

Studies on Carboxy-Terminated Liquid Natural Rubber in NBR

U. DILEEP, SHANTI A. AVIRAH

Mahatma Gandhi University Regional Research Centre, Department of Chemistry, Mar Athanasius College, Kothamangalam 686666, Kerala, India

Received 24 August 2000; Accepted 25 July 2001

ABSTRACT: Maleic anhydride was chemically attached to depolymerized natural rubber by a photochemical reaction. The product Carboxy Terminated Liquid Natural Rubber (CTNR) was characterized by $^1\text{H-NMR}$, IR, GPC, and TGA. The efficiency and permanence of CTNR were compared with conventional plasticizers in NBR vulcanizates. This polymeric plasticizer was found to be less volatile and more resistant to oil extraction. The vulcanizates showed improved aging resistance compared to vulcanizates containing conventional plasticizers. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 261–267, 2002; DOI 10.1002/app.10322

Key words: Carboxy Terminated Liquid NR; plasticizer

INTRODUCTION

One of the most exciting and at times ingenious areas of research during the past decade has been the preparation of low molecular weight telechelic polymers that are susceptible to future modification. Such materials are a prerequisite for the production of new materials like adhesives, binders for rocket propellents, polyurethanes, polymer-bound antioxidants, coupling agents, plasticizers etc.¹ Several methods are described in the literature for the preparation of low molecular weight polymers with reactive end groups.^{2,3} Such functional groups in a rubber can impart increased strength by increasing the intra- and interchain forces.⁴ Nitrile rubber-based polymers used in the fabrication of seals for use in contact with mineral oil-based hydraulic fluids require

selective compounding. The viscosity, tackiness, and processibility of NBR compounds can be adjusted through the use of plasticizers. At the same time these compounds reduce the mechanical properties, swell resistance, and dimensional stability of the vulcanizates, and they are volatile and extractable by oils. A polymeric plasticizer could alleviate this problem.⁵ This article describes the cost effective preparation of Carboxy Terminated Liquid Natural Rubber (CTNR) and subsequent use of the product in NBR compounds as a reactive polymeric plasticizer. The natural rubber part of the CTNR gets attached to the NBR during sulphur vulcanization, and the plasticizer become nonvolatile and nonextractable. The efficiency and permanence of this polymeric plasticizer were compared with that of conventional plasticizer in silica and carbon black-filled NBR vulcanizates.

Correspondence to: S. A. Avirah (mac@giasmdol.vsnl.net.in).

Contract grant sponsor: University Grants Commission, New Delhi, India.

Journal of Applied Polymer Science, Vol. 84, 261–267 (2002)
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EXPERIMENTAL

Acrylonitrile butadiene rubber (NBR-JSR 230) was supplied by Apar Polymers Ltd. India. Nat-

Table I Formulations for Testing the Optimum Concentration of CTNR

Ingredients (phr)	1	2	3	4	5	6	7	8	9	10	11	12
Acrylonitrile-butadiene Rubber (NBR)	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4	4	4	4	4	4	4
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Styrenated phenol	1	1	1	1	1	1	0	0	0	0	0	0
Vulkanox-4020	0	0	0	0	0	0	1	1	1	1	1	1
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2
Silica	40	40	40	40	40	40	0	0	0	0	0	0
Carbon black (HAFN 330)	0	0	0	0	0	0	40	40	40	40	40	40
Diethyl phthalate (DOP)	0	5	0	0	0	0	0	5	0	0	0	0
Depolymerized natural rubber	5	0	0	0	0	0	5	0	0	0	0	0
CTNR	0	0	2.5	5	8	10	0	0	2.5	5	8	10
Mercaptobenzothiazole	1	1	1	1	1	1	1	1	1	1	1	1
Tetramethylthiuramdisulphide	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cure characteristics												
Optimum cure time (min)	3.9	4.42	4.26	3.52	3.48	3.41	5.2	7.07	5.42	4.53	3.59	3.44

ural rubber (NR; ISNR-5) was supplied by RRII, Kottayam. Compounding ingredients, ZnO, stearic acid, dioctylphthalate, silica, and carbon black (HAF, N330), were commercial grade. Mercaptobenzothiazole (MBT), tetramethylthiuram disulphide (TMTD), and Vulkanox 4020 (*N*-phenyl-*N'*-(1,3 dimethylbutyl) (*p*-phenylenediamine), were rubber grade supplied by Bayer India Ltd. Maleic anhydride, methanol, acetone, toluene, were of reagent grade and used as such. Transformer oil and engine oil were commercial grade.

Preparation of Carboxy-Terminated Liquid Natural Rubber (CTNR)

NR (200 g) was masticated for 30 min at 50°C. One hundred grams of it was dissolved in 1 L

toluene, and the solution was charged into the photochemical reactor, a glass vessel of 3 L capacity fitted with a water condenser and a mechanical stirrer. A high-pressure mercury vapor lamp in a quartz immersion well was placed in the solution. After 50 h exposure, to a part of the depolymerized natural rubber solution, 20 g maleic anhydride dissolved in methanol was added slowly with stirring, and irradiation was continued. Samples taken after 1, 3, 5, 7, 9, 10, 11, 12, and 15 h of exposure after adding maleic anhydride were poured into an excess of methanol with stirring, liquid rubber precipitated. The unreacted maleic anhydride was removed by repeated reprecipitation using a toluene-methanol (1 : 1 v/v) mixture, and the product was dried in a vacuum oven. CTNR was obtained in the form of

Table II Formulations for Testing the Properties of CTNR

Ingredients (phr ^a)	A	B	C	D	E	F
Acrylonitrile-butadiene Rubber	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4
Magnesium oxide	1	1	1	1	1	1
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5
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	40	40	0	0	0
Carbon black (HAF N330)	0	0	0	40	40	40
Diethyl phthalate (DOP)	5	0	1	5	0	1
CTNR	0	5	5	0	5	5
Mercaptobenzothiazole	1	1	1	1	1	1
Tetramethylthiuramdisulphide	0.5	0.5	0.5	0.5	0.5	0.5

^a Parts per hundred rubber.

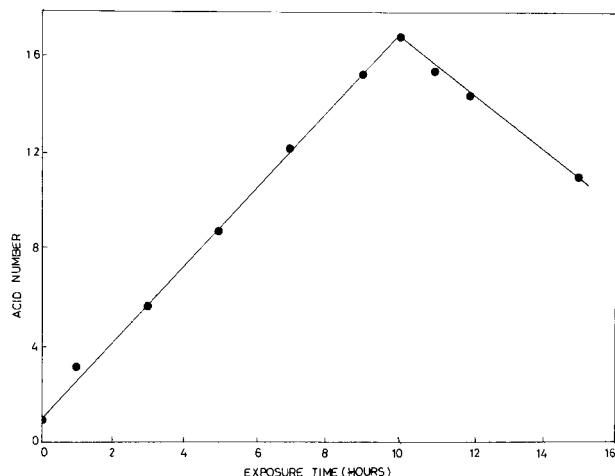


Figure 1 Variation of carboxyl content (acid number) with exposure time.

brown viscous liquid. Samples taken after different times of exposure were analyzed for —COOH content as acid number.⁶ Maximum COOH content was obtained for samples produced after exposure for 10 h, so time of UV irradiation after adding maleic anhydride was fixed at 10 h. Carboxy-Terminated Liquid Natural Rubber (CTNR) was prepared by irradiating depolymerized natural rubber with maleic anhydride for 10 h. The rest of the depolymerized rubber solution was irradiated continuously. Samples were taken after 1, 3, 5, 7, 9, 10, 11, 12, and 15 h of exposure, precipitated as above, and determined the COOH content.

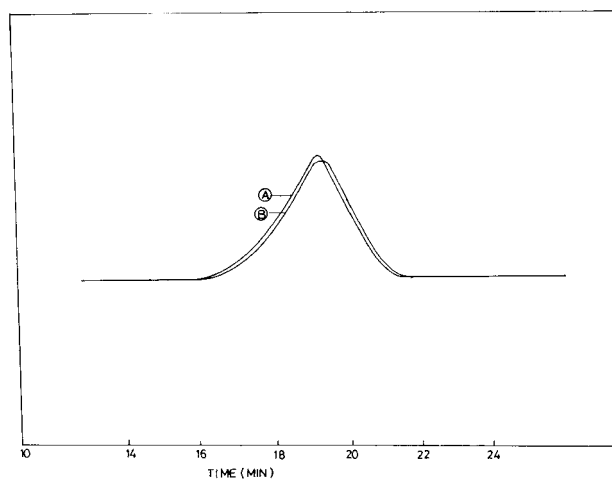


Figure 2 GPC traces of (A) CTNR and (B) depolymerized NR.

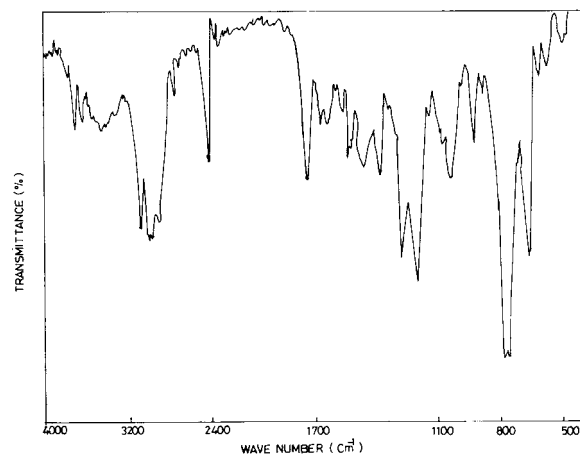


Figure 3 IR spectrum of depolymerized NR.

Analysis of Carboxy-Terminated Liquid Natural Rubber (CTNR)

Analysis of CTNR was carried out by infrared spectroscopy (IR), proton magnetic resonance spectroscopy ($^1\text{H-NMR}$), thermogravimetric analysis (TGA), and gel permeation chromatography (GPC).

IR spectra were taken on a Perkin-Elmer Model 882 IR spectrometer.

The $^1\text{H-NMR}$ spectra of the samples were recorded from a solution in CDCl_3 using a JEOL-EX 90 spectrometer.

TGA was carried out using a Universal VI.12 ETA instrument at a heating rate of 20°C per min.

Molecular weight of CTNR and depolymerized natural rubber was determined on a Water Associates GPC model 2000.

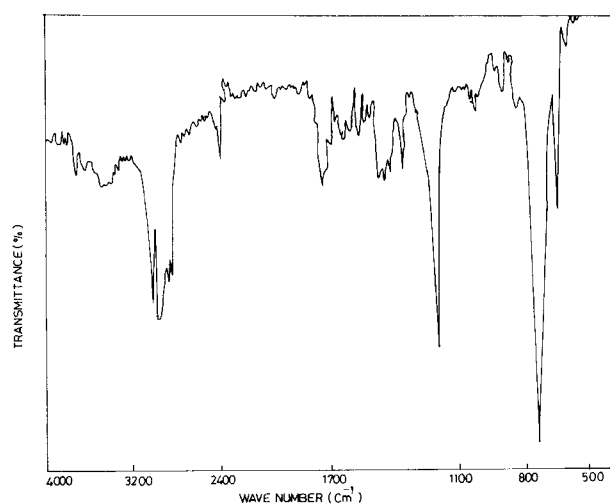


Figure 4 IR spectrum of CTNR.

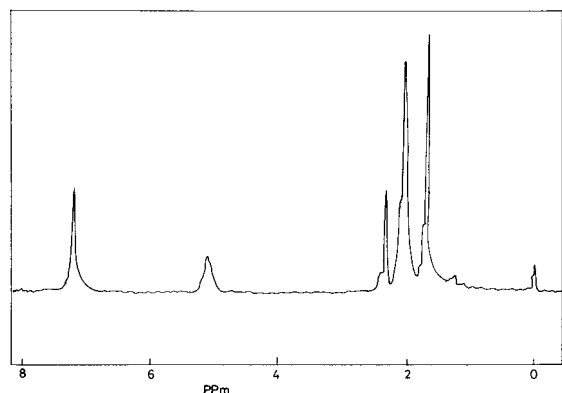


Figure 5 $^1\text{H-NMR}$ spectrum of depolymerized NR.

The optimum concentration of CTNR for attaining maximum properties in silica and carbon black-filled NBR compounds were determined by varying the amount of CTNR in the mix as per the formulations in Table I. The optimum cure times of the compounds were determined on a Mon Santo Moving Die Rheometer-2000.

CTNR was added in NBR as per formulations given in Table II.

Rubber compounds were molded in an electrically heated laboratory hydraulic press at 150°C up to their optimum cure time.

Dumb-bell-shaped tensile test pieces were punched out of these compression-molded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Prolific Universal Testing Machine model 1.3 D using a crosshead speed of 500 mm/min conforming to ASTM D412 (1980). The hardness (shore A) of the molded samples was tested using a Zwick 3115

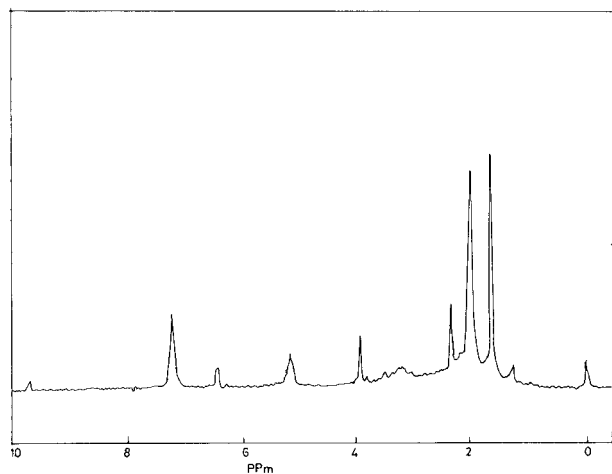


Figure 6 $^1\text{H-NMR}$ spectrum of CTNR.

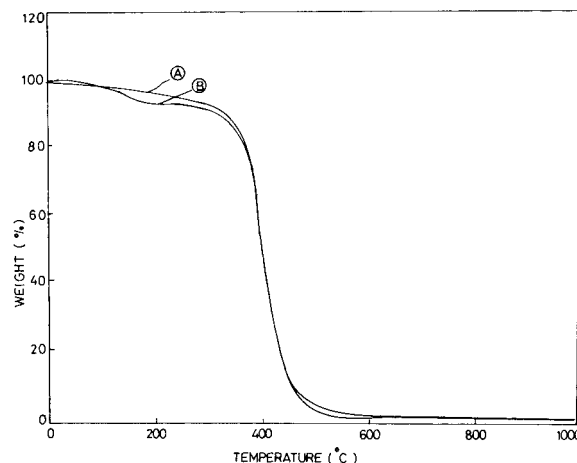


Figure 7 TGA traces of (A) Depolymerized NR and (B) CTNR.

hardness tester in accordance with ASTM D-2240. The compression set of the samples was calculated with ASTM D-395 methods. Rebound resilience of the vulcanizates was evaluated using a Dunlop Tripsometer (BS 903, part 22, 1950). Abrasion loss was tested by using a DIN Abrader. The heat build up of the vulcanizates were measured using Goodrich Flexometer conforming to ASTM D 623-67 Method A. Retention in tensile properties, compression set, heat buildup, resilience, and abrasion loss of the vulcanizates were evaluated after aging the samples at 100°C for 24 h. Oil resistance of the NBR vulcanizates containing CTNR was studied by keeping the samples in transformer oil and engine oil at room temperature for 48 h and finding the retention in tensile properties and hardness. Swelling in oil of the vulcanizates containing CTNR was studied by keeping a known weight of the sample in transformer oil and engine oil for 48 h at room temperature and then measuring the increase in weight.

RESULTS AND DISCUSSION

Figure 1 shows the variation in acid number with exposure time in presence of and in the absence of maleic anhydride. The acid number increases first, reaches a maximum, and then decreases at an exposure time of 10 h. This shows that after an optimum time of exposure, all the maleic anhydride molecules are attached to the depolymerized natural rubber. The decrease in acid number (carboxyl content) after an optimum time of expo-

Table III Variation in Properties with the Concentration of CTNR as per the Formulations in Table I

Properties	1	2	3	4	5	6	7	8	9	10	11	12
Tensile strength (N/mm ²)	4.69	6.45	10.16	12.59	10.92	8.86	9.5	17.5	17.6	20.93	15.3	14.5
Elongation at break (%)	387	505	420	558	542	482	454	434	485	498	405	384
Modulus at 300% elongation (N/mm ²)	3.44	6.18	8.53	8.57	7.35	6.63	5.18	11.8	9.3	9.75	10.3	11.1
Hardness (Shore A)	58	56	58	57	55	59	64	69	67	68	67	69

sure may be due to the decarboxylation reaction in presence of UV light.

Figure 2 shows the GPC traces of depolymerized NR (\overline{M}_w 56,530) and CTNR (\overline{M}_w 56,631). The molecular weight of CTNR is very close to that of depolymerized NR.

Figures 3 and 4 show the IR spectra of depolymerized NR and CTNR, respectively. The IR spectrum of depolymerized NR shows peaks at 3028 cm⁻¹ and 2971 cm⁻¹ corresponding to aliphatic CH, at 1664 cm⁻¹ due to C=C, at 1458 cm⁻¹ and 1380 cm⁻¹ due to —CH₃ and at 765 cm⁻¹ due to —C(CH₃)=CH. The IR spectrum of CTNR shows additional peaks at 3000–2500 cm⁻¹ due to bonded —O—H stretching in an acid, 1702 cm⁻¹ (s) due to —C=O stretching and 1611 cm⁻¹ due to carboxylate anion stretching. This indicates the chemical binding of maleic anhydride onto depolymerized NR during UV irradiation. There is no change observed in the absorption band of the isoprene unit. The attachment of maleic anhydride molecule may be at α -methylene carbon atom of depolymerized NR.

Figure 5 shows ¹H-NMR spectrum of depolymerized NR. There are peaks at $\delta = 5.1$ (—C=C), $\delta = 1.2$ (—CH₂) and $\delta = 1.65$ ppm

(—CH₃). Figure 6 shows ¹H-NMR spectrum of CTNR, which shows additional peak at $\delta = 9.768$ (carboxylic proton). The peak due to acidic proton at $\delta = 2$ –2.5 ppm may be masked by the presence of the —C=C— group in CTNR. This again indicates the chemical binding of maleic anhydride onto depolymerized NR.^{2,7}

Figure 7 shows the thermograms of CTNR and depolymerized NR. The 6.5% weight loss in CTNR at 221°C may be due to the decarboxylation.

Table III shows the variation in tensile strength, elongation at break, modulus at 300% elongation, and hardness of the vulcanizates given in Table I. Tensile strength, elongation at break, and modulus are found to increase with the concentration of CTNR, reaches a maximum and then decreases in silica filled vulcanizates. Tensile strength and elongation at break shows the same trend in carbon black-filled vulcanizates, but modulus values are comparable. The decrease in properties after an optimum level may be due to the incompatibility of the natural rubber part of CTNR with NBR. The hardness values are comparable for all these vulcanizates. This shows that CTNR can be used as a plasticizer in NBR.

Table IV Variation in Tensile Properties and Hardness before and after Aging of the Compounds Shown in Table II

	A	B	C	D	E	F
Before aging						
Tensile strength (N/mm ²)	6.55	12.8	14.6	18.18	21.17	22.42
Elongation at break (%)	520	562	580	439	512	530
Modulus at 300% elongation (N/mm ²)	6.19	9.12	10.13	11.94	9.82	10.5
Hardness (Shore A)	56	57	59	69	68	69
After aging at 100°C for 24 h						
Tensile strength (N/mm ²)	4.42	8.83	11.24	15.51	18.82	20.02
Elongation at break (%)	323	396	408	300	361	412
Modulus at 300% elongation (N/mm ²)	5.02	9.91	11.86	13.82	15.05	14.32
Hardness (Shore A)	62	64	66	72	73	74

Table V Variation in Properties before and after Aging

	A	B	C	D	E	F
Before aging						
Rebound resilience (%)	51.87	53.79	55.12	45.94	46.33	48.89
Heat buildup ($\Delta T^{\circ}\text{C}$)	33	32	30	46	45	41
Compression set (%)	13.81	13.61	12.72	15.65	12.8	10.81
Abrasion loss (mm^3)	174.8	180	184	95.4	99.8	103.1
After aging at 100°C for 24 h						
Rebound resilience (%)	51.15	53.26	54.87	44.63	45.66	48.25
Heat buildup ($\Delta T^{\circ}\text{C}$)	32	30	29	44	44	40
Compression set (%)	9.16	7.81	7.02	9.61	8.11	6.98
Abrasion loss (mm^3)	175.8	169.9	175.8	98.9	95.4	96.3

The optimum cure times of the compounds is found to decrease with the amount of CTNR, as shown in Table I. This may be due to the ionic cross linking involving CTNR and NBR.

Table IV shows the tensile properties of the vulcanizates shown in Table II, before and after aging for 24 h at 100°C . Tensile strength and elongation at break of the vulcanizates were found to be better, when dioctyl phthalate (DOP) was replaced by CTNR. Modulus values are comparable for all these vulcanizates. Superior tensile properties were observed when DOP was partially replaced by CTNR. Traces of MgO is found to improve the vulcanizate properties.⁴ The retention in tensile properties, after aging, of the vulcanizates containing CTNR, is due to the lower volatility of CTNR. The increase in modulus and hardness, after aging, is attributed to the postcuring of NBR. This again shows that CTNR is a good plasticizer for NBR.

Table V shows the variation in rebound resilience, heat buildup, compression set, and abrasion loss of the compounds shown in Table II, before and after aging. The rebound resilience and heat buildup values of both silica and carbon black-filled NBR vulcanizates containing CTNR are better than those containing DOP alone. This may be due to the NR part of CTNR. Abrasion loss values are slightly higher for the vulcanizates containing CTNR; but, abrasion resistance is superior for the vulcanizates containing CTNR after aging.

Table VI shows the variation in tensile strength, elongation at break, modulus, and hardness of the vulcanizates A, C, D, and F given in Table II, before and after extraction of the samples in transformer oil and engine oil. The retention in tensile properties after oil extraction shown by both the silica and carbon black-filled vulcanizates containing CTNR is due to the

Table VI Properties before and after Oil Extraction for 48 h at Room Temperature

	A	C	D	F
Tensile strength (N/mm^2)	6.55	14.6	18.18	22.42
Elongation at break (%)	520	580	439	530
Modulus at 300% elongation (N/mm^2)	6.19	10.13	11.94	10.5
Hardness (Shore A)	56	59	69	69
After extraction in transformer oil				
Tensile strength (N/mm^2)	4.42	14.2	17.84	21.2
Elongation at break (%)	454	488	415	498
Modulus at 300% Elongation (N/mm^2)	4.83	11.53	11.99	11.33
Hardness (Shore A)	53	56	65	68
After extraction in engine oil				
Tensile strength (N/mm^2)	4.48	14.41	16.98	20.9
Elongation at break (%)	432	488	383	490
Modulus at 300% elongation (N/mm^2)	4.95	11.38	13.8	10.8
Hardness (Shore A)	51	56	66	66

Table VII Percent Weight Increase in Oil

Type of Oil	A	C	D	F
Transformer oil	0.173	0.758	0.093	0.226
Engine oil	0.156	0.189	0.097	0.185

lower extractability of the polymeric plasticizer by oils.

Table VII shows the percentage increase in weight of the vulcanizates A, C, D, and F shown in Table II, in transformer oil and engine oil. The lower increase in weight of the vulcanizates containing the conventional plasticizer may be due to the leaching of the plasticizer by oils. The compounds containing CTNR gets attached to NBR during vulcanization, making it nonextractable.

CONCLUSIONS

1. Maleic anhydride can be chemically attached to depolymerized natural rubber by a photochemical reaction.
2. The product CTNR can replace the conventional plasticizers either partially or fully in NBR compounds.
3. This polymeric plasticizer could reduce

heat buildup improve rebound resilience, compression set, and aging resistance of the NBR vulcanizates.

4. Oil resistance of NBR vulcanizates could be improved by the use of CTNR.
5. A combination of conventional plasticizer and CTNR is found to be promising.

The authors wish to express their gratitude to the University Grants Commission, New Delhi, India, for financial support.

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