Chapter II
Utilization of Cardanol in NR Processing

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2.1 Introduction
In this chapter, possible uses of cardanol in natural rubber processing are investigated. The plasticizer property of cardanol is compared with that of a conventional plasticizer, aromatic oil, at various filler contents, viz. 10-50 phr HAF black and 5-25 phr precipitated silica (Section 2.2.3). The antioxidant property of cardanol was compared (Section 2.2.4) with that of trimethyl quinoline and styrenated phenol in gum samples. Ageing studies were done for evaluating the thermal resistance (Section 2.2.4). Co-activator and accelerator properties were compared with those of stearic acid and N-cyclohexyl-2-benzothiazole suphenamide (Sections 2.2.5 and 2.2.6) respectively.

2.2 Experimental work

2.2.1 Raw Materials

a) Elastomers

Natural rubber – ISNR – 5 (1) was obtained from Rubber Research Institute of India; Kottayam, Kerala. Specifications of ISNR-5 are given below.

Mooney viscosity ML (1+4) at 100°C - 82
Dirt content, % by mass, max - 0.05
Volatile matter, % by mass, max - 1
Nitrogen, % by mass, max - 0.07
Ash, % by mass, max - 0.60
Initial plasticity, min - 30
Plasticity retention index - 60

1. Zinc Oxide (activator) was supplied by M/s Meta Zinc Ltd., Mumbai and Goderej Soaps Pvt Ltd., Mumbai. It had the following specifications.

Specific gravity - 5.5
ZnO content - 98%
2. **Stearic acid** (co-activator) used in the present study was supplied by Goderej Soaps Pvt Ltd., Mumbai and had the following specifications.

- Specific gravity: \(0.85 \pm 0.01\)
- Melting point: 50-69°C
- Acid number: 185-210
- Iodine number: 9.5
- Ash content: 0.1%

3. **N-cyclo hexyl 2-benzothiazole sulphenamide (CBS)** (accelerator) used in the present study was obtained from Polyolefine Industries, Mumbai.

4. **Tetramethyl thiuram disulphide (TMTD)** (accelerator) used in the present study was supplied by Flexys, Netherlands. It had the following specifications.

- Melting point: 108°C
- Moisture content: 0.12%
- Ash content: 0.03%

5. **High Abrasion Furnace black (N330)** used in the present study was supplied by M/s Philips Carbon Black India Ltd., Cochin, India. It had the following specifications.

- Appearance: black granules
- DBP absorption: 102cc/100g
- Pour density: 376kg/m³
- Iodine number: 82

6. **Precipitated silica** used was of commercial grade supplied by Sameera Chemicals, Kottayam. The specifications are given below.

- pH (5% aqueous solution): 6.3
- Specific gravity: 2.03
- SiO₂ in dried sample: 90%
- Loss on heating (105°C): -5.5%
7. **Aromatic oil** obtained from Hindustan Organic Chemicals Ltd. Kochi, had the following specifications:

- **Specific gravity**: 0.98
- **Aniline point**: 43.00
- **Ash content % by mass**: 0.01
- **Viscosity gravity constant**: 0.96

8. **Refined CNSL** conforming to Indian Standard 1 S: 840 (1964) was supplied by Vijayalaksmi Cashew Exports, Kollam, India. Cardanol was separated from commercial grade CNSL by distillation under reduced pressure (1mmHg). The pale yellow fraction collected at 206-208°C was cardanol.

9. **Sulphur** (cross linking agent), was supplied by Standard Chemicals Co. Pvt. Ltd. Chennai. The sample used had the following specifications:

- **Specific gravity**: 2.05
- **Acidity, max**: 0.01%
- **Ash, max**: 0.015

10. **Styrenated phenol (SP)** was supplied by Olympic Chemicals, Maharashtra, India.

11. **Diethylene glycol (DEG)** was supplied by E. Merk Limited, India.

**c) Solvents used for Soxhlet extraction**

1. **Toluene** was supplied by Fine Chemicals Ltd., Mumbai and had the following specifications:

- **Boiling Point**: 95°C
- **Acidity**: 0.012
- **Alkalinity**: 0.012
- **Non volatile matter**: 0.002%

2. **Acetone (AR)** was supplied by Qualigens Fine Chemicals, India. It had the following specifications:

- **Minimum assay**: 99.5
- **Wt / ml at 20°C**: 0.789 - 0.791
2.2.2 Quality evaluation

Different evaluation methods employed for vulcanizate properties are the following:

a. Cure characteristics: The cure characteristics of the mixes were determined using Rubber Processing Analyser (RPA 2000) supplied by Alpha Technologies, USA, as per ASTM Standard, D 2084-01. The instrument uses two directly heated opposing biconical dies with a die gap of 0.487 that are designed to achieve a constant shear gradient over the entire sample chamber. The lower die is oscillated at 50rpm and the torque transducer on the upper die senses the force being transmitted through the rubber. Rheometric scorch time ($t_{s2}$) is the time required for the torque value to increase by two units above the minimum torque. It is a measure of the scorch safety of the rubber compound. Rheometric induction time ($t_{sl}$) is the time required for the torque value to increase by one unit above the minimum torque. It indicates the minimum time required to start the cure reaction. The optimum cure time corresponds to the time to achieve 90 percent ($t_{90}$) of the cure. It is calculated using the equation 2.1 (3):

$$\text{Optimum cure (} t_{90} \text{)} = 0.9 (M_b - M_o) + M_o$$  \hspace{1cm} (2.1)

where $M_b$ and $M_o$ are the maximum and minimum torques respectively.

i) Cure rate index

Cure rate index which is a measure of the rate of cure, was calculated using the formula (4)

$$CRI = \frac{100}{t_{90} - t_{s2}}$$  \hspace{1cm} (2.2)

where $t_{90}$ and $t_{s2}$ are cure time and scorch time respectively.

ii) Alpha value

Alpha ($\alpha$) represents filler specific constant independent of the cure system and closely related to the morphology of the filler (5-7). This parameter has been used
to characterize the filler structure existing in vulcanizates, in particular for carbon blacks. A low value of $\alpha$ indicates good filler dispersion.

$$\frac{D_{\text{max}} - D_{\text{min}}}{D^0_{\text{max}} - D^0_{\text{min}}} - 1 = \alpha \frac{m_{\text{filler}}}{m_{\text{rubber}}}$$  \hspace{1cm} (2.3)

where, $D_{\text{max}}$ and $D_{\text{min}}$ correspond to the maximum and minimum rheometric torques of compounds with filler, $D^0_{\text{max}}$ and $D^0_{\text{min}}$ that without filler and $m_{\text{filler}}$ and $m_{\text{rubber}}$, mass of filler and mass of rubber respectively.

iii) Kinetics of vulcanization

The kinetics of vulcanization was studied from the rheographs by the method (8) given below. The general equation for the kinetics of a first order chemical reaction is

$$\ln (a - x) = -kt + \ln a$$  \hspace{1cm} (2.4)

where, $a$ = initial reactant concentration, $x$ = reacted quantity of reactant at time $t$, and $k$ = first order rate constant.

For the vulcanization of rubber, the rate of crosslink formation is monitored by measuring the torque developed during vulcanization. The torque obtained is proportional to the modulus of rubber. So the following substitutions can be made

$$(a - x) = M_h - M_t$$  \hspace{1cm} (2.5)
$$a = M_h - M_0$$  \hspace{1cm} (2.6)

$M_h$ and $M_0$ maximum and minimum rheometric torques, and $M_t$ - Rheometric torque at time $t$. So the equation becomes

$$\ln (M_h - M_t) = -kt + \ln (M_h - M_0)$$  \hspace{1cm} (2.7)

This equation is of the general form of a straight line. Therefore, if the plot of $\ln (M_h - M_t)$ Vs. time $t$ is a straight line graph, it means that the cure reaction follows first order kinetics. The cure reaction rate constant ($k$) is directly obtained from the slope of the respective straight lines.

The energy of activation $E_{\text{act}}$ of curing was determined using Arrhenius equations (9) given below
\[ k = Ae^{-\frac{E_a}{RT}} \]  

\[ \log k = \log A - \frac{E_a}{2.303RT} \]  

(2.8)  

(2.9)

where, \( A \) is the Arrhenius constant, \( E_a \), the activation energy, \( R \), the universal gas constant and \( T \), the absolute temperature.

The rubber compounds were subsequently vulcanized up to the optimum cure time in an electrically heated hydraulic press with 30cm x 30cm platens at the required temperature and 11.6 MPa. The mouldings were cooled quickly in water at the end of the curing and stored in a cool dark place for 24 h. prior to physical testing.

b. Tensile properties: The tensile tests were done on dumb-bell shaped specimens punched out from the vulcanized sheets. The measurements were carried out on a ‘Shimadzu’ Universal Testing Machine (10KN) model AG 50 kN with a grip separation of 40mm, using a crosshead speed of 500mm/min. as per ASTM D 412. The reinforcing index was calculated using the formula (30)

\[
\text{Reinforcing index} = \frac{N}{N_0} \times \frac{100}{m_{\text{filler}}} \quad \ldots \ldots \quad 4.10
\]

Where \( N \) and \( N_0 \) indicate any property of filled and gum samples respectively and \( m_{\text{filler}} \) the mass of filler per 100 g rubber. Reinforcing index is a measure of the reinforcing effect of filler on the rubber.

c. Tear resistance: This test was carried out as per ASTM D 624 using type C, un-nicked test pieces with a 90° angle on one side and tab ends punched out from the vulcanized sheets parallel to the mill grain direction. The test was carried out on the ‘Shimadzu’ Universal Testing Machine (10KN) with a grip separation of 40mm, using a crosshead speed of 500mm/min.

d. Hardness: The hardness (Shore A) of the moulded samples was determined using Zwick 3114 Hardness Tester in accordance with ASTM D 2240-05. The tests were performed on unstressed samples of 30mm diameter and 6mm
thickness. The readings were taken after 10s of indentation since firm contact had been established with the specimen.

e. **Abrasions loss**: The abrasion resistance of the samples was determined using a DIN Abrader (DIN 53516). Samples having a diameter of 6 ± 0.2mm and a thickness of 6mm were kept on a rotating sample holder and a 10N load was applied. Initially a pre-run was given for the sample and its weight taken. The weight after final run was also noted. The abrasion loss in cc/hr. was calculated using the formula

\[
\text{Abrasions loss} = \frac{\text{loss of weight}}{\text{sp. gravity}} \times 60 \times \frac{2.2}{2.2}
\]

for an abrasion time of 2.2 minutes.

f. **Rebound resilience**: Rebound resilience is the ratio of energy given up on recovery from deformation to the energy required to produce the deformation. It is expressed as percentage and is measured using a Vertical Rebound Resilience Tester as per ASTM D 2632-01. A plunger weighing 28±0.5g is dropped from a height of 40cm to the sample of thickness 12.5mm and the rebound height is measured.

\[
\text{Resilience} = \frac{R_h}{D_h} \times 100
\]

where, \(R_h\) is the rebound height and \(D_h\) the drop height

g. **Soxhlet extraction**: Known weights of different samples of vulcanized rubber were packed in Wattman I filter paper and extracted in a Soxhlet apparatus using toluene as solvent and the loss of weight (%) was noted.

h. **FTIR spectroscopy**: FTIR spectra of the Soxhlet extract of the cardanol based vulcanizate and cardanol itself were taken on Fourier Transform Infrared Spectroscope Bruker-Tensor 27 (Netherlands) and compared.
Similar studies were made on a cardanol sample after reaction with sulphur in order to identify chemical changes if any. The sample was heated for half an hour with sulphur at 100°C and cooled prior to testing.

i. **Crosslink density**: Crosslink density was determined on both aromatic oil based and cardanol based samples loaded with 30phr HAF using toluene as per ASTM D 6814-02\textsuperscript{1}. The process was repeated for aged samples after varying periods of ageing.

j. **Free sulphur analysis**: Free sulphur analysis was carried out as per ASTM D297 on both cardanol based and aromatic oil based vulcanizates each containing 30phr HAF black. The analysis was also carried out on samples aged up to 4 days.

k. **Thermo gravimetric analysis**: Thermo gravimetric analysis was carried out on both cardanol based and aromatic oil based vulcanizates with 30phr HAF on a TGA Q50 V6.4 Build 193 instrument (Netherlands), at a heating rate of 20°C/minute over a range of 30-800°C.

l. **Differential scanning calorimetric analysis**: Differential scanning calorimetric analysis was carried out on both cardanol based and aromatic oil based samples vulcanized with 30phr HAF on STAR\textsuperscript{e} SW 8.10 equipment at a heating rate of 10°C/ min. over a range of 100°C to +155°C.

m. **Mooney viscosity**: Mooney viscosity was measured on a Model EKTRONTEK, TAIWAN Mooney Viscometer.

n. **Ageing tests**: Oxidative ageing tests were carried out for ten days in accordance with ASTM D573-04, in an air oven at two temperatures, viz.70°C and 100°C. After 24 hours of conditioning at ambient temperature, tensile strength and tear resistance of the samples were determined as per ASTM D 412 and 624 respectively apart from other indicators like free sulphur content, extractable matter etc.
2.2.3 Compounding and curing of NR

The mixing of the ingredients was done according to ASTM D 3182-3189 at a friction ratio of 1:1.22. The mill opening was set at 0.2mm and NR was passed through the rolls twice without banding. This was then banded on the slow roll with the mill opening at 1.44mm and was increased to 1.9 mm as the band became smooth. The temperature of the rolls was maintained at 70±5°C. The compounding ingredients were added as per procedure given in ASTM D3184-89 in the following order: activator, filler, plasticizer, accelerator and curing agents. Before the addition of accelerator and sulphur, the batch was thoroughly cooled.

After mixing, the compound was homogenised by passing the rolled stock endwise six times at a mill opening of 0.8mm. The mill was opened to give a minimum stock thickness of 6mm and the stock was passed through the rolls four times folding it back on itself each time.

The cure times of the mixes were determined as per ASTM Standard D 2084-01 using Rubber Processing Analyser, RPA 2000 supplied by Alpha Technologies, USA.

The rubber compounds were then vulcanized up to the optimum cure time in an electrically heated hydraulic press with 30cm x 30cm platens at 150°C and 11.6 MPa. The mouldings were cooled quickly in water at the end of the curing cycle and stored in a cool dark place for 24 h prior to physical testing.

2.2.4 Cardanol as plasticizer in NR compounds

A) HAF black
In this study samples were prepared as per details given in Section 2.2.3. The formulations employed are given in Table 2.1. Initially specimens were prepared using aromatic oil as plasticizer. Subsequently all studies were repeated replacing aromatic oil by cardanol. All the samples were tested for different properties as per details mentioned in Section 1.13.
Table 2.1. - Formulations with varying HAF black content

<table>
<thead>
<tr>
<th>Sample</th>
<th>NR (phr)</th>
<th>ZnO (phr)</th>
<th>St.acid (phr)</th>
<th>HAF (phr)</th>
<th>Ar. oil/cardanol (phr)</th>
<th>TQ (phr)</th>
<th>CBS (phr)</th>
<th>S (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>0.8</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>20</td>
<td>2</td>
<td>1</td>
<td>0.8</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>30</td>
<td>3</td>
<td>1</td>
<td>0.8</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>40</td>
<td>4</td>
<td>1</td>
<td>0.8</td>
<td>2.5</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>50</td>
<td>5</td>
<td>1</td>
<td>0.8</td>
<td>2.5</td>
</tr>
</tbody>
</table>

B) Precipitated silica

In this study silica filled samples were prepared as per details given in Section 2.2.3 using formulations given in Table 2.2. Initially, specimens were prepared using aromatic oil as plasticizer and all studies were repeated replacing aromatic oil by cardanol. All the samples were tested for different properties as per details mentioned in Section 1.13.

Table 2.2 Formulations with varying silica content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NR, phr</th>
<th>ZnO, phr</th>
<th>St.acid, phr</th>
<th>DEG, phr</th>
<th>Silica, phr</th>
<th>Ar. Oil/cardanol, phr</th>
<th>CBS, phr</th>
<th>TMTD, phr</th>
<th>S, phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>5</td>
<td>0.5</td>
<td>0.6</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
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<td>1</td>
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<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>15</td>
<td>1.5</td>
<td>0.6</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>20</td>
<td>2.0</td>
<td>0.6</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>25</td>
<td>2.5</td>
<td>0.6</td>
<td>0.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

C) Ageing studies

Samples were prepared as described in Section 2.2.2 according to formulations given in Tables 2.1 and 2.2. Oxidative ageing was carried out as per ASTM D573-04 using an air oven at 100°C. Specimens were subjected to ageing for 1, 2, 3, 4 70
and 5 days. Physical properties of the specimens before and after ageing were determined after 24 hours of conditioning at ambient temperature. Graphs were plotted for property vs no. of days of ageing for both plasticizers.

D) Optimization of cardanol content

Optimization of cardanol percentage was done for both HAF black filled and silica filled samples. For the optimization of cardanol, samples containing optimum filler loadings, 30phr HAF black and 15 phr silica (Sections 2.5.1 and 2.5.2) were used. Different samples were moulded at a constant filler content and different cardanol percentages, viz. 0.25 to 15% of the filler content as given in Tables 2.3 and 2.4.

Table 2.3: HAF black formulations with varying cardanol content

<table>
<thead>
<tr>
<th>Sample</th>
<th>NR (phr)</th>
<th>ZnO (phr)</th>
<th>St.acid (phr)</th>
<th>HAF black (phr)</th>
<th>Cardanol (phr)</th>
<th>TQ (phr)</th>
<th>CBS (phr)</th>
<th>S (phr)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.5</td>
</tr>
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<td>2</td>
<td>30</td>
<td>1.5</td>
<td>1</td>
<td>0.8</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>30</td>
<td>2.25</td>
<td>1</td>
<td>0.8</td>
<td>2.5</td>
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<td>4.25</td>
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<td>0.8</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 2.4 Silica formulations with varying cardanol content

<table>
<thead>
<tr>
<th>Sample</th>
<th>NR (phr)</th>
<th>ZnO (phr)</th>
<th>St.acid (phr)</th>
<th>DEG (phr)</th>
<th>Silica (phr)</th>
<th>Cardanol (phr)</th>
<th>CBS (phr)</th>
<th>TMTD (phr)</th>
<th>S (phr)</th>
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<tbody>
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<td>1</td>
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<td>0.75</td>
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E) Comparative study of cardanol and CNSL as plasticizers

As in Section 2.2.3, mixes were prepared using formulations given in Table 2.5 and the properties of the vulcanizate were determined and compared with vulcanizates in which cardanol was used as plasticizer. Mechanical properties were determined as described in Section 1.13. Oxidative ageing tests were carried out as per ASTM D573-04 using an oven at 100°C. Specimens were subjected to ageing for 1, 2, 3, 4 and 5 days. Physical properties of the specimens before and after ageing were determined after 24 hours of conditioning at ambient temperature. Property vs days of ageing graphs were plotted and compared for samples using each of cardanol and CNSL as plasticizers.

**Table 2.5 Formulations with varying HAF black content**

<table>
<thead>
<tr>
<th>Sample</th>
<th>NR (phr)</th>
<th>ZnO (phr)</th>
<th>St.acid (phr)</th>
<th>HAF (phr)</th>
<th>CNSL/cardanol (phr)</th>
<th>TQ (phr)</th>
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<td>1</td>
<td>0.8</td>
<td>2.5</td>
</tr>
</tbody>
</table>

2.2.5 Cardanol as antioxidant

This study was conducted to investigate whether cardanol possesses any antioxidant property for NR. The study was conducted in gum and silica filled samples using the formulations given in Table 2.6 and 2.7.

A) Antioxidant property of cardanol for NR gum compound

Oxidative ageing studies were carried out as per ASTM D573-04 using an oven at 70°C both in the case of silica filled and gum samples. Specimens were subjected to ageing for 1, 2, 3, 4 and 5 days. Physical properties of the specimens before and after...
after ageing were determined after 24 hours of conditioning at ambient temperature. Graphs were plotted for property vs days of ageing for all the three cases where cardanol, SP and TQ were used as antioxidants.

**TABLE 2.6 Formulation for gum samples**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Quantity (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td>4</td>
</tr>
<tr>
<td>Cardanol / SP / TQ</td>
<td>1</td>
</tr>
<tr>
<td>CBS</td>
<td>0.8</td>
</tr>
<tr>
<td>S</td>
<td>2.5</td>
</tr>
</tbody>
</table>

**B) Antioxidant property of silica filled NR compounds**

**TABLE 2.7 Formulation for silica filled samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>NR (phr)</th>
<th>ZnO (phr)</th>
<th>St.acid (phr)</th>
<th>DEG (phr)</th>
<th>Silica (phr)</th>
<th>A/B/C (phr)</th>
<th>CBS (phr)</th>
<th>TMTD (phr)</th>
<th>S (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>5</td>
<td>0.5</td>
<td>0.6</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>10</td>
<td>1.0</td>
<td>0.6</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>15</td>
<td>1.5</td>
<td>0.6</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>20</td>
<td>2.0</td>
<td>0.6</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>25</td>
<td>2.5</td>
<td>0.6</td>
<td>0.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

A- Cardanol  B- Aromatic oil  C- {Cardanol as plasticizer + SP (1phr)}

**2.2.6 Cardanol as co-activator for NR gum**

This study was conducted to investigate whether cardanol possesses any co-activator property when used as a substitute for stearic acid in NR gum formulation. The formulation used for the co-activator study is given in Table 2.8. The cure characteristics and mechanical properties when stearic acid is replaced by
cardanol or a combination of 1phr each of cardanol and stearic acid as co-activators were found out.

**Table 2.8 Formulation for cardanol as co-activator**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Quantity (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td>4</td>
</tr>
<tr>
<td>Co-activator</td>
<td>2</td>
</tr>
<tr>
<td>CBS</td>
<td>0.8</td>
</tr>
<tr>
<td>S</td>
<td>2.5</td>
</tr>
</tbody>
</table>

**2.2.7 Cardanol as accelerator for NR gum**

The accelerator property of cardanol was investigated for curing NR gum samples using the formulation given in Table 2.9. The accelerator property was estimated by noting the cure characteristics.

**Table 2.9 Formulation for cardanol as accelerator**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Quantity (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td>4</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>Cardanol / CBS</td>
<td>0.8</td>
</tr>
<tr>
<td>S</td>
<td>2.5</td>
</tr>
</tbody>
</table>

**2.2.8 Sulphurless curing**

**Table 2.10 Formulations for DCP curing of NR gum**

<table>
<thead>
<tr>
<th></th>
<th>NR (phr)</th>
<th>Cardanol (phr)</th>
<th>DCP (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>
NR was compounded with dicumyl peroxide as per formulation in Table 2.10 and vulcanized as per ASTM standard, D 2084-01 and physical properties of samples determined according to details given in Section 1.13. A similar study was done without cardanol and the properties compared.

2.3 Results and discussion

2.3.1 Performance of cardanol as plasticizer for NR

A) HAF black filler

1. Cure characteristics

The cure characteristics of the mixes were determined at 150°C and 11.6 MPa using Rubber Processing Analyser RPA 2000 supplied by Alpha Technologies, USA, as per ASTM Standard, D 2084-01.

![Cure curves of cardanol and aromatic oil based samples with 30phr HAF black loading.](image)

Fig. 2.1 Cure curves of cardanol and aromatic oil based samples with 30phr HAF black loading.

Fig. 2.1 is a comparison of cure curves of 30phr HAF black filled compounds. Similar values of torque are attained for both plasticizers. The cure characteristics are given in Table 2.11.
Table 2.11 Cure characteristics of 30 phr HAF black filled samples

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>( t_{10} ) min</th>
<th>( t_{50} ) min</th>
<th>( t_{90} ) min</th>
<th>( t_s^2 ) min</th>
<th>CRI ( \text{min}^{-1} )</th>
<th>Min. torque, dNm</th>
<th>Max. torque, dNm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardanol</td>
<td>2.25</td>
<td>3.81</td>
<td>7.41</td>
<td>3.6</td>
<td>1.23</td>
<td>26.53</td>
<td>0.016</td>
</tr>
<tr>
<td>Ar. oil</td>
<td>2.39</td>
<td>3.88</td>
<td>7.79</td>
<td>3.64</td>
<td>1.44</td>
<td>26.88</td>
<td>0.072</td>
</tr>
</tbody>
</table>

The minimum torque value, which indicates viscosity of the compound, is much less for the cardanol based samples. Hence cardanol is a better plasticizer for NR. The scorch time, cure time, \( t_{10} \) and \( t_{50} \) are comparable for both samples. Even though the cure rate index is slightly lower for the cardanol based sample, the \( \alpha \)-value which is a measure of filler agglomeration is lower for cardanol based sample and is indicative of better filler dispersion.

Table 2.12 Minimum and maximum torque values during cure for HAF black filled samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Torque, dNm</th>
<th>10phr</th>
<th>20phr</th>
<th>30phr</th>
<th>40phr</th>
<th>50phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardanol</td>
<td>minimum</td>
<td>0.05</td>
<td>0.05</td>
<td>0.02</td>
<td>0.01</td>
<td>0.2</td>
</tr>
<tr>
<td>Aromatic oil</td>
<td>minimum</td>
<td>0.11</td>
<td>0.05</td>
<td>0.07</td>
<td>0.09</td>
<td>0.3</td>
</tr>
<tr>
<td>Cardanol</td>
<td>maximum</td>
<td>3.53</td>
<td>3.4</td>
<td>4.4</td>
<td>5.32</td>
<td>6.6</td>
</tr>
<tr>
<td>Aromatic oil</td>
<td>maximum</td>
<td>3.94</td>
<td>4.2</td>
<td>4.6</td>
<td>5.69</td>
<td>7.5</td>
</tr>
</tbody>
</table>
Table 2. 12 gives minimum and maximum torque values during cure for HAF black filled samples. It is seen that the minimum torque value, which is indicative of the viscosity of the compound is in general lower for cardanol based samples.

Fig. 2.2 Variation of cure time with HAF black content

Figure 2.2 shows the variation of cure time with HAF black content. A marginally lower cure time is obtained for the cardanol based sample. The latter can be the result of chemical interactions between cardanol and natural rubber/sulphur, which can accelerate the overall curing process. Various possibilities exist for cross-linking between the side chains of cardanol and also between these and natural rubber\(^\text{10}\) chains through sulphidic linkages and/or free radical mechanisms.

Fig. 2.3 Variation of \(\alpha\)-value with HAF black content
Figures 2.3 and 2.4 give a comparison of $\alpha$ and scorch values of cardanol and aromatic oil based samples with varying HAF black content. Lower $\alpha$ values for cardanol based samples indicate that cardanol is a better medium for dispersing HAF black providing a higher degree of plasticization than aromatic oil. The lower $\alpha$ values also show that filler agglomeration takes place to a much smaller extent in cardanol based compounds resulting in better utilization of filler. The lower viscosity of cardanol, 45 centipoise compared to 3400 centipoise for aromatic oil, may lead to better flow properties and consequently better wetting of filler rubber interface compared to aromatic oil. A slight lowering of scorch values in the presence of cardanol points to a more reactive compound.

Fig 2.4 Variation of scorch value with HAF black loading
Fig 2.5 Variation of cure rate index with HAF black loading

Cure rate index with HAF black loading (Fig 2.5) shows that CRI values of cardanol based samples are comparable to the values for aromatic oil. Kinetics of cure reactions of 30phr HAF black filled cardanol and aromatic oil based compounds show that they obey first order kinetics as $\ln(M_h - M_t)$ vs $t$ plot gives a straight line with rate constant $k = 0.43935$ and $0.43117$ respectively.

Fig. 2.6 $\ln(M_h - M_t)$ vs $t$ for cardanol based sample: $k = 0.43935$, where $k$ is the first order rate constant
b) **Tensile properties:** Fig. 2.8 shows the variation of tensile strength of HAF reinforced natural rubber, for both cases. Both plasticizers show similar tensile strengths aromatic oil giving slightly higher values at 30phr black and above.

![Fig. 2.8 Variation of tensile strength (MPa) with HAF black loading](image)
Fig. 2.9 Variation of elongation at break (%) with HAF black content

Also comparative data on the effect of filler content on elongation at break (Fig. 2.9) show equivalent performance by both plasticizers. Fig. 2.10 shows that the variation of 300% modulus with HAF black content for both cases is similar up to 40phr filler content and at 50phr the cardanol based sample has a clear superiority. For the cardanol-based sample, the 300% modulus value increases linearly with increase in filler content. The tensile properties, in general, show that cardanol is equivalent to aromatic oil as plasticizer.

Fig. 2.10 Variation of modulus at 300% elongation with HAF black content
c) **Tear strength**: The tear strength of samples employing both plasticizers has also been measured as a function of HAF black filler content (Fig. 2.11). The tear strength values of the cardanol based samples are marginally higher. This points to a better reinforcing action by the filler in the presence of cardanol. This can be the result of more effective wetting of the filler-rubber interface by cardanol or better dispersion of the filler in comparison with aromatic oil.
Fig. 2.13 Variation of reinforcing index on the basis of tear strength with HAF black loading

Figs. 2.12 and 2.13 indicate the variation of reinforcing index with filler content on the basis of tensile and tear strength respectively. They are similar for both plasticizers.

d) Abrasion loss: Fig. 2.14 shows the variation of abrasion loss with HAF black filler content for both cases. Both curves are close to each other.

Fig. 2.14 Variation of abrasion loss with HAF black content
e) **Hardness**: Surface hardness values (Fig. 2.15) of specimens employing both plasticizers are also similar.

f) **Resilience**: Fig. 2.16 shows the variation of resilience with increase in HAF black filler loadings for both cases. Both curves are similar.
Fig. 2.17 Results of Soxhlet extraction of 30phr HAF black loaded samples using toluene as solvent

g) Soxhlet extraction: The data given in Fig. 2.17 after Soxhlet extraction of cured samples are also significant. Cardanol based samples contain very little extractable matter both before ageing and after an ageing period of three days. Even after ageing for three days, the cardanol based sample gives almost the original value.

Fig. 2.18 FT-IR spectrum of cardanol
Fig. 2.19 FT-IR spectrum of the extract of cardanol based vulcanizate (30 phr HAF black) in toluene

Fig. 2.20 FT-IR spectrum of sulphur treated cardanol

h) FT-IR spectra: Figs.2.18 and 2.19 show the IR spectra of cardanol and the Soxhlet extract of the cardanol based vulcanizate respectively. A comparison of the
two shows no sign of cardanol in the extract, as the –OH absorption peak of cardanol observed at 3338cm⁻¹ is absent in the spectrum of the extract. This shows that in the case of cardanol, loss of plasticizer during service is not likely. Fig.2.20 shows the FTIR spectrum of cardanol after heating with elemental sulphur. Comparison of Figs. 2.18 and 2.19 shows suppression of the peak at 3090cm⁻¹ resulting from the disappearance of =C-H stretch of the aliphatic side chain of cardanol. This points to a vulcanization type reaction cardanol has undergone with sulphur.

i) Crosslink density: Fig. 2.21 is a plot of crosslink density of both samples at various stages of ageing. Crosslink density is slightly less in cardanol based samples compared to aromatic oil based samples. The presence of cardanol molecules has led to a lower extent of crosslinking between the rubber chains. This can be viewed as an extreme case of plasticization or steric hindrance due to the bulky nature of cardanol molecules. But since properties of the cardanol based sample are similar or even better, this is not a matter of concern.

![Crosslink density graph](image)

Fig. 2.21 Variation of crosslink density (mmol / kgRH⁶) of 30phr HAF black loaded vulcanizate on ageing at 100°C

* Rubber hydrocarbon
Fig. 2.22 Variation of free sulphur content in 30phr HAF black loaded vulcanizate on ageing at 100°C

j) Free sulphur content: Variation of free sulphur content estimated at various stages of ageing shown in Fig.2.22 is supportive of this. Initially free sulphur content of the cardanol- based sample is much less than the aromatic oil based sample. But after the first day of ageing, there is a sharp increase in free sulphur content presumably due to the breakage of cardanol-sulphur linkages. It is likely that the sulphur is subsequently utilized by natural rubber to form more crosslinks. By the second day of ageing, both samples show practically the same free sulphur content after a sharp fall in the case of the cardanol- based samples. Both samples show almost equal free sulphur values for the rest of the ageing period.

k) Thermogravimetric analysis: Figs.2.23 and 2.24 show the thermograms of samples plasticized by cardanol and aromatic oil respectively. The onset point of degradation of the cardanol based sample is higher than that of aromatic oil based sample. 50% degradation temperature (T<sub>50</sub>) is higher for aromatic oil based sample.
Fig. 2.23 Thermogram of 30 phr HAF black loaded cardanol based NR vulcanizate
The thermal properties are to some extent governed by the presence of the plasticizer. In this case, cardanol has a potential point of weakness in the linear aliphatic side chain. This may explain the lower amount of residue in the case of the cardanol based sample. The thermal data are given in Table 13.

Fig. 2.24 Thermogram of 30 phr HAF black loaded ar.oil based sample
Table 2.13 Thermal data of 30 phr black loaded samples

<table>
<thead>
<tr>
<th>Property</th>
<th>Cardanol</th>
<th>Aromatic oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>On set point of degradation</td>
<td>308.68</td>
<td>299.6</td>
</tr>
<tr>
<td>Temperature of 50% degradation</td>
<td>401.5</td>
<td>407.05</td>
</tr>
<tr>
<td>Maximum degradation temperature</td>
<td>389.96</td>
<td>389.26</td>
</tr>
<tr>
<td>Maximum rate of degradation (% / °C)</td>
<td>1.207</td>
<td>1.094</td>
</tr>
<tr>
<td>Residue (%)</td>
<td>22.89</td>
<td>28.04</td>
</tr>
</tbody>
</table>

I) Differential scanning calorimetric analysis: The DSC data (Table 2.14) show no difference in the $T_g$ and $T_m$ values when cardanol and aromatic oil are used as plasticizers whereas $\Delta H_m$ is slightly higher for the cardanol based sample. The differential scans of cardanol and aromatic oil based samples are given in Figs.2.25 and 2.26 respectively.

Table 2.14 DSC data of 30 phr HAF black filled samples

<table>
<thead>
<tr>
<th>Property</th>
<th>Cardanol</th>
<th>Aromatic oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition - onset (°C)</td>
<td>-63.39</td>
<td>-63.24</td>
</tr>
<tr>
<td>Glass transition - midpoint (°C)</td>
<td>-60.83</td>
<td>-60.49</td>
</tr>
<tr>
<td>$T_m$ - onset (°C)</td>
<td>79.26</td>
<td>79.66</td>
</tr>
<tr>
<td>$T_m$ - peak(°C)</td>
<td>94.8</td>
<td>93.39</td>
</tr>
<tr>
<td>$T_m$ - end set (°C)</td>
<td>103.94</td>
<td>102.43</td>
</tr>
<tr>
<td>$\Delta H_m$ (mJ/mg)</td>
<td>1.6414</td>
<td>1.417</td>
</tr>
</tbody>
</table>
Fig. 2.25 Differential scan of 30 phr HAF black loaded sample containing cardanol

Fig. 2.26 Differential scan of 30 phr HAF black loaded sample containing aromatic oil
B) Optimization of cardanol content for 30phr HAF black filled sample

a) Variation of cure characteristics with cardanol content (% of HAF black)

There is not much variation in cure time (Fig. 2.27) with cardanol content whereas α value (Fig. 2.28) which is a measure of filler agglomeration is a minimum when cardanol is 7.5% of HAF black. Again, the rate of cure as indicated by the cure rate index curve (Fig. 2.29) shows a somewhat steady but slow increase with cardanol content. The positive influence of cardanol on the curing process is indicated by this.

Fig. 2.27 Variation of cure time with cardanol content

Fig. 2.28 Variation of α value with cardanol content
b) Variation of physical properties with cardanol content

Fig 2.30 shows that maximum tensile strength is obtained at 5% cardanol content (of HAF black weight). Fig. 2.31 shows that elongation at break increases roughly with increase in cardanol content. The variation of modulus at 300% elongation (MPa) is given in Fig 2.32. The modulus slightly decreases with cardanol content. Tear strength (N/mm) (Fig 2.33), also shows a prominent maximum value at 5% cardanol content. Tear strength is sharply influenced by the filler content and its dispersion.
Fig. 2.31 Variation of elongation at break (%) with cardanol content

Fig 2.32 Variation of modulus at 300% elongation (MPa) with cardanol content
Fig. 2.33 Variation of tear strength (N/mm) with cardanol content

Figures 2.30 and 2.33 indicate that the optimum amount of cardanol (plasticizer) based on tensile and tear properties of the vulcanizate is 5% of filler. The elongation at break shows a mild increasing tendency (Figure 2.31) at higher cardanol contents due to excessive plasticization. The lowering of tensile modulus (Figure 2.32) with increasing cardanol content is also based on this. A lower requirement of plasticizer (5% as against 10% for aromatic oil) improves the economic viability of the concept.

Fig. 2.34 Variation of abrasion loss (cc/hr.) with cardanol content
Abrasion loss (Fig 2.34) and resilience (Fig 2.36) increase with increase in cardanol content whereas hardness (Fig 2.35) is almost steady.

**Fig. 2.35 Variation of hardness (shore A) with cardanol content**

**Fig. 2.36 Variation of resilience (%) with cardanol content**
C) Ageing at 100°C of HAF black filled samples

a) 10 phr HAF black filled NR

Fig. 2.37 Variation of tensile strength with no. of days of ageing

Fig. 2.38 Variation of elongation at break with no. of days
Fig. 2.39 Variation of modulus at 300% elongation with no. of days

Fig. 2.40 Variation of tear strength with no. of days
b) 20phr HAF black filled NR

![Graph of tensile strength variation](image1.png)

**Fig. 2.41 Variation of tensile strength with no. of days**

![Graph of elongation at break variation](image2.png)

**Fig. 2.42 Variation of elongation at break with no. of days**
Fig. 2.43 Variation of modulus at 300% elongation no. of days

Fig. 2.44 Variation of tear strength with no. of days
c) 30phr HAF black filled NR

Fig. 2.45 Variation of tensile strength with no. of days

Fig. 2.46 Variation of elongation at break with no. of days
Fig. 2.47 Variation of modulus at 300% elongation with no. of days

Fig. 2.48 Variation of tear strength with no. of days
d) 40phr HAF black filled NR

Fig. 2.49 Variation of tensile strength with no. of days

Fig. 2.50 Variation of modulus at 300% elongation with no. of days
Fig. 2.51 Variation of elongation at break with no. of days

Fig. 2.52 Variation of tear strength with no. of days
e) 50phr HAF black filled NR

**Fig. 2.53** Variation of tensile strength with no. of days

**Fig. 2.54** Variation of elongation at break (%) with no. of days
Fig. 2.55 Variation of tear strength of with no. of days

Figures 2.37 to 2.55 indicate the ageing behaviour of samples containing different plasticizers and varying percentages of HAF black filler. The behaviour of all cardanol based samples show remarkable similarity in the case of tensile strength, tear strength, maximum strain and 300% modulus. These properties show a rapid fall after the first day of ageing to be followed by a rapid increase on the second day. With the exception of 300% modulus, all properties tend to fall beyond this point. In general, the properties measured are better for the cardanol based samples for almost the whole period of ageing. Since fairly rigorous conditions have been employed for ageing, the thermal age resistance of the cardanol based samples is seen to be remarkably good. The aromatic oil based samples show a rapid decline throughout the ageing period. The fall in properties after the first day of ageing, may be the result of reversal or modification of chemical reactions that had taken place between cardanol and sulphur during the curing process indicated by the FTIR spectra in Fig. 2.20 of Section 2.3.1. It can be hypothesized that the sulphur liberated by this process is utilized subsequently by the rubber, which is reflected by improved properties after the second day of ageing. Variation of free sulphur content estimated at various stages of ageing shown in Fig. 2.22 of Section 2.3.1 is supportive of this.
D) Silica filled compounds
a) Curing studies

Fig. 2.56 is a comparison of typical cure curves for both cases. Higher torque values are attained for aromatic oil during cure. The lower values of torque attained during cure by the cardanol containing compound point to a lower shear modulus and a more effective plasticizing action.

Fig. 2.56 Cure curves of cardanol and aromatic oil based samples with 15 phr silica loading.

Fig. 2.57 Variation of cure time with silica loading
Curing studies indicate that the variation of cure time (Fig. 2.57) with silica content is similar for both processing oils.

![Graph showing the variation of cure rate index (CRI) with silica loading for cardanol and aromatic oil](image)

**Fig. 2.58 Variation of CRI with silica loading**

Fig. 2.58 gives the variation of CRI with silica loading. The cure rate is slightly higher for cardanol based compounds indicating the possibility of a role for cardanol in the curing process. Fig. 2.59 shows a comparison of the variation of $\alpha$-value with silica content. Lower $\alpha$ values are obtained for cardanol based samples indicating that cardanol is a better medium for dispersing silica and it provides a higher degree of plasticization than aromatic oil. The lower $\alpha$, values also show that filler agglomeration takes place to a much smaller extent in cardanol based vulcanizates resulting in better utilization of filler. The lower viscosity of cardanol may also lead to better flow properties and consequently better wetting of the filler rubber interface compared to aromatic oil.
Fig. 2.59 Variation of $\alpha$ value with silica loading

Kinetics of cure reactions of 15phr silica filled cardanol and aromatic oil based compounds (Figs. 2.60 and 2.61) show that they obey first order kinetics as $\ln(M_h - M_t)$ vs $t$ plot gives a straight line with rate constant $k = 2.10$ and 2.11 respectively. This shows that cardanol does not alter the kinetics of cure reactions when used as plasticizer.

Fig. 2.60 $\ln(M_h - M_t)$ vs $t$ for cardanol based compound containing 15phr silica; $k=2.10$
Fig. 2.61 $\ln (M_t - M_i)$ vs $t$ for aromatic oil based compound containing 15phr silica; $k=2.11$

**b. Tensile Strength:** Fig. 2.62 shows the variation of tensile strength of silica reinforced natural rubber for both cases. The curves are similar and 15phr silica appears to be the optimal filler content for both cases. The performance of cardanol is almost equivalent to that of aromatic oil. But a deviation from the pattern is noticed beyond 20phr silica. At 20phr, there is a fall in tensile strength for the cardanol case. It is possible that there is a need to optimize the percentage of cardanol at higher filler contents. Fig. 2.63 shows the change in elongation at break on using cardanol in place of aromatic oil. Here also both plasticizers behave similarly although values for aromatic oil are higher for low silica content (5-10%). Similar values were obtained from 300% modulus (Fig.2.64) measurements on both samples. The tensile properties, in general, show that cardanol is not inferior to aromatic oil as plasticizer.
Fig. 2.62 Variation of tensile strength (MPa) with silica content

Fig. 2.63 Variation of elongation at break (%) with silica content
c) **Tear Strength:** The tear strength of samples employing both plasticizers has been measured as a function of silica content (Fig. 2.65). Both cases show almost equivalent performance although at 25phr silica content aromatic oil has some superiority. Similar to the case of tensile strength (Fig. 2.62)
Fig. 2.66 Variation of reinforcing index on the basis of tensile strength

Fig. 2.67 Variation of reinforcing index on the basis of tear strength

Figs. 2.66 and 2.67 indicate the variation of reinforcing index with filler content on the basis of tensile and tear strength respectively. They are similar for both plasticizers. On comparing Figs. 2.12 and 2.13 with Figs. 2.66 and 2.67, the
reinforcing effect of silica and HAF black are similar although very low percentages like 5% are not studied in the case of HAF black.

d) **Resilience**: The variation of resilience with silica content (Fig. 2.68) is similar for both plasticizers. A slight decrease in resilience with increase in silica content is observed in both cases.

![Graph of Resilience vs Silica Content](image)

**Fig. 2.68 Variation of resilience with silica loading**

e) **Hardness**: Surface hardness (Fig.2.69) of specimens employing both plasticizers also shows only minor variations.

f) **Abrasion loss**: Abrasion loss is slightly less when cardanol is used at higher silica contents. Fig. 2.70 shows the variation of abrasion loss with silica content.
Natural rubber

Fig. 2.69 Variation of hardness with silica loading

Fig. 2.70 Variation of abrasion loss with silica loading

g) Soxhlet extraction: Fig.2.71 is a plot of the weight loss on Soxhlet extraction of NR samples plasticized by the two different materials. In general, cardanol gives less toluene soluble material in the vulcanizate for most of the range.
Fig. 2.71 Weight loss on Soxhlet extraction of silica loaded samples using toluene as solvent

**h) Thermogravimetric analysis:** Thermogravimetric analysis (Table 2.15) shows that the thermal stability of both samples is similar.

**Table 2.15 TGA of 15 phr silica filled samples**

<table>
<thead>
<tr>
<th>Property</th>
<th>Cardanol</th>
<th>Aromatic oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>On set point of degradation</td>
<td>320.07</td>
<td>311.92</td>
</tr>
<tr>
<td>Temperature of 50% degradation</td>
<td>391.84</td>
<td>392.92</td>
</tr>
<tr>
<td>Maximum degradation temperature</td>
<td>385.10</td>
<td>385.44</td>
</tr>
<tr>
<td>Maximum rate of degradation (%/°C)</td>
<td>1.374</td>
<td>1.365</td>
</tr>
<tr>
<td>Residue (%)</td>
<td>13.37</td>
<td>14.10</td>
</tr>
</tbody>
</table>
E) Optimization of cardanol content in 15phr silica filled sample

a) Variation of cure characteristics with cardanol content (% of silica)

Fig. 2.72 Variation of cure time (min) with cardanol content

Fig. 2.73 Variation of cure rate index with cardanol content
b) Variation of mechanical properties with cardanol content

Fig. 2.74 Variation of alpha value with cardanol content

Fig. 2.75 Variation of tensile strength (MPa) with cardanol content
Fig. 2.76  Variation of tear strength (N/mm) with cardanol content

Fig. 2.77  Variation of modulus at 300% elongation (MPa) with cardanol content
Fig. 2.78 Variation of elongation at break (%) with cardanol content

Fig. 2.79 Variation of resilience (%) with cardanol content
Fig. 2.80 Variation of abrasion loss (cc/hr.) with cardanol content

Figs 2.72 – 2.74 give the variation of cure characteristics with cardanol content. The CRI (Fig.2.73) shows a sharp increase from 5 - 10 % but remains steady for the rest of the range. There is not much difference in cure characteristics with increase in cardanol content. Figs 2.75- 2.80 give the variation of mechanical properties with cardanol content. The tensile strength and tear strength are not very sensitive to silica content. Still an optimal behaviour is noticed at 10phr. Modulus and elongation at break values are sharply influenced by cardanol content. Similarly resilience (Fig. 2.79) and abrasion loss (Fig. 2.80) are also affected by cardanol %.
F) Ageing of silica based vulcanizates at 100°C

i) 5phr silica based vulcanizates

Fig. 2.81 Variation of tensile strength (MPa) with no. of days

Fig. 2.82 Variation of elongation at break (%) with no. of days
Fig. 2.83 Variation of tear strength (N/mm) with no. of days

ii) 10phr silica based vulcanizates

Fig. 2.84 Variation of tensile strength (MPa) with no. of days
Fig. 2.85 Variation of elongation at break (%) with no. of days

Fig. 2.86 Variation of tear strength (N/mm) with no. of days
iii) 15phr silica based vulcanizates

Fig. 2.87 Variation of tensile strength (MPa) with no. of days

Fig. 2.88 Variation of elongation at break (%) with no. of days
iv) 20phr silica based vulcanizates

Fig. 2.89 Variation of tear strength (N/mm) with no. of days

Fig. 2.90 Variation of tensile strength (MPa) with no. of days
Natural rubber

Fig. 2.91 Variation of elongation at break (%) with no. of days

Fig. 2.92 Variation of tear strength (N/mm) with no. of days
v) 25phr silica based vulcanizates

**Fig. 2.93** Variation of tensile strength (MPa) with no. of days

**Fig. 2.94** Variation of elongation at break (%) with no. of days
Figs. 2.81 to 2.95 indicate the ageing behaviour of samples containing different amounts of fillers and employing each plasticizer. After ageing for 10 days at 100°C, the cardanol-based vulcanizate shows superiority in tensile properties over the aromatic oil based samples. For the most part, especially in the case of tensile strength and tear strength, the cardanol based samples show better performance. Though the elongation at break is lower for cardanol based vulcanizates (all cases) after the first day of ageing, it is higher for the rest of the ageing period. Hence embrittlement during ageing is less likely in the case of cardanol. Crosslinking between cardanol and NR chains via sulphur linkages cannot be ruled out. But the sulphur-cardanol linkages may be sensitive to the prolonged ageing process, resulting in the liberation of sulphur. In almost all cases of tensile strength, tear strength and some cases of elongation at break, the graph for cardanol goes through a maximum on the third day of ageing. This makes an interesting comparison with the case of black filled samples when the maximum were most often noticed on the second day of ageing.
Chapter II

G) Ageing of 15phr silica based samples at 70°C

Fig. 2.96 Variation of tensile strength (MPa) with no. of days

Fig. 2.97 Variation of elongation at break (%) with no. of days
Figs. 2.96 to 2.98 indicate the ageing behaviour (70°C) of samples employing each plasticizer. After ageing for 10 days at 70°C, the cardanol-based vulcanizate shows a clear superiority in tensile properties over the aromatic oil based samples. Towards the end of the ageing period (10 days), the tear strength (Fig.2.98) of the aromatic oil based rubber shows rapid degradation whereas the cardanol based product shows an almost steady value.

Ageing at 70°C may not offer conditions rigorous enough to break any cardanol sulphur linkages already formed during cross linking. Hence the absence of ups and downs earlier observed in the case of 100°C ageing for black filled and silica filled samples.
Chapter II

H) Weathering studies on 30phr HAF black filled samples

Fig. 2.99 Variation of tensile strength (MPa) with no. of months

Fig. 2.100 Variation of elongation at break (%) with no. of months
The tensile properties (Fig. 2.99 – 2.101) and tear strength (Fig. 2.102) values indicate the comparative performance of cardanol and aromatic oil as plasticizers after weathering 30phr HAF black filled samples in outdoor conditions for one year. The studies show that the comparative performance is similar for both cases. But the tear strength retention (Fig. 2.102) is noticeably better for cardanol based samples.
I) Comparative study of cardanol and CNSL as plasticizers for NR

Fig. 2.103 Variation of tensile strength with HAF black content

Fig. 2.104 Variation of tensile strength with HAF black content
Natural rubber

Fig. 2.105 Variation of elongation at break (%) with HAF black content

Fig. 2.106 Variation of modulus at 300% elongation (MPa) with HAF black content
Fig. 2.107 Variation of tear strength (N/mm) with HAF black content

Fig. 2.108 Variation of hardness (Shore A) with HAF black content
Fig. 2.109 Variation of resilience (%) with HAF black content

This section reports results on plasticization by CNSL in place of aromatic oil. Cardanol is the main ingredient of CNSL which also contains cardol, methyl cardol and tarry materials. Since CNSL is cheaper and more readily available than cardanol, its performance in comparison with cardanol has been studied.

Figs.2.103-2.109 indicate the comparative performance of cardanol and CNSL at various filler contents. In general, the performance of CNSL is comparable to that of cardanol. However, CNSL, being a crude agro-byproduct, can have a varying composition depending on place of origin and method of processing. Hence cardanol is to be preferred. Moreover, CNSL can undergo changes during storage and has a much higher viscosity.
Chapter II

J) Ageing of cardanol and CNSL based samples at 100°C

![Graph showing variation of tensile strength (MPa) with number of days for cardanol and CNSL.](image)

**Fig. 2.110** Variation of tensile strength (MPa) with no. of days

![Graph showing variation of elongation at break (%) with number of days for cardanol and CNSL.](image)

**Fig. 2.111** Variation of elongation at break (%) with no. of days

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Figs. 2.110-2.113 indicate the comparative ageing behaviour of cardanol and CNSL plasticized samples. 30phr HAF black filled samples were used in both cases. Even though the performance of samples plasticized by both plasticizers are comparable, CNSL is not favoured as a plasticizer because of inconsistency in composition. The marginally better tensile and tear strength after ageing in the case of CNSL based vulcanizates are attributed to the presence of a larger amount of polymeric matter.
Chapter II

2.3.2 Cardanol as antioxidant in NR

(a) Antioxidant property of cardanol in NR gum compounds

Cardanol being a substituted phenol, antioxidant activity can be expected from its use. It may function as a primary antioxidant whereby it can donate the phenolic proton and stabilize the phenoxy radical by electron delocalization in the aromatic ring.

![Cure curves of NR gum samples](image)

**Fig. 2.114 Cure curves of NR gum samples.**

**Table 2.16: Cure characteristics with cardanol as antioxidant in gum samples**

<table>
<thead>
<tr>
<th></th>
<th>$t_{2}$ (min)</th>
<th>$t_{10}$ (min)</th>
<th>$t_{50}$ (min)</th>
<th>$t_{90}$ (min)</th>
<th>Max. torque (dNm)</th>
<th>Min. torque (dNm)</th>
<th>CRI (min)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardanol</td>
<td>5.80</td>
<td>3.63</td>
<td>5.10</td>
<td>8.61</td>
<td>3.19</td>
<td>0.01</td>
<td>35.8</td>
</tr>
<tr>
<td>SP</td>
<td>7.01</td>
<td>4.14</td>
<td>5.63</td>
<td>8.97</td>
<td>2.756</td>
<td>0.035</td>
<td>51</td>
</tr>
<tr>
<td>TQ</td>
<td>6.64</td>
<td>4.05</td>
<td>5.5</td>
<td>8.73</td>
<td>2.879</td>
<td>0.55</td>
<td>47.8</td>
</tr>
</tbody>
</table>

Fig. 2.114 gives the cure curves of NR gum samples containing 1) cardanol 2) TQ and 3) SP as antioxidant. Similar cure curves are obtained for all the three samples.
with the cardanol based sample showing the maximum torque. From the measurement of cure characteristics of NR gum compounds containing 1) cardanol 2) TQ and 3) SP as antioxidant, it is seen that the minimum torque and cure rate index values (Table 2.16) are lowest for the cardanol based sample whereas the maximum torque is found to be highest for the cardanol based sample. The presence of SP leads to the highest CRI value.

b) Ageing of gum samples at 100° C

Figures 2.115-2.118 show the results of ageing tensile and tear samples containing different antioxidants, viz. cardanol, TQ and SP in NR gum compounds at 100° C for 48 hours.

![Graph showing tensile strengths of gum samples containing cardanol, TQ, and SP before and after ageing.]

**Fig. 2.115** Tensile strengths of gum samples containing cardanol / SP / TQ as antioxidants before and after ageing.
Chapter II

Fig. 2.116  Elongation at break (%) of gum samples containing cardanol / SP / TQ as antioxidants before and after ageing.

Fig. 2.117  Modulus at 300% elongation of gum samples containing cardanol / SP / TQ as antioxidants before and after ageing.
In the matter of retaining tensile and tear strengths on 48h ageing, all antioxidants give similar performance. But it must be remembered that usual amounts of cardanol will be more than this in the role of plasticizer. This leads to still better performance by cardanol.

c) Ageing at 70°C of gum samples for 5 days

Fig. 2.119 Variation of tensile strengths of NR gum samples containing cardanol / SP / TQ as antioxidants
Chapter II

Fig. 2.120 Variation of modulus at 300 % elongation of NR gum samples containing cardanol / SP / TQ as antioxidants

Fig. 2.121 Variation of tear strengths of NR gum samples containing cardanol / SP / TQ as antioxidants

The tensile and tear properties (Figs. 2.119-2.121) of cardanol, TQ and SP based vulcanizates on ageing are similar after five days of ageing at 70°C. Thermal analysis of natural rubber gum vulcanizates (Table 2.17) with each of TQ, SP and cardanol as antioxidants gives similar thermal stability in all cases. Figs. 2.122-
2.124 give the thermograms of NR gum samples containing SP, cardanol and TQ as antioxidant respectively.

**Table 2. 17: TGA of NR gum samples with different antioxidants**

<table>
<thead>
<tr>
<th>Property</th>
<th>Cardanol</th>
<th>SP</th>
<th>TQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset point of degradation (°C)</td>
<td>305.93</td>
<td>311.03</td>
<td>310.24</td>
</tr>
<tr>
<td>Temp at 50% degradation (°C)</td>
<td>385.43</td>
<td>386.12</td>
<td>386.31</td>
</tr>
<tr>
<td>Temp at maximum rate of degradation (°C)</td>
<td>382.15</td>
<td>383.22</td>
<td>382.39</td>
</tr>
<tr>
<td>Maximum rate of degradation (% / °C)</td>
<td>1.679</td>
<td>1.623</td>
<td>1.554</td>
</tr>
<tr>
<td>Residue (%)</td>
<td>4.401</td>
<td>4.218</td>
<td>4.376</td>
</tr>
</tbody>
</table>

![Fig. 2.122 Thermogram of NR gum sample containing SP as antioxidant](image-url)
Fig. 2.123 Thermogram of NR gum sample with cardanol as antioxidant

Fig. 2.124 Thermogram of NR gum sample with TQ as antioxidant

d) Ageing of silica filled samples of varying filler contents at 100°C for 5 days

Figs. 2.125 - 2.129 indicate results of tensile strength tests on samples containing
a) cardanol as plasticizer without any added antioxidant. b) aromatic oil as plasticizer without any added antioxidant c) aromatic oil as plasticizer and SP as added antioxidant. The results indicate that in general after five days of ageing silica filled samples at 100°C, the antioxidant activity has not stopped the samples from loss of tensile strength. However, for most cases, cardanol still retains a
marginal superiority over the other two cases. The difference in behaviour is more noticeable as the filler content and consequently the cardanol content go up, say at 25phr (Fig. 2.144).

![Graph of tensile strength variation](image1)

**Fig. 2.125** Variation of tensile strength (MPa) of 5phr silica filled samples with no. of days

![Graph of tensile strength variation](image2)

**Fig. 2.126** Variation of tensile strength (MPa) of 10phr silica filled samples with no. of days
Fig. 2.127 Variation of tensile strength (MPa) of 15phr silica filled samples with no. of days

Fig. 2.128 Variation of tensile strength (MPa) of 20phr silica filled samples with no. of days
Fig. 2.129 Variation of tensile strength (MPa) of 25phr silica filled samples with no. of days

Fig. 2.130 Variation of tear strength (N/mm) of 5phr silica filled samples with no. of days
Fig. 2.131 Variation of tear strength (N/mm) of 10phr silica filled samples with no. of days

Fig. 2.132 Variation of tear strength (N/mm) of 15phr silica filled samples with no. of days
Fig. 2.133 Variation of tear strength (N/mm) of 20phr silica filled samples with no. of days

Fig. 2.134 Variation of tear strength (N/mm) of 25phr silica filled samples with no. of days

Figs. 2.130 - 2.134 indicate the tear strength values of similar samples on ageing. Generally the cardanol based samples show superior ageing behaviour with respect to tear strength. This effect becomes more apparent as the cardanol content goes up steadily with the silica filler content.
Figs. 2.135 – 2.139 indicate results of tensile strength tests on samples containing a) cardanol as plasticizer without any added antioxidant b) aromatic oil as plasticizer without any added antioxidant c) cardanol as plasticizer and SP as added antioxidant. The properties are found to be better when cardanol is used as plasticizer only. Styrenated phenol is found to reduce the antioxidant property of cardanol.

**Fig. 2.135** Variation of tensile strength (MPa) of 5phr silica filled samples with no. of days

**Fig. 2.136** Variation of tensile strength (MPa) of 10 phr silica filled samples with no. of days
Fig. 2.137 Variation of tensile strength (MPa) of 15 phr silica filled samples with no. of days

Fig. 2.138 Variation of tensile strength (MPa) of 20 phr silica filled samples with no. of days
Fig. 2.139 Variation of tensile strength (MPa) of 25 phr silica filled samples with no. of days

Figs. 2.140 -2.144 indicate the tear strength values of similar samples on ageing. Generally the cardanol based samples show superior ageing behaviour with respect to tear strength. For low levels of silica content, the quantity of cardanol used as plasticizer is proportionately less. Hence the effect is not pronounced at low levels of silica filler content.

Fig. 2.140 Variation of tear strength (MPa) of 5 phr silica filled samples with no. of days
Fig. 2.141 Variation of tear strength (MPa) of 10 phr silica filled samples with no. of days

Fig. 2.142 Variation of tear strength (MPa) of 15 phr silica filled samples with no. of days
Fig. 2.143 Variation of tear strength (MPa) of 20 phr silica filled samples with no. of days.

Fig. 2.144 Variation of tear strength (MPa) of 25 phr silica filled samples with no. of days.
2.3.3 Cardanol as co-activator

Co-activator property of cardanol in comparison with a conventional co-activator, stearic acid was determined by comparing cure characteristics and physical properties of the vulcanizates.

a) Cure characteristics

Figure 2.145 gives the cure curves when 1) cardanol 2) stearic acid and 3) (cardanol+stearic acid) are used as co-activators. Similar curves are obtained in all the three cases of which the highest torque is obtained when cardanol is used as co-activator.

![Cure curves for different co-activators in NR](image)

Fig. 2.145 Cure curves for different co-activators in NR

The scorch time, cure time, t_10 and t_50 (Table 2.18) are found to be slightly higher for cardanol based samples. Similarly, the maximum and minimum torque values are also higher, whereas the CRI is found to be least when cardanol is used as co-activator. Hence, judging from cure characteristics, cardanol possesses only moderate co-activator property.
### Table 2. 18 Cure characteristics of cardanol and / stearic acid as co-activator in gum compounds

<table>
<thead>
<tr>
<th>Co-activator</th>
<th>$t_{10}$, min</th>
<th>$t_{50}$, min</th>
<th>$t_{52}$, min</th>
<th>$t_{90}$, min</th>
<th>Max. torque, dNm</th>
<th>Min. torque, dNm</th>
<th>CRI, Min-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic acid</td>
<td>3.28</td>
<td>4.29</td>
<td>5.5</td>
<td>7.03</td>
<td>2.64</td>
<td>0.032</td>
<td>64.93</td>
</tr>
<tr>
<td>Cardanol</td>
<td>3.92</td>
<td>5.41</td>
<td>6.7</td>
<td>8.76</td>
<td>2.82</td>
<td>0.059</td>
<td>48.54</td>
</tr>
<tr>
<td>(Cardanol + Stearic acid)</td>
<td>4.02</td>
<td>5.43</td>
<td>6.83</td>
<td>8.55</td>
<td>2.72</td>
<td>0.045</td>
<td>58.1</td>
</tr>
</tbody>
</table>

### Table 2. 19 Physical properties when cardanol and / stearic acid is used as co-activator in gum compounds

<table>
<thead>
<tr>
<th>Co-activator</th>
<th>Tensile strength, MPa</th>
<th>Tear strength, N/mm</th>
<th>Elongation at break, %</th>
<th>Modulus at 300% elongation, MPa</th>
<th>Resilience, %</th>
<th>Hardness, Shore A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardanol</td>
<td>24.8</td>
<td>41.6</td>
<td>1067</td>
<td>1.68</td>
<td>73</td>
<td>35</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>24.71</td>
<td>37.25</td>
<td>1121</td>
<td>1.35</td>
<td>72</td>
<td>34</td>
</tr>
<tr>
<td>(Stearic acid + Cardanol)</td>
<td>21.89</td>
<td>35.9</td>
<td>1003</td>
<td>1.89</td>
<td>68</td>
<td>37</td>
</tr>
</tbody>
</table>
b) Physical properties

Table 2.19 gives a comparison of physical properties when 1) cardanol 2) stearic acid or 3) cardanol + stearic acid are used as co-activators in NR gum compounds. The physical properties of cardanol based samples are comparable to that of stearic acid based ones. Thus it can be concluded that cardanol possesses co-activator property.

In order to investigate interactions between cardanol and Zn$^{++}$ ion, mixtures of 1) cardanol + ZnO and 2) Zn Cl$_2$ + cardanol were prepared and their IR spectra compared with the spectra of pure a) cardanol b) ZnO and c) Zn Cl$_2$. The IR spectra of the samples were taken on the same day. On comparison of 1) cardanol (Fig. 2.18) and 2) cardanol + ZnO (Fig. 2.146), it is seen that the O-H stretching frequency of cardanol is shifted from 3360.35 to 3350.66 cm$^{-1}$ indicating an interaction between cardanol and Zn$^{++}$. As the $\pi$- $\pi$ bond absorptions of Zn$^{++}$ and oxygen are in the region 500-400 cm$^{-1}$ and as the absorptions in the region are subtle, the IR spectrum of Zn Cl$_2$ + cardanol (Fig. 2.147) is compared with the absorptions of 1) cardanol and 2) ZnCl$_2$. The O-H stretching frequency of cardanol is shifted from 3360.35 to 3398.78. It is also seen that the absorptions of ZnCl$_2$ in (Zn Cl$_2$+cardanol) in the region 500-400 cm$^{-1}$ are shifted towards the absorptions of ZnO indicating that $\pi$- $\pi$ bonding occurs between the oxygen of cardanol and Zn$^{++}$. Hence interaction between cardanol and ZnO is indicated. This can be the result of a complex formation between cardanol and Zn$^{++}$ ion.
Chapter II

Fig. 2.18 FTIR spectrum of cardanol

Fig. 2.146 FTIR spectrum of (cardanol + ZnO)
c) Optimization of cardanol content for co-activator effect

Cure characteristics of gum compounds were determined (Table 2.20) for varying amounts of cardanol as co-activator. Minimum cure time is obtained when 1phr cardanol is used as co-activator.

Table 2.20 Cure characteristics for different cardanol percentages

<table>
<thead>
<tr>
<th>Cardanol, phr</th>
<th>ta, min</th>
<th>t10, min</th>
<th>t50, min</th>
<th>t90, min</th>
<th>Max., torque dNm</th>
<th>Min., torque dNm</th>
<th>CRI, min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>5.5</td>
<td>3.28</td>
<td>4.29</td>
<td>7.04</td>
<td>2.64</td>
<td>0.032</td>
<td>69.93</td>
</tr>
<tr>
<td>1.5</td>
<td>4.62</td>
<td>2.87</td>
<td>3.89</td>
<td>6.05</td>
<td>2.785</td>
<td>0.006</td>
<td>69.9</td>
</tr>
<tr>
<td>1</td>
<td>4.57</td>
<td>2.91</td>
<td>3.85</td>
<td>6.01</td>
<td>2.86</td>
<td>0.039</td>
<td>69.44</td>
</tr>
<tr>
<td>0.5</td>
<td>5.56</td>
<td>3.67</td>
<td>4.55</td>
<td>7.02</td>
<td>2.678</td>
<td>0.094</td>
<td>68.49</td>
</tr>
<tr>
<td>0.25</td>
<td>5.05</td>
<td>3.07</td>
<td>4.09</td>
<td>6.48</td>
<td>2.677</td>
<td>0.035</td>
<td>69.9</td>
</tr>
</tbody>
</table>
TGA shows (Table 2.21) that thermal stability when cardanol is used as co-activator is similar to that when stearic acid is used. The respective thermograms are given in Figs. 2.148 and 2.149.

Table 2.21: Thermal analysis when cardanol is used as co-activator

<table>
<thead>
<tr>
<th>Property</th>
<th>Cardanol</th>
<th>Stearic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset point of degradation (°C)</td>
<td>302.63</td>
<td>272.36</td>
</tr>
<tr>
<td>Temp at maximum rate of degradation (°C)</td>
<td>381.71</td>
<td>384.53</td>
</tr>
<tr>
<td>Temp of 50% degradation (°C)</td>
<td>387.5</td>
<td>389.6</td>
</tr>
<tr>
<td>Maximum rate of degradation (%/°C)</td>
<td>1.601</td>
<td>1.59</td>
</tr>
<tr>
<td>Residue (%)</td>
<td>4.254</td>
<td>4.571</td>
</tr>
</tbody>
</table>

Fig. 2.148 Thermogram of NR gum vulcanizate containing stearic acid as co-activator.
Fig. 2.149 Thermogram of NR gum vulcanizate containing cardanol as co-activator.

Fig. 2.150 Variation of cure time (min) with cardanol content
Figs. 2.150-2.152 indicate the variation of cure time, maximum torque and cure rate index respectively with cardanol content (co-activator). Cure time is found to be a minimum for 1-1.5phr cardanol, whereas maximum torque is obtained for 1 phr cardanol. The cure rate index is not much affected by cardanol content in this concentration range.
2.3.4 Cardanol as accelerator

Table 2.22 Cure Characteristics when cardanol is used as accelerator

<table>
<thead>
<tr>
<th>Accelerator</th>
<th>( t_{52} ) (min)</th>
<th>( t_{10} ) (min)</th>
<th>( t_{50} ) (min)</th>
<th>( t_{90} ) (min)</th>
<th>Max. torque (dNm)</th>
<th>Min. torque (dNm)</th>
<th>CRI (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBS</td>
<td>6.7</td>
<td>3.92</td>
<td>5.41</td>
<td>8.76</td>
<td>2.815</td>
<td>0.059</td>
<td>48.54</td>
</tr>
<tr>
<td>Cardanol</td>
<td>-</td>
<td>1.77</td>
<td>15.32</td>
<td>26.42</td>
<td>0.542</td>
<td>0.062</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Table 2.22 gives the cure characteristics when CBS is replaced by cardanol in gum compound. Cardanol does not show any accelerator property.

2.3.5 Sulphurless curing

When cardanol is used along with DCP for NR curing (Tables 2.23, 2.24 and Fig. 2.153), no positive effect is noticed.

![Cure curves of sulphurless curing](image)

Fig.2.153 Cure curves of sulphurless curing
### Table 2.23 Cure characteristics for DCP curing

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>$t_{10}$, min</th>
<th>$t_{50}$, min</th>
<th>$t_{90}$, min</th>
<th>$t_{91}$, min</th>
<th>Min. torque, dNm</th>
<th>Max. torque, dNm</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCP</td>
<td>1.24</td>
<td>5.33</td>
<td>18.75</td>
<td>8.11</td>
<td>0.13</td>
<td>1.653</td>
</tr>
<tr>
<td>DCP + cardanol</td>
<td>1.13</td>
<td>5.79</td>
<td>19.28</td>
<td>17.54</td>
<td>0.023</td>
<td>1.163</td>
</tr>
</tbody>
</table>

### Table 2.24 Mechanical properties for DCP curing

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Tensile strength, MPa</th>
<th>Elongation at break (%), 300%</th>
<th>Modulus at 300%, MPa</th>
<th>Tear strength, N/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCP</td>
<td>5.6</td>
<td>995</td>
<td>0.79</td>
<td>15.8</td>
</tr>
<tr>
<td>DCP + cardanol</td>
<td>4.17</td>
<td>1129.9</td>
<td>0.66</td>
<td>12.21</td>
</tr>
</tbody>
</table>

### 2.4 Conclusions

Comparing the cure characteristics of HAF black filled NR for different plasticizers, the minimum torque values which indicate the viscosity are lower for cardanol plasticized compounds than aromatic oil plasticized compounds. The cure times of cardanol based samples are lower and the cure rate indices are higher. Similarly, the alpha value, which is a measure of filler agglomeration, is lower for cardanol based samples indicating better filler dispersion. The tensile properties in general show that cardanol is somewhat superior to aromatic oil as a plasticizer especially at higher filler contents. The tear strengths of cardanol based samples are marginally superior. The extractable matter in cardanol based samples is lower than that of aromatic oil based samples. The crosslink densities of cardanol based samples are somewhat lower. Optimization of cardanol content shows that optimum mechanical properties are obtained when cardanol is 5% of HAF black. Better ageing behaviour is observed for cardanol based samples on the basis of
ageing for five days in an air oven at 100°C. Kinetics of cure reactions of 30phr HAF Black filled compounds is similar for both cardanol and aromatic oil based samples with similar rate constants. Plasticization by CNSL is comparable to that of cardanol. Ageing behaviour of CNSL is somewhat superior to that of cardanol. The mechanical properties of cardanol based samples show a rapid fall after the first day of ageing to be followed up by rapid increase on the second day.

In the case of silica filled samples lower values of torque are attained during cure for cardanol based sample. Again cure times and alpha values are lower whereas the CRI values higher for the cardanol based samples. Kinetics of cure reactions of 15phr silica filled compounds are similar for both cardanol and aromatic oil based samples with equivalent rate constants. The mechanical properties and thermal stability are similar for both cardanol and aromatic oil based samples. The extractable matter in cardanol based samples is lower. Optimum amount of cardanol is about 10% of silica. Mechanical properties are superior for cardanol based samples after ageing 1) at 100°C for five days and 2) at 70°C for ten days.

Comparison of the antioxidant property of cardanol with TQ and SP in NR gum samples shows that thermal stability of the cardanol based sample is similar to that of TQ and SP based samples. The tensile and tear properties of cardanol, TQ and SP based vulcanizates after ageing at 70°C are similar after five days of ageing.

On comparing cure characteristics and mechanical properties the co-activator property of cardanol is comparable to stearic acid. Cardanol does not show any accelerator property.
REFERENCES

2. A.I. Medalia and G. Kraus, In: 'Science and Technology of Rubber' Eds. 8