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MODIFIED RADIATION VULCANISED NATURAL RUBBER

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Abstract

Radiation vulcanisation is a process to produce prevulcanised natural rubber(NR) latex free of toxic residual chemicals. Some of the factors that control the efficiency of vulcanisation of NR latex by gamma irradiation are initial molecular weight of rubber, green strength of rubber, 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 gel content 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. It is observed that on exposure of fresh NR latex to low doses of gamma radiation there is an increase in gel content favouring enhanced level of vulcanisation. Due to concentration of latex by a creaming process there is reduction in non-rubber ingredients that help in formation of coherent latex films. Unlike centrifugal process, the number of smaller rubber particles in latex after creaming is higher in creamed fraction. All these factors contribute to enhanced mechanical properties of Radiation Vulcanised Natural Rubber Latex (RVNRL). It is observed that RVNRL could be more easily blended with synthetic latex because there is formation of graft copolymer and an enhancement in colloidal stability after irradiation. On blending RVNRL with high styrene content styrene butadiene copolymer latex (HSBL) the modulus increase depending on its concentration mainly due to the rigidity of rubber present. RVNRL of improved mechanical properties are obtained by using creamed NR latex that has higher gel content and by blending RVNRL with HSBL.

Introduction

Natural rubber latex (NRL) forms the raw material for the production different types of gloves, foam, elastic thread, rubber band, balloon etc. For this the latex needs to be subjected to a process of vulcanisation. Latex is vulcanised either by compounding with sulphur and accelerators or by exposure to gamma radiation. 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 causes allergic response [1,2,3]. The main drawback is the lower modulus. Some of the factors that control the efficiency of vulcanisation of NR latex by gamma irradiation are initial molecular weight of rubber, green strength of rubber, the amount of non -rubber ingredients present and number of particles in NR latex.[2] 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 formation of fatty acid soaps and micro gel, Ammonium soaps formed due to reaction of ammonia with hydrolytic products of phospholipids adsorb on surface of rubber particle and leads to improvement in colloidal stability[4]. The formation of micro gel is attributed to interaction of non - rubber components that is proteins and phospholipids bonded to the rubber molecules.[5] Due to formation of micro gel the green strength of the rubber increases. The green strength can be increased by increasing the gel content. The dynamic mechanical properties of the films depend on the non rubber ingredients and gel content of latex.

The modulus and tensile strength can be improved by using latex concentrate of higher green strength as the raw material and by suitable leaching operations. It is also possible to get improvement in modulus by direct radiation grafting cum cross linking of NR latex in presence of a monomer like methyl methacrylate (MMA) with MMA content in the range of 50-60 phr.[6] On the other hand direct blending of RVNRL with up to 25 parts MMA grafted natural rubber latex, showed only marginal improvement in modulus.

If polymers of suitable polarity are mixed, the blend is expected to provide enhanced mechanical properties including modulus. The present work is an attempt in this line and reports the use of high styrene content styrene butadiene copolymer in improving the modulus of RVNRL films prepared from latex of higher gel content.

Experimental

High ammonia preserved field latex was obtained from Pilot crumb rubber factory, RRII. High styrene content styrene butadiene copolymer latex (HSBL), Ploilite SBL 2058, was obtained from M/s Eliokem Pvt Ltd Mumbai, India (total solids content = 29.32 %, pH =11.3).The latex was subjected to a creaming process using ammonium alginate.

Table 1. 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 (P_0)	30	--	33	-
Gel content,%	2	-	36	-

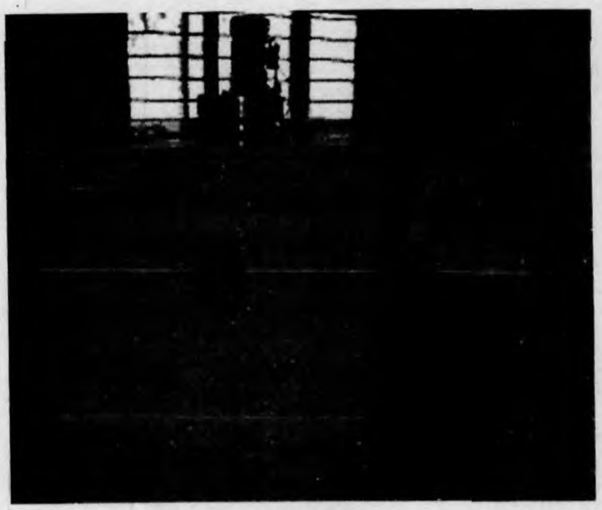

Fig. 1. Gamma chamber 5000 cc

Radiation vulcanisation was effected by gamma rays using Gamma Chamber - 5000 cc. Natural rubber latex(NRL)was collected 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 using a gamma chamber 5000 cc.(Fig.1). 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 irradiation. Latex blends were prepared by blending NRL 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.

Table 2a. Viscosity of pure RVNRL and 90/10 RVNRL/HSBL (based on dry rubber) latex blends at different shear rates

Shear rate, (sec^{-1})	Control viscosity mPa.s		Sample viscosity mPa.s	
	Pure RVNRL	90/10 blend	Pure RVNRL	90/10 blend
60	0.05	0.10	0.05	.09
120	0.05	0.05	0.05	.06
180	0.03	0.03	0.03	.03

Results and discussion

1. Particle size distribution of latex

The particle size varies from about 100 nm 2000 nm for both un-irradiated latex sample and irradiated sample. The bimodal distribution is unchanged but the amount of smaller particles increase after irradiation. After creaming for both un-irradiated and pre-irradiated latex the particle size decreases 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 particle. The nitrogen content before and after creaming is shown in Table 1. As observed the nitrogen content decreases after creaming.

2. 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 level of DRC. 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[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. The pre-irradiated latex has particles which are of smaller size and hence creaming efficiency is slightly lower than un- irradiated latex.

3. Flow characteristics(Haake viscometer)

The data on flow characteristics of viscosity versus shear rate of the pure RVNRL and blends with HSBL in 90/10 and 80/20 proportions are shown in Table 2a and that of rubber solutions at the same concentration is given in Table 2b.

For pure latex the viscosity is constant over different shear rates and hence shows Newtonian behaviour. For the blends the viscosity is slightly higher and viscosity shows variation with shear rate. At lower shear rates viscosity is higher and decreases with shear rate for both the latex samples. The flow characteristics change on blending and there is deviation from the Newtonian behaviour. It is seen that the flow is non-Newtonian for the rubber solutions as noted earlier [7]. The viscosity decreases as shear rate increases. It is also noted that the viscosity increases after irradiation and is attributed to gel formation.

Table 2b. Viscosity of 0.3 % (w/v) rubber solutions in toluene

Shear rate (sec^{-1})	Un-irradiated	Pre-irradiated
60	3.5	5.5
120	3	4.5
180	2.5	3.5

4. Raw rubber properties

The raw rubber properties of rubber obtained by pre-irradiation in comparison with control sample is given in Table 1. It is observed that the nitrogen content remains

Table 3. 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

almost same after irradiation .But it decreases after creaming for both radiated and unirradiated sample. The decrease is higher for the creamed latex that was subjected to a pre-irradiation process. *There is an increase in initial plasticity (P_0) 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 radiation[3]. Consequently there is a decrease in nitrogen content after creaming as low molecular weight nitrogenous materials go into serum fraction and 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 phospholipid groups present in the molecules. Thus, these crosslinks make it possible to form three dimensional network structures in NR[8]. This cross linking along with other likely cross links formed in presence of gamma radiation lead to an increase in gel content. An increase in P_0 for irradiated samples can be due to formation of gel during irradiation.

5. Mechanical properties of RVNRL

5.1. Pure RVNRL

The gum strength of NR increases after pre irradiation. This is attributed to the increase in gel content as shown in Table 3. The enhancement in green strength due to enhancement of entanglement and gel formation is reported earlier [2,8].

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 hysterisis loss is higher for the control compared with sample; consequently tension set is also lower for the sample. A higher cross linking is obtained after pre-irradiation as observed from solvent swelling.

It is expected that during pre-irradiation several changes take place. This includes chain entanglements, micro gel formation and partial removal of proteins. All these changes contribute to enhancement in mechanical properties.

Modified RVNRL can be directly used for production of latex based household gloves (Fig. 2).

5.2. Blends of RVNRL with HSBL

On blending RVNRL with HSBL (90/10 based on dry rubber content) the modulus increased

Fig. 2. Household gloves made from radiation vulcanised latex

Table 4. 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	2.56	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

significantly (Table 4). 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 % in the blend, the modulus increased sharply and the vulcanizate became hard and more plastic natured. The increase in modulus is mainly due to the rigidity of the styrene butadiene copolymer.[9] Latex of higher modulus can be used for production of latex based product like elastic thread.

Conclusion

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 like higher elastic modulus, lower hysterisis loss and lower permanent set. The flow characteristics of the latex change after blending RVNRL with low proportion of HSBL and the latter becomes more non Newtonian. 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).

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Carbon Black/Silica Master Batch From Fresh Natural Rubber Latex

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A new process for production of carbon black/silica master batches with enhanced mechanical properties has been developed. The unit operations in the process are the preparation of filler slurry, in presence of suitable surfactant, addition of the slurry to the fresh natural rubber latex under stirring, coagulation of the mixture by the addition of acid, dewatering of the coagulum, and drying to obtain filler incorporated NR. The competence of the new technique was established by comparing the characteristics of carbon black/silica incorporated NR by mill mixing process (control). The mechanical properties of the vulcanizates obtained from the latex stage and dry rubber incorporated mixes were evaluated. The effect of ageing on the mechanical properties was also studied. Mixed filler containing master batch prepared by the new process showed good cure characteristics as compared to the dry rubber incorporated mix. The mechanical properties like tensile strength, modulus, tear strength, abrasion resistance and hardness were superior for the vulcanizates prepared by the new method. The heat build – up values were considerably low for the latex filler master batches. Comparatively better ageing resistance was also recorded by these vulcanizates. The silica filled mixes showed comparatively very good mechanical properties in the absence of any coupling agent. The improvement in mechanical properties shown by the silica/carbon black master batches over the conventional mill mixed compounds was attributed to better filler dispersion evidenced from the result of filler dispersion data.