

## Studies on Carboxy-terminated Natural Rubber in Filled NR and NR Latex Vulcanizates

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### ABSTRACT

Carboxy-terminated liquid natural rubber (CTNR) was prepared by a photochemical reaction, involving masticated natural rubber and maleic anhydride. CTNR is tried as a modifier in filled NR and NR latex vulcanizates. The ageing and oil resistance of the NR vulcanizates and the ageing resistance of the NR latex vulcanizates were studied and compared with those containing conventional plasticizer and depolymerized NR. CTNR can improve the tensile properties, ageing and oil resistance of NR vulcanizates and the tensile properties and ageing resistance of the NR latex vulcanizates. The vulcanizates containing CTNR are found to possess better rubber-filler interaction.

#### Key Words:

carboxy-terminated liquid NR;  
plasticizer;  
natural rubber latex;  
ageing;  
oil resistance;  
rubber-filler interaction.

### INTRODUCTION

The use of fillers, both as reinforcing fillers like carbon black, silica, etc. and non-reinforcing fillers like clay, calcium carbonate, etc. in latex products is limited; because, they affect the mechanical properties adversely [1-3]. The reduction in vulcan-

izate properties may be due to the lack of rubber-filler interaction [4,5]. In order to improve the rubber-filler interaction, coupling agents and modifiers are used in dry rubber compounding. Earlier workers have studied the reinforcement of silica

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filler in NR, in the presence of silane coupling agents [6,7]. In order to manufacture cooler running tyres with low rolling resistance and to avoid environmental pollution and huge power consumption, the tyre industry is fast trying to replace carbon black with silica or any other non-black fillers [8]. In this study, carboxy-terminated liquid natural rubber (CTNR) has been tried as a potential modifier for improving the mechanical properties of filled natural rubber (NR), and filled natural rubber latex (NR Latex) vulcanizates. The resistance to ageing and oil extraction and the rubber-filler interaction of the vulcanizates, in the presence of CTNR are also proposed to be investigated as well.

## EXPERIMENTAL

### Materials

Natural rubber (NR): ISNR-5 (Mooney Viscosity ML (1+4) 1000°C), NR-latex; was supplied by RRII, Kottayam, Kerala. The compounding ingredients such as: zinc oxide (ZnO), magnesium oxide (MgO), stearic acid, aromatic oil, carbon black (HAF N-330) and silica were of commercial grade. Mercaptobenzothiazole (MBT), zinc diethyl-dithiocarbamate (ZDC), tetramethylthiuramdisulphide (TMTD) styrenated phenol (SP), Vulkanox 4020 (*N*-phenyl-*N'*-(1,3 dimethylbutyl)

*p*-phenylenediamine), were of rubber grade; supplied by Bayer (I) Ltd. Potassium hydroxide and toluene used were of Analar grade supplied by E. Merck (I) Ltd. The carboxy-terminated liquid natural rubber (CTNR) was prepared in the laboratory by the UV irradiation of 100 g masticated NR in 1 L toluene and 20 g maleic anhydride. The unreacted maleic anhydride was removed by repeated reprecipitation, using toluene-methanol (1:1 v/v) mixture and the product CTNR was characterized by <sup>1</sup>H NMR, IR, GPC and TGA [9].

The optimum concentration of CTNR, for reaching maximum tensile properties, in silica filled and carbon black filled NR vulcanizates and that in silica filled and clay filled NR latex compounds were determined by varying the amount of CTNR in the mix as per the formulations given in Tables 1-4, respectively. The amount of plasticizer can be reduced by the use of the low molecular weight CTNR.

The NR compounds were moulded in an electrically heated laboratory hydraulic press at 150°C up to their optimum cure times. The optimum cure times of the NR compounds were determined on a Monsanto moving die rheometer-2000. Typical cure curves for the vulcanizates F<sub>1</sub> and F<sub>2</sub> in the Tables 1 and 2, respectively are given as Figures 1 and 2. Dumb-bell shaped tensile test pieces were punched out of these compres-

**Table 1.** Formulations for testing the optimum concentration of CTNR in silica filled NR vulcanizates.

Ingredients (phr*)	A <sub>1</sub>	B <sub>1</sub>	C <sub>1</sub>	D <sub>1</sub>	E <sub>1</sub>	F <sub>1</sub>	G <sub>1</sub>	H <sub>1</sub>	I <sub>1</sub>	X <sub>1</sub>
Natural rubber	100	100	100	100	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4	4	4	4	4
Magnesium oxide	2	2	2	2	2	2	2	2	2	2
Styrenated phenol	1	1	1	1	1	1	1	1	1	1
Stearic acid	2	2	2	2	2	2	2	2	2	2
Silica	40	40	40	40	40	40	40	40	40	40
Aromatic oil	5	4.5	3	0	0	0	0	0	0	0
Depolymerized NR	0	0	0	0	0	0	0	0	0	5
CTNR	0	2	4	6	8	10	12	14	20	0
Mercaptobenzothiazole.	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Tetramethyl thiuramdisulphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Optimum cure time (min)	1:45	1:46	1:40	1:38	1:36	1:35	1:31	1:28	1:21	1:49

(\*) parts per hundred rubber.

**Table 2.** Formulations for testing the optimum concentration of CTNR in carbon black filled NR vulcanizates.

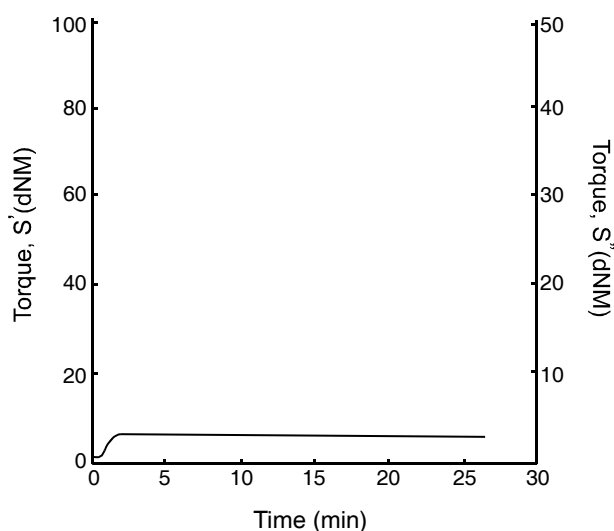
Ingredients (phr <sup>*</sup> )	A <sub>2</sub>	B <sub>2</sub>	C <sub>2</sub>	D <sub>2</sub>	E <sub>2</sub>	F <sub>2</sub>	G <sub>2</sub>	H <sub>2</sub>	I <sub>2</sub>	X <sub>2</sub>
Natural rubber	100	100	100	100	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4	4	4	4	4
Magnesium oxide	2	2	2	2	2	2	2	2	2	2
Vulkanox 4020	1	1	1	1	1	1	1	1	1	1
Stearic acid	2	2	2	2	2	2	2	2	2	2
Carbon black (HAFN 330)	40	40	40	40	40	40	40	40	40	40
Aromatic oil	5	4.5	3	0	0	0	0	0	0	0
Depolymerized NR	0	0	0	0	0	0	0	0	0	5
CTNR	0	2	4	6	8	10	12	14	20	0
Mercaptobenzothiazole.	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Tetramethyl thiuramdisulphide	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Optimum cure time (min)	1:57	1:56	1:48	1:44	1:39	1:34	1:28	1:21	1:19	1:56

(<sup>\*</sup>) parts per hundred rubber.

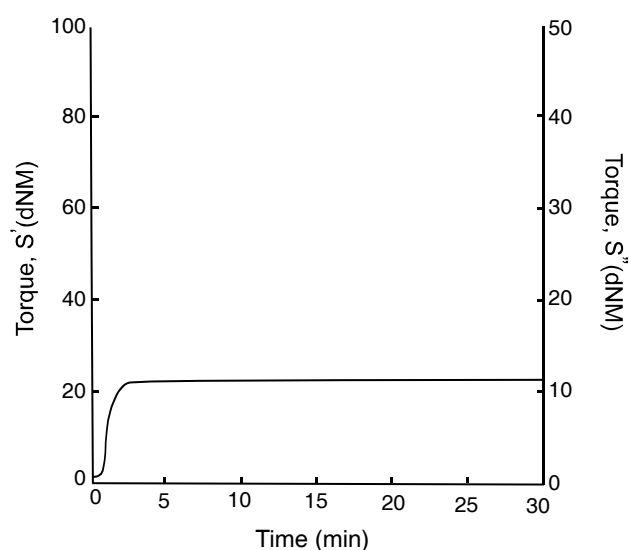
sion moulded NR sheets along the mill grain direction. The NR latex compounds were moulded on glass trays in the form of sheets. The vulcanization of the latex sheets were carried out in the laboratory oven at 120°C. The time for optimum cure was determined by vulcanizing the sheets for different durations of time at 120°C and determining the tensile strength of the vulcanizates in each case. The NR latex compounds were cured at 120°C for different durations of time from 10 to

80 min, preceded by a 1 h rise to that temperature. The maximum tensile properties were found for those compounds cured for 40 min, at the above said conditions.

The tensile properties of both the NR and the NR latex vulcanizates were evaluated on a Prolific Universal Testing Machine model 1.3D; using a cross-head speed of 500 mm/min conforming to ASTM D 412 (1980). The Shore A hardness of the moulded samples were tested using a Zwick 3115 hardness tester in



**Figure 1.** Typical cure curve for the silica filled NR vulcanizate (F<sub>1</sub>) of Table 1.



**Figure 2.** Typical cure curve for the carbon black filled NR vulcanizate (F<sub>2</sub>) of Table 2.

**Table 3.** Formulations for testing the optimum concentration of CTNR in silica filled NR latex vulcanizates.

Ingredients (phr)	A <sub>3</sub>	B <sub>3</sub>	C <sub>3</sub>	D <sub>3</sub>	E <sub>3</sub>	F <sub>3</sub>	G <sub>3</sub>	H <sub>3</sub>	I <sub>3</sub>	X <sub>3</sub>
Natural rubber latex	167	167	167	167	167	167	167	167	167	167
Potassium hydroxide (10%)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Zinc oxide (50%)	1	1	1	1	1	1	1	1	1	1
Styrenated phenol (50%)	2	2	2	2	2	2	2	2	2	2
Silica (40%)	40	40	40	40	40	40	40	40	40	40
Dispersol VL	5	5	5	5	5	5	5	5	5	5
Depolymerized NR	0	0	0	0	0	0	0	0	0	5
CTNR (50%)	0	2	4	6	8	10	12	14	20	0
Zinc diethyldithiocarbamate (50%)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Tetramethylthiuram disulphide (10%)	1	1	1	1	1	1	1	1	1	1
Sulphur (50%)	3	3	3	3	3	3	3	3	3	3

accordance with ASTM D- 2240.

The retention in tensile properties and hardness of NR vulcanizates and NR latex vulcanizates containing CTNR were evaluated after ageing the samples for 24 h at 100°C.

The oil resistance of the NR vulcanizates containing CTNR; was determined by keeping the samples in transformer oil and engine oil for 48 h at room tem-

perature and finding the retention in tensile properties and hardness. Swelling in oil of these vulcanizates was studied by keeping a known weight of the samples in transformer oil and engine oil for 48 h at room temperature.

The rubber-filler interaction of the NR and NR latex vulcanizates was studied by varying the amount of filler in the mix as per the formulations given in Tables 5 and 6, respectively [10,11].

**Table 4.** Formulations for testing the optimum concentration of CTNR in clay filled NR latex vulcanizates.

Ingredients (phr)	A <sub>4</sub>	B <sub>4</sub>	C <sub>4</sub>	D <sub>4</sub>	E <sub>4</sub>	F <sub>4</sub>	G <sub>4</sub>	H <sub>4</sub>	I <sub>4</sub>	X <sub>4</sub>
Natural rubber latex	167	167	167	167	167	167	167	167	167	167
Potassium hydroxide (10%)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Zinc oxide (50%)	1	1	1	1	1	1	1	1	1	1
Styrenated phenol (50%)	2	2	2	2	2	2	2	2	2	2
Clay (40%)	40	40	40	40	40	40	40	40	40	40
Dispersol VL	5	5	5	5	5	5	5	5	5	5
Depolymerized NR	0	0	0	0	0	0	0	0	0	5
CTNR (50%)	0	2	4	6	8	10	12	12	20	0
Zinc diethyldithiocarbamate (50%)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Tetramethylthiuram disulphide (10%)	1	1	1	1	1	1	1	1	1	1
Sulphur (50%)	3	3	3	3	3	3	3	3	3	3

**Table 5.** Formulations for testing the rubber-filler interaction in silica filled and carbon black filled NR vulcanizates.

Ingredients (phr)	A	B	C	D	E	F
Natural rubber	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4
Magnesium oxide	2	2	2	2	2	2
Styrenated phenol	1	1	1	0	0	0
Vulkanox 4020	0	0	0	1	1	1
Stearic acid	2	2	2	2	2	2
Silica	40	60	80	0	0	0
Carbon black	0	0	0	40	60	80
Aromatic oil	0	0	0	0	0	0
CTNR	10	10	10	10	10	10
Mercaptobenzothiazole	0.6	0.6	0.6	0.6	0.6	0.6
Tetramethylthiuram disulphide	0.2	0.2	0.2	0.2	0.2	0.2
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

## RESULTS AND DISCUSSION

Table 7 shows the variation in tensile properties and hardness of the silica filled NR vulcanizates, as per the formulations given in Table 1. The tensile properties are found to increase with the amount of CTNR, and then level off; at about 10 phr, and then they show a

slight decrease. The increase in tensile properties may be attributed to the better rubber-filler interaction promoted by the presence of CTNR. The decrease in properties, after an optimum level, may be due to the plasticizing effect of CTNR. It can also be seen that the improvement in tensile properties of the vulcanizates containing CTNR is not due to the depolymerized NR part of CTNR. The hardness; however, is found to have comparable values for all the vulcanizates. Table 8 shows the variation in tensile properties and hardness of the carbon black filled NR vulcanizates, as per the formulations even in Table 2. It can be seen that the tensile properties and hardness values are found to show a similar trend as being shown by the silica filled NR vulcanizates.

Tables 9 and 10 show the variation in tensile properties and hardness, before and after ageing, of the vulcanizates A<sub>1</sub>, F<sub>1</sub>, X<sub>1</sub>, A<sub>2</sub>, F<sub>2</sub> and X<sub>2</sub> in Tables 1 and 2, respectively. The retention in tensile properties of the vulcanizates containing CTNR, may be due to the lower volatility of CTNR and greater compatibility of CTNR with NR. The hardness values are found to be comparable for all these vulcanizates.

Table 11 shows the variation in tensile properties and hardness values of the compounds A<sub>1</sub>, F<sub>1</sub>, A<sub>2</sub> and F<sub>2</sub> in Tables 1 and 2, before and after oil extraction. The vulcanizates containing CTNR is found to show superior resistance to oil extraction, in comparison to

**Table 6.** Formulations for testing the rubber-filler interaction in silica filled and clay filled NR latex vulcanizates.

Ingredients (phr)	A	B	C	D	E	F	G	H
Natural rubber latex	167	167	167	167	167	167	167	167
Potassium hydroxide (10%)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Zinc oxide (50%)	1	1	1	1	1	1	1	1
Styrenated phenol (50%)	2	2	2	2	2	2	2	2
Silica (40%)	40	60	80	100	0	0	0	0
Clay (40%)	0	0	0	0	40	60	80	100
Dispersol VL	5	5	5	5	5	5	5	5
CTNR (50%)	10	10	10	10	10	10	10	10
Zinc diethyldithiocarbamate (50%)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Tetramethylthiuram disulphide (10%)	1	1	1	1	1	1	1	1
Sulphur (50%)	3	3	3	3	3	3	3	3

**Table 7.** Variation in tensile properties and hardness of silica filled NR vulcanizates as per the formulations given in Table 1.

Properties	A <sub>1</sub>	B <sub>1</sub>	C <sub>1</sub>	D <sub>1</sub>	E <sub>1</sub>	F <sub>1</sub>	G <sub>1</sub>	H <sub>1</sub>	I <sub>1</sub>	X <sub>1</sub>
Tensile strength (N/mm <sup>2</sup> )	8.83	10.46	11.74	13.96	15.94	17.5	17.2	16.9	16.1	8.18
Elongation-at-break (%)	686.1	704	712	720	730	726	681	620.1	590	626
Modulus at 300% elongation (N/mm <sup>2</sup> )	1.49	1.56	1.68	1.93	2.08	2.25	2.20	2.19	2.10	1.41
Hardness (Shore A)	33	36	37	35	37	40	41	40	37	35

**Table 8.** Variation in tensile properties and hardness of carbon black filled NR vulcanizates as per the formulations given in Table 2.

Properties	A <sub>2</sub>	B <sub>2</sub>	C <sub>2</sub>	D <sub>2</sub>	E <sub>2</sub>	F <sub>2</sub>	G <sub>2</sub>	H <sub>2</sub>	I <sub>2</sub>	X <sub>1</sub>
Tensile strength (N/mm <sup>2</sup> )	23.36	25.04	25.44	25.82	26.08	27.84	27.10	26.79	26.0	22.84
Elongation-at-break (%)	606.4	608.8	635.2	620	618.6	616.8	616	619	621.3	608
Modulus at 300% elongation (N/mm <sup>2</sup> )	5.88	6.93	6.11	7.71	7.08	6.99	6.99	7.11	6.98	5.69
Hardness (Shore A)	56	55	55	57	56	59	58	58	56	57

**Table 9.** Variation in tensile properties and hardness, before and after ageing, of the silica filled NR vulcanizates.

Before ageing	A <sub>1</sub>	F <sub>1</sub>	X <sub>1</sub>
Tensile strength (N/mm <sup>2</sup> )	8.83	17.5	8.18
Elongation-at-break (%)	686.1	726	626
Modulus at 300% elongation (N/mm <sup>2</sup> )	1.49	2.25	1.41
Hardness (Shore A)	33	40	35
After ageing at 100°C for 24 h	A <sub>1</sub>	F <sub>1</sub>	X <sub>1</sub>
Tensile strength (N/mm <sup>2</sup> )	6.62	15.78	5.08
Elongation-at-break (%)	478.1	553.5	349
Modulus at 300% elongation (N/mm <sup>2</sup> )	1.10	2.86	0.98
Hardness (Shore A)	35	41	41

**Table 10.** Variation in tensile properties and hardness, before and after ageing, of the carbon black filled NR vulcanizates.

Before ageing	A <sub>2</sub>	F <sub>2</sub>	X <sub>2</sub>
Tensile strength (N/mm <sup>2</sup> )	23.36	27.84	22.84
Elongation-at-break (%)	606.4	616.8	608
Modulus at 300% elongation (N/mm <sup>2</sup> )	5.88	6.99	5.69
Hardness (Shore A)	56	59	57
After ageing at 100°C for 24 h	A <sub>1</sub>	F <sub>1</sub>	X <sub>1</sub>
Tensile strength (N/mm <sup>2</sup> )	16.23	22.48	17.66
Elongation-at-break (%)	412.4	444.8	298
Modulus at 300% elongation (N/mm <sup>2</sup> )	5.09	7.32	3.07
Hardness (Shore A)	58	66	52

**Table 11.** Properties of vulcanizates before and after oil extraction.

Before oil extraction	A <sub>1</sub>	F <sub>1</sub>	A <sub>2</sub>	F <sub>2</sub>
Tensile strength (N/mm <sup>2</sup> )	8.83	17.5	23.36	27.84
Elongation-at-break (%)	686.1	726	606.4	616.8
Modulus at 300% elongation (N/mm <sup>2</sup> )	1.49	2.25	5.88	6.99
Hardness(Shore A)	33	40	56	59
After oil extraction in transformer oil at room temperature for 48 h	A <sub>1</sub>	F <sub>1</sub>	A <sub>2</sub>	F <sub>2</sub>
Tensile strength (N/mm <sup>2</sup> )	1.31	9.26	8.52	12.20
Elongation-at-break (%)	270.1	305	260	300
Elongation (N/mm <sup>2</sup> )	0.53	1.16	2.99	4.56
Hardness (Shore A)	21	30	41	46
After oil extraction in engine oil at room temperature for 48 h	A <sub>1</sub>	F <sub>1</sub>	A <sub>2</sub>	F <sub>2</sub>
Tensile strength (N/mm <sup>2</sup> )	1.49	10.11	7.98	13.18
Elongation-at-break (%)	282	330	261	316
Modulus at 300% elongation (N/mm <sup>2</sup> )	0.71	1.71	3.08	4.31
Hardness (Shore A)	24	32	40	50

**Table 12.** Percentage increase in weight of the vulcanizates in oils.

Type of oil	A <sub>1</sub>	F <sub>1</sub>	A <sub>2</sub>	F <sub>2</sub>
Transformer oil	53.18	52.38	47.59	33.02
Engine oil	50.62	47.93	45.78	34.09

**Table 13.** Variation in tensile properties and hardness of the silica filled NR latex vulcanizates as per the formulations given in Table 3.

Properties	A <sub>3</sub>	B <sub>3</sub>	C <sub>3</sub>	D <sub>3</sub>	E <sub>3</sub>	F <sub>3</sub>	G <sub>3</sub>	H <sub>3</sub>	I <sub>3</sub>	X <sub>3</sub>
Tensile strength (N/mm <sup>2</sup> )	17.01	17.75	18.01	9.38	20.4	22.08	1.95	21.45	21.01	7.03
Elongation-at-break (%)	902.3	906.5	918.1	922	939.6	948.4		946.4		946
Modulus at 300% elongation (N/mm <sup>2</sup> )	7.63	7.84	7.99	8.61	9.41	9.99	9.49	9.44	9.44	7.11
Hardness (Shore A)	16	17	20	20	22	25	25	24	22	16

**Table 14.** Variation in tensile properties and hardness of the clay filled NR Latex vulcanizates as per the formulations given in Table 4.

Properties	A <sub>4</sub>	B <sub>4</sub>	C <sub>4</sub>	D <sub>4</sub>	E <sub>4</sub>	F <sub>4</sub>	G <sub>4</sub>	H <sub>4</sub>	I <sub>4</sub>	X <sub>4</sub>
Tensile strength (N/mm <sup>2</sup> )	15.68	15.79	16.01	17.21	17.32	17.95	17.91	17.01	16.98	15.71
Elongation-at-break (%)	820.8	833	844.7	915.7	985.6	915.8	908.6	909.1	900.8	818.3
Modulus at 300% elongation (N/mm <sup>2</sup> )	4.75	4.79	5.76	6.85	7.08	7.25	7.21	6.93	6.99	4.19
Hardness (Shore A)	18	19	20	24	26	29	29	28	26	19

**Table 15.** Properties, before and after ageing, of the NR latex vulcanizates, as per the formulations given in Tables 3 and 4.

Before ageing	A <sub>3</sub>	F <sub>3</sub>	A <sub>4</sub>	F <sub>4</sub>
Tensile strength (N/mm <sup>2</sup> )	17.01	22.08	15.68	17.95
Elongation-at-break (%)	902.3	948.4	820.8	915.8
Modulus at 300 % elongation (N/mm <sup>2</sup> )	7.63	9.99	4.75	7.25
Hardness (Shore A)	16	25	18	29
After ageing at 100°C for 24 h	A <sub>3</sub>	F <sub>3</sub>	A <sub>4</sub>	F <sub>4</sub>
Tensile strength (N/mm <sup>2</sup> )	6.21	18.54	4.58	10.52
Elongation-at-break (%)	649.7	729.3	506.4	558.6
Modulus at 300 % elongation (N/mm <sup>2</sup> )	3.74	5.99	1.28	2.10
Hardness (Shore A)	12	22	7	15

those containing aromatic oil. This may be attributed to the lower extractability of the polymeric CTNR by the oils.

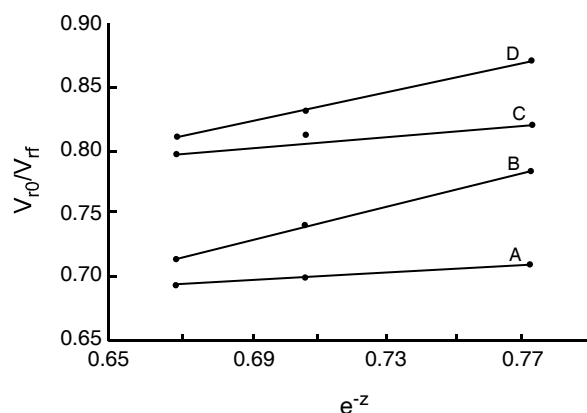
Table 12 shows the percentage increase in weight of the vulcanizates A<sub>1</sub>, F<sub>1</sub>, A<sub>2</sub> and F<sub>2</sub> in Tables 1 and 2. Lower increase in weight of the vulcanizates containing CTNR may be due to the higher swelling resistance of these vulcanizates in oils.

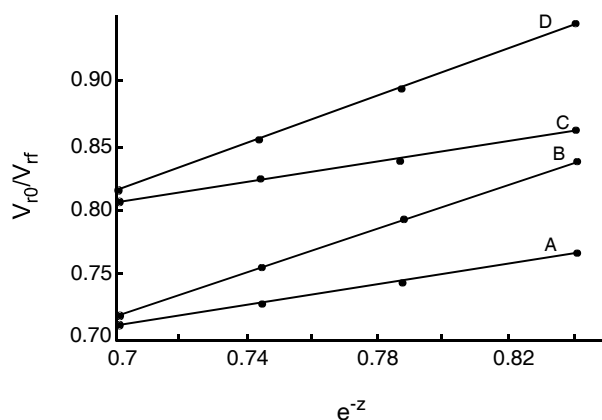
Table 13 shows the variation in tensile properties and hardness of the silica filled NR latex vulcanizates, as per the formulations given in Table 3. The tensile strength, elongation and modulus values are found to

increase with the concentration of CTNR, level off at an optimum concentration of 10 phr and then they are found to have a slight decrease. The decrease in properties is due to the plasticizing effect of CTNR. The hardness values are comparable for all the vulcanizates. A similar trend is shown by the clay filled NR latex vulcanizates as shown in Table 14.

Table 15 shows the variation in tensile properties and hardness of the vulcanizates A<sub>3</sub>, F<sub>3</sub>, A<sub>4</sub> and F<sub>4</sub> given in Tables 3 and 4, before and after ageing. The vulcanizates containing CTNR is found to show superior ageing resistance compared to those without CTNR. This may be due to the better rubber-filler interaction in presence of CTNR.

Figure 3 shows the variation of  $V_{ro}/V_{rf}$  with respect to  $e^{-z}$ ; of the silica and carbon black filled NR vulcan-

**Figure 3.** Variation of  $V_{ro}/V_{rf}$  with respect to  $e^{-z}$ ; of the silica and carbon black filled NR vulcan-



**Figure 4.** Variation of  $V_{ro}/V_{rf}$  with respect to  $e^{-z}$ ; of the silica and clay filled NR latex vulcanizates.

izates as per the formulations in Table 5. The vulcanizates containing CTNR is found to exhibit higher slope indicating the higher swelling resistance and better rubber-filler interaction by the addition of CTNR in the mix.

Similarly, Figure 4 shows the variation of  $V_{ro}/V_{rf}$  with respect to  $e^{-z}$ ; of the silica and clay filled NR latex vulcanizates; as per the formulations given in Table 6. Here also a higher slope is obtained for the vulcanizates containing CTNR; indicating better rubber-filler interaction in the presence of CTNR.

## CONCLUSION

- Carboxy-terminated liquid natural rubber (CTNR) can improve the tensile properties of filled NR and NR latex vulcanizates.
- The ageing and oil resistance of NR vulcanizates can be improved by the addition of CTNR.
- The ageing resistance of NR latex vulcanizates can be improved by the addition of CTNR-CTNR can improve the rubber-filler interaction in NR and NR latex vulcanizates-CTNR can act as a polymeric plasticizer in filled NR vulcanizates.

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