

# A Comparative Study of Cardanol and Aromatic Oil as Plasticizers for Carbon-Black-Filled Natural Rubber

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**ABSTRACT:** Cardanol is the main ingredient of cashew nut shell liquid, an agro-byproduct. Its comparative merits vis-a-vis aromatic oil for plasticizing HAF-black-filled natural rubber (NR) is the subject of this article. Aromatic oil is the conventional plasticizer employed for such compounding requirements. The mechanical properties, ageing behavior, and torque time curves during cure of NR plasticized by both these materials are compared under identical

conditions. It has been established that cardanol, when used as plasticizer, gives rise to similar tensile properties, shorter cure times, and superior ageing behavior compared to aromatic oil. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4835–4841, 2006

**Key words:** FTIR; ageing; mechanical properties; crosslinking; vulcanization

## INTRODUCTION

Cardanol is the main ingredient of cashew nut shell liquid (CNSL), a byproduct of the cashew industry. As an agro-byproduct it has the advantages of low cost and renewable supply<sup>1–5</sup> and can replace phenol in many applications. Cardanol is obtained by vacuum distillation of commercial grade CNSL conforming to Indian Standard, I S: 841-1964. The structure of cardanol is given in Figure 1.

The potential for application of cardanol in rubber processing has been highlighted by many workers from time to time.<sup>6–10</sup> The properties of natural rubber (NR) modified with phosphorylated cashewnut shell liquid have been found to be superior to that employing another plasticizer, 2-ethyl hexyl diphenyl phosphate (Santicizer 141)<sup>11</sup> by Pillai and coworkers. The adhesive properties of blends of cardanol formaldehyde resin with poly chloroprene are another recently explored subject.<sup>12</sup>

Plasticizer molecules penetrate into the polymer matrix and establish polar attractive forces between them and the chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the segmental mobility, thereby reducing the  $T_g$  value.<sup>13</sup> Aromatic oil imparts the best processability to NR. Chlorinated paraffinic hydrocarbons are sometimes used as flame retardant

plasticizers, e.g., Cereclor (ICI). Several other substances have plasticizing ability and are used for special situations.<sup>14</sup> In the present work, the comparative performance of cardanol and aromatic oil, a conventional plasticizer has been investigated in terms of the mechanical and thermal properties of the final vulcanizate and parameters like crosslink density, free sulfur content, cure characteristics, etc. No attempt has been made to elucidate chemical interactions if any between NR chains and cardanol molecules.

## EXPERIMENTAL

### Raw materials

NR was obtained from Rubber Research Institute of India; Kottayam. Zinc oxide (activator) and stearic acid (coactivator) were supplied by M/s Meta Zinc, Mumbai, and Goderej Soaps, Mumbai, respectively. Cyclo hexyl benzothiazil sulfenamide and tetramethyl thiuram disulphide (accelerator) used in the present study were obtained from Polyolefins Industries, Mumbai. Sulfur (crosslinking agent) was supplied by Standard Chemicals, Chennai. High Abrasion Furnace black (N330) used in the present study was supplied by M/s Philips Carbon Black India, Cochin.

Aromatic oil obtained from Hindustan Organic Chemicals, Kochi, had the following specifications: Sp. gravity, 0.98; Aniline point, 43.00; Ash content % by mass, 0.01; viscosity gravity constant, 0.96.

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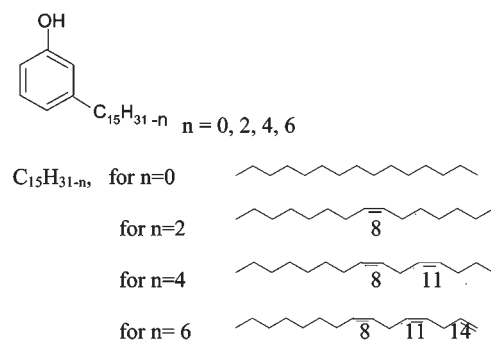


Figure 1 Structure of cardanol.

Refined CNSL conforming to Indian Standard 1 S: 840 (1964) was supplied by Pierce Leslie Limited, Cochin, in 200 L barrels. Cardanol was separated from commercial grade CNSL by distillation under reduced pressure (1 mmHg). The pale yellow fraction collected at 206–208°C was cardanol.<sup>15</sup>

### Compounding

Mixes were prepared on a laboratory size two-roll mixing mill ( $16 \times 33 \text{ cm}^2$ ) at a friction ratio of 1:1.25. A nip gap of 0.2 mm was set and the temperature maintained at  $(70 \pm 5)^\circ\text{C}$ . The compounding ingredients were added as per procedure given in ASTM D 3184-89 (2001) and over a time period of 18 min. For this work only carbon filler was employed. The formulations employed are given in Table I and each formulation was repeated with cardanol replacing aromatic oil.

### Curing

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. Subsequently, the rubber compounds were vulcanized up to the optimum cure time at  $150^\circ\text{C}$  and 11.6 MPa. The moldings 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.

### TESTING

The tensile tests were determined on dumb-bell shaped specimens and tear tests on Type C, unnicked test pieces with  $90^\circ$  angle on one side and with tab ends punched out from the vulcanized sheets. The measurements were carried out on a Shimadzu Universal Testing Machine (10 KN) with a grip separation of 40 mm, using a crosshead speed of 500 mm/min as per ASTM D412 and 624, respectively.

The hardness (Shore A) of the molded samples was determined using Zwick 3114 hardness tester in accordance with ASTM D 2240-05. The tests were performed on unstressed samples of 30 mm diameter and 6 mm thickness. The readings were taken after 10 s of indentation after firm contact had been established with the specimen. The abrasion resistance of the samples was determined using a DIN Abrader (DIN 53,516). Samples having a diameter of  $6 \pm 0.2 \text{ mm}$  and a thickness of 6 mm were kept on a rotating sample holder and a 10N load was applied. Initially a prerun was given for the sample and its weight taken. The weight after final run was also noted. The abrasion loss in cc/h was calculated using the formula

$$\text{abrasion loss} = (\text{loss of wt./sp. gr.}) \times 60/2.2 \text{ for an abrasion time of 2.2 min}$$

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  $28 \pm 0.5 \text{ g}$  is dropped from a height of 40 cm to the sample of thickness 12.5 mm and the rebound height is measured.

Soxhlet extraction was carried out by packing known weights of different samples of vulcanized rubber in Wattman I filter paper and extracting in a Soxhlet apparatus using toluene as solvent and the loss of weight (%) was noted.

FTIR spectra of the Soxhlet extract of the cardanol-based vulcanizate and cardanol were taken on Fourier

TABLE I  
NR Formulations for Varying HAF-Black Content

Sample	NR (phr)	ZnO (phr)	St. acid (phr)	HAF (phr)	Aromatic oil/ cardanol (phr)	TQ (phr)	CBS (phr)	S (phr)
1	100	5	2	10	1	1	0.8	2.5
2	100	5	2	20	2	1	0.8	2.5
3	100	5	2	30	3	1	0.8	2.5
4	100	5	2	40	4	1	0.8	2.5
5	100	5	2	50	5	1	0.8	2.5

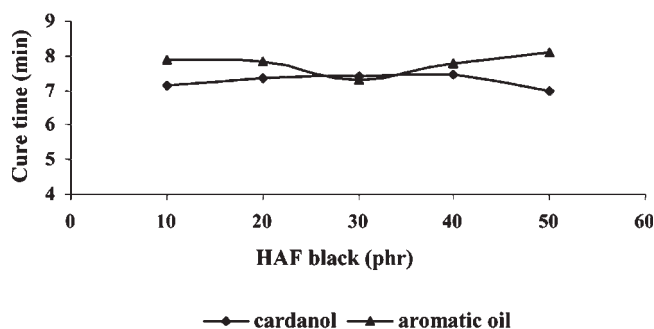


Figure 2 Variation of cure time (min) with HAF-black loading.

transform infrared spectroscope Bruker-Tensor 27 (Netherlands) and compared. Similar studies were made on a cardanol sample after reaction with sulfur to identify chemical changes if any. The sample was heated for half an hour with sulfur at 100°C and cooled prior to testing.

Oxidative ageing tests were carried out for 10 days in accordance with ASTM D573-04, in an air oven at 100°C. After 24 h 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 free sulfur content, extractable matter, etc.

Crosslink density was determined on both aromatic-oil-based and cardanol-based samples loaded with 30 phr HAF using toluene as per ASTM D 6814-02<sup>e1</sup>. The process was repeated for aged samples after varying periods of ageing.

Free sulfur analysis was carried out as per ASTM D297 on both cardanol-based and aromatic-oil-based cured samples each containing 30 phr HAF-black. The analysis was carried out on samples aged up to 4 days.

## RESULTS AND DISCUSSION

The variation of cure time with HAF-black filler for both plasticizers is depicted in Figure 2. Both plasti-

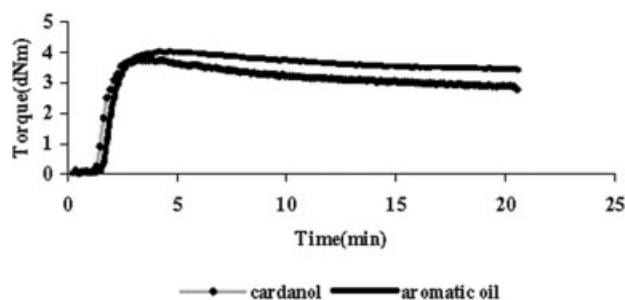


Figure 3 Cure curves for both cardanol- and aromatic-oil-based samples with 30 phr HAF-black loading.

TABLE II  
Minimum and Maximum Torque Values during Cure for Cardanol- and Aromatic-Oil-Based Samples with Varying Filler Content

Sample	Torque (dNm)	10 (phr)	20 (phr)	30 (phr)	40 (phr)	50 (phr)
Cardanol	Minimum	0.045	0.052	0.016	0.013	0.157
Aromatic oil	Minimum	0.114	0.052	0.072	0.091	0.251
Cardanol	Maximum	3.526	3.413	4.38	5.324	6.606
Aromatic oil	Maximum	3.938	4.2	4.64	5.688	7.469

cizers give similar cure times for different filler contents. This shows that cardanol does not interfere with the curing process of NR.

Figure 3 is a comparison of cure curves for both cases. Similar values of torque are attained for both plasticizers. The minimum torque values (Table II), which indicate viscosity of the compound, are lower for cardanol-based samples. Hence, cardanol is a better plasticizer for NR.

Figure 4 shows the tensile behavior of specimens containing varying amounts of HAF-black for both plasticizers. The shapes of the curves are similar. The tensile strength is maximum at 30 phr HAF-black in both cases falling to lower values at higher filler contents. This effect is well known<sup>16</sup> and can be attributed to poor wetting of the reinforcement particles at filler contents above the optimum. Also comparative data on the effect of filler content on elongation at break versus filler content and 300% modulus versus filler content show equivalent performance by both plasticizers.

The tear strength of samples employing both plasticizers has also been measured as a function of HAF-black filler content (Fig. 5). As in the case of tensile strength, the tear strength 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 in comparison with aromatic oil. Abrasion loss, surface hardness, and resilience curves for both

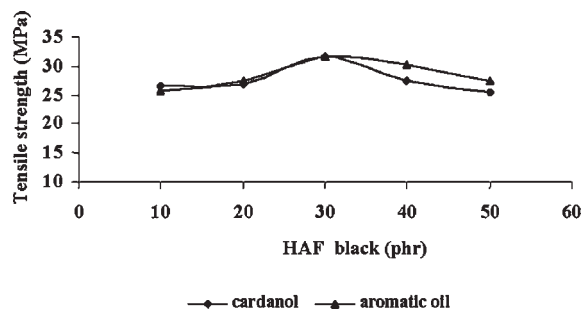


Figure 4 Variation of tensile strength (MPa) with HAF-black loading (phr).

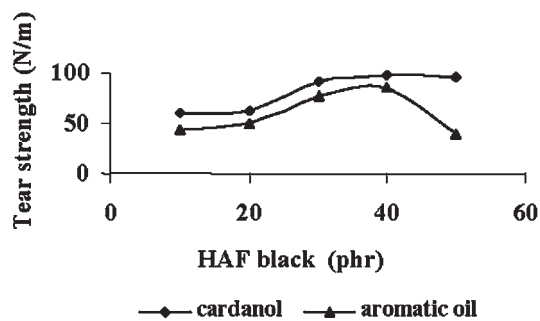


Figure 5 Variation of tear strength (N/m) with HAF-black loading (phr).

plasticizers for different filler contents show remarkable similarity and are not reproduced here.

Figures 6–9 indicate the ageing behavior of samples containing different plasticizers. The behavior of the cardanol-based samples show remarkable similarity in the case of tensile strength, tear strength, elongation at break, 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 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 chemical reactions that had taken place between cardanol and sulfur during the curing process indicated by the FTIR spectra in Figure 14. Many vulcanized vegetable oils (factices) customarily used for rubber processing are known to be unstable at temperatures normally employed for rubber vulcanization.<sup>17</sup> It can be hypothesized that the sulfur liberated by decom-

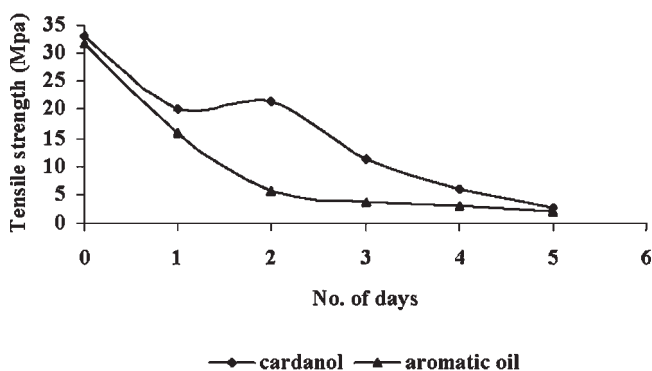


Figure 6 Ageing at 100°C: Variation of tensile strength (MPa) of 30 phr carbon-black-filled vulcanizate with number of days.

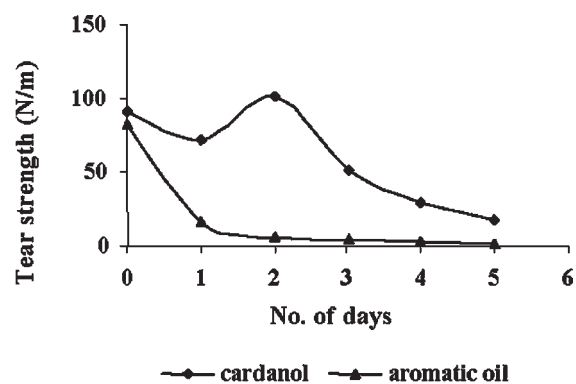


Figure 7 Ageing at 100°C. variation of tear strength (N/m) of 30 phr HAF-black-filled vulcanizate with number of days.

position of this product is utilized subsequently by the rubber, which is reflected by improved properties after the second day of ageing. Considering that cardanol has several sites of unsaturation this is a definite possibility.

Variation of free sulfur estimated at various stages of ageing shown in Figure 10 is supportive of this. Initially, free sulfur 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 sulfur content presumably due to the breakage of cardanol-sulfur linkages. It is likely that the sulfur is subsequently utilized by NR to form more crosslinks. By the second day of ageing, both samples show practically the same free sulfur content after a sharp fall in the case of the cardanol-based samples. Both samples show almost equal free sulfur values for the rest of the ageing period.

The data given in Figure 11 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 3 days. Even after ageing for 3 days, the cardanol-

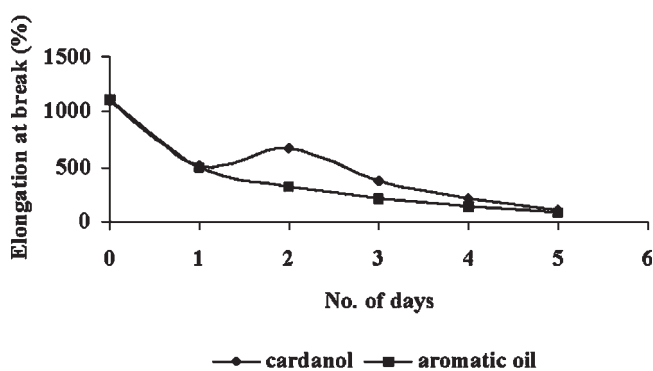


Figure 8 Ageing at 100°C. Variation of elongation at break (%) of 30 phr HAF-black-filled vulcanizate with number of days.

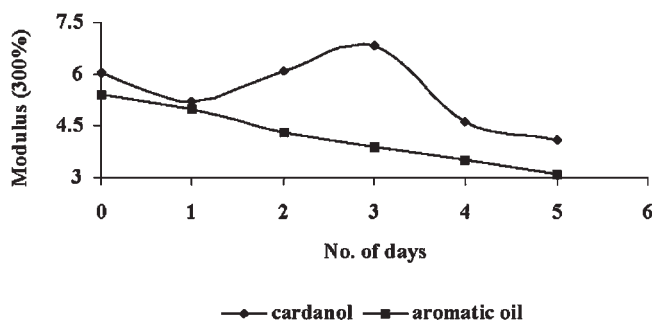


Figure 9 Ageing at 100°C. Variation of 300% modulus of 30 phr HAF-black-filled vulcanizate with number of days.

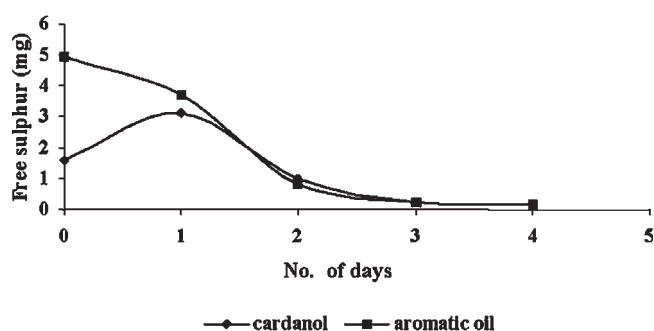


Figure 10 Results of free sulfur analysis of HAF-black-loaded (30 phr) vulcanizate.

based sample gives almost the original value. Any changes undergone by the cardanol-sulfur reaction product during ageing do not still lead to extraction of the cardanol.

Figures 12 and 13 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  $3338\text{ cm}^{-1}$  is absent in

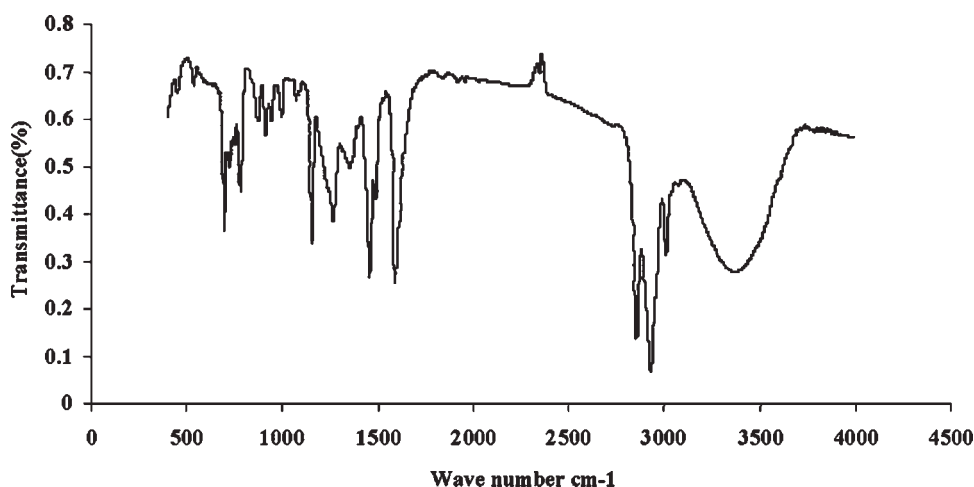


Figure 12 FTIR spectrum of cardanol.

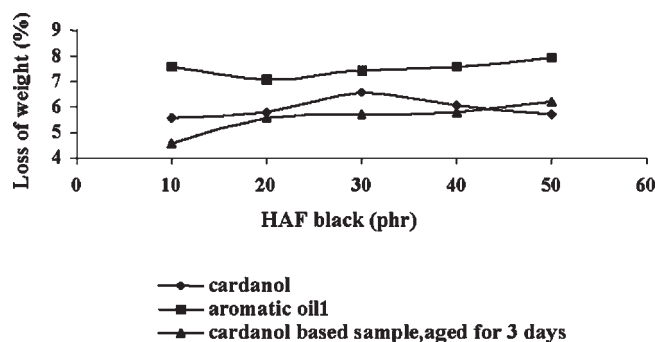


Figure 11 Results of Soxhlet extraction of 30 phr HAF-black-loaded samples using toluene as solvent.

the spectrum of the extract. This shows that in the case of cardanol, loss of plasticizer during service is not likely. Figure 14 shows the FTIR spectrum of cardanol after heating with elemental sulfur. Comparison of Figures 13 and 14 shows suppression of the peak at  $3090\text{ cm}^{-1}$  resulting from the disappearance of  $=\text{C}-\text{H}$  stretch of the aliphatic side chain of cardanol. This points to a vulcanization type reaction cardanol has undergone with sulfur.

Figure 15 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. But since properties of the cardanol-based sample are similar or even better, this is not a matter of concern.

## CONCLUSIONS

The mechanical properties in general show that cardanol and aromatic oil are almost equivalent when used

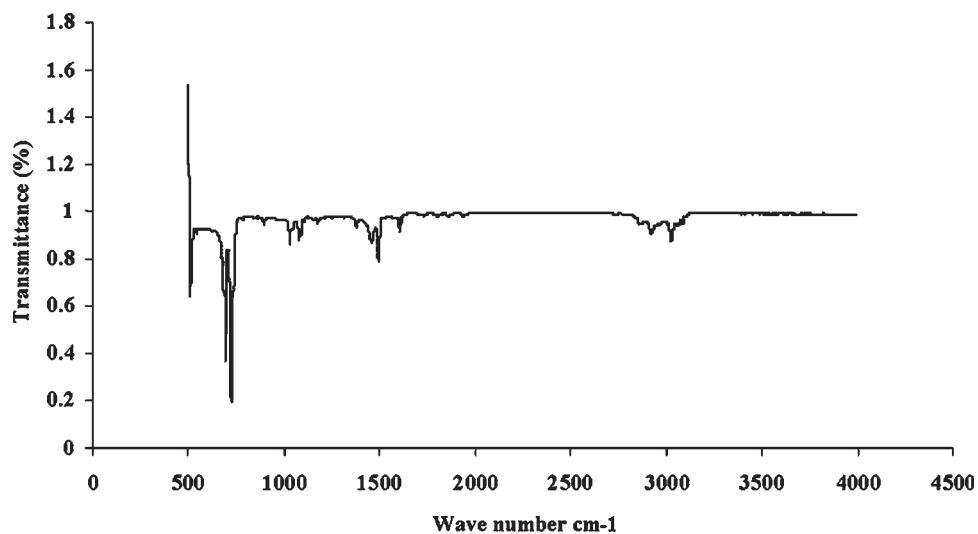


Figure 13 FTIR spectrum of the extract of cardanol-based vulcanizate (30 phr HAF-black) in toluene.

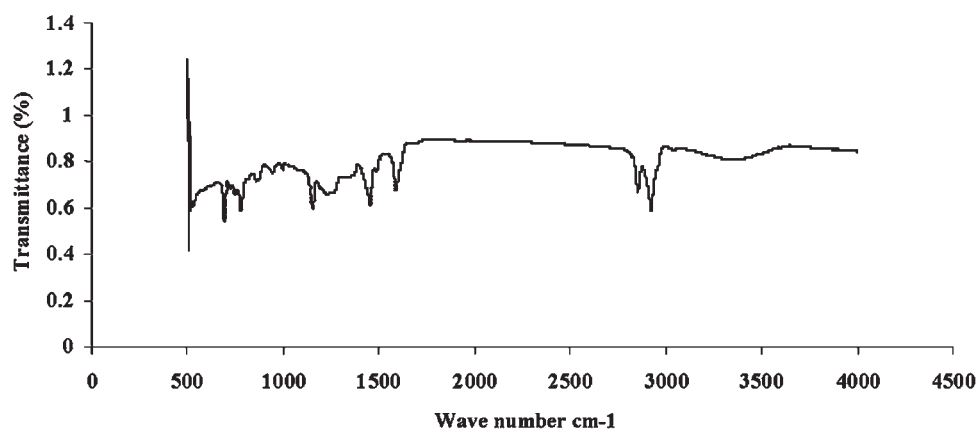


Figure 14 FTIR spectrum of cardanol sulfur vulcanizate.

for plasticizing NR reinforced with various percentages of HAF-black. Marginally superior performance is observed for cardanol in the case of tear strength. Ageing studies in both cases establish that cardanol

leads to a vulcanizate of better thermal stability indicated by superior mechanical properties in the early stages of ageing. Since cardanol does not get extracted by toluene from the cured NR, there is no likelihood of plasticizer loss during the service period. Thus, cardanol has clear superiority over aromatic oil for plasticizing NR containing HAF-black.

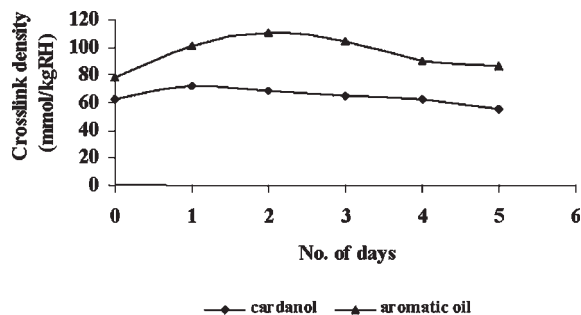


Figure 15 Variation of crosslink density (mmol/kg RH) of 30 phr HAF-black-loaded vulcanizate on ageing.

## References

1. Lubi, M. C.; Thomas, E. *Thachil Des Monomers Polym* 2000, 3, 123.
2. Wassermann, D.; Dawson, C. R. *Ind Eng Chem* 1945, 37, 396.
3. Carraher, C. E.; Sperling, L. H. *Polymer Applications of Renewable Resource Materials*; Plenum: New York, 1981.
4. Roy, S. S.; Kundu, A. K.; MaMaili, S. *J Appl Polym Sci* 1988, 36, 1283.
5. Manjula, S.; Sudha, J. D.; Bera, S. C.; Pillai, C. K. S. *J Appl Polym Sci* 1985, 30, 1767.
6. Truong, T. D.; Nguyen, V. K. *Tap Chi Hoa Hoc* 1995, 33, 36.

7. Ghosh, A. K.; Das, C. K.; Banerjee, S. *Polym Commun* 1984, 25, 152.
8. Ghosh, A. K.; Banerjee, S. *Indian J Technol* 1975, 13, 362.
9. Sanghi, L. K.; Battacharjee, A. S.; Banerjee, S. *J Inst Rubber Ind* 1974, 8, 188.
10. Truong, T. D.; Nguyen, V. K.; Quang, K. D. *J Macromol Sci Pure Appl Chem* 1996, 33.
11. Menon, A. R. R.; Pillai, C. K. S.; Nando, G. B. *Eur Polym J* 1998, 34, 923.
12. Alen, V. L.; Thomas, T. E. *J Adhes Sci Technol* 2004, 18, 181.
13. Gowariker, V. R.; Viswanathan, N. V.; Sreedhar, J. *Polymer Science*; New Age International: New Delhi, 1986; reprint 2005.
14. Blow, C. M. *Rubber Technology and Manufacture*, 2nd ed.; Butterworth Scientific: London, 1982.
15. Durrani, A. A.; Davis G. L.; Sood, S. K.; Tychopoulos, V.; Tyman, J. H. P. *J Chem Technol Biotechnol* 1982, 32, 618.
16. Maurice, M. *Rubber Technology*, 3rd ed.; Van Nostrand Reinhold: New York, 1987; p 80.
17. Hoffman, W. *Rubber Technology Hand Book*; Hanser: New York, 1989; p 306.