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Quality improvement of radiation vulcanised natural rubber latex

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Introduction

Vulcanisation of natural rubber latex with gamma radiation can provide latex products free from chemical toxicity¹ and carcinogenic nitrosamines². Some of the factors that control the efficiency of vulcanisation of NR latex by gamma irradiation are initial molecular weight of rubber ³-⁴, green strength of rubber ⁵, the amount of non—rubber ingredients present and number of particles in NR latex. Generally latex concentrate is stored for about three weeks to achieve an improvement in molecular weight and hence green strength. 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 creaming of latex to reduce the non-rubber ingredients. The creamed latex is then vulcanised by exposure to gamma radiation in presence of n-butyl acrylate as sensitiser.

Experimental

Natural rubber latex (NRL) was collected and exposed to low doses of gamma radiation. The latex was then subjected to a creaming process by using ammonium alginate as the creaming agent. The creamed latex was exposed to a dose of 15 kGy at a dose rate of 1.26 kGy/h, to produce radiation vulcanised natural rubber latex (RVNRL). The creamed latex was compounded with 0.3 phr potassium hydroxide as stabiliser and 5 phr n-butyl acrylate (n-BA) as sensitizer prior to radiation vulcanisation. Latex blends were prepared by blending RVNRL and HSBL 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.

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Results and discussion

Latex properties

a) Particle size distribution of latex

The particle size distribution of fresh NR latex and latex exposed to small doses of radiation after creaming is shown in Fig. 1. After creaming for both unirradiated and pre-irradiated latex the particle size decrease considerably and comparatively lower sized particles are obtained for the pre-irradiated latex. The proportion of bigger sized particles is high in creamed latex prepared from fresh NR latex. 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.

b) Creaming characteristics

It is observed that a higher level of creaming is observed for fresh NR latex without prior irradiation as observed by a higher DRC of creamed fraction. The smaller sized particles of latex increase after irradiation and after creaming. Adsorption of macromolecules of creaming agent promotes reversible agglomeration of latex particles by reducing the effective density of electric charge at the particle interface ⁶. The particles thus come together and cohere 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. The pre-irradiated latex has particles which are of smaller size and hence creaming efficiency is slightly lower than un irradiated latex.

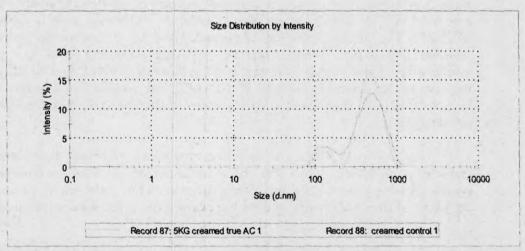


Figure 1: Particle size distribution of creamed latex prepared from fresh and pre-irradiated latex





Raw rubber properties

The raw rubber properties of rubber obtained after creaming of fresh and preirradiated latex—are given in Table 1. It is observed that the nitrogen content remains almost same after irradiation. But it decreases after creaming for both irradiated and unirradiated samples. It is also noted that on exposure of fresh NR latex to gamma radiation gel content increases with irradiation dose. It is also observed that solution viscosity is higher for pre-irradiated latex compared to fresh latex. It is expected that there can be slight cross linking involving proteins leading to gel formation. An increase in Po (initial plasticity) for irradiated samples can be due to formation of gel during irradiation. A slight cross linking between rubber chains also contribute to increase in Po and increase in intrinsic viscosity. Due to the chemical changes in the non rubber ingredients there is an increase in acetone extractables. Earlier reports show that proteins get degraded on exposure to radiation. ⁵

Mechanical properties of blend

The gum strength of NR increases after pre irradiation. This is attributed to the increase in gel content as shown in Table 1. The enhancement in green strength due to enhancement of entanglement and gel formation is reported earlier ^{5, 7}. In the case of latex, there is gel formation during storage and is attributed to the chemical branching that form at both chain ends of the rubber molecule and due to this the green strength of rubber increases during the preservation of the latex in the presence of ammonia. The mechanical properties are better for RVNRL prepared after pre-irradiation. The pre-irradiated RVNRL sample shows a higher tensile strength, modulus and good elongation. On blending RVNRL with HSBL (90/10 based on dry rubber content) the modulus increased significantly (Table 3). Further improvement in modulus was obtained after pre-irradiation. The tensile strength was only marginally reduced by adding HSBL. When the proportion of HSBL was increased from 10 to 20 %, the modulus increased sharply and the vulcanizates became hard and more plastic natured. The increase in modulus is mainly due to the rigidity of the styrene butadiene copolymer.

Table 1: Raw rubber properties

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	
Intrinsic viscosity of the rubber solution	2.67		4.67	

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Table 2: Mechanical properties of RVNRL

Properties	Control (Creamed PFL)	Sample (pre-irradiated Creamed PFL)	
Gum strength, MPa	1.54	3.0	
Modulus 300%, MPa	0.85	1.1	
Modulus 500%, MPa	1.14	1.6	
Tensile strength, MPa	22.0	25.32	
Elongation at break,%	1379	1283	
Solvent swelling, % (after 24 hours)	230	170	
Tension set after 1 hour at 300 % elongation	10	6	

Summary

The green strength of NR latex increase after exposing fresh latex to low doses of gamma radiation and is attributed to gel formation. RVNRL prepared from latex of higher gel content has a higher tensile strength and modulus along with better dynamic properties. The tensile strength and modulus of RVNRL films increase significantly after blending RVNRL prepared from latex exposed to small doses of gamma radiation, with 10 parts of high styrene content styrene butadiene copolymer latex (HSBL).

Table 3: Mechanical properties of the blend

Parameter	Control RVNRL/HSBL (based on drc*)		Sample 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

^{*}dry rubber content

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