Dichlorocarbene Modification of Natural Rubber and Its Role as a Modifier in Blends of Natural Rubber and Hydrogenated Nitrile Rubber

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Received 18 June 2004; accepted 31 May 2005
DOI 10.1002/app.23184

ABSTRACT: Dichlorocarbene modification of natural rubber (NR) carried out by alkaline hydrolysis of chloroform in presence of cetyl trimethyl ammonium bromide as phase-transfer catalyst was investigated. Extent of chemical reaction was characterized by estimation of chlorine content and FTIR studies. Rate of dichlorocarbene addition depends on the time and temperature of reaction. Reaction carried out at 60°C for 2 h yielded a material with a chlorine content of 15%. Chemical modification of NR was accompanied by introduction of chlorine through cyclopropyl ring to the main chain of NR as revealed from FTIR studies. As level of chlorination increased, the physical nature of NR changed from a soft flexible state to a hard nontacky form. Blends of NR with hydrogenated nitrile rubber (HNBR) containing three to seven parts of dichlorocarbene-modified NR (DCNR) of chlorine content 15% could be prepared by conventional mill mixing. Incorporation of DCNR into blends of NR and HNBR promoted polar interaction between the chlorine segments and acrylonitrile segments of the blend as shown from the shift in characteristic IR absorption peaks and shift in T_g from DSC studies. As a consequence, DCNR acted as an interface modifier in blends of NR and HNBR. Blends of NR and HNBR containing DCNR showed a considerable improvement in cure behavior, physical properties, and ageing characteristics in oil, ozone, and high temperature compared to pure blends of NR and HNBR. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4401–4409, 2006

Key words: elastomers; modification; blends; immiscibility; mechanical properties

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INTRODUCTION

Modified forms of natural rubber (NR) and polar rubbers play a vital role to enhance vulcanizate characteristics of blends of NR and polar rubbers like acrylonitrile butadiene rubbers (NBR). Methyl methacrylate-grafted NR (MG 30) and chloroprene rubber (CR) impart improved physical characteristics, when added in small proportions to blends of NR and NBR, due to the polar–polar interactions that are possible in the blends. NBR/ethylene propylene rubber (EPR) and CR/EPR blends mix more rapidly in the presence of small amounts of chlorinated polyethylene.[1,2]

The double bonds present in NR provide active sites for chemical modification.[3,4] The reaction of carbenes with olefins to form cyclopropyl derivatives had been used to modify elastomers. Pinazzi and Levesque[5] and Barentsvich et al.[6] found that carbene addition had a significant influence on the properties of polydienes. Dichlorocarbene modification on styrene butadiene rubber (SBR) is reported to increase the solvent and flame resistance.[7] In addition, it plays a significant role in improving blend characteristics of SBR with polar rubbers like CR and NBR.[8] Thus, it seems rational that dichlorocarbene-modified NR (DCNR) would impart enhanced physical characteristics in blends of NR with a polar rubber like hydrogenated NBR (HNBR).

HNBR is widely used as vibration dampers, timing belts, power transmission belts, and bearings because of its ideal balance of properties like excellent heat and oil resistance coupled with good mechanical properties.[9–11] It combines the oil and fuel resistance of NBR with the heat and oxidation resistance of EPDM rubber. NR is a versatile elastomer and finds application in a variety of products. Good strength, high fatigue resistance, high resilience, and low heat build-up make it a good polymer in various engineering products. But, it has very poor oil, ozone, and heat resistance. Blends of NR and HNBR would be ideal choice for applications requiring good high temperature oil ageing characteristics in dynamic conditions with low temperature flexibility like seals, gaskets, etc. Normally, blends of NR with polar rubbers result in materials with inferior physical properties because of incompatibility arising from a difference in solubility parameter and cure rate. These problems are alleviated to an extent by use of compatibilizers that reduce the interfacial tension between the polymers, proper blending methods, judicious choice of curative,

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Journal of Applied Polymer Science, Vol. 101, 4401–4409 (2006)

TABLE I
Formulation for Preparation of DCNR

ISNR 5	10 g
Toluene	300 ml
Chloroform	30 ml
50% NaOH	35 ml
CTAB	0.85 g
Time	0–25 h
Temperature	40, 50, and 60°C

and by vulcanization of one of the phases prior to final processing.

In this work, an attempt is made to modify NR by dichlorocarbene addition through the alkaline hydrolysis of chloroform using cetyl trimethyl ammonium bromide (CTAB) as a phase transfer agent and to evaluate its effect in blends of NR and HNBR for improvements in vulcanizate characteristics.

EXPERIMENTAL

Materials

NR used in this study was ISNR 5 grade obtained from Pilot Crumb Rubber Factory, Rubber Board, Kottayam, India. HNBR used was Zetpol 2010 grade obtained from Nippon Zeon Company, Japan, with 36% bound ACN content, iodine value 11 g/100 g and Mooney viscosity ML(1 + 4)100°C − 85.

Preparation of DCNR

The DCNR used was prepared by alkaline hydrolysis of chloroform, using CTAB as phase-transfer catalyst according to the method suggested by Makoscza and Wawrzyniewicz[12] and developed by Joshi et al.[13] NR dissolved in toluene was taken in a three-necked round-bottom flask fitted with a magnetic stirrer. To this, the phase-transfer catalyst was added and the mixture was stirred well. Chloroform was added drop wise followed by a 50% solution of sodium hydroxide, with constant stirring. The reaction product was separated from solution and washed with hot and cold water until free of chlorine. The product was coagulated with isopropyl alcohol. The reaction conditions, such as concentration of reagents, temperature, and time, are given in Table I. The modification was monitored at different intervals by measurement of chlorine content, using Volhard titration method.[14] DCNR of chlorine contents 15%, 20%, and 35% were used in this investigation.

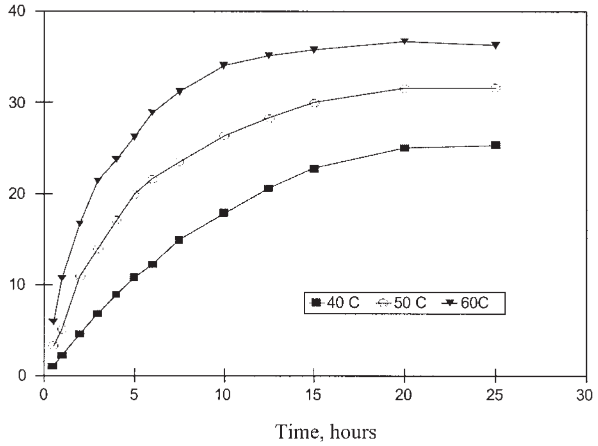


Figure 1 Plots of percentage of chlorine *versus* time, at temperatures of 40, 50, and 60°C.

TABLE II
Formulations of the Mixes

Ingredients	NR	HNBR	NH	NHC3	NHC7	NHB	HHC7B
NR	100	—	50	50	50	50	50
HNBR	—	100	50	50	50	50	50
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMTD	1.5	1.5	1.5	1.5	1.5	1.5	1.5
MBT	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	0.5	0.5	0.5	0.5	0.5	0.5	0.5
DCNR[a]	—	—	—	3.0	7.0	—	7.0
GPF, N660						50	50
Naphthenic oil						1.5	1.5
DOP						1.5	1.5

TMTD, tetramethylthiuram disulfide; MBT, mercaptobenzothiazole; DOP, dioctyl pthalate.

[a] DCNR of three levels of modification.

Preparation of rubber blends

The formulations of the mixes are given in Table II. Rubber compounds were prepared on a laboratory size two-roll mill (15 × 30 cm^2) at a friction ratio of 1:1.25 as per ASTM D 3182–89. The temperature of the rolls was controlled by passing cold water. For the preparation of the blend, NR and HNBR were first

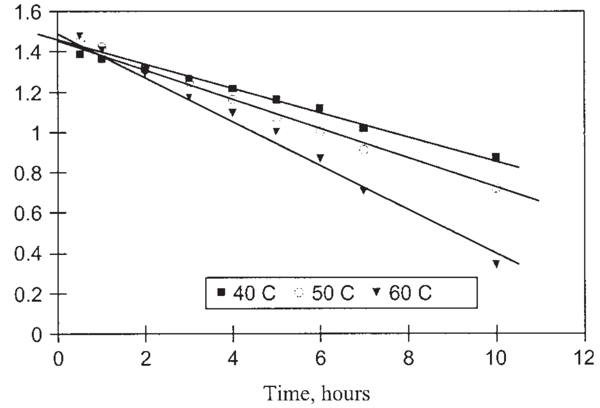


Figure 2 Rate of dichlorocarbene modification based on plots of log ($C_\infty - C_t$) versus time.

TABLE III
IR Absorption Data for DCNR

IR absorption wave length (cm^{-1})	NR	DCNR	IR spectral assignment
723	Present	Low intensity	*cis*-CH═CH—
914	Present	Absent	—CH═CH$_2$
964	Present	Present	*trans*-CH═CH—
780	Absent	Present	C—Cl
1020	Absent	Present	Cyclopropyl ring
1377	Present	Present	—CH$_3$

masticated, blended together, and then the compounding ingredients were added as per standard mixing procedure. For the modified blend, DCNR was masticated, blended with HNBR, and then blended with NR. Cure characteristics were studied using a Monsanto rheometer R100 at 150°C according to ASTM D 2705. The rubber compounds were vulcanized to their respective optimum cure time in a hydraulic press at 150°C at a pressure of 45 kg/cm^2 on the mold.

Characterization techniques

IR spectra were recorded by a Shimadzu 8101 Fourier transform infrared spectrophotometer, using pyrolysate of the samples. Samples were heated in a fusion tube and the condensed vapors are collected on the surface of sodium chloride cell to form a uniform film, and this film was used to record the IR spectra. DSC studies were carried out using a differential scanning calorimeter model Toledostar SW7 supplied by Mettler Co., Germany, at a heating rate of 20°C/min in nitrogen atmosphere. T_g was taken as the mid point of the tangent of the curve, with maximum slope in the regions of transition. The tensile properties and tear resistance of the vulcanized blends were measured using Instron tensile testing machine 4148, at a cross head speed of 500 mm/min. Air ageing resistance was assessed by measuring the change in physical properties after ageing at 120°C for 5 days as per ASTM D 572–99. Oil ageing was carried out by immersion of the samples in ASTM oils No. 1, 2, and 3 at 70°C for 5 days as per ASTM D471–98. Ozone ageing was conducted at a temperature of 38.5°C and concentration of 50 pphm using an ozone chamber (MAST Development Co., USA) as per ASTM D 1149–81. The other mechanical properties were determined by the relevant ASTM standards.

RESULTS AND DISCUSSION

Preparation and characterization of DCNR

Effect of time and temperature on chlorination

The extent of reaction based on chlorine content at three different temperatures 40, 50, and 60°C are shown in Figure 1. The dichlorocarbene addition is fast in the initial stages but decreases at later stages of reaction. The rate of reaction almost levels off after about 17 h. As temperature of reaction increases, rate of reaction as measured by chlorine content increases.

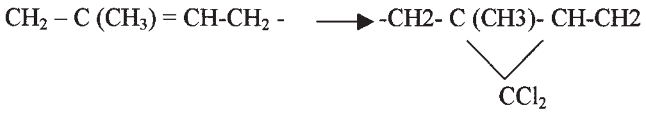
Figure 2 shows change in chlorine content, expressed as log $(C_\propto - C_t)$ versus time, where $C_\propto$ is the maximum chlorine percentage obtained at a particular temperature and C_t is the chlorine percentage at a particular time t. Linearity of the plots show that modification reaction proceeds according to first-order kinetics. Calculated rate constant (k) of the reactions are 1.33×10^{-5}, 2.48×10^{-5}, and 3.33×10^{-5} at 40, 50, and 60°C, respectively. The activation energy of reaction calculated from linear plots of log k *versus* $1/T$ is found to be 39.7 kJ/mol.

FTIR characterization

The band of interest for characteristic absorption is in the region 1050–740 cm^{-1} and is given in Tables III and IV. As modification proceeds, there is change in absorption due to cis double bond (—CH═CH—) and vinyl group (—CH═CH$_2$) while absorption due to trans double bond remains unchanged. Two new peaks appeared in the modified rubber; one at 780 cm^{-1} due to incorporation of chlorine (—C—Cl) and another at 1020 cm^{-1} due to presence of cyclopropyl ring. The cis double bonds are readily attacked by dichlorocarbene, and even at low levels of modification, the intensity due to double bonds is greatly reduced. The IR absorption characteristics are consistent with formation of cyclopropyl rings and loss of unsaturation of NR, and the modification is given in Scheme 1.

TABLE IV
IR Absorption Peak Ratios for DCNR

Chlorine (%)	cis-CH═CH—/—CH$_3$ 723/1377	C—Cl/—CH$_3$ 780/1377	trans-CH═CH—/—CH$_3$ 964/1377	Cyclopropyl/—CH$_3$ 1020/1377
15	0.0416	0.0416	0.2183	0.0410
20	0.0196	0.0590	0.2176	0.049
30	723 peak absent	0.0937	0.2180	0.0968



$$CH_2 - C\,(CH_3) = CH\text{-}CH_2\text{ -} \longrightarrow \text{-CH2- }\underbrace{\text{C (CH3)- CH}}_{CCl_2}\text{-CH2}$$

Scheme 1 Chemical change taking place during dichlorocarbene modification.

Effect of addition of DCNR in NR/HNBR blend

Cure characteristics

Cure characteristics of the pure and DCNR-incorporated 50/50 NR/HNBR blend compounds are given in Table V. The blend containing seven parts of DCNR of 15% chlorine content records a higher rheometric torque, for both gum and filled blends, showing the formation of additional crosslinks in the presence of DCNR. With the incorporation of DCNR, there is marginal increase in cure time. As expected, cure time decreases in presence of filler. Interactions leading to chemical reactions between chlorine-containing polymers and HNBR without the aid of vulcanizing agents resulting in an increase in rheometric torque has been reported earlier.[15] In presence of DCNR, the mix is more homogeneous and the curatives are possibly more evenly distributed, resulting in the formation of more crosslinks. Mixes containing higher levels of chlorine (20–35%) show a lower rheometric torque as compared with pure blend (Fig. 3). As the extent of chlorination increases the DCNR becomes harder and does not mix uniformly in NR. So characteristics of blends containing DCNR of 15% chlorine content are only studied.

IR spectroscopic studies

IR spectra of NR/HNBR blends are given in Figure 4 and spectral data are given in Table VI. HNBR shows characteristic IR absorption at 2237 cm^{-1} for —C≡N linkage and at 1641 cm^{-1} for C═O linkage. Formation of C═O and —CHO groups in HNBR have been reported earlier to be due to oxidative degradation.[16] Examination of Figure 4 reveals two regions that show marked difference in their absorption for modified blend in comparison with pure blend: 2200–3000 cm^{-1} and 1800–1500 cm^{-1} regions, which corresponds to the absorption of —C≡N and C═O, respectively. Absorption due to —C≡N stretching at 2237 cm^{-1} in pure NR/HNBR blend is shifted to 2240 cm^{-1} for the blend containing DCNR. Pure blend also shows an absorption at 1641 cm^{-1} due to —(C═O) stretching, which is shifted to 1645 cm^{-1} in modified blend. The absorption at 1017 cm^{-1} due to —(C—O) stretching in pure blend shifts to 1019 cm^{-1} in presence of DCNR. These observations indicate that there is interaction between the DCNR and HNBR.

TABLE V
Cure Characteristics of the Blend at 150°C

Mix	Minimum torque (dN m)	Maximum torque (dN m)	Optimum cure time (min)
NH	4.0	35.5	6.00
NHC3	5.0	37.5	6.25
NHC7	5.0	39.0	9.00
NHB	9.5	45.5	4.50
HNC7B	10.0	51.0	7.00

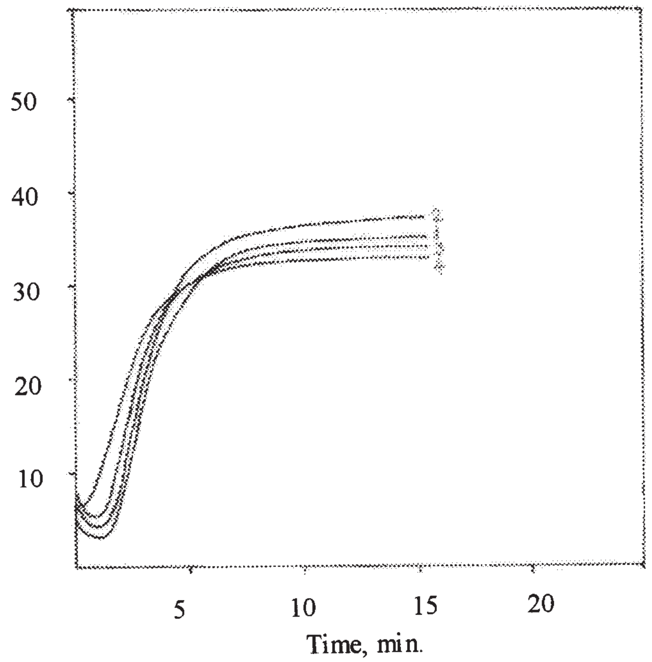


Figure 3 "Monsanto" rheographs of 1.50/50 NR/HNBR blend and blends containing seven parts DCNR of varying chlorine content 2.15%, 3.20%, and 4.35%.

The addition of DCNR could promote dipole interaction in blends. Such interactions are known to affect the characteristic IR absorption peaks as reported earlier.[17,18] Tabb and Koenig[19] described a shift in —(C—O) absorption frequencies of dioctylpthalate (DOP) due to its interaction with polyvinylchloride. Coleman et al.[20] have attributed a shift in —(C—O) absorption band of poly(methyl methacrylate) due to interactions involving carbonyl group in compatible blend of poly(vinylidene fluoride) and poly(methyl methacrylate).

DSC studies

DSC traces of pure NR/HNBR blend and blend containing two different levels of DCNR of 15% chlorine content are shown in Figure 5 and results are summarized in Table VII. DCNR shows a T_g at −5°C. The blends exhibit two separate T_g's one at about −63°C

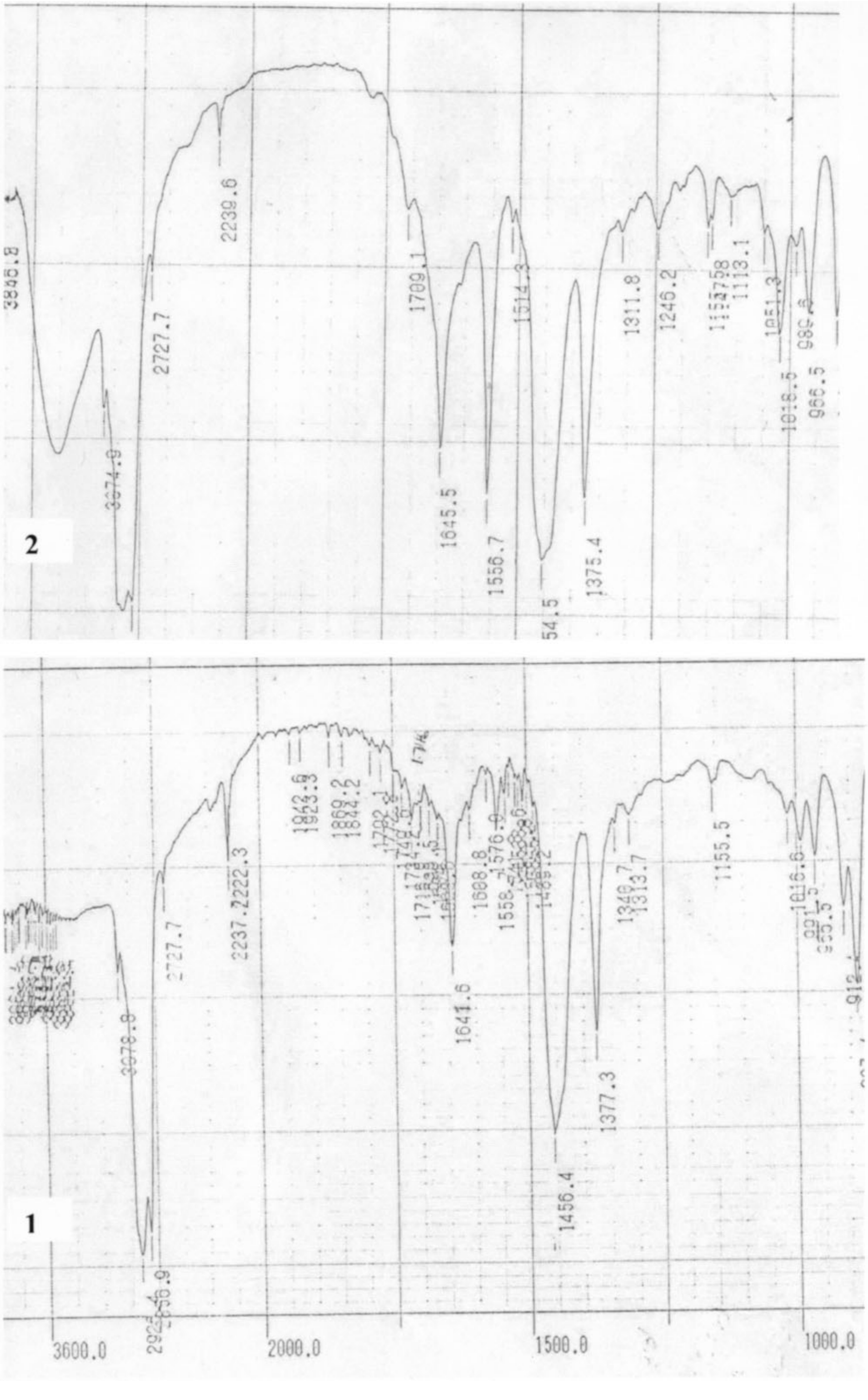


Figure 4 IR spectrographs of (1) NH and (2) NHC7.

and the other at about −25°C, which corresponds to the glass-transition temperature of NR and HNBR, respectively. The presence of two peaks for transitions of NR and HNBR in the binary blends reveals that blends of NR and HNBR are not compatible completely. There is only slight change in T_g of both NR and HNBR on addition of DCNR. This indicates that DCNR is not a very good compatibilizer. With the addition of DCNR to the blend, T_g of both NR and HNBR shifts to a slightly higher temperature. Shifting

TABLE VI
Characteristic IR Absorption for the Blends of NR/HNBR

Mix	IR absorption, wave length, cm^{-1}	Peak assignment
HNBR	2237	—C═N stretch
	1641	)C═O stretch
	1017	—C—O stretch
NH	2237	—C═N stretch
	1641	)C═O stretch
	1017	—C—O stretch
NHC7	2240	—C═N stretch
	1645	)C═O stretch
	1019	—C—O stretch

TABLE VII
DSC Peaks of NR, HNBR, DCNR (15% Chlorine Content), and Blends

Sample	T_{g1} (°C)	T_{g2} (°C)
NR	−63.7	—
HNBR	—	−24.4
DCNR	−5.0	
NH	−63.6	−25.9
NHC3	−63.0	−25.1
NHC7	−63.0	−24.8

of T_g of a blend constituent to a higher temperature due to interaction with compatibilizer has been reported earlier.[21] This observation suggests the possibility of interactions between DCNR and the blend constituents and thus it acts as an interface modifier in blends of NR/HNBR.

Physical properties

The physical properties of NR/HNBR blends of different composition (vulcanized using the same formulation as in Table II) are summarized in Table VIII. Blends record inferior mechanical properties with respect to tensile strength, compression set, and heat build-up as compared to pure NR and HNBR. Among the different blends, 50/50 blend maintain comparatively better mechanical properties and hence this blend ratio is chosen for further study.

The mechanical properties of the 50/50 blends with different concentrations of DCNR of 15% chlorine content are given in Table IX. Compared to pure blends, DCNR added blends show better mechanical properties. As in the case of tensile strength, tear strength also improves on addition of DCNR. This is due to the formation of uniformly distributed finer domains that tend to elongate at higher strains and effectively prevent tear propagation. The compression set decreases and resilience increases due to the enhanced level of crosslink formation. It is also noted that improvement in physical properties are more prominent in presence of filler. The 50-phr GPF black-filled blend containing DCNR show considerable enhancement in tensile strength, modulus, tear strength, and resilience. The compression set and heat build-up characteristics are superior as compared to the pure blend. This is probably due to the reinforcing effect of filler as a result of better uniform distribution of filler among the two phases in presence of DCNR.

Even though it is an immiscible blend as seen from DSC traces, there is interaction between DCNR and HNBR as observed from IR data and also higher level of crosslinking in presence of DCNR as both NR and DCNR has sufficient double bonds to give a satisfactory level of cure. Due to these facts, even though NR/HNBR blend is immiscible, there is considerable enhancement of physical properties in presence of DCNR.

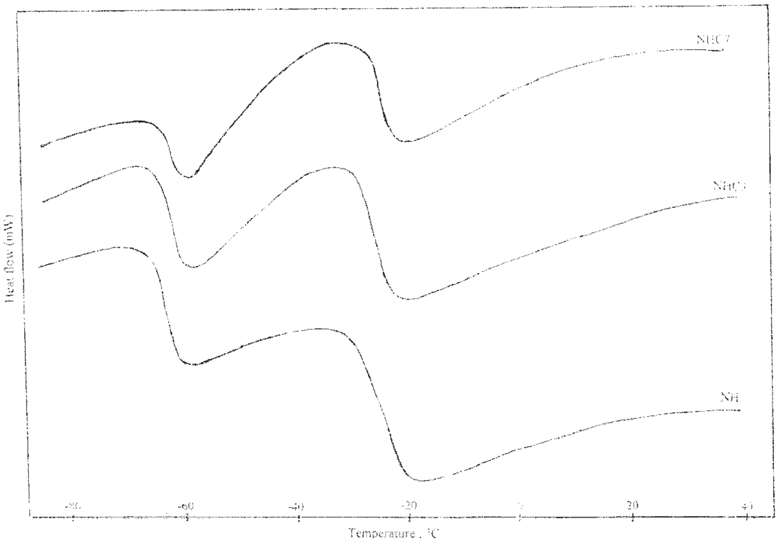


Figure 5 DSC traces of NH, NHC3, and NHC7.

TABLE VIII
Physical Properties of NR/HNBR Blend with Different Blend Composition

Parameter	NR	NH 75/25	NH 50/50	NH 25/75	HNBR
Tensile strength (MPa)	18.0	10.74	10.64	14.2	21.1
Elongation-at-break (%)	730	750	740	740	720
Modulus 100% (MPa)	0.85	0.88	0.93	1.04	1.10
Modulus 300% (MPa)	1.83	1.55	1.52	1.15	1.45
Tear strength (kN/m)	20.8	20.6	20.5	19.1	16.9
Hardness (Shore A)	37	40	44	45	49
Resilience (%)	72	70	69	67	65
Compression set at 70°C for 22 h (%)	8.3	26.92	46.2	69.4	30.1
Heat build-up, ΔH (°C)	6	16	56	57	25
Dynamic set (%)	0.08	2.24	10.19	10.36	2.27

TABLE IX
Physical Properties of NR/HNBR Blends

Parameter	NH	NHC3	NHC7	NHB	NHC7B
Tensile strength (MPa)	10.6	11.9	12.3	13.85	16.49
Modulus 100% (MPa)	0.93	1.12	1.13	1.82	1.84
Modulus 300% (MPa)	1.5	1.53	1.58	3.57	4.41
Elongation-at-break (%)	740	730	690	570	550
Tear strength (kN/m)	20.5	21.8	23.9	33.83	51.49
Hardness (Shore A)	44	45	45	60	61
Resilience (%)	69	70	70	54	56
Compression set at 70°C for 22 h (%)	46.2	40.9	39.0	58.4	45.6
Heat build-up, ΔH (°C)	56	48	47	63	57
Dynamic set (%)	10.19	9.37	8.89	10.8	5.77

TABLE X
Physical Properties of NR/HNBR Blends after Ageing at 120°C for 5 Days

Parameter	NR	HNBR	NH	NHC3	NHC7	NHB	NHC7B
Tensile strength (MPa)	0.93	18.0	1.93	3.76	6.07	5.79	10.2
Modulus 100% (MPa)	0.37	1.29	1.64	1.68	2.04	2.36	5.92
Modulus 300% (MPa)	—	1.47	1.88	2.04	3.46	—	—
Elongation-at-break (%)	260	680	310	360	360	280	290

Ageing characteristics

Air ageing. The tensile properties after ageing in hot air at 120°C for 5 days are shown in Table X. As known already, HNBR has excellent ageing characteristics[22] compared to NR. After ageing, the blend showed very poor tensile properties. However, the blend containing seven parts of DCNR showed a comparatively higher percent retention of modulus and tensile strength compared to pure blend. The ageing resistance of DCNR containing blend is further improved by incorporation of filler. The better ageing properties of the DCNR added blend should be due to the enhanced homogeneity during mixing and the formation of enhanced crosslinks as a result of the interface modification by DCNR as discussed earlier.

Oil ageing. The oil ageing characteristics in ASTM oils (presented in Table XI) indicate that addition of DCNR in NR/HNBR blends have comparatively good ageing characteristics based on additive average. The increased oil ageing characteristics are due to the higher level of crosslinking and increased polarity in the presence of DCNR.

TABLE XI
Oil Swelling in ASTM Oils 1, 2, and 3 after Ageing at 70°C for 5 Days and Percent Change in Mass

	ASTM oils		
Mix	No. 1	No. 2	No. 3
NR	124.41	207.68	280.81
HNBR	0.96	7.83	18.95
NH	47.39	80.44	155.56
NHC3	44.12	79.89	151.62
NHC7	42.47	79.03	145.32

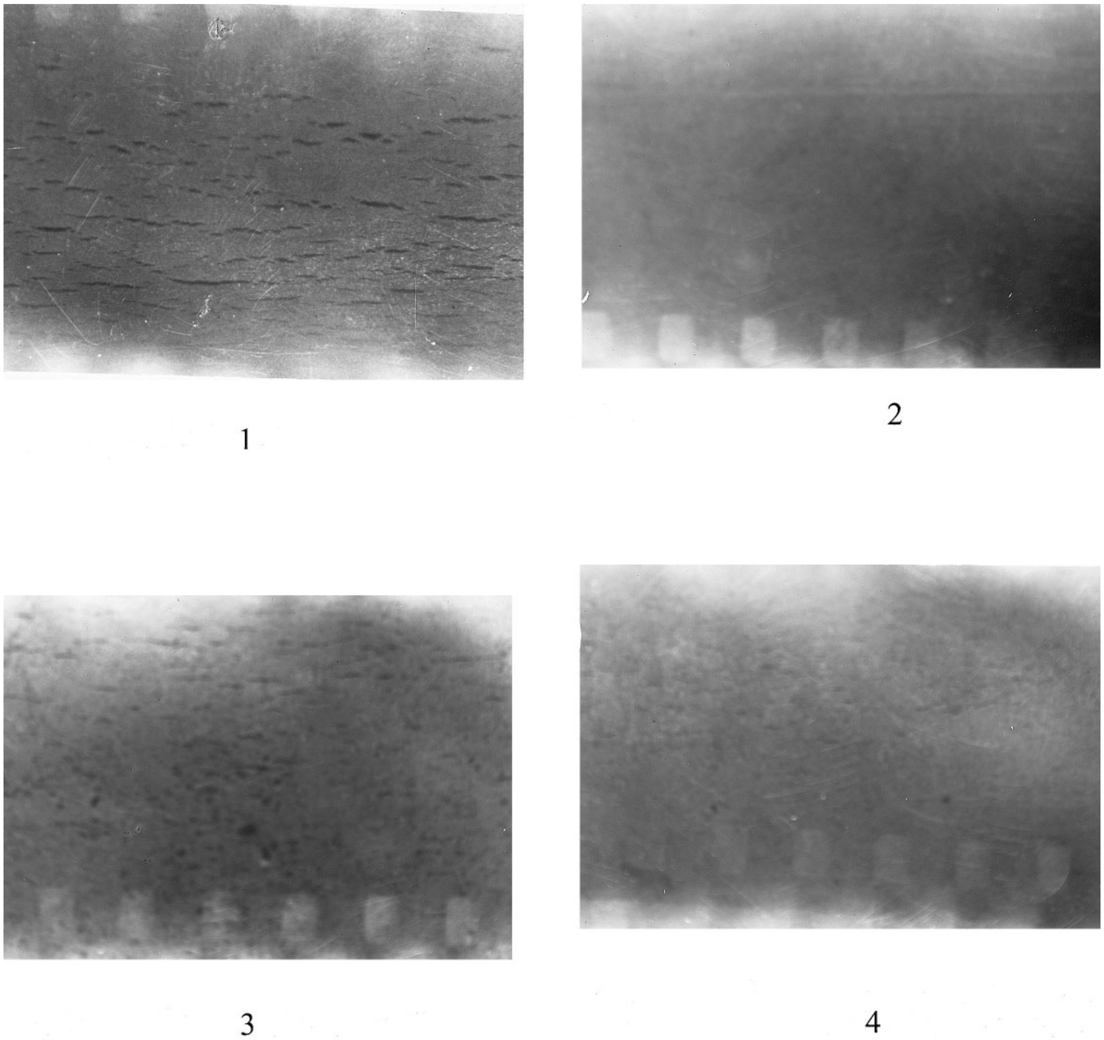


Figure 6 Samples exposed to ozone ageing at a concentration of 50 pphm. (1) NR, (2) HNBR, (3) NH, and (4) NHC7.

Ozone ageing. Ozone ageing characteristics as observed from the cracks developed after exposure for 40 h are shown in Figure 6. The crack initiation occurs in pure NR after about an hour of exposure in ozone while in blends the cracks initiation is after about 10 h. The development of crack growth is greatly reduced in blends containing DCNR.

CONCLUSIONS

DCNR having a chlorine content varying from 15 to 35% was prepared by the alkaline hydrolysis of chloroform using CTAB as phase-transfer catalyst. It was found that DCNR acted as an interface modifier in blends of NR and HNBR due to the polar–polar interactions possible. Consequently, blends of NR and HNBR containing three to seven parts of DCNR had enhanced physical properties and very good resistance to oil, high temperature, and ozone ageing as compared with pure blends.

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