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QUALITY IMPROVEMENT OF RADIATION VULCANISED NATURAL RUBBER LATEX

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An attempt was made to improve the green strength of fresh natural rubber latex by exposure to low doses of γ radiation followed by centrifuging to reduce the non-rubber ingredients. The centrifuged latex was then vulcanised by exposure to γ-radiation in presence of n-butyl acrylate as sensitizer. The non-rubber ingredients were further removed by suitable leaching operations. As a result of the chemical changes accompanied by exposure of latex to γ-radiation, the extractable protein content of the radiation vulcanised natural rubber latex (RVNRL) films decreased to acceptable levels (below 50 $\mu g\ g^{-1}$). The mechanical properties of RVNRL also improved by using centrifuged natural rubber latex having high gel content or by blending with sulphur vulcanised natural rubber latex (SVNRL).

Keywords: Leachable protein, Prevulcanisation, Radiation vulcanisation, Shrinkage

INTRODUCTION

Natural rubber latex can be vulcanised by exposure to γ-rays from a Co^{60} source to obtain radiation vulcanised natural rubber latex (RVNRL). This latex can be used for the production of rubber based products in the way similar to that adopted for sulphur pre-vulcanised latex. Radiation vulcanized natural rubber latex (RVNRL) possesses several advantages over the sulphur vulcanized, such as the absence of nitrosamine compounds, better transparency, very low cytotoxicity and less rubber proteins that cause allergic response (Keong *et al*., 2009; Varghese *et al*., 2000; Makuchi, 2003). The main drawback of RVNRL is the lower modulus and comparatively lower tensile strength. Some of the factors that control the efficiency of vulcanisation of NR latex by γ-irradiation are initial molecular weight of rubber, green strength and the amount of non-rubber ingredients present. An increase in green strength contributes to higher tensile strength of RVNRL films. Generally latex concentrate is stored for about three weeks to achieve an improvement in molecular weight and hence green strength. Both colloidal stability and green strength of rubber in latex concentrate increase during storage. This is due to the formation of fatty acid soaps and microgel. Ammonium soaps formed due to

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reaction of ammonia with hydrolytic products of phospholipids get adsorbed on the surface of rubber particle and leads to improvement in colloidal stability (Blackley, 1997). The formation of microgel is attributed to interaction of rubber molecules with non-rubber components like proteins and phospholipids (Sakdapipanich *et al*., 1999). Due to formation of microgel, the green strength of the rubber films increases.

The modulus and tensile strength of RVNRL films can be improved using latex concentrate of higher green strength as the raw material and by blending with latex having better mechanical properties. The present work is an attempt in this line and reports the use of latex with higher gel content as raw material for production of RVNRL and blending with sulphur pre-vulcanised latex for quality improvement of RVNRL.

MATERIALS AND METHODS

High ammonia preserved field latex obtained from Pilot Latex Processing Centre (PLPC) Chethackal of Rubber Research Institute of India (RRII) was exposed to low doses of γ-radiation (4 kGy) in the RVNRL Pilot plant. The latex was then concentrated using centrifuging and creaming processes. Centrifugation was done using Alfa-Laval 510 latex centrifuging machine. The bowl speed of the machine was 7000 rpm. The creaming was carried out using ammonium alginate as the creaming agent.

RVNRL was prepared by exposing latex concentrate to γ-radiation to a dose of 15 kGy at a dose rate of 4.85 kGy h^{-1}. The latex was compounded with 0.3 phr potassium hydroxide as stabiliser and 5phr n-butyl acrylate (n-BA) as sensitizer before exposure to γ-radiation. A control RVNRL was also prepared without any pre-irradiation process.

Sulphur pre-vulcanised latex (SVNRL) was prepared in the conventional way by heating centrifuged latex mixed with the compounding ingredients at 60 °C for three hours (Table 1). Latex blends were prepared by blending RVNRL and SVNRL so as to have dry rubber content in the ratio 90/10 and 80/20.

Table 1. **Formulation used for sulphur pre-vulcanisation of natural rubber latex**

Ingredient		Parts by mass	
		Dry	Wet
60%	Concentrated latex	100	167
10%	KOH solution	0.4	4
25%	(w/v) Sodium dodecyl sulphate solution	0.2	0.8
50 %	Zinc oxide dispersion	0.25	0.5
50 %	Zinc diethyldithiocarbamate dispersion	1.0	2.0
50 %	Sulphur dispersion	1.25	2.5

The particle size distribution of the latex samples was determined using a particle size analyser (Malvern Zetasizer, Nano S, U.K). The Zeta-potential was measured using a zeta potential analyser (Malvern Zetasizer, Nano Z, U.K) and the FTIR measurements were carried out using a FTIR spectrometer (Varian-660 IR).

The properties of RVNRL and RVNRL/SVNRL blends were evaluated by measuring the latex quality parameters and strength of the films obtained by casting and dipping techniques. The dried films obtained by casting were leached in water at room temperature for four hours and further dried for four hours at 70 °C before testing. Solvent absorption was conducted using toluene as the solvent for 48 hours at room temperature. The tensile strength, elongation at break and modulus were determined by using a universal testing machine (Houns field, HSK-S). Hysterisis studies and permanent set were determined by using a universal testing machine (Zwick-1474). The dumb bell specimens were subjected to a strain of 300 per cent and the set was determined after three cycles.

The raw rubber properties were determined as per BIS standards. The mechanical properties of the films were determined as per the ASTM standards. The presence of nitrogen (N) and extractable protein (EP) content of the films were determined by ASTM D 3533 and ASTM D 5712 respectively.

RESULTS AND DISCUSSION

Particle size distribution of latex

The particle size distribution of fresh and pre-irradiated latices before and after creaming is shown in Figure 1. The particle size varies from 100 to 2000 nm for fresh latex and 100 to 1000 nm for pre-irradiated latex. The bimodal distribution is unchanged and the amount of smaller particles increases after irradiation. After creaming, for both un-irradiated and pre-irradiated latex the bimodality is preserved and the peak for the low particle diameter becomes very prominent for the pre-irradiated creamed latex. The particle size of centrifuged latex prepared from un-irradiated and pre- irradiated latex also follows a similar pattern.

During irradiation it is possible that some chemical changes take place for the proteinaceous materials and this may be contributing to reduction of size after creaming. Particle size of centrifuged latex also follows a similar pattern. The reduction in particle size can be attributed to removal of proteins present on the rubber particle. The nitrogen content before and after creaming is shown in Table 2. As observed the nitrogen content decreases after creaming. The Zeta-potential value though comparable is slightly lower for pre-irradiated creamed latex compared to conventional creamed latex suggesting that some proteins present on the surface that provided colloidal stability are removed. (Zeta-potential of conventional creamed latex is -67.3 and that of pre-irradiated creamed latex is -65.7).

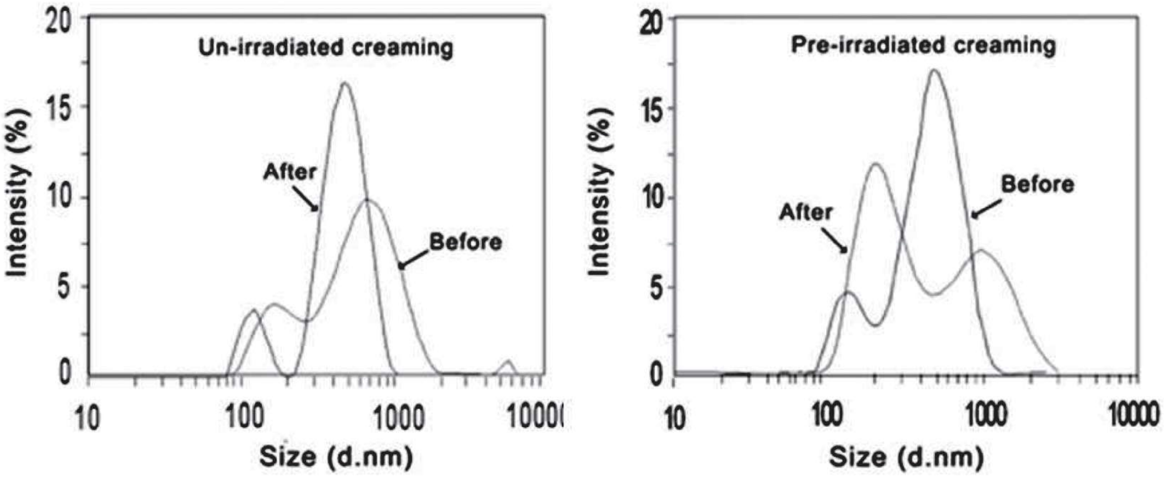

Fig 1. The particle size distribution of fresh NR latex and latex exposed to small doses of γ-radiation before and after creaming

Table 2. **Raw rubber properties of un-irradiated and pre- irradiated latex samples**

Parameter	Control (un-irradiated)		Sample(pre-irradiated)	
	Before creaming	After creaming	Before creaming	After creaming
Nitrogen content (%)	0.50	0.46	0.49	0.24
Acetone extractables (%)	3.53	4.25	3.42	4.19
Initial plasticity (P_0)	30	-	33	-
Gel content (%)	2	-	36	-

Concentration characteristics

The centrifuging process results in latex of higher dry rubber content (drc) compared to creaming process. In creaming, higher drc is observed for NR latex without prior irradiation. (drc of pre-irradiated and creamed latex was about 45 per cent and that of conventional creamed latex was about 49 per cent). Irradiation favours the size reduction of latex particles. Adsorption of macromolecules of creaming agent promotes reversible agglomeration of latex particles by reducing the effective electric charge density at the particle interface (Sakdapipanich *et al*., 1999; Blackley, 1997). The particles thus come together and coher loosely. These agglomerated particles grow and form clusters of rubber particles. These clusters grow until their buoyancy is sufficient to get the rubber particles separated from the network leading to creaming of latex. However, smaller the size of rubber particles more is the resistance to creaming.

The concentration process is governed by (Equation 1)

$$V = \frac{2g\,(\rho_s - \rho_r)\,r^2}{9\eta} \quad \ldots\ldots\ldots\ldots \quad (1)$$

V = Velocity with which the rubber particles rise (cm sec^{-1})

g = Gravitational force (cm sec^{2-1})

ρ_s = Density of serum

ρ_r = Density of rubber particles

r = Effective radius of rubber particles (cm)

η = Viscosity of the serum (poise)

In the centrifugal process the separation of latex into centrifuged fraction is governed by centrifugal force unlike in a creaming process where it is governed by gravitational force. Hence the drc obtained by centrifugation is higher than that obtained by creaming process, even when the particle size of latex becomes lower. (drc of pre-irradiated and centrifuged latex was about 62 per cent)

Raw rubber properties

The raw rubber properties of rubber obtained by pre-irradiation in comparison with control sample are given in Table 2. It was observed that the nitrogen content remains almost same after irradiation but it decreases after concentration for both irradiated and un-irradiated sample. The decrease is higher for the concentrated latex that was subjected to a pre-irradiation process. There is an increase in initial plasticity (Po) of rubber recovered from latex subjected to pre-irradiation. It is also noted that on exposure of fresh NR latex to γ-radiation, gel content increases.

Earlier reports show that proteins get degraded on exposure to γ-radiation (Maku-chi, 2003; Varghese *et al.*, 2000). Consequently there is a decrease in nitrogen content after concentration as low

Table 3. **Mechanical properties of RVNRL**

Properties	Films by casting			Films by dipping
	Control (centrifuged un irradiated PFL)*	Sample (pre-irradiated centrifuged PFL)*	$Ca(NO_3)_2$ Leaching for 4 h at room temperature	
Gum strength (MPa)	1.54	3.0	-	-
300% Modulus (MPa)	0.85	1.1	1.1	0.9
500% Modulus (MPa)	1.14	1.6	1.65	1.14
Tensile strength (MPa)	21.0	23.02	25.5	20.02
Elongation at break (%)	1380	1285	1280	1290
Toluene swelling (%) (after 24 h)	230	170	160	-
Tension set after 1 hour at 300% elongation	10	6		-

*4 h leaching in cold water

molecular weight nitrogenous materials go into serum fraction. NR molecules are presumed to be linked with phospholipids and other groups that associate with protein to form crosslinking by intermolecular hydrogen bonding. It is expected that branching of NR molecules occur due to the phospholipid groups present in the molecules. Thus these crosslinks make it possible to form three dimensional network structures in NR (Kawahara *et al.*, 2002). This crosslinking is expected to happen during irradiation. It is also expected that there is crosslinking between rubber molecules due to γ-radiation. Both these reactions lead to an increase in gel content. An increase in initial plasticity (Po) for irradiated samples can be due to formation of gel during irradiation.

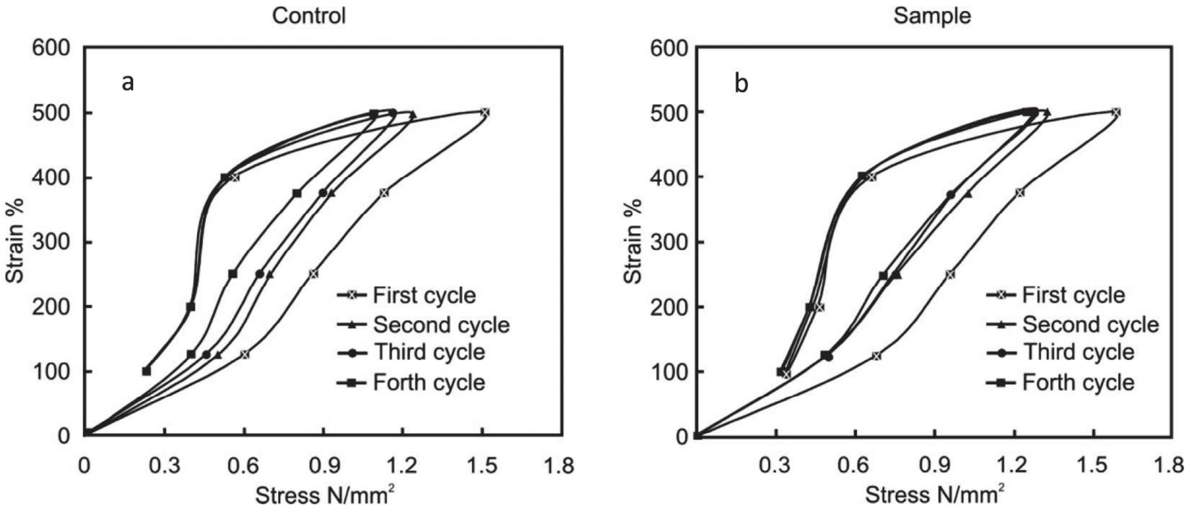

Fig. 2. Hysteresis loss under cyclic deformations a. RVNRL film from un-irradiated latex b. RVNRL film from pre-irradiated latex

Properties of RVNRL

Pure RVNRL films – Mechanical properties – effect of leaching

The gum strength of NR increases after pre-irradiation. This is attributed to the increase in gel content as shown in Table 2.

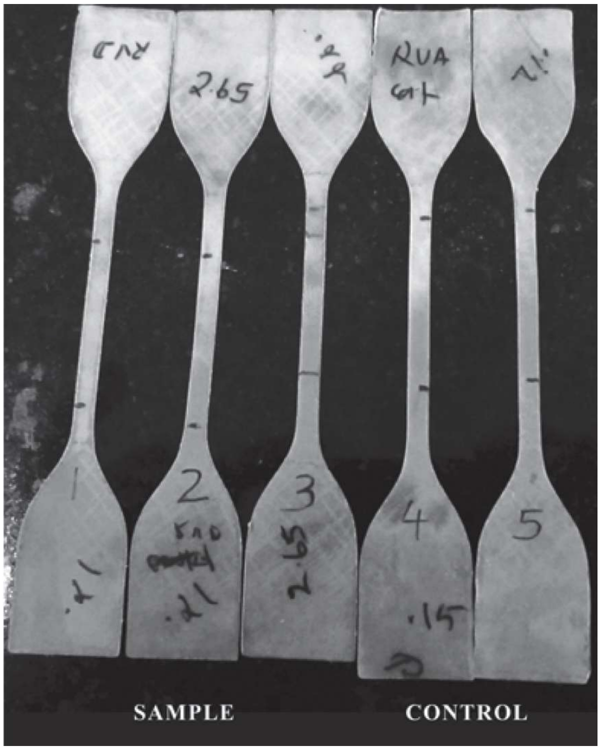

Fig. 3. Permanent set after three cyclic deformations at 0 to 300% elongation

The enhancement in green strength due to enhancement of entanglement and gel formation is reported earlier (Kawahara *et al*., 2002; Alex *et al*., 2010).

RVNRL films prepared after pre-irradiation showed a higher modulus, tensile strength and lower elongation at break and tension set (permanent set) (Table 3). The stress-strain behaviour during cyclic deformation at an elongation of 300 per cent is shown in Figures 2. a and b. As observed from the figure the hysterisis loss is higher for the conventional RVNRL in comparison with the modified RVNRL, as the area under the hysterisis loop is lower for sample (pre-irradiated) compared to control (conventional RVNRL). Due to this permanent set is also higher for conventional RVNRL films compared with modified RVNRL films (Fig. 3).

It is expected that during pre-irradiation several changes take place. This includes chain entanglements, microgel formation and partial removal of proteins. These factors are expected to contribute to an enhancement in mechanical properties.

Leaching of RVNRL films in water helps in enhancement of strength characteristics

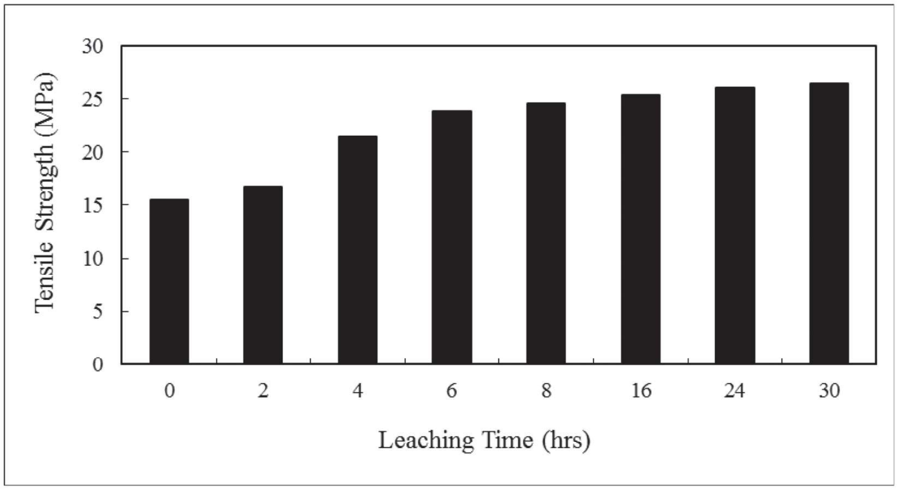

Fig. 4. Leaching effect of RVNRL films in water with respect to time

as shown in Figure 4. The strength of RVNRL films are known to depend on intra-particle crosslinking (chemical crosslinking) and inter-particle entanglement (physical crosslinking). The inter-particle entanglement mainly depends on leaching and drying conditions of NR latex film (Maku-chi, 2003). As reported earlier the non-rubber ingredients which inhibit better fusion of the rubber particles is removed during the leaching process (Maku-chi, 2003).

Leaching of films in calcium nitrate solution (2.5%) for four hours was also found to enhance the tensile strength as shown in Table 3. It is expected that inter-particle crosslinking will improve tensile strength in the presence of calcium ions, due to ionic bonding involving calcium ions. Enhancement in the strength characteristics during immersion of films in calcium nitrate solution could thus be attributed to formation of additional crosslinks.

Table 4. **Shrinkage of RVNRL and SVNRL films**

Sample	SVNRL (cm^2)	RVNRL (cm^2)
Initial surface area of the glass plate	157.33	157.33
The surface area of the film	134 4	147.3
% change in surface area	14.6	6.3

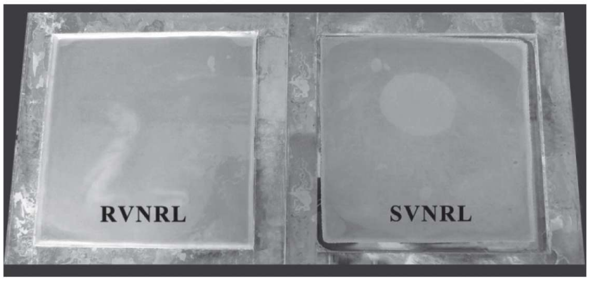

Fig. 5. Shrinkage of RVNRL and SVNRL

Modified RVNRL films prepared by dipping process using formic acid as a coagulant is given in Table 3. A lower tensile strength was obtained by this process. There is variation in time for film formation using the two techniques and the variation in strength of films produced by these two processes could be attributed to this though the actual mechanism is not clear.

Shrinkage

It is observed that shrinkage is lower for the films prepared from RVNRL compared to films prepared using SVNRL (Table 4, Fig. 5). In radiation processing n-butyl acrylate is used as a sensitizer and it is expected that some amount of n-butyl acrylate (n-BA) gets grafted to the rubber molecules during the process of radiation vulcanisation (Hossain and Chowdhury, 2010). The IR spectra of RVNRL film (Fig. 6)

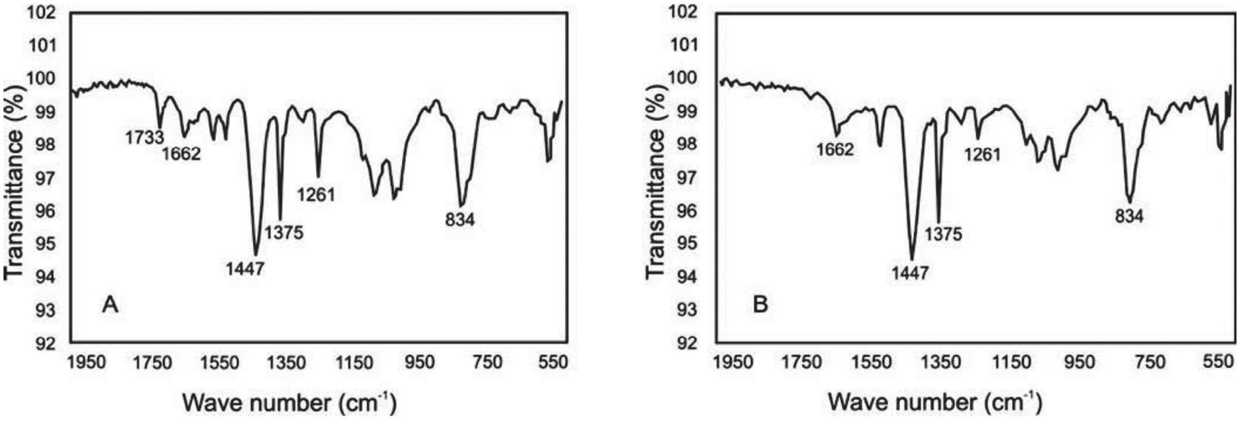

Fig. 6. IR spectrum of RVNRL (a) and SVNRL (b)

shows the major transmittance peak of C=O functional group (1733 cm^{-1}) of the n-BA grafted to NR latex. It is also expected that during the vulcanisation process by exposure of γ radiation, free radicals are formed due to knocking out of electrons. These free radicals formed leads to crosslinks. Thus in the case of RVNRL C-C bonds are formed during vulcanisation while during sulphur vulcanisation polysulphidic, disulphidic and or monosulphidic are formed. The difference in shrinkage behaviour may be attributed to difference in the type crosslinks.

Ageing studies

Ageing characteristics of films obtained by casting technique are given in Table 5. It is observed that even in the absence of added antioxidants comparatively good retention of tensile strength, modulus, and elongation at break are obtained after ageing for seven days at 70 ^{0}C.

Blending of sulphur pre-vulcanised latex (SVNRL) with RVNRL

Pure sulphur pre vulcanised natural rubber latex (SVNRL) shows a higher tensile strength than RVNRL films. Irrespective of the difference in the method of production and cross linked structures perfect blending is possible between RVNRL and SVNRL.

It is well known that in sulphur prevulcanisation involves formation of polysulphidic, disulphidic and monosulphidic crosslinks between rubber molecules that offer very high tensile strength for the films. As the proportion of SVNRL in the RVNRL/SVNRL blend increase from 10 to 20 parts the tensile strength increase proportionately (Table 6).

Leachable proteins

In RVNRL, the leachable proteins are below specified level (Table 7). During irradiation the protein content of latex is disintegrated resulting in an increase in water extractable protein content. Consequently after leaching the residual water extractable protein content in films decrease.

CONCLUSIONS

On exposure of fresh NR latex to low doses of γ-radiation there was an increase

Table 5. **Effect of ageing on mechanical properties of RVNRL films**

Property	Un aged	3 days aged	5 days aged	7 days aged
100% Modulus (MPa)	0.41	0.64	0.58	0.37
300% Modulus (MPa)	0.77	1.14	0.96	0.86
500% Modulus (MPa)	1.37	1.63	1.35	1.29
700% Modulus (MPa)	3.38	3.67	2.42	3.01
Tensile strength (MPa)	25.1	22.7	21.8	18.7
Elongation at break (%)	1260	1205	1260	1210

Table 6. **Mechanical properties of the blends**

Parameter	RVNRL/SVNRL			
	100/0	90/10	80/20	0/100
300% Modulus (MPa)	1.1	1.1	1.1	1.1
500% Modulus (MPa)	1.5	1.5	1.55	1.58
Tensile strength (MPa)	24.02	24.12	24.80	29.6
Elongation at break (%)	1280	1290	1300	1400

Table 7. **Leachable proteins**

Type of RVNRL film	Extractable protein content µg g^{-1}
RVNRL films unleached	312
RVNRL films (After leaching in water for 24 h)	40
RVNRL/SVNRL films 80/20 (After leaching in water for 24 h)	45
RVNRL/SVNRL films 60/40 (After leaching in water for 24 h)	48

in gel content favouring enhanced level of vulcanisation and degradation of proteins to low molecular weight fractions and a part of which get removed during the concentration process. The centrifuging process results in latex of higher dry rubber content compared to creaming process. Leaching of the films obtained from radiation vulcanised natural rubber latex in water and calcium nitrate solution enhances the mechanical properties due to additional crosslink formation and due to leaching out of certain non-rubber ingredients. The leachable proteins in RVNRL films can be reduced to negligible level by suitable leaching operations. Films obtained by casting technique shows higher tensile strength compared to films obtained by dipping process.

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