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SUPERIOR PROCESSING RUBBER FROM RADIATION CROSS-LINKED NATURAL RUBBER LATEX

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Superior processing (SP) natural rubber was prepared by blending different proportions of fresh and radiation vulcanised natural rubber latex, followed by coagulation and drying. The Mooney viscosity of SP rubber increased as the proportion of cross-linked rubber increased. Cross-linked and uncross-linked rubber blended in 20/80 proportion (P20) recorded very good mechanical and processing characteristics compared to pure NR. The better processing characteristics were attributed to the higher viscous nature of the modified rubber in gum and carbon black filled mixes. It was observed that the P20 rubber had a higher level of vulcanisation than the pure NR. The improved processability and vulcanisation characteristics were ensured from the analysis of viscoelasticity cure characteristics, physical property evaluation and filler dispersion characteristics. Blending of fresh natural rubber latex and radiation vulcanised latex in suitable proportions offer a very simple method to produce SP rubber with enhanced processing characteristics and mechanical properties.

Keywords: Radiation vulcanisation, Natural rubber latex, Processing rubber, Viscoelasticity.

INTRODUCTION

The latex which is called prevulcanised latex became indispensable for the manufacture of latex products like toy balloons, Rubber band, gloves, latex foam etc. Later an application of this cross-linked latex as a process aid (called superior processing rubber) in the form of dried rubber after coagulating the latex blend of uncrosslinked and cross linked latex was explored. (Karunaratne and Fernando, 1985). The Superior Processing (SP) rubber consists of well mixed vulcanised and unvulcanised rubber. They can be compounded in the manner similar to ordinary grades of natural rubber, with better processing properties. (George *et al.*, 2000). Generally there is little loss of physical properties of the final vulcanisate but they show improved processing characteristics and ability to retain dimensional stability. The SP rubber is prepared using latex cross-linked by sulphur and accelerators in the latex stage. Field latex suitably compounded with the various compounding ingredients is steam heated using a water bath to the desired level of crosslinking, cooled and then intimately mixed with the required quantity of fresh field latex. The blended latex is coagulated with acid.

NR latex can be cross-linked by exposure to gamma radiation in presence of suitable sensitizers. The latex is called

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radiation vulcanised natural rubber latex (RVNRL). This latex has several advantages over conventional sulphur vulcanised one. The advantages include better latex stability (longer shelf life possible), less or toxicity (free from nitrosamines and accelerators induced allergies), better clarity of products (better colouration), cleaner industrial effluents (less environmental pollution), lower ash content (less environmental pollution), absence or of toxic gases on combustion (safer disposal of used products). An advantage of crosslinking by radiation vulcanisation is the degradation of proteins to water soluble hydrolytic products that can be easily removed during coagulation. (Keong, *et al.*, 2009; Varghese *et al.*, 2003; Makuchi, 2003).

Partial removal of proteins from latex is known to improve the dynamic properties of rubber vulcanizates. Sulphur prevulcanisation involves preparation of different compounding ingredients, its addition to latex without affecting colloidal stability and heating the compounded latex at higher temperature. So it is expected that blending of cross-linked and uncross-linked rubbers based on RVNRL would offer better mechanical and dynamic properties than blend of cross-linked and uncross-linked rubbers based on accelerated sulphur cross-linked system. The work presented in this paper is an attempt in this line.

MATERIALS AND METHODS

Field latex collected from the RRII Experiment Station was used as the raw material. The latex was irradiated with γ radiation using the Pilot plant facility of Rubber Research Institute of India. The irradiation was carried out in presence of n-butyl acrylate as a sensitizer having a total dose of 15 kGy. The fresh latex is mixed with RVNRL at different proportions and coagulated with 5 per cent sulphuric acid and made into crepe and dried at 70 °C to obtain modified rubber. The proportion of uncross-linked/cross-linked rubber was 100/0, 80/20, 60/40, 40/60, 20/80 which are designated as PNRL, P20, P40, P60 and P80 respectively.

The stability of latex in terms of zeta potential was studied using Zeta Analyser MALVERN Nano-S. The particle size of latex was determined using a MALVERN Nano-Z particle size Analyser.

Properties of the rubber were determined using standard test methods. The Mooney viscosity was determined using Mooney viscometer model V-MV 3000. The other processing related parameters were determined using RPA 2000. Cure characteristics, dynamic and mechanical properties were evaluated as per standard methods. The filler- filler interaction characteristics were studied by evaluating Payne effect using DMA 50 N and filler dispersion was assessed by using a Dynisco Dispergrader Plus. Ageing studies were done as per the standard ASTM method.

RESULTS AND DISCUSSIONS

1. Stability of latex

It was observed that radiation vulcanized latex could be mixed well with fresh NR latex without affecting colloidal stability. The zeta potential values are shown in Table 1. The latex samples remain stable while blending resulting in uniform mixing of latex. A high zeta potential is shown by fresh field latex. The zeta potential is slightly lower for RVNRL and blends. Earlier reports show that fresh latex has a higher zeta potential than concentrated latex (from which RVNRL is prepared) due to the higher proportion of phospholipids, carbohydrates and proteins inherently

Table 1. **Processing characteristics of natural rubber latex**

Particulars	Mooney viscosity ML (1+ 4) at 100 °C	Zeta potential mV	Mean particle diameter, nm
P20	67	-51.95	438
P40	68	-48.3	455
P60	72	-48.8	500
P80	80	-56.4	510
NR alone	87	-62.9	520
RVNRL alone	-	-58.9	380

present. (Jitalda *et al.*, 2011). The average particle size of pure RVNRL, fresh NR latex and blended latices vary from 380 nm to 530 nm. (Table 1) There is no noticeable level of aggregation of particles, as the particle size changes only marginally after blending.

2. Raw rubber properties

The raw rubber properties of the blended rubber are shown in Table 2. It is observed that the gel content, acetone extractables, Initial plasticity (P_0) and Mooney viscosity increased with increased proportion of cross-linked rubber. However PRI was not influenced with higher proportion of cross-linked rubber. The higher amount of acetone extractables in blends of cross-linked and uncross-linked could be associated with the non-rubber ingredients formed in latex during its processing into RVNRL or due to the added ingredients like fatty acid soaps *etc.*

Mooney viscosity depends on factors like molecular weight, molecular weight distribution, branching, green strength, gel content *etc.* and as such cannot characterize the viscous and elastic response separately. A material of less elasticity can have better processing characteristics. (Jiri Malac, 2011)

3. Processing characteristics

The Mooney viscosity values are given in Table 1. The Mooney viscosity that gives an insight into processability ranges from 67-72 for pure NR and NR mixed with 20 and 40 per cent cross-linked NR. The difficulty of mixing SP 80 is due to the comparatively higher viscosity because of the presence of cross-linked rubber as Mooney viscosity is inversely correlated to

Table 2. **Raw rubber properties of blends of cross-linked and non-cross-linked rubber**

NRL/ RVNRL	Sample notations	Gel content (%)	Acetone extract (%)	Initial plasticity (P_0)	Plasticity retention Index, PRI	Mooney viscosity ML (1+4) 100 °C
100/0	PNRL	1.42	2.17	43	95	70
80/20	P20	9.87	2.70	44	73	72
60/40	P40	34.35	2.71	52	83	77
40/60	P60	54.54	2.29	59	86	83
20/80	P80	73.03	2.34	70	83	96

processing characteristics. Mooney units are recorded at comparatively low shear rates while RPA testing is conducted at very high shear rates and better knowledge about processing characteristics of rubbers can be obtained using Rubber Process Analyzer. (Dick and Liotta, 2004; Stevens and Dick, 2001).

The RPA frequency sweep measured at 100 per cent strain for tan δ and elastic torque are shown in Figs. 1-2. As a general observation elastic torque S′ increases with frequency. The elastic responses remained are almost the same for pure NR and for the blend containing 20 parts of cross-linked rubber. The elastic torque recorded for mixes containing 40 and 60 parts cross-linked rubber was only slightly higher compared to pure NR (Fig. 1). However P80 recorded a very high elastic torque. Hence it is expected that it is very difficult to process P80. As seen from Fig. 2 a higher tan δ is shown by both pure NR and NR containing 20 parts cross-linked rubber. Rubber samples that have higher tan δ and lower elastic torque are known to have better processing characteristics than natural rubber samples with lower tan δ when samples of very close Mooney viscosities are compared. (Stevens and Dick, 2001).

The plots of elastic torque versus strain percentage are given in Fig. 3. At lower and at higher strain percentage NR and NR containing 20 parts cross-linked rubber showed almost same S′. Earlier reports show that rubbers with comparable Mooney viscosities can show a difference in processability and the rubber that records higher elastic torques at higher strains have lesser sticky nature during processing. It was

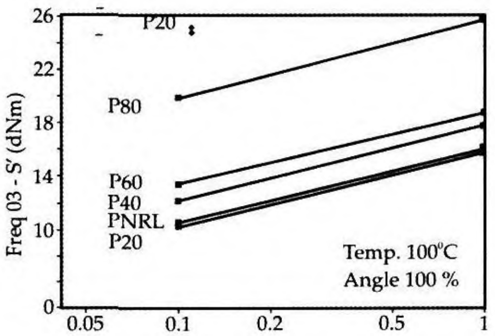

Fig. 1. RPA frequency sweep of raw NR and blends of raw and cross-linked NR for s′ at a strain of 100 per cent.

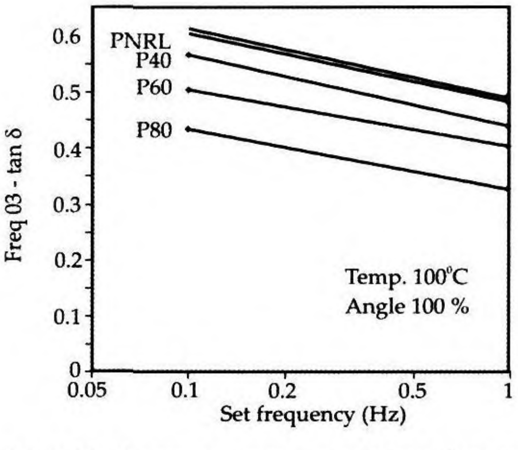

Fig. 2. RPA frequency sweep of raw NR and blends of raw and cross-linked NR at a strain of 100 per cent.

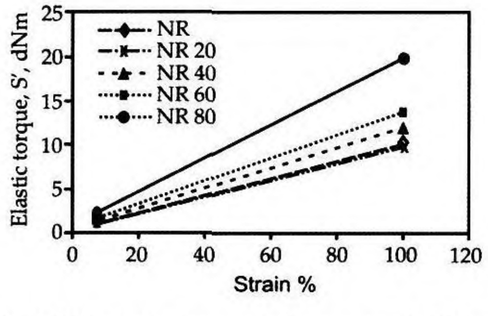

Fig. 3. RPA strain sweep at a frequency of 0.1 Hz of raw NR and blends of raw and cross-linked NR.

observed that mixing ease remained the same up to 60 parts cross-linked rubber while for P80; the mill breakdown was very less due to the very high Mooney viscosity.

4. Processability of compounded rubber with relation to viscoelastic parameters

The RPA frequency sweep for compounded rubber (Table 3) measured at a strain level of 100 per cent noticeably higher tan δ for P20 and P40 compared to NRL (Fig. 3). At higher frequencies also a higher tan δ was shown by P20 and P40 but there was lower difference in the tan δ values for the different mixes.

When tested at lower amplitude for strains in the viscoelastic region of P20 recorded a noticeably higher damping than ISNR 5 at higher frequencies (Fig. 4). However at lower frequencies the tan δ was higher for NR compared to P20.

It is known that the elastic response can vary when rubber is tested at different strains. The rubber molecules are more entangled in the viscoelastic region (6.98%) while at higher levels (100 %) there is no entanglement of NR molecular chains and a better understanding of processability is obtained when tests are conducted at high strains.

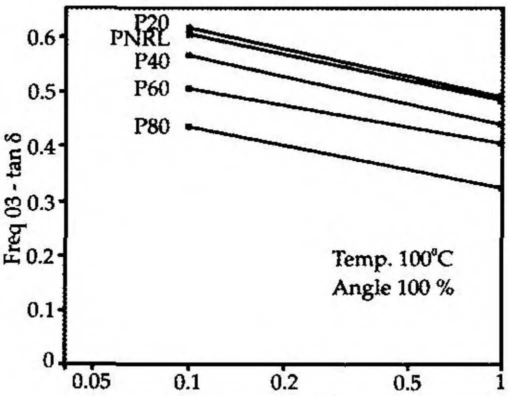

Fig. 4. RPA frequency sweep for tan δ of compounded NR as per ACS1 formulation for NR and blends of raw and cross-linked NR at a strain of 100 per cent.

Table 3. ***Formulation of ACS I and carbon black filled mixes***

Ingredients	ACS I	Carbon black filled
Rubber	100	100
ZnO	6	5
Stearic Acid	0.5	1
MBT*	0.5	-
Antioxidant	-	1.2
SRF black	-	40
Napthenic oil	-	2
CBS**	-	0.9
Sulphur	3.5	2.5

*Mercaptobenzothiazole
**Cyclohexylbenzothiazolesulfenamide

A similar observation is seen for plots of elastic torque versus frequency. A lower S′ was observed for P20 and P40.

These data show that there is higher viscous component for P 20 compared to NR that corresponds to lower dies-well during processing operation like extrusion and hence better processing characteristics.

It is well known that RPA measures both elastic and viscous properties. The torque transmitted through the sample is measured as complex torque S* which is the sum of elastic component S′ (elastic torque) and viscous component S″ (viscous torque).

$$S'/S'' = \tan\delta \quad \text{—— (1)}$$

So a higher tan δ or lower S′ corresponds to more viscous component in the viscoelastic material. A low die swell is well known to correlate with higher viscous component in the viscoelastic material.

Table 4. **Cure characteristics of ACS1 mixes**

Particulars	Torque minimum, dN.m		Torque maximum dN.m		Optimum cure time minutes	
	ACS 1	Carbon black	ACS 1	Carbon black	ACS 1	Carbon black
PNRL	0.20	1.20	4.24	16.20	21.22	8.78
P20	0.16	1.76	6.96	17.79	28.64	10.80
P40	0.52	2.63	4.24	18.32	24.08	10.98
P60	0.57	2.75	5.08	17.43	29.65	11.06
P80	1.00	2.15	5.03	15.70	29.65	9.91

Table 5. **Mechanical properties of carbon black filled mixes**

Particulars	P20	P40	P60	P80	PNRL (Pure NR)
Modulus , MPa	2.77	2.95	2.98	2.69	2.44
Tensile strength, MPa	24.49	22.61	22.61	21.37	20.09
Elongation at break, %	615	580	585	585	640
Tear strength, kN/m	113	108	98	83	83
Hardness , Shore A	62	62	62	60	58
DIN abrasion loss, mm^3	135	132	133	144	125
Compression set, % 22 h at 70 ^0C	40.9	41.5	42.6	42.2	41.0
Heat build-up, "T , ^0C	18	19	18	17	17
Solvent absorbed, % (after 24 hours in toluene)	192	190	183	180	193

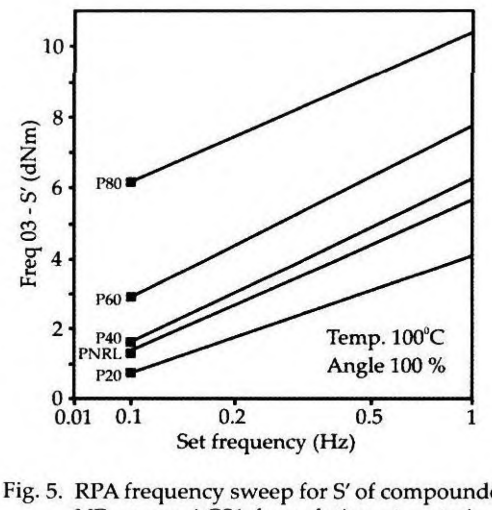

Fig. 5. RPA frequency sweep for S' of compounded NR as per ACS1 formulation at a strain of 100 per cent.

5. Cure characteristics

The cure characteristics as per ACS1 and carbon black filled mixes are shown in Table 4.

As observed higher crosslinking is observed for P20 both for ACS1 mixes and in carbon black filled mixes. However as the amount of cross-linked rubber increases the level of vulcanization does not improve. It is already observed that due to high Mooney viscosity there were difficulties during mill mixing. It is expected that cross-linked rubber contains predominantly carbon-carbon crosslinks with small amount of grafted sensitizer. The latex is colloidally stable and during mixing it is expected that they mix very homogeneously. The reason for a higher level of cure is not very clear but there is the

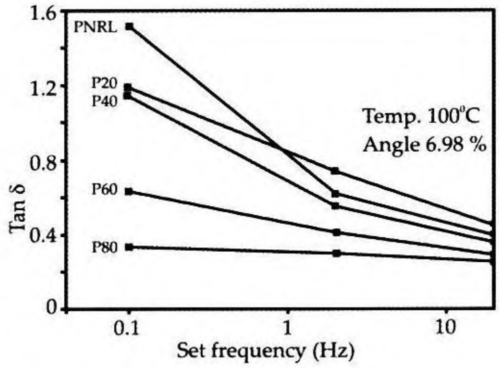

Fig. 6. RPA frequency sweep for tan δ of compounded NR as per ACS1 formulation at a strain of 6.98 per cent.

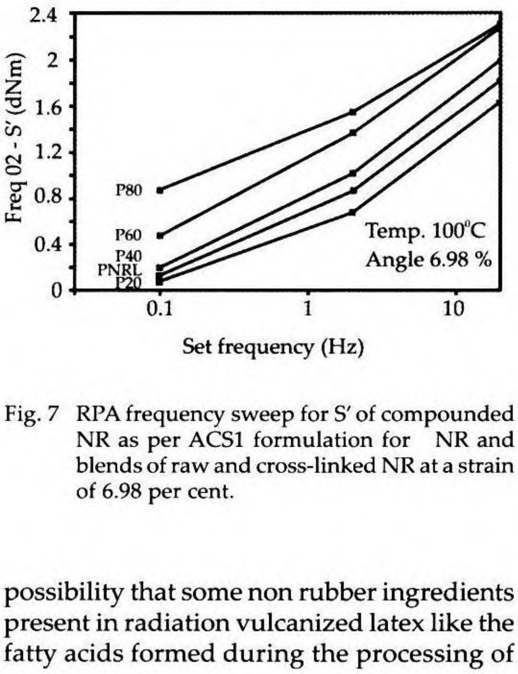

Fig. 7 RPA frequency sweep for S' of compounded NR as per ACS1 formulation for NR and blends of raw and cross-linked NR at a strain of 6.98 per cent.

possibility that some non rubber ingredients present in radiation vulcanized latex like the fatty acids formed during the processing of

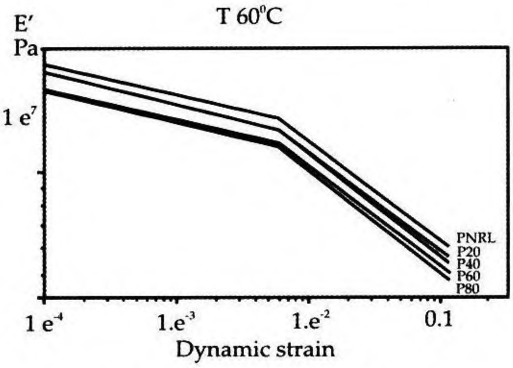

Fig. 8. Payne effect of different vulcanizates.

RVNRL could activate the cure. It is well known that during preservation of latex by ammonia the phospholipids hydrolyze to form free fatty acids.

6. Physical properties

A higher tensile strength, tear strength and modulus is shown by P20 in comparison with control NR. The filler dispersion characteristics as obtained from a Dispersion Analyser are given in Table 6. The filler dispersion characteristics as obtained from measurement of Payne effect is given in Fig. The data from the curves of elastic modulus versus frequency and the rating from Dispersion Analyser show that incorporation of cross-linked rubber did not adversely affect filler dispersion.

The enhancement in mechanical properties could be attributed to higher level of crosslinking and good filler dispersion.

Table 6. **Filler dispersion using Dispergrader**

Test parameter	P20	P40	P60	P80	PNRL
	X=7.6	X=9.0	X=8.6	X=8.2	X=7.3
	Y=9.9	Y=10	Y=10	Y=10	Y=9.8
Dispersion %	99.5	99.9	99.9	99.9	98.0

CONCLUSION

Blending of radiation vulcanised natural rubber latex (RVNRL) with fresh field latex in definite proportions followed by coagulation and drying gives a modified form of rubber that has enhanced processing characteristics. This modified form of rubber containing 20 parts of cross-linked and 80 parts uncross-linked rubber exhibits very good mechanical properties as compared to conventional natural rubber.

REFERENCES

George, B., Alex, R. and Mathew, N.M. (2000). Modified forms of natural rubber. In: *Natural Rubber Agromanagement and Crop Processing* (Eds. P.J. George and C. Kuruvilla Jacob). Anaswara Printing and Publishing Company Kochi, India. pp. 457-458.

Sansatsadeekul, J., Sakdapipanich, J. and Rojrutai, P. (2011). Characterisation of associated proteins and phospholipids in natural rubber latex. *Journal of Bioscience and Bioengineering*, **111**(6): 628-634.

Malac, J. (2011). Mooney viscosity Mooney elasticity and processability of raw natural rubber. *Journal of Material Science and Engineering with Advanced Technology*, **3**(1): 67-87.

Dick, J. and Liotta, T. (2004). New Useful ASTM test methods and standards now available internationally. *Rubber World*, **229** (4): 30.

Karunaratne, S.W. and Fernando, W.S.E. (1985). A linear gel/polymer system based on radiation prevulcanised natural rubber latex. Journal of Rubber Research Institute of Sri Lanka **64**, 1985 p 29-32.

Keong, C.C., Zin, W.M.W. Ibrahim, P. and Ibrahim, S. (2009). 9th National Symposium on polymeric materials (NSPM), Radiation prevulcanised natural rubber latex: cytotoxicity and safety evaluation on animal IOP publishing Ltd, IOP Conf Series: *Materials Science and Engineering*, **11**: 012002, pp. 1-5.

Makuchi, K. Ed. (2003). An Introduction to Radiation Vulcanisation of Natural Rubber Latex, T R I Global Company Ltd, Bangkok 10320, Thailand, 69 p. and 104 p.

Stevens, C. A., Dick, J. S. (2001). Factory testing and control of raw natural rubber and mixed batches using Rubber process Analyser. *Rubber world and Kautchuk Gummi Kunststoffe*, **54** (1-2): 29.

Varghese, ,S. Katsumura,Y., Mukuuchi, K. and Yoshii, F. (2000). Production of soluble protein free latex by radiation process. *Rubber Chemistry and Technology*, **73**: 80-88.