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Studies on radiation vulcanized natural rubber latex

Radiation vulcanization is a process to produce prevulcanized natural rubber latex free of toxic residual chemicals. In this work an attempt is made to improve green strength of fresh NR latex by exposure to low doses of gamma radiation followed by concentration of latex to reduce the non-rubber ingredients and to use this as the raw material for production of RVNRL in the conventional way

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[1,2,3]. The main drawback is the lower modulus and comparatively lower strength. Some of the factors that control the efficiency of vulcanization of NR latex by gamma irradiation are initial molecular weight of rubber, green strength of rubber and the amount of non –rubber ingredients present[2]. An increase in green strength contributes to higher tensile strength of RVNRL films and for this latex concentrate is stored for about twenty days before converting the same to RVNRL. During storage of ammonia preserved latex there is formation of micro gel that enhances the green strength of the rubber.

The modulus and tensile strength can be improved by using latex concentrate of higher green strength as the raw material and by suitable 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 suitable natural and synthetic latex.

Experiment

High ammonia preserved field latex (PFL) was obtained from PLPC Chethackal. High styrene content styrene butadiene copolymer latex (HSBL), Ploilite SBL 2058, was obtained fro. Eliokem Pvt Ltd Mumbai, India (total solids content = 29.32 %, pH =11.3).

Radiation vulcanization was effected by gamma rays using RVNRL Pilot plant at RRII. Natural rubber latex (NRL) was collected and exposed to low doses of gamma radiation. The latex was then subjected to a concentration using both creaming and

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centrifugation. The creaming process was done by using ammonium alginate as the creaming agent. The centrifugation was done by using. Alfa-Laval 510 latex centrifuging machine, operating at 7000 rpm. The concentrated latex was exposed to a dose of 15 kGy in the standard method to obtain Radiation vulcanized natural rubber latex (Modified RVNRL). A conventional RVNRL without pre-irradiation process was also prepared. Sulphur prevulcanized latex (SVNRL) was prepared in the conventional way by heating centrifuged latex mixed with the compounding ingredients at 60°C for 3 hours as per the formulation given in **Table 1**. Latex blends were prepared by blending RVNRL with HSBL/SVNRL so as to have dry rubber content in the ratio 90/10, 80/20.

The particle size distribution of the latex samples were determined using Malvern Zetasizer Nano Series (Nano S) particle size analyzer. The quality of RVNRL was evaluated by measuring the latex quality parameters and strength of RVNRL films obtained by casting technique. Solvent absorption was conducted using toluene as the solvent and duration was 48 h at room temperature. The properties of latex and dry rubber films were carried out as per standard test methods.

Results and discussion

1. Particle size distribution of latex

The particle size distribution of fresh and pre-irradiated latex before and after creaming is shown in **Figure 1.** The particle size varies from about 100 to 2000 nm for fresh latex sample and from about 100 to 1000 nm for pre-irradiated sample. 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 particle size decrease considerably. 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. The reduction in particle size can be attributed to removal of proteins present on the rubber particles. The nitrogen content before and after creaming is shown in **Table 2**. As observed the nitrogen content decreases after creaming.

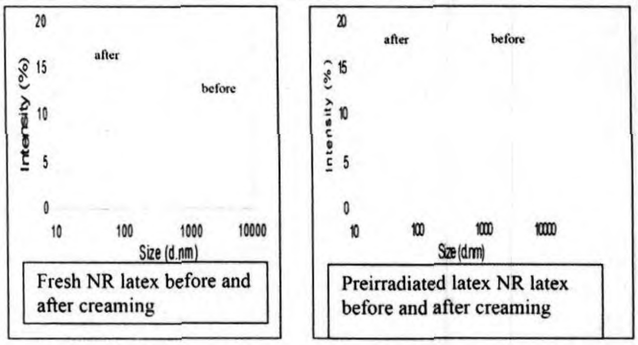

Figure 1 The particle size distribution of fresh NR latex and latex exposed to small doses of gamma radiation before and after creaming

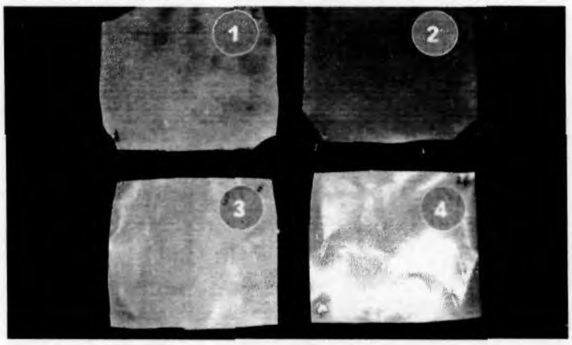

Figure 2. Photograph of RVNRL films 1) Pure RVNRLl, 2) 90/10 RVNRL/HSBL 3) 75/25 RVNRL/HSBL 4) 60/40 RVNRL/HSBL

2. Concentration characteristics

It is observed that a higher level of creaming is observed for fresh NR latex without prior irradiation as observed by a higher level of DRC. (DRC of pre-irradiated and creamed latex was about 45% and that of conventional creamed latex was about 49%). While by centrifuging process, since the conditions could be adjusted, the DRC was higher.

The smaller sized particles of latex incr after irradiation. Adsorption of macromolecules of creaming agent promotes reversible agglomeration of latex particles by reducing the effective density of electric charge at the particle interface[4,5]. 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 cause them break free from the network leading to creaming of latex. However, smaller the size of rubber particles more is the resistance to creaming. In the centrifugal process the separation of latex into centrifuged fraction is governed by centrifugal force unlike in a

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creaming process where it is governed by gravitational force. (Equation 1. Hence the DRC obtained by centrifugation is higher than that obtained by creaming process. (DRC of pre-irradiated and centrifuged latex was about 62 %)

The concentration process is govern. by

$$V = \frac{2g\,(Ds-Dr)r^2}{9\,\eta} \quad \text{............ (1)}$$

V = Velocity with which the rubber particles rise (cm/sec)

g = Gravitational force (cm/sec^2)

Ds = Density of serum

Dr = Density of rubber particles

r = Effective radius of rubber particles

η = Viscosity of the serum (poise)

3. Raw rubber properties

The raw rubber properties of rubber obtained by pre-irradiation in comparison with control sample are given in **Table 2**. It is 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 Po of rubber recovered from latex subjected to pre-irradiation. It is also noted that on exposure of fresh NR latex to gamma radiation gel content increases.

Earlier reports show that proteins get degraded on exposure to gamma radiation3. Consequently, there is a decrease in nitrogen content after concentration as low molecular weight nitrogenous materials go into serum fraction and hence there is an increase in acetone extractable fraction in the rubber. NR molecules are presumed to be linked with phospholipids and other groups that associate with protein to form cross-linking by intermolecular hydrogen bonding. It is expected that branching of NR molecules occur due to the phospholipids groups present in the molecules. Thus these cross-links make it possible to form three dimensional network structures in NR[6]. This cross-linking leads to an increase in gel content and is expected to happen during irradiation. An increase in initial plasticity (Po) for irradiated samples can be due to

Tab Formulation used for sulphur prevulcanisation of natural rubber latex

Ingredients	Wet Weight,g
Concentrated latex	167
KOH solution (10 %)	4
Sodium dodecyl sulphate solution (25% w/v)	0.8
Zinc Oxide (50 % dispersion)	0.5
Zinc diethyldithiocarbamate (50 % dispersion)	2.0
Sulphur (50 % dispersion)	2.5

Table 2 Raw rubber properties of un-irradiated and pre- irradiated latex sample

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	30	-	33	-
Gel content,%	2	-	36	

Table 3 Mechanical properties of RVNRL

Properties	Casted film Conventional RVNRL	Casted film modified RVNRL	Dipped film modified RVNRL
Gum strength, MPa	1.54	3.0	-
Modulus 300%, MPa	0.85	1.1	0.9
Modulus 500%, MPa	1.14	1.6	1.14
Tensile strength, MPa	22.0	24.02	20.02
Elongation at break,%	1380	1285	1290
Toluene Solvent swelling, %	230	170	-
Tension set after 1 hour at 300 % elongation	10	6	

Table 4 Mechanical properties of the blend

Parameter	Sample RVNRL/ HSBL(based on drc)		Control RVNRL/ HSBL(based on drc)	
	90/10	80/20	90/10	80/20
Modulus 300%, MPa	1.83	2.564	2.08	3.25
Modulus 500%, MPa	3,64	5.02	4.24	6.51
Modulus 700%, ,MPa	8.18	9.72	9.14	12.45
Tensile strength, MPa	18.18	12.89	25.51	16.62
Elongation at break, %	910	805	1055	800

formation of gel during irradiation.

4. Properties of RVNRL

Pure RVNRL films – Mechanical properties

The gum strength of NR increases after pre-irradiation. This is attributed to the increase in gel content as shown in **Table 2**. An enhancement in green strength due to enhancement of entanglement and gel formation is reported earlier [2,6,7].

RVNRL films prepared after pre-irradiation showed a higher modulus, tensile strength and lower elongation at break and tension set (Permanent set) (**Table 3**). It is expected that during pre-irradiation several changes take place. This includes chain entanglements, micro gel formation and degradation of proteins. The enhancement in mechanical properties is attributed to this.

Table 5 Mechanical properties of the blend

Parameters	RVNRL/SVNRL			
	100/0	90/10	80/20	0/100
Modulus 300%, MPa	1.1	1.1	1.1	1.1
Modulus 500%, 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

Modified RVNRL films prepared by dipping process using formic acid as a coagulant is given in **Table 3**. A lower tensile strength is 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.

4. Blends of RVNRL with HSBL (High styrene content styrene butadiene copolymer latex)

On blending RVNRL with HSBL (90/10 based on dry rubber content) the modulus increased significantly (**Table 4**). Further improvement in modulus was obtained after pre-irradiation. The tensile strength was only marginally reduced by adding HSBL in low concentrations. When the proportion of HSBL was increased from 10 to 20, the modulus increased sharply and the vulcanizate became hard and plastic nature. The increase in modulus is mainly due to the rigidity of the styrene butadiene copolymer[9]. When the proportion of HSBL was increased from 10 to 25 and 40 parts the vulcanizate became very hard and more plastic natured. (**Fig. 2**)

Blending of Sulphur prevulcanized latex (SVNRL) with RVNRL

Pure SVNRL showed a higher tensile strength than RVNRL. The crosslinked structures are different in the two methods. In the production of RVNRL a sensitiser is used for enhancing radiation induced vulcanization[8]. As the proportion of SVNRL in the RVNRL/SVNRL blend increased from 10 to 20 parts the tensile strength increased proportionately. (**Table 5**)

Final results

The green strength of NR latex increases after exposing freshly preserved latex to low doses of gamma radiation and is attributed to gel formation. RVNRL prepared from latex of higher gel content has a higher t e strength and modulus along with better dynamic properties like lower permanent set. The tensile strength and modulus of RVNRL films increase after suitable leaching process and by blending with high styrene content styrene butadiene copolymer and sulphur prevulcanized latex.

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