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Role of High Styrene Content Styrene Butadiene Copolymer in Improving the Mechanical Properties of Radiation Vulcanised Natural Rubber Latex

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***Abstract*: The present paper attempts to improve the mechanical properties of radiation vulcanised natural rubber latex (RVNRL) films by blending with high styrene content styrene butadiene copolymer latex (HSBL) and leaching the casted film. The modulus of the films increased by several folds as the concentration of HSBL increased but simultaneously the tensile strength decreased. Comparatively very good modulus and tensile strength were obtained when RVNRL and HSBL were mixed in 90/10 proportion based on dry rubber content. This improvement is attributed to the factors that the two latices can mix homogeneously to a good extent and the polarity difference between the two is not very high. In addition, there can be entanglement of grafted n-butyl acrylate chains with HSBL polymer chains.**

***Key words*: Radiation vulcanisation, high styrene content styrene butadiene copolymer**

I. INTRODUCTION

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]. The main drawback is the lower modulus. The modulus and tensile strength can be improved by using latex concentrate of higher green strength [2] 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 [3]. On the other hand direct blending of RVNRL with upto 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.

II. EXPERIMENTAL

Centrifuged latex (High Ammonia- Cenex) was prepared at Pilot Latex Processing Centre (PLPC) of Rubber Research Institute of India (RRII) using alfa-laval 510 latex centrifuging machine, operating at 7000 rpm. Latex of varying particle size was obtained by using skim screws of 9.5 (Cenex 1) and 13 cm (Cenex 2) length. 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)

Radiation vulcanisation was effected by gamma rays using Gamma Chamber- 5000. Natural rubber latex (NRL) having 22 days maturity was exposed to a total dose of 15 kGy at a dose rate of 1.26 kGy/h after diluting to a dry rubber content of 55%. NRL 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, 75/25 and 60/40. 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. Leaching was conducted by immersing the films in 2.5 % calcium nitrate solution for one hour. The properties of latex and dry rubber films were carried out as per standard test methods.

III. RESULTS AND DISCUSSION

A. Particle size and tensile strength

The particle size distribution of the latices used is given in Fig.1. Latex of varying particle size is obtained by using skim screws of 9.5 (Cenex 1) and 13 cm (Cenex 2).

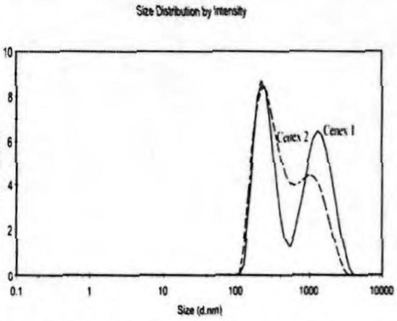

Fig. 1. Particle size distribution of cenex

Cenex 1 contains comparatively larger particle size as compared to cenex 2. For cenex 1 particle size varies from about 100 to 4000 nm while for cenex 2 it varies from about 100 to 3500 nm. HSBL contains comparatively very small particles and the particle size varies from about 58 nm to 105 nm with an average of 78 nm. A shorter screw length encourages a greater difference in density between skim and cream and hence the cream tends to have increased rubber content and the proportion by volume of skim also increases. Consequently particle size of latex obtained by using short screw is higher. A comparatively higher tensile strength and modulus were obtained for cenex 1 (Table I). It is known that for NR latex, molecules present in bigger particles are highly branched and that in smaller particles are linear. The rubber molecules of large rubber particles are presumably terminated with functional group containing fatty acid esters to form long chain branching [5]. This chemical reaction which occurs during storage of ammonia preserved latex plays a major role in improving green strength of rubber [6]. The higher tensile strength of RVNRL prepared using Cenex 1 can be attributed to this. When films are immersed in calcium nitrate solution it is possible that calcium ions participate in an inter particle cross-linking process leading to formation of more cross-links[2]. Due to this the strength of RVNRL improves after the leaching process.

B. Effect of blending HSBL

On blending RVNRL with HSBL (90/10 based on dry rubber content) the modulus increased significantly (Table II). Further improvement in modulus was obtained after leaching. The tensile strength was only marginally reduced by adding HSBL. The improvement in modulus was more prominent when NRL was mixed with HSBL and irradiated but tensile strength was significantly reduced. This may be due to the fact that styrene butadiene copolymer interferes with the free radical formation. Free radical formation is easier in isoprene units[7] as compared to styrene butadiene copolymer units due to presence of aromatic moiety.

C. Effect of proportion of HSBL

When the proportion of HSBL was increased from 10 to 25 and 40 parts, the modulus increased sharply and the vulcanizate became hard and more plastic natured. (Fig. 2). The increase in modulus is mainly due to the rigidity of the styrene butadiene copolymer. The modulus increased further after leaching in calcium nitrate solution due to the formation of more cross links (Table III).

D. Swelling characteristics

Solvent swelling data which is related to the cross links formed is given in Table IV. The solvent uptake decreases after leaching the films in calcium nitrate solution showing that additional cross links are formed during this process. However as HSBL content in the blend is increased, uptake of solvent is also increased mainly due to the higher are almost dissolved as toluene is a good solvent for both NR and styrene butadiene copolymer. Hence the two polymers can proportion of unvulcanised polymer in the blend. At 40 parts HSBL, the samples are highly swollen to the extent that they mix to a good level of homogeneity as the polarity differences between the two are not very high

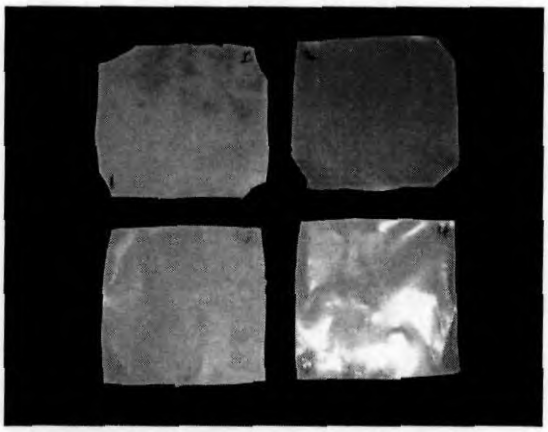

Fig.2. Photograph of RVNRL films 1) Pure RVNRLl, 2) 90/10 RVNRL/HSBL 3) 75/25 RVNRL/HSBL 4) 60/40 RVNRL/HSBL

E. Latex properties before and after gamma irradiation

The properties of NR latex before and after irradiation are shown in Table V. It is seen that the dry rubber content and mechanical stability time (MST) of latex increase while the viscosity changes only slightly after gamma irradiation.

It is known that during irradiation n-butyl acrylate is polymerised and becomes a part of the vulcanised matrix [7-8]. The improvement in modulus can also be attributed to the fact that there can be entanglement of such graft chains with HSBL chains. The increase in MST after irradiation is due to the adsorption of radiation decomposed non rubber ionic components on to the rubber particles [2].

IV. CONCLUSIONS

The modulus of RVNRL film could be significantly improved by blending the prevulcanised latex with 10 parts of high styrene content styrene butadiene copolymer latex (HSBL). The addition of HSBL did not reduce the tensile strength significantly. Higher proportions of HSBL led to films of higher modulus, but the films became less rubbery. The modulus and tensile strength of RVNRL films containing 10 parts of the high styrene copolymer was further improved by leaching in calcium nitrate solution.

TABLE I
EFFECT OF PARTICLE SIZE OF CENEX ON TENSILE PROPERTIES OF RVNRL

Parameter	Cenex 1		Cenex 2	
	Unleached	Leached	Unleached	Leached
M300, MPa	1.02	1.07	1.01	1.05
M500, MPa	1.40	1.49	1.32	1.46
M700, MPa	2.60	2.73	2.32	2.62
Tensile strength, MPa	23.0	26.6	22.1	25.5
Elongation at break, %	1398	1350	1322	1313

TABLE II
EFFECT OF BLENDING WITH HSBL

Parameter	Mixed NRL and HSL in 90/10 proportion and irradiated *		Irradiated NRL and mixed with HSL in 90/10 proportion *	
	Cenex 1	Cenex 2	Cenex 1	Cenex 2
M300, MPa	1.49 (1.38)	1.3 (1.37)	1.74 (1.79)	1.26 (1.74)
M500, MPa	2.94 (2.98)	2.45 (2.46)	2.51 (2.65)	2.49 (2.51)
M700, MPa	6.86 (6.15)	6.01 (5.33)	4.85 (5.08)	4.74 (4.85)
Tensile Strength, MPa	17.35 (16.5)	13.82 (17.9)	22.05 (25.55)	22.00 (22.10)
Elongation at break, %	950 (1004)	1020 (1090)	1260 (1270)	1214 (1260)

**values in the brackets are for the samples leached in 2.5 % calcium nitrate solution for 1 hour*

TABLE III
EFFECT OF CONCENTRATION OF HSBL ON MECHANICAL PROPERTIES OF RVNRL (CENEX 1)

Parameter	90/10 *	75/25 *	60/40 *
M300, MPa	1.74 (1.79)	3.56 (3.62)	7.76 (6.83).
M500, MPa	2.51 (2.65)	5.71 (6.99)	12.30 (-)
M700, MPa	4.85 (5.08)	9.65 (12.68)	-(-)
Tensile strength, MPa	22.05 (25.55)	20.13 (15.62)	15.12 (8.84)
Elongation at break, %	1260 (1270)	1000 (400)	540 (320)

**values in the brackets are for the samples leached in 2.5 % calcium nitrate solution for 1 hour*

Table IV
SWELLING DATA OF PURE RVNRL AND RVNRL/HSBL BLEND

Parameter	Proportion of HSBL in the blend (based on dry rubber content)			
	0	10	25	40
Solvent absorption before leaching in calcium nitrate solution, ml/g	4.92	5.8	Highly swollen	Highly swollen and almost dissolved
Solvent absorption after leaching in calcium nitrate solution, ml/g	4.66	5.24	Highly swollen	Highly swollen and almost dissolved

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