization of NRL

The emulsions of sensitizer and stabiliser were prepared and were slowly added to the centrifuged latex. The total solid content of the latex was 50 per cent. The irradiation dose given was 15 k.Gy. After irradiation, the antioxidant dispersion was added. Formulation for the preparation of RVNRL was presented in Table 1.

Table 1. **Formulation of RVNRL**

Ingredients	Parts by weight	
	Dry	Wet
60 per cent centrifuged latex	100	167
10 per cent potassium hydroxide	0.1	1.0
n-butyl acrylate	5.0	5.0
50 per cent antioxidant	1.0	2.0

Radiation induced peroxide vulcanization of NRL (Irradiation method)

The vulcanization of RVNRL was carried out in presence of peroxide whereby γ-irradiation was used as the sensitising agent. The latex was irradiated at various doses ranging from 2-16 k.Gy. The latex was formulated as given in Table 2.

Table 2. **Formulation of RIPV**

Ingredients	Parts by weight	
	Dry	Wet
60 per cent centrifuged latex	100	167
10 per cent potassium hydroxide	0.10	1.0
n-butyl acrylate	2.5	2.5
75 per cent t-butyl hydroperoxide	0.10	0.13
50 per cent antioxidant	2.5	5.0

Peroxide vulcanization of NRL (chemical method)

The formulation used was given in the Table 3. The required amount of latex was mixed with peroxide emulsion (peroxide was mixed with 5g of 20 per cent potassium laurate solution and 50 ml water) followed by 20 per cent fructose solution. The latex compound was diluted to 50 per cent total solid. Prevulcanization was carried out at 70°C in a round bottom flask immersed in a water bath. Small amount of ammonia was added during the reaction to compensate the loss due to evaporation losses. Samples of the latex were taken at regular intervals, chilled rapidly, dried at room temperature, and were used for swelling measurements.

Table 3. **Formulation of PVNRL (chemical method)**

Ingredients	Parts by weight	
	Dry	Wet
60 per cent centrifuged latex	100	167
75 per cent t-butyl hydroperoxide	0.8	1.2
20 per cent potassium laurate	0.2	1.0
20 per cent fructose	1.0	5.0
50 per cent antioxidant	1.25	2.5

Preparation of RVNRL films

The latex was filtered through a sieve. The films were cast 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 and 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 were stored in desiccators for further testing.

Testing of vulcanizates

Crosslink density measurement

Crosslink density of RVNRL film was determined by equilibrium swelling measurement. Volume fraction of rubber (V_r) was calculated using the Ellis and Welding equation and crosslink density was calculated on the basis of Flory and Rehner equation (Flory and Rehner, 1943).

$$V_r = \frac{D/\rho_p}{D/\rho_p + A_o/\rho_s} \qquad \ldots\ldots\ldots\ldots 1$$

$$M_c = \frac{-\rho_p V_s V_r^{1/3}}{\ln(1-V_r) + V_r + 0.42\,(V_r)^2} \qquad \ldots\ldots\ldots\ldots 2$$

$$\upsilon = \frac{1}{2\,M_c} \qquad \text{............3}$$

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

Particle size distribution

The change in particle size, size distributions and specific surface area of the latex particles were measured using a particle size analyzer (Mastersizer 3000, Malvern, UK) by dynamic light scattering (DLS) technique as per ISO 13320:2009. Size distribution was determined as the average of five replicates. The polydispersity index or width of particle size distribution of the dispersion was expressed by span.

$$\text{Span} = \frac{[D\,(v, 90) - D\,(v, 10)]}{D\,(v, 50)} \qquad \text{............ 4}$$

Mechanical properties

The tensile properties of the test specimens were tested using dumbbell shaped specimens according to the ASTM D-412 on an Instron 3343 universal testing machine at a crosshead speed of 500 mm per minute.

Fourier Transform Infrared 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 600-4000 cm^{-1} according to ASTM D 2702- 05 (2011).

RESULTS AND DISCUSSION

Optimization of the peroxide

Optimization of the t-butyl hydroperoxide was carried out with different doses of peroxide at a radiation dose of 10 k.Gy and the results are given in Table 4.

Table 4. **Tensile strength of RIPV with various amounts of t-BHPO at 10 k.Gy**

Amounts of t-BHPO (phr)	Tensile strength (MPa)
0.1	22.1
0.3	15.3
0.5	Latex gds coagulated

It was observed that sample with 0.1 phr peroxide showed maximum tensile strength. The earlier reports are also in line with this finding, (Ibrahim *et al.*, 2018a). Hence hereafter radiation vulcanization is carried out with 0.1phr t-BHPO.

Crosslink density

Table 5 shows the crosslink density of radiation induced peroxide vulcanizates (RIPV), radiation vulcanized NRL (RVNRL) and peroxide vulcanized NRL (PVNRL).

Table 5. **Crosslink density of RVNRL, PVNRL and RIPV**

Sample	Irradiation dose (k.Gy)	Crosslink density x 10^{-5} mol/cm^3
RVNRL	15	4.20
PVNRL	Chemical method	3.86
RIPV	2	1.36
RIPV	6	2.76
RIPV	10	4.18
RIPV	12	4.12
RIPV	14	4.05

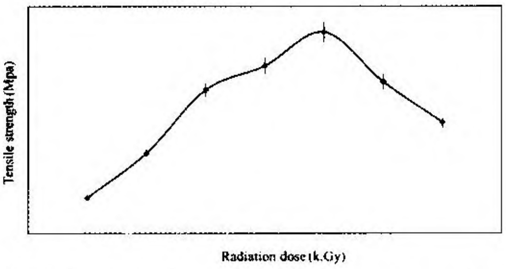


Fig. 1. Variation in tensile strength with radiation dose for RIPV vulcanizates

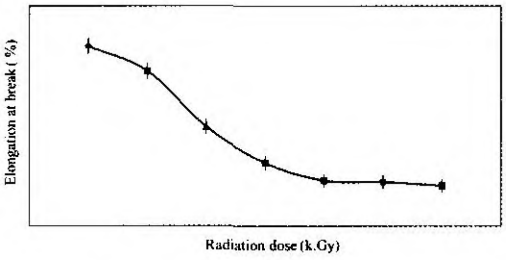


Fig. 2. Variation in elongation at break with radiation dose for RIPV vulcanizate

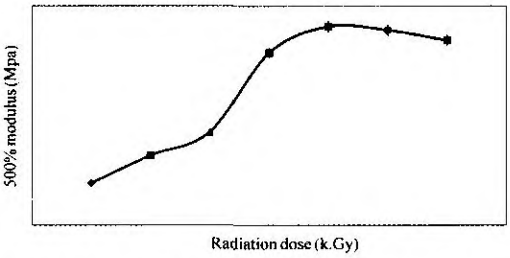


Fig. 3. Variation in 500 per cent modulus with radiation dose for RIPV vulcanizates

The results showed that the crosslink density of RIPV was increased with increasing radiation dose up to 10 k.Gy and thereafter it decreases. The results also showed that on addition of t-butyl hydroperoxide the dose required for vulcanization is reduced from15 to 10 k.Gy. This indicates that n-BA upon irradiation produces free radicals which preferably decomposes peroxide. Hydroperoxide thus introduces a large number of free radicals, which leads to crosslink formation between the polymer chains.

Mechanical properties

Modulus and tensile strength are considered as the two parameters which have technological importance. Modulus values are always referred as the degree of crosslinking in products while tensile strength is referred as ability to withstand stress.

Table 6 shows the tensile properties of vulcanizates of RVNRL, PVNRL and RIPV.

The results showed that RIPV gives higher tensile strength at 10k. Gy when compared to RVNRL. There are two factors supporting to this observation. First factor is irradiation time. Longer irradiation time may cause polymerization of n-BA and hydrolysis of peroxide. Thus, the concentration of n-BA and hydroperoxide decreases during irradiation and the rate of vulcanization become lower (Ibrahim *et al.*, 2018a).

Second factor is chemical and physical (inter particle) crosslinking. Chemical

Table 6. **Mechanical properties of RVNRL and PVNRL**

Sample	Irradiation dose (k.Gy)	Tensile strength (MPa)	Elongation at break (%)	500 % Modulus (MPa)
RVNRL	15	21.37	1100	3.28
RIPV	10	22.1	962	2.72
PVNRL	Chemical method	17.41	1023	2.12

crosslinking increases with the increasing irradiation dose. The chain entanglement (physical crosslinking) depends upon the free rubber chain ends at the surface of each rubber particle. The length of the free rubber chain decreases with the increasing dose. Thus the tensile strength of RIPV film increases upto 10k.Gy and then decreases with the increasing dose. The decrease in properties may be due to the denaturation of latex proteins thereby latex loses its chemical stability.

The crosslinking mechanism in RVNRL involves bombardment of high energy radiation with rubber molecules. The excited molecules thus produce free radicals through energy transfer, which leads to crosslinking reaction between molecules. By irradiation, monomer molecules (nBA) were also excited and the homopolymer thus formed may graft with rubber molecules. The tensile strength of RVNRL is low compared to RIPV. This may be due to long linear side chain of n-BA, which may hinder the formation of crosslink between the rubber molecules. This is confirmed by FT-IR spectra which will be discussed later (George *et al.*, 2003).

In RIPV, the elongation at break decreases with increasing dose. Lower elongation at break of RIPV vulcanizates is due to the increased restrictions imposed on the flexibility of molecular chains by additional crosslinks. Modulus also increased with increasing irradiation dose due to high crosslink density.

The tensile strength of peroxide vulcanized natural rubber latex (PVNRL) film is low when compared to others. It is explained that the inhomogeneous distribution of crosslinks in peroxide crosslinked NR latex resulted from the non-uniform adsorption of peroxide in the rubber particles. Consequently, the alkoxy radicals generated in the aqueous phase react with the rubber molecules on the surface of the latex particles followed by abstraction of hydrogen atoms to produce rubber radicals which readily combined to form cross-links. This rigid C-C crosslink caused increased stiffness and less relaxed network. This is due to less mobility of the polymer chains. The rigid C-C crosslink restrict the orientation of the macromolecular chains of NR when stretched and consequently lowered mechanical properties Craciun *et al.*, 2016). Another potential problem is that carbon-centered radicals can readily react with oxygen. This reaction will produce hydroperoxides and can form partially vulcanized tacky surfaces (Akiba and Hashim, 1997).

FT-IR spectroscopy

FT-IR spectra of centrifuged latex (CL), RVNRL, PVNRL and RIPV (irradiated at 10 k.Gy) are shown in Figure 4 and the important peaks resolved are given in Table 7. The spectrum was scanned in the frequency range 400- 4000 cm^{-1}.

The characteristics peaks of *cis*-1, 4-isoprene units: The absorption bands at 1665cm^{-1} due to –C=C- stretching; the peak at 1440 cm^{-1} associated with the bending of C-H in –CH_2; 1373 cm^{-1} absorption band due to C-H bending in CH_3; the strongest band in the low energy region of *cis* spectrum belong to =C-H out of plane bending mode at 842 cm^{-1}.

In RVNRL, there is additional absorption bands at 1735 and 1074 cm^{-1} corresponding to –C=O and –C-O stretching vibration of n-butyl acrylate (n-BA). The IR spectra indicate that crosslinking of NR takes place through graft polymerization of n-BA into NR. The intensity of the absorption bands at 1033 and 1154 cm^{-1} (-C-C- stretch) slightly

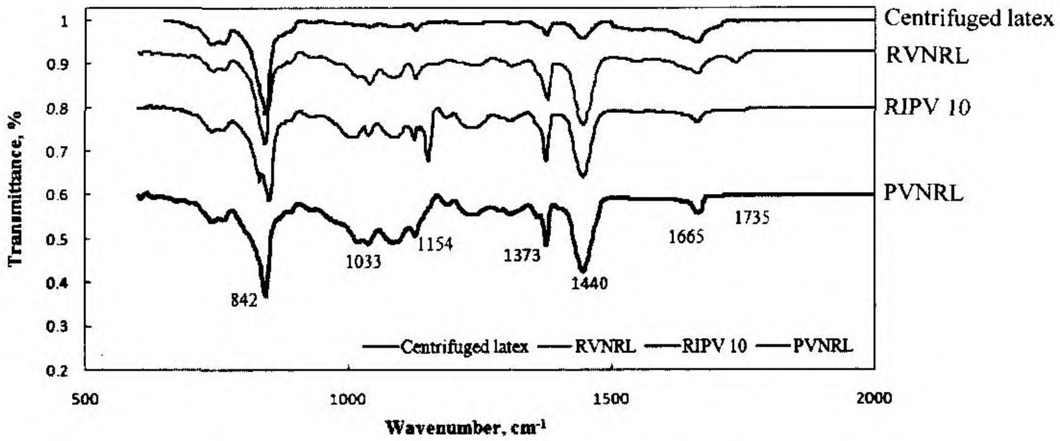


Fig. 4. FT-IR spectra of centrifuged latex, RVNRL, RIPV 10 and PVNRL

increases which confirms the formation of -C-C- bond between rubber molecules. This indicates that direct crosslinking of NR molecules also takes place.

In RIPV, the intensity of the absorption band at 1735 cm^{-1} (-C=O stretch) slightly decreases but intensity of absorption band at 1150 cm^{-1} (-C-C- stretch) increases compared to RVNRL and PVNRL. This indicates that more C-C crosslink formed in RIPV compared to RVNRL and PVNRL. This may be due to the fact that hydroperoxide introduce more free radicals that will abstract hydrogen from rubber hydrocarbon and form more C-C crosslinks (Ibrahim *et al.*, 2018b).

The FT-IR spectra of PVNRL showed that the intensity of the absorption bands at 1035 and 1157 cm^{-1} (-C-C- stretch) slightly increases which confirms that new -C-C- bond is formed. In PVNRL, less C-C crosslinks are formed compared to others. This can result in reduced mechanical property.

Sorption curve (Effect of nature of crosslinks)

The absorption of polymer with solvent is very much essential to understand the extent of crosslinking. The crosslinking in polymer can act as one of the controlling factor in transport behaviour.

The sorption curves of crosslinked NR using different vulcanizing systems (RVNRL, PVNRL and RIPV) is given in Figure 5. Sorption curves indicate the plot between Q_t (mole % uptake of solvent per

Table 7. **FT-IR spectroscopic data for important peaks in natural rubber**

Absorption bands, cm^{-1}	Assignment
838	=C-H- out of plane bending
1033, 1124	-C-CH_3 in-plane deformation vibration
1373	-CH_3 asymmetric deformation
1441	-CH_2 deformation
1652	-C=C – stretching
1747	-C=O stretching

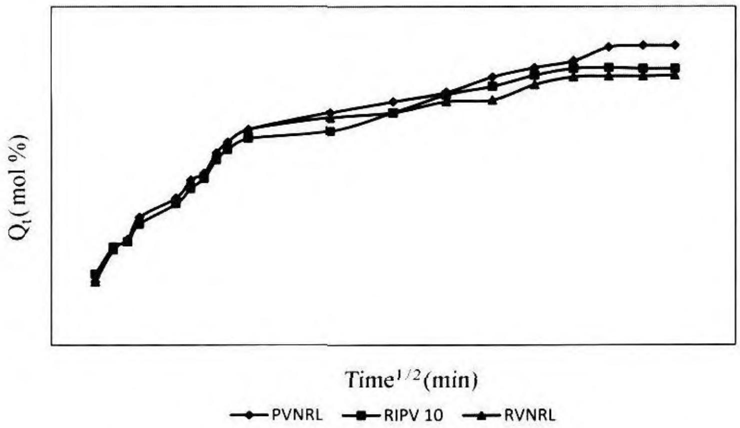
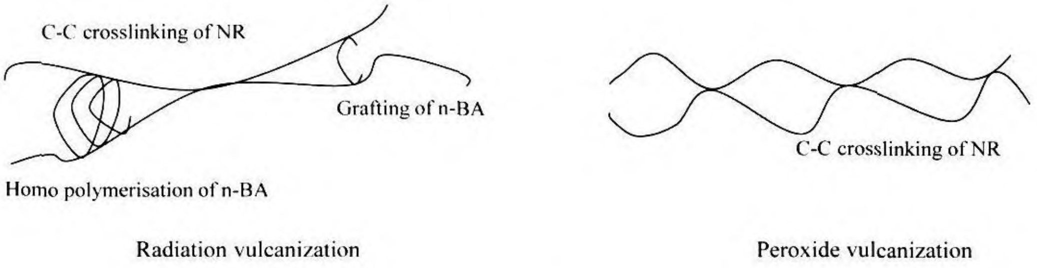


Fig 5. Swelling behaviour of RVNRL, RIPV and PVNRL in toluene



Scheme 1: Radiation vulcanization and peroxide vulcanization of natural rubber latex

100 g of the material) against square root of time. The uptake is rapid in the initial zone in all compositions. This indicates that swelling rate is very high in this area. Thereafter the sorption rate decreases leading to a plateau. This corresponds to equilibrium swelling. It is also clear that Q_t values decreases in the order PVNRL > RVNRL > RIPV. The difference in the solvent uptake values may be due to the formation of bonds between rubber chains during vulcanization. Figure 6 depicts the general figure of vulcanized networks.

The nature of crosslinking is one of the major controlling factors in the mechanical properties of polymers. Scheme 1 indicates the proposed mechanism involved in the radiation crosslinking with n-BA and peroxide crosslinking of NRL. There are three types of crosslinking in radiation vulcanized NRL. (a) direct crosslinking of NR molecules (b) crosslinking through grafted poly (n-BA) (c) physical crosslinking with homopolymerised poly (n-BA). Radiation vulcanized film showed lowest solvent uptake. It seems that during

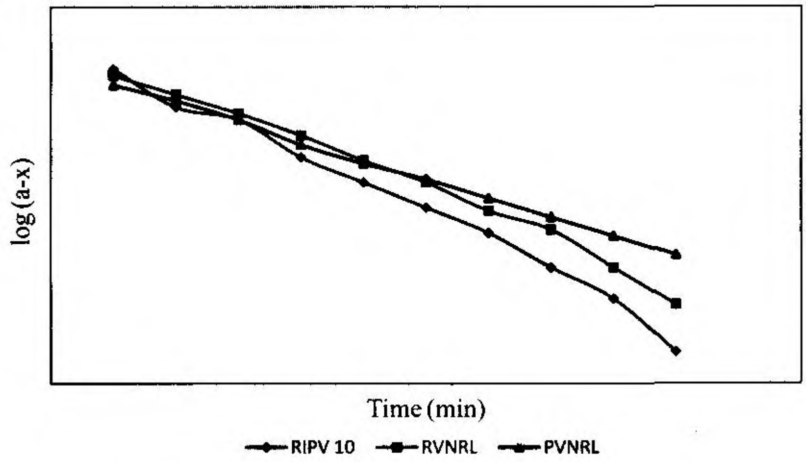


Fig. 6. First order kinetics of RVNRL, PVNRL and RIPV 10

peroxide vulcanization rather than crosslinking, oxidation of chains also will happen and this will be greater in PVNRL than RIPV 10. Due to such oxidation, effective crosslinking will be less in peroxide crosslinked vulcanizates.

Vulcanization kinetics

The kinetics order of the vulcanized film can be studied using the first order kinetics equation. The plot between log (a-x) against time is a straight line. From the graph, the order of the reaction can be obtained from

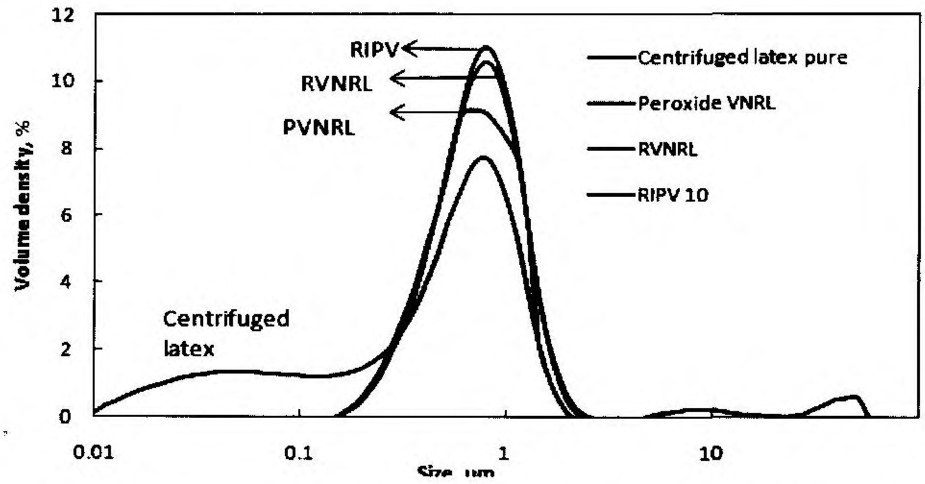


Fig. 7. Particle size distribution of centrifuged NRL, PVNRL, RVNRL and RIPV 10

Table 8. **Particle size distribution of various forms of NR latex**

	Volume percentage of particles (nm)		
	Below		Above
	500	500-1000	1000
Centrifuged latex pure	11.9	73.4	12.4
RVNRL		87.4	12.3
PVNRL		80.3	19.7
RIPV 10		88.1	12.2

the slope and the rate constant from the intercept. Figure 6 indicates that RVNRL, PVNRL and RIPV followed first order kinetics.

Particle size distribution

The volume distribution of rubber particles in centrifuged latex, RVNRL, PVNRL and RIPV 10 were obtained by dynamics light scattering method and are shown in Figure 7. The particle size distributions were grouped into three discrete categories (Table 8) and designated as sizes below 500 nm (nano range), 500-1000 nm (submicron) and above 1000 nm (coarse).

The results showed that the portion of the lower sized particles decreases on irradiation. In centrifuged latex, 11.9 per cent of the particles are in the nanoparticle range, 73.4 per cent in sub-micron range and 12.4 per cent in the coarse range. A narrow distribution is observed after irradiating the samples. After irradiation, volume percentage of the nano-range particles decreases whereas the quantity of submicron particles increased. Natural rubber latex is comprised of rubber hydrocarbon and non rubber materials. Radiation causes the decomposition of protein in NR latex which causes agglomeration of particles (Sizue *et al.*, 2003). This may be the reason for decrease of nano region upon radiation.

In peroxide vulcanized compound also, higher particles were seen due to agglomeration.

Thermal ageing

The resistance of the rubber vulcanizates to thermal ageing is considered as an essential requirement for better service performance of the products. The mechanical properties of RVNRL, PVNRL and RIPV10 before and after ageing for 22h at 100°C are given in Table 9.

The results showed that RVNRL and PVNRL vulcanized films registered appreciable reduction in tensile strength whereas RIPV showed only a slight change in tensile strength upon thermal ageing. In PVNRL, as the crosslinking was conducted at elevated temperature, thereby the rubber hydrocarbon chain is more prone to oxidation.

The best retention in tensile properties was displayed by RIPV due to the higher thermal resistance of strong C-C crosslinks. This indicates that RIPV film contain more rigid C-C crosslinks compared to RVNRL and PVNRL.

Table 9. **After ageing properties (100°C for 22h)**

Sample	Tensile strength (MPa)		Retention	Temperature of vulcanization, °C
	Before ageing	After ageing	(%)	
RVNRL	21.3	18.4	86.3	Room temperature
PVNRL	17.4	13.0	74.7	70
RIPV 10	22.1	21.2	95.9	Room temperature

CONCLUSION

The effect of radiation induced peroxide vulcanization on the mechanical properties of NR latex was evaluated. RVNRL with t-BHPO gave higher tensile strength at 10k.Gy when compared to RVNRL and PVNRL. Irradiated natural rubber latex prepared using a hydroperoxide along with n-BA was more stable than latex irradiated with n-BA alone. The addition of hydroperoxide is a more practical method to reduce the vulcanization dose from 15k.Gy to10 k.Gy. The FT-IR spectra showed that C-C crosslinks predominate in RIPV 10 than RVNRL and PVNRL and chain oxidation was less. Solvent diffusion studies also supported this finding. Thermal ageing study showed that the best retention in tensile properties was shown by RIPV vulcanizates. In peroxide vulcanization, hydrocarbon chain undergoes oxidation which on thermal ageing causes high reduction in properties.

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