

Dichlorocarbene Modification of Natural Rubber

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Dichlorocarbene modified natural rubber (NR) was prepared by aqueous alkaline hydrolysis of chloroform in a toluene solution of NR. The factors affecting the modification reaction were examined. The modified NR was characterised and its properties such as thermal stability and flammability were determined.

The processibility of the modified NR and the physical properties of the vulcanisates were determined. Various cure systems were used to prepare the vulcanisates.

The properties of NR could be modified by reactions involving its double bonds. The conversion of the double bonds through reactions with various reagents could result in improvements in ageing resistance (oxidation and thermal stability), flame retardancy, solvent resistance and other properties.

The addition of dichlorocarbene to polymers¹⁻³ including NR⁴ has been reported. However, very little work has been published on the technological properties of the modified NR. This paper describes the method of preparation used, the properties of the raw rubber and vulcanisates of the dichlorocarbene modified NR.

PREPARATION OF DICHLOROCARBENE MODIFIED NATURAL RUBBER

Dichlorocarbene modified NR was prepared by the method of alkaline hydrolysis of chloroform developed by Makosza *et al.*⁵ and improved upon by Joshi *et al.*⁴ The hydrolysis was carried out using strong aqueous sodium hydroxide (50%), a phase transfer agent and chloroform in a toluene solution of NR. Three samples of dichlorocarbene modified NR were prepared under the conditions shown in *Table 1*. Later preparations used Cetrimide instead of decyltrimethylammonium bromide as the transfer agent.

CHARACTERISATION OF DICHLOROCARBENE MODIFIED NATURAL RUBBER

Iodine Number

The iodine number is defined as the number of grammes of iodine absorbed by 100 g of polymer under specified conditions. It is a measure of the unsaturation in the polymer. The theoretical iodine number for NR is 373.6. The iodine number was used to calculate the extent of the dichlorocarbene reaction. The extent of reaction is defined here as the percentage of originally present double bonds transformed into *gem*-dichlorocyclopropanes. *Table 2* shows the calculated values of iodine number and chlorine content reflecting the theoretical extent of reaction. *Table 3* shows the iodine number and extent of reaction of the three samples of dichlorocarbene modified NR.

Chlorine Content

The dichlorocarbene reaction introduces two chlorine atoms per addition hence the chlorine content can be used as a method of determining the extent of reaction. The results for the three samples of modified NR prepared are shown in *Table 4*.

The extent of reaction calculated by the two methods (iodine number and chlorine

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TABLE 1. PREPARATION OF DICHLOROCARBENE MODIFIED NATURAL RUBBER

Sample	SMR 5 (g)	Toluene (ml)	CHCl ₃ (ml)	NaOH (ml)	Transfer agent (g)	Time (h)
1	2	100	2.5	6	0.2	4
2	5	250	6.3	15	0.4	24
3	5	250	6.3	15	0.4	48

Reaction temp: 40°C (under nitrogen atmosphere)
Transfer agent: decyltrimethylammonium bromide

TABLE 2. EXTENT OF REACTION, IODINE NUMBER AND CHLORINE CONTENT

Extent of reaction (%)	Iodine number (gI ₂ /100 g)	Chlorine content (% wt)
0	373.6	0
10	299.5	9.3
20	240.2	16.78
30	191.4	22.93
40	150.6	28.06
50	116.0	32.49
60	86.17	36.17
70	60.42	39.42
80	37.79	42.27
90	17.79	44.77
100	0.0	47.02

TABLE 3. IODINE NUMBER AND EXTENT OF REACTION OF MODIFIED NATURAL RUBBER

Sample	Iodine number ^a	Extent of dichlorocarbene reaction (%)
1	249	18.2
2	216	24.3
3	107	52.7

^aWij's solution with chloroform as solvent

content) differed by about 5% and the iodine number method consistently gave higher values. Both methods have experimental difficulties and for routine checks, the chlorine content method is preferred since it is more rapid and convenient. In

all later work, the chlorine content method was used.

TABLE 4. CHLORINE CONTENT AND EXTENT OF REACTION OF MODIFIED NATURAL RUBBER

Sample	Chlorine content ^a (% wt)	Extent of reaction (%)
1	11.47	12.7
2	16.95	20.3
3	31.58	47.8

^aFurnace fusion method

Infra-red Spectra

Infra-red spectra of thin sample films (from toluene solution) were recorded. The bands of interest are those due to carbon-carbon double bond at 1660 cm⁻¹, the carbon-chlorine at 760 cm⁻¹ and the cyclopropyl ring⁶ at 1010 cm⁻¹. The 1660 cm⁻¹ band decreased with increasing extent of reaction and the 760 cm⁻¹ and 1010 cm⁻¹ bands increased with increasing extent of reaction. The spectra were consistent with the formation of dichlorocyclopropyl rings and the loss of unsaturation.

EFFECTS OF EXPERIMENTAL CONDITIONS ON THE DICHLOROCARBENE ADDITION TO NATURAL RUBBER

The amount of bound chlorine, which is related to the extent of reaction, in the modified NR and the physical nature of the rubber depended very much on the experimental conditions. Some observations on

the effects of experimental conditions on the dichlorocarbene addition to NR are discussed here.

Concentration of reagents affected the rate and temperature of the reaction. Very high concentration of reagents caused rapid reaction and rapid heat generation. The reaction mixture shown in *Table 5* generated sufficient heat to cause the mixture to boil and yield a charred product. Cooling the reaction vessel in a bath of cold running water to 28°C, resulted in the same mixture producing a mass of brown material which has a chlorine content of 43.01% in 1 hour.

TABLE 5. COMPOSITION OF A HIGH CONCENTRATION REACTION MIXTURE FOR THE PREPARATION OF MODIFIED NATURAL RUBBER

Compound	Amount
SMR 5	40 g (0.6 m isoprene unit)
Cetrimide (cetyltrimethyl- ammonium bromide)	1.7 g (0.06 m)
Chloroform	215 g (1.8 m)
Sodium hydroxide	180 g (4.5 m)) added as
Water	180 g) 50% solution
Toluene	1.5 litres

The composition used for the preparation of most of the modified rubber used in this work is shown in *Table 6*.

TABLE 6. COMPOSITION FOR THE PREPARATION OF DICHLOROCARBENE MODIFIED NATURAL RUBBER (REACTION TEMP: 50°C)

Compound	Amount
SMR 5	40 g
Cetrimide	1.7 g
Chloroform	144 g
Sodium hydroxide	48 g)
Water	48 g) as 50% solution
Toluene	1.5 litres

The plots of bound chlorine content against the reaction time of three compositions are shown in *Figure 1*. These plots show the influence of the transfer agent (Cetrimide) and the dichlorocarbene generating reagents. The former affected the final level of reaction and the latter had a strong influence on the rate of reaction.

The reaction temperature is another important factor in determining the extent of reaction. For example, using the composition given in *Table 6* and under similar conditions, the modified NR obtained had bound chlorine contents of 3.7% at 40°C and 5.2% at 50°C in 6 hours.

The dichlorocarbene reaction is also affected by oxygen. A rubber sample prepared under conditions as in *Sample 2* in *Table 1* but in an oxygen atmosphere has 6.18% bound chlorine compared to the 16.95% found in *Sample 2* under nitrogen.

Samples of modified NR used in the work described later were prepared in the presence of air.

PROPERTIES OF DICHLOROCARBENE MODIFIED NATURAL RUBBER

Physical Nature

Modified NR samples with chlorine content greater than 25% were hard materials and showed very little rubbery characteristics. This is in contradiction to a report⁴ that such rubber with 39% chlorine is still rubbery. Freshly prepared modified NR (>25% chlorine) could be dissolved in solvents and plastic-like films could be cast from these solutions. The best solvent was chloroform. The solubility of the modified rubbers depended on the bound chlorine content. Highly modified rubbers had very low solubility of less than ½%. Films cast from solutions of modified rubber were less flexible compared to polyethylene films.

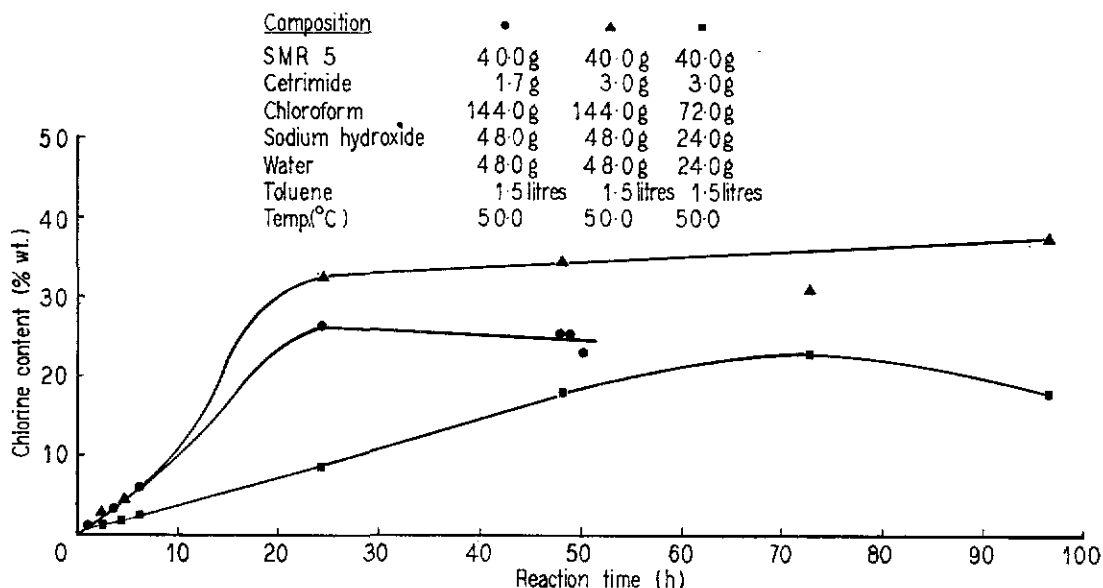


Figure 1. Changes in chlorine content with reaction time.

The hardness of the modified rubber did not correlate very well with chlorine content and was affected by the reaction conditions.

Solution Viscosity

The limiting viscosity numbers, $[\eta]$ of the modified rubbers were determined according to BS 1673, Part 6. The viscosity numbers were plotted against the solution concentrations and the straight lines were extrapolated to zero concentration to obtain the limiting viscosity numbers (Figure 2). The results are tabulated in Table 7. The limiting

TABLE 7. LIMITING VISCOSITY NUMBERS OF DICHLOROCARBENE MODIFIED NATURAL RUBBER

Chlorine content (% wt)	$[\eta]^a$ (dl/g)
0 (unmodified NR)	5.25
4.13	4.15
6.53	3.55
11.83	2.65
16.63	1.58

^aIn toluene at 25°C

viscosity numbers decreased with increasing chlorine contents of the modified NR and there is a linear correlation as shown in Figure 3. The modified NR solution viscosity data showed the Huggins relationship⁷, i.e. the slope of the viscosity number against concentration relationship (see Figure 2) for a given polymer-solvent combination is approximately proportional to the square of the limiting viscosity number of the polymer:

$$\frac{d}{dc} \frac{\eta_{sp}}{c} = k[\eta]^2 \quad k = \text{Huggins constant}$$

The Huggins relationship for modified NR is shown in Figure 4. The Huggins constant, k was found to have an average value of 0.57.

The drop in the limiting viscosity number with increasing chlorine content of the modified NR could be due to factors such as modification of the polymer structure and changes in the molecular weight and molecular weight distribution. It has been

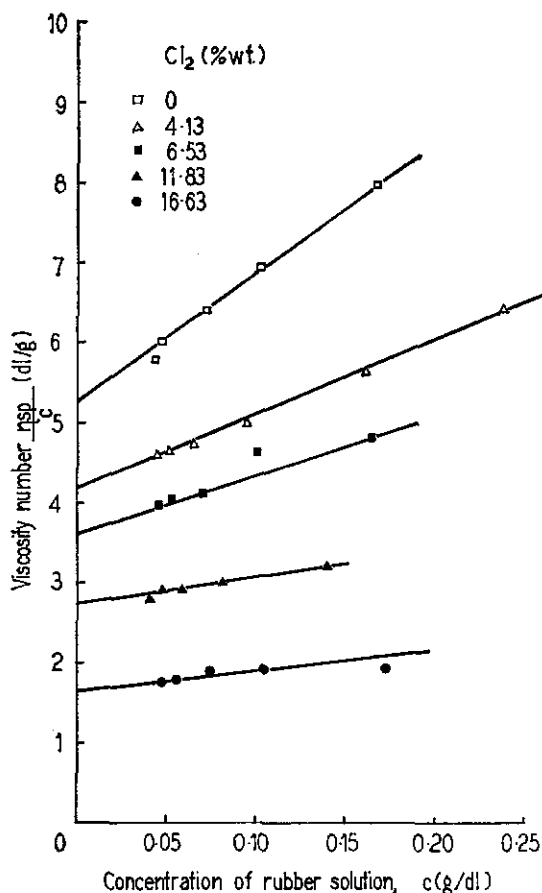


Figure 2. Determination of limiting viscosity number of modified natural rubber.

observed³ that the viscosity data for NR which has undergone chemical chain scission generally showed a lower Huggins constant than 0.57. Thus, it is probable that the change in the limiting viscosity numbers of the dichlorocarbene modified NR is due mainly to modification of the polymer structure.

Thermal Stability

It was reported⁴ that dichlorocarbene modified NR with chlorine content greater

than 46% is thermally stable up to 150°C. Hydrogen chloride was one of the gaseous products liberated in the degradation of the rubber at 200°C.

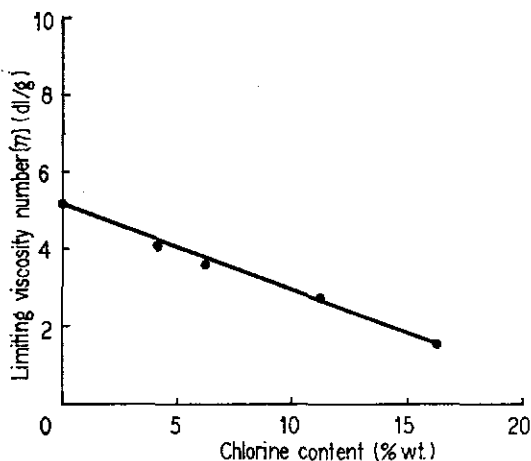


Figure 3. Changes in limiting viscosity number with chlorine content.

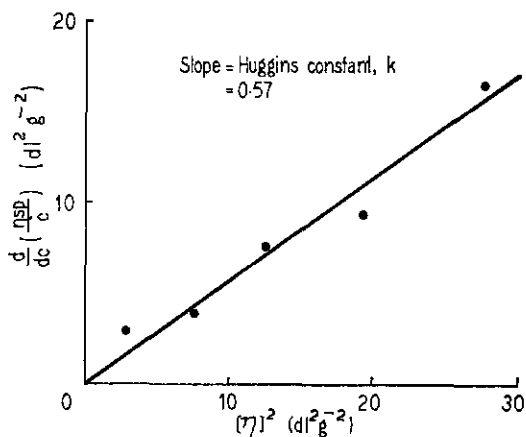


Figure 4. Huggins relationship for modified natural rubber.

Work here showed that dichlorocarbene modified NR with chlorine content between 20% and 37% is thermally unstable. Charring occurred in the temperature range of 80°C to 140°C. A sample of modified NR with 32.75% chlorine was heated at 100°C in an ageing oven in an open vessel and another sample in an evacuated (10^{-2} mm Hg) sealed tube. The changes in the samples are recorded in *Table 8*.

Thermal degradation of the modified NR was, as expected, worse in air than in an evacuated sealed tube.

Flammability

Halogenation of polymers increases their flame retardancy. The flame retardancy of the polymer depends on the halogen content and type. The flame retardancy of eleven dichlorocarbene modified NR were examined by simple burning tests. The results are shown in *Table 9*.

The simple burning test showed that dichlorocarbene modified NR could be broadly classified into three groups:

- No flame retardancy (below 8% chlorine)
- Slight retardancy in ignition and burning rate (8% - 30% chlorine)
- Retardancy in ignition and self-extinguishing (above 30% chlorine).

TABLE 9. BURNING OF DICHLOROCARBENE MODIFIED NATURAL RUBBER

Chlorine content (% wt)	Burning characteristics ^a
2.57	Burnt like ordinary NR
3.98	Burnt like ordinary NR
5.00	Burnt like ordinary NR
5.22	Burnt like ordinary NR
8.36	Ignition slightly more difficult, burnt like ordinary NR
17.49	Ignition more difficult, slower burning than ordinary NR
22.89	Ignition more difficult, slower burning than ordinary NR
31.14	Difficult ignition, extinguished when removed from flame
34.73	Difficult ignition, extinguished when removed from flame
37.37	Difficult ignition, extinguished when removed from flame

^aIgnition by a small blue bunsen flame

One method of quantitative measurement of flammability is the Critical Oxygen Index Technique (ASTM D2863-74). Critical Oxygen Index (COI) is defined as the minimum concentration of oxygen, expressed as volume percent in a mixture of oxygen and nitrogen, that will just support flaming combustion of a material initially at room temperature under the conditions of the

TABLE 8. CHANGES IN MODIFIED NATURAL RUBBER (32.75% CHLORINE) AT 100°C

Time (days)	In air	In vacuo
1	Light yellow to brown colour, showed porosity and brittleness	Slightly more yellowish
2	Light yellow to brown colour, showed porosity and brittleness	Slightly more yellowish
5	Dark brown colour	Slightly more yellowish
7	Dark brown colour	More yellowish
12	Almost black colour	Slight brownish
14	Black	Brown colour, some porosity
30	Black	Dark brown

method. The method was basically designed to test plastics. It has been successfully used for testing rubber⁹. The apparatus used for testing dichlorocarbene modified NR was the Stanton Redcroft FTA. Some synthetic rubbers were also tested. The test results are shown in *Table 10*.

Substances with COI well above 20.8 (the percentage of oxygen in air) are classified as relatively safe while substances with COI less than 20.8, which continue to burn in oxygen-deficient air are not safe as building materials. *Figure 5* is a plot of the COI against the chlorine content of the dichlorocarbene modified NR. It shows that at least 27.5% chlorine is required to impart

the flame retardant property to NR. Synthetic rubbers such as Hypalon 20, Neoprene AD, Viton B and Silopren RS are flame retardant based on the COI concept.

TECHNOLOGICAL EVALUATION

Conventional Sulphur Vulcanisation

Simple gum mixes using the conventional sulphur system (Rubber 100, ZnO 5, Stearic acid 3, S 2.5, CBS 0.5) were prepared from a series of dichlorocarbene modified NR. In preliminary testing, mixing was done on a micro-mill. Mixing was difficult and some samples charred. Some mixes were very hard and turned black after short storage. Determining the cure conditions was another

TABLE 10. CRITICAL OXYGEN INDEX OF MODIFIED NATURAL RUBBER AND SOME SYNTHETIC RUBBER

Rubber	Hetero gp content	COI ^a (%)
Unmodified NR	-	17.0
Dichlorocarbene modified NR		
A	5.40% Cl ₂	18.3
B	16.34% Cl ₂	18.9
C	24.12% Cl ₂	19.9
D	29.16% Cl ₂	22.2
E	32.41% Cl ₂	23.1
Chlorobutyl (Butyl HT 1066)	1.1% - 1.3% Cl ₂	18.2
Bromobutyl (Bromobutyl 2)	2% - 3% Br ₂	18.9
Hypalon 20	27% Cl ₂ , 1.2% S	21.8
Neoprene AD	40.1% Cl ₂	28.3
NBR (Krynac 803)	34% CN	17.6
Viton B	65% F ₂	71.9
Silopren RS	38% Si	22.9
SBR (Intol 1500)	-	17.1
BR (Intene 55NF)	-	16.7
IR (Natsyn 400)	-	16.8
EPDM (Vistalon 6505)	-	17.2

^aTested on uncompounded raw rubber according to ASTM D2863-74

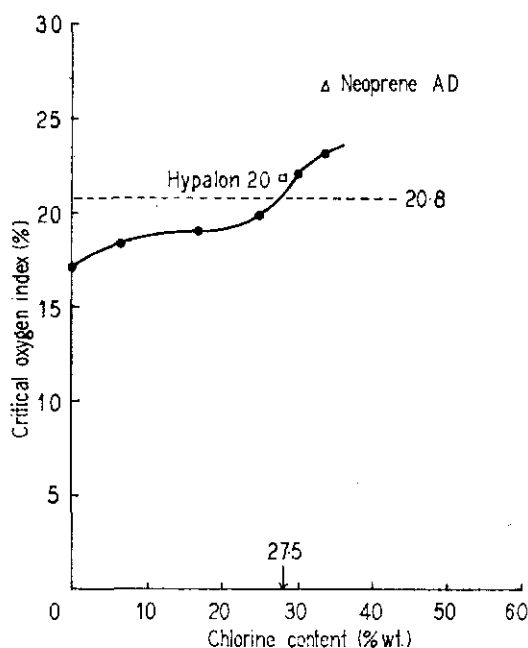


Figure 5. Critical oxygen index of dichlorocarbene modified natural rubber.

difficult process because of charring of samples during the heating-up process in the Monsanto Rheometer or Shawbury Curometer. Cure conditions used were based on Shawbury Curometer results. Processing difficulties were related to the chlorine content of the modified NR. Satisfactory test pieces could be prepared from modified NR with chlorine content less

than 20%. Table 11 shows some tensile results of the vulcanisates.

Dichlorocarbene modified NR, even at very low levels of modification, has much lower tensile strength than NR. Increasing the level of modification beyond 5% drastically reduced the tensile strength. On ageing, the tensile strength dropped further for all samples except the one with 17.92% chlorine, which showed an increase.

Two samples of modified NR were mixed on the normal laboratory mill and more tests were done. Results are shown in Table 12.

With limited results it is not possible to draw firm conclusions. It could, however, be noted that the sample with higher chlorine content has shorter scorch time, higher hardness, lower resilience and poorer ageing resistance. The evaluation has produced the following conclusions:

- The unaged and aged tensile properties are lower than a similar NR vulcanisate.
- The hardness is similar to NR vulcanisate.
- The resilience is lower than NR vulcanisate (75% compared to 85%).
- The hardness is not significantly affected by ageing.

TABLE 11. TENSILE PROPERTIES OF MODIFIED NATURAL RUBBER VULCANISATES

Chlorine content (% wt)	Cure time at 140°C (min)	Tensile strength (MPa)	Elongation at break (%)	Aged ^a tensile strength (MPa)
2.07	40	20.44	700	2.11
3.08	40	20.64	720	2.45
4.91	60	20.56	740	3.22
8.21	40	17.29	910	3.66
12.20	40	6.67	990	3.18
17.92	20	6.38	435	9.62

^aSeven days at 70°C

Other Vulcanisation Systems

Brief investigations of modified NR with four other cure systems were carried out. The systems were: TMTD/ZnO, peroxide,

EV and ZnO; ZnO was tried as a curing agent because of the chlorine atoms in the rubber. Mixing was done on a micro-mill. The tensile properties are shown in *Table 13*.

TABLE 12. TECHNOLOGICAL PROPERTIES OF MODIFIED NATURAL RUBBER

Property	Sample 1	Sample 2
Chlorine content (% wt)	10.65	8.66
Scorch time (min)	8.0	23.6
Cure time at 140°C (min)	40.0	60.0
Tensile strength (MPa)	8.0	8.5
Tensile strength, aged 7 days at 70°C (MPa)	3.6	6.3
Elongation at break (%)	740.0	830.0
Elongation at break, aged (%)	455.0	780.0
Hardness (IRHD)	36.0	34.5
Hardness, aged (IRHD)	34.0	-
Resilience ^a (%)	73.0	75.0
Resilience ^a , aged (%)	65.3	-

^aDunlop triposometer at 23°C

TABLE 13. TENSILE PROPERTIES OF MODIFIED NATURAL RUBBER VULCANISED WITH DIFFERENT CURE SYSTEMS

Item	ZnO	TMTD/ZnO	Peroxide	TMTD/ZnO	Peroxide	EV
Modified NR						
12.46% Cl ₂	-	-	-	-	10.0	10.0
12.61% Cl ₂	-	-	-	20.0	10.0	10.0
17.92% Cl ₂	25.0	-	-	-	-	-
23.66% Cl ₂	-	25.0	25.0	-	-	-
ZnO	1.25	1.0	-	0.8	-	1.0
Stearic acid	-	0.75	-	0.6	-	0.6
TMTD	-	1.0	-	0.8	-	-
TBTD	-	-	-	-	-	0.16
MOR	-	-	-	-	-	0.40
Sulphur	-	-	-	-	-	0.16
Dicup	-	-	0.63	-	0.5	-
Cure (min/°C)	60/140	15/140	30/140	60/140	60/150	60/140
Tensile strength (MPa)	3.52	6.00	5.30	4.50	6.00	3.00
Elongation at break (%)	200	175	155	620	400	320

The tensile strength of these vulcanisates were between 3 and 6 MPa. This is the same range as with the conventional sulphur system. Zinc oxide and the EV systems were not efficient as could be seen by comparison with corresponding samples in *Table 11*. The TMTD/ZnO and peroxide systems were not significantly inferior to the conventional sulphur system and have the advantage that satisfactory vulcanisates could be produced from modified NR with 23.66% chlorine.

Blends of Modified Natural Rubber

Blends of modified NR with different chlorine contents were evaluated using a conventional sulphur system. The blends were 1:1 mixtures. The blending of the rubbers was not difficult but problems in the mixing stage were the same as those stated earlier. The tensile properties of the blends are shown in *Table 14*.

The blending experiments showed that modified NR containing more than 20% chlorine, which on their own would not give satisfactory vulcanisates but charred, could be blended with rubbers with less than 20% chlorine to give satisfactory vulcanisates. The blending of two modified NR both of which have chlorine content below 20% gave vulcanisates with tensile strength slightly higher than the average of the two individual modified NR. For blends in which one component has more than 20% chlorine, the tensile strength were between 3 and 5 MPa.

Blends of modified NR with normal NR were also evaluated in the conventional sulphur system. The blending and mixing were not very difficult but uniform dispersion was very difficult to achieve. The vulcanised test pieces showed poor dispersion of the rubbers. Some tensile properties were obtained as shown in *Table 15*. The large

TABLE 14. TENSILE PROPERTIES OF BLENDS OF MODIFIED NATURAL RUBBER VULCANISATES

Chlorine content ^a (% wt)	Cure time and temperature	Tensile strength (MPa)		Elongation at break (%)
		Unaged	Aged ^b	
4.76 6.36	40 min/140°C	23.72	5.41	740
4.91 17.92	40 min/140°C	13.76	15.08	750
4.91 17.92	60 min/140°C	19.12	12.22	740
6.53 23.66	45 min/120°C	4.82	4.44	730
6.53 23.66	60 min/120°C	4.43	3.83	630
6.53 23.66	15 min/140°C	4.18	3.03	640
16.63 28.09	20 min/120°C	3.76	charred	400
16.63 28.09	40 min/120°C	3.08	charred	250

^aChlorine content of individual modified NR in the blend at 1:1 ratio

^bSeven days at 70°C

TABLE 15. TENSILE PROPERTIES OF MODIFIED/NORMAL NATURAL RUBBER BLEND VULCANISATES

Modified/normal NR ratio	Modified NR ^a chlorine content (% wt)	Cure	Tensile strength ^b (MPa)	Elongation at break (%)
1 : 1	4.13	60 min/140°C	22.50, 9.00, 2.62	770, 610, 380
1 : 1	16.62	60 min/140°C	17.50, 7.65, 10.00	770, 780, 730
1 : 1	28.09	60 min/120°C	4.47, 6.50	530, 660
1 : 4	28.09	60 min/140°C	17.80, 9.50	760, 710

^aChlorine content of the modified NR in the blend^bOf individual test pieces

variations in the results reflected the poor dispersion of the rubbers.

CONCLUSION

Dichlorocarbene modification of NR by the aqueous alkaline hydrolysis of chloroform in the presence of a transfer agent gave lower yields when oxygen was present. The physical nature of the modified NR was dependent on the experimental conditions and the amount of bound chlorine. The limiting viscosity numbers of the modified NR dropped linearly with the chlorine contents. Huggins constant, k , for the modified NR solution in toluene at 25°C is 0.57. Modified NR had poor thermal stability. These modified NR samples were flame retardant when the chlorine contents were above 27.5%.

The processibility of the modified NR was poor. Vulcanisates had low tensile properties which deteriorated on ageing. However, the damping property had been improved without increase in hardness. This might be advantageous for vibration mountings for light delicate instruments.

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