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Plasticisation of Carbon Black Filled Acrylonitrile-butadiene Rubber Using Cardanol

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The comparative performance of cardanol, the main ingredient of cashew nut shell liquid (CSNL) for plasticising carbon black-filled acrylonitrile – butadiene rubber (NBR) is presented. The performance of dioctyl phthalate (DOP), a common plasticiser for NBR was compared with that of cardanol in terms of the cure characteristics, mechanical properties, thermal ageing properties, crosslink density and extractability. While both these plasticisers showed almost equivalent performance in respect of most properties, a clear superiority was noted for cardanol in the case of extractability after varying periods of ageing at 100°C. This alludes to the resistance of cardanol-plasticised NBR to ageing and a lessened possibility of it being leached out / blooming out on prolonged use. The demonstrated usefulness of cardanol, a renewable, agro-byproduct for NBR processing is significant.

Key words: FT-IR; ageing; mechanical properties; crosslinking; vulcanisation

Cardanol is a naturally occurring phenol present in cashew nut shell liquid (CNSL), a by-product of the cashew nut industry. It has the advantages of low cost and renewable supply[1-5] and can replace phenol in many applications. Cardanol is obtained by vacuum distillation of commercial grade CNSL conforming to *Indian Standard IS: 841-1964* (*Table 1*), and the structure of cardanol is given in *Figure 1*. The results of studies evaluating the performance of cardanol for plasticising HAF black and silica-filled natural rubber were reported earlier[6,7]. The potential for application of cardanol in rubber processing has also been highlighted by many workers from time to time[8-14].

Plasticisers are low molecular weight non-volatile substances, which when added to a polymer; improves its flexibility and processability[15]. Plasticisers are generally used in NBR compounds to improve processing and low temperature properties. Typically they are ester compounds, aromatic oils and polar derivatives and can be extractable or non extractable depending upon the end use applications[16]. Examples are dibutyl phthalate, dibutyl sebacate, dioctyl phthalate, and trixylyl phosphate. Polyesters, polyester ethers, polyester polyethers, pentaerythritol ester and xylene formaldehyde resins are all used. The viscosity, tackiness and processability of NBR compounds can be altered by the use of

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plasticisers which at the same time also influence the elasticity, low temperature flexibility and swelling resistance of the vulcanisates. In concentrations up to 30 p.h.r., typical plasticisers based on ethers, esters or polythioethers are very effective in increasing the rebound elasticity and low temperature flexibility of vulcanisates[17]. However, all plasticisers reduce the mechanical properties and swell resistance of the vulcanisates and volatilise at high temperatures. For high temperature resistance of NBR, plasticisers of low volatility, such as butyl carbitol formal and polyester polythioethers which simultaneously improve low temperature flexibility, should be used[18]. Several other substances with plasticising ability are used under special situations[16] which bequeath other properties to make compounding easier or to give an improved final product. In the present work, the comparative performance of cardanol and DOP, a conventional plasticiser has been investigated in terms of the mechanical and thermal properties of the final vulcanisate and parameters like crosslink density, free sulphur content, cure characteristics and extractability.

EXPERIMENTAL

Raw Materials

Acrylonitrile-butadiene rubber, Aparene N-50 with 44% acrylonitrile content and Mooney viscosity, ML 80-95, were obtained from Apar Polymers Ltd., Mumbai, India. Zinc Oxide (activator) and Stearic acid (co-activator) were supplied by M/s Meta Zinc Ltd., Mumbai and Goderej Soaps Pvt Ltd., Mumbai respectively. Cyclo hexyl benzothiazil sulphenamide (CBS) and tetramethyl thiuram disulphide (TMTD) (accelerator) were procured from Polyolefins Industries, Mumbai. Sulphur (cross linking agent), was supplied by Standard Chemicals Co. Pvt. Ltd. Chennai. High Abrasion Furnace black (N330) used in the present study was supplied by M/s Philips Carbon Black India Ltd., Cochin.

Dioctyl Pthalate used in the present study was of commercial grade supplied by Rubo-Synth Impex Pvt. Ltd., Mumbai. The viscosity of the sample was 60 m Pa.s.

TABLE 1. INDIAN STANDARDS SPECIFICATION FOR CNSL

Characteristic	Requirement
Specific gravity	0.95-0.97
Viscosity at 30°C, cp (max)	550
Moisture % by wt. (max)	1.0
Matter insoluble in toluene, % by wt. (max)	1.0
Loss in wt. on heating, % by wt. (max)	1.0
Ash, % by wt. (max)	1.0
Iodine value (max)	
(a) Wij's method	250
(b) Catalytic method	375
Polymerisation	
Time, min (max)	4
Viscosity at 30°C, cp (min)	30
Viscosity after acid washing at 30°C, cp (min)	200

Refined CNSL (*Table 1*) conforming to *Indian Standard 1S: 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°C–208°C was cardanol[19].

Compounding

Mixes were prepared on a laboratory size two roll mixing mill (16 × 33 cm) at a friction ratio of 1:1.25. A nip gap of 0.2 mm was set and the temperature maintained at 70 ± 5°C. The compounding ingredients were added as per procedure given in *ASTM D 3184-89 (2001)* and over a time period of 29 min. In the present study, only carbon black filler was employed. The formulations employed are given in *Table 2* and each of it was repeated with cardanol replacing dioctyl pthalate.

Curing

The cure characteristics of the mixes were determined using a Rubber Processing Analyser RPA 2000 supplied by Alpha Technologies, USA, as per *ASTM* standard, *D 2084-01*. Subsequently, the rubber compounds were vulcanised up to the optimum cure time at 150°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, un-nicked test pieces with a 90° angle on one side and with tab ends punched out from the vulcanised 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 *ASTM 624* respectively.

Soxhlet extraction was carried out by packing known weights of vulcanised rubber in Whatman No. 1 filter paper and extracting in a Soxhlet apparatus using toluene as solvent and the loss of weight (%) was noted.

FT-IR spectra of the Soxhlet extract of the cardanol-based vulcanisate and cardanol were obtained using Fourier Transform Infrared Spectroscope Bruker-Tensor 27 (Netherlands) and compared. Similar studies[6] were made on a cardanol sample after reaction with sulphur in order to investigate chemical changes if any. The sample was heated for half an hour with sulphur at 100°C and cooled prior to testing.

TABLE 2. NBR FORMULATIONS FOR VARYING CARBON BLACK CONTENT

Sample	NBR (p.h.r.)	S (p.h.r.)	ZnO (p.h.r.)	St.acid (p.h.r.)	HAF (p.h.r.)	Cardanol DOP (p.h.r.)	TQ (p.h.r.)	CBS (p.h.r.)	TMTD (p.h.r.)
1	100	1.5	4.5	1.75	10	1	1	1	0.5
2	100	1.5	4.5	1.75	20	2	1	1	0.5
3	100	1.5	4.5	1.75	30	3	1	1	0.5
4	100	1.5	4.5	1.75	40	4	1	1	0.5
5	100	1.5	4.5	1.75	50	5	1	1	0.5

Oxidative ageing tests were carried out for ten days in accordance with *ASTM D573-04*, in an air oven at 100°C. After 24 hours of conditioning at ambient temperature, tensile strength and tear resistance of the samples were determined as per *ASTM D412* and *ASTM D624*, respectively, apart from free sulphur content and extractable matter.

Crosslink density was determined on both DOP-based and cardanol-based samples loaded with 30 p.h.r. HAF black using toluene as per *ASTM D6814-02*$^{\epsilon 1}$. The process was repeated for aged samples after varying periods of ageing.

Free sulphur analysis was carried out as per *ASTM D297* on both cardanol-based and DOP-based vulcanisates each containing 30 p.h.r. HAF-black. The analysis was carried out on samples aged up to four days.

RESULTS AND DISCUSSION

The variation of cure time with HAF-black filler for both plasticisers is shown in *Figure 2*. Both plasticisers gave similar cure times for different filler contents. This showed that cardanol did not interfere with the curing of NBR.

Figure 3 is a comparison of cure curves for both cases. Similar values of torque was attained for both plasticisers. The minimum torque values (*Table 3*), which was indicative

TABLE 3. MINIMUM AND MAXIMUM TORQUE VALUES DURING CURE FOR CARDANOL AND DOP BASED SAMPLES WITH VARYING FILLER CONTENT

Sample	Torque (dNm)	10 (p.h.r.)	20 (p.h.r.)	30 (p.h.r.)	40 (p.h.r.)	50 (p.h.r.)
Cardanol	minimum	0.284	0.346	0.431	0.588	0.660
DOP	minimum	0.280	0.359	0.493	0.555	0.699
Cardanol	maximum	5.230	6.534	7.162	7.930	8.096
DOP	maximum	4.423	7.106	7.333	7.851	8.368

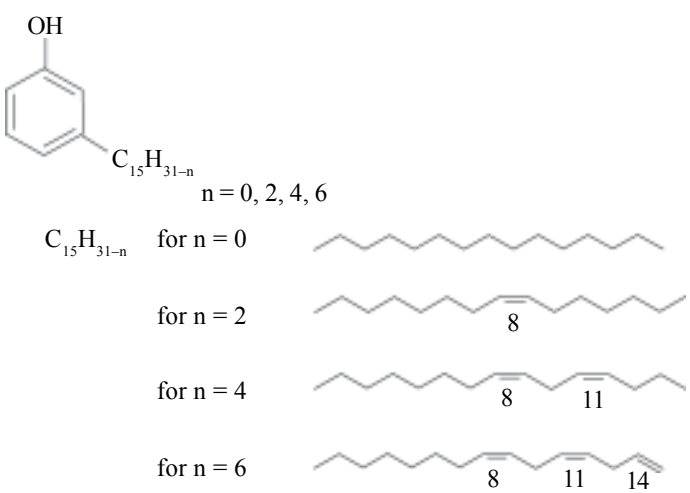

Figure 1. Structure of cardanol.

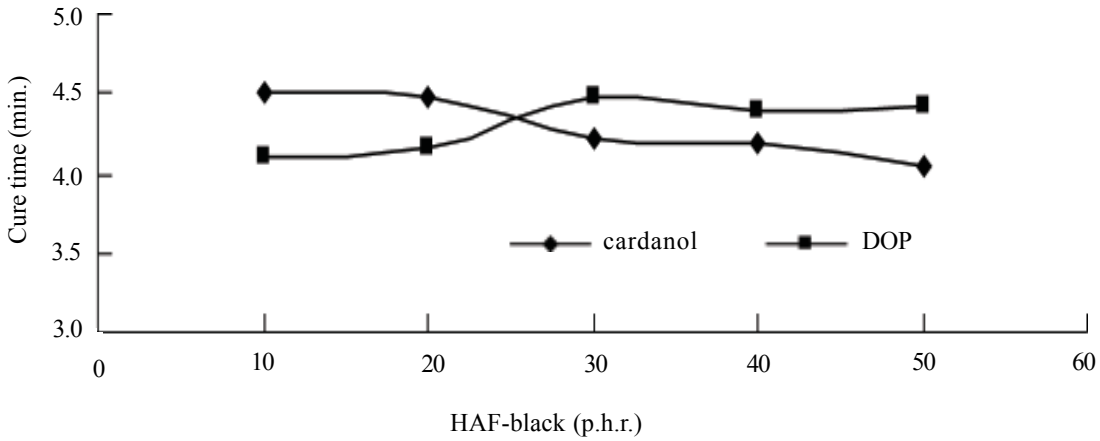

Figure 2. Variation of cure time (min) with HAF-black loading.

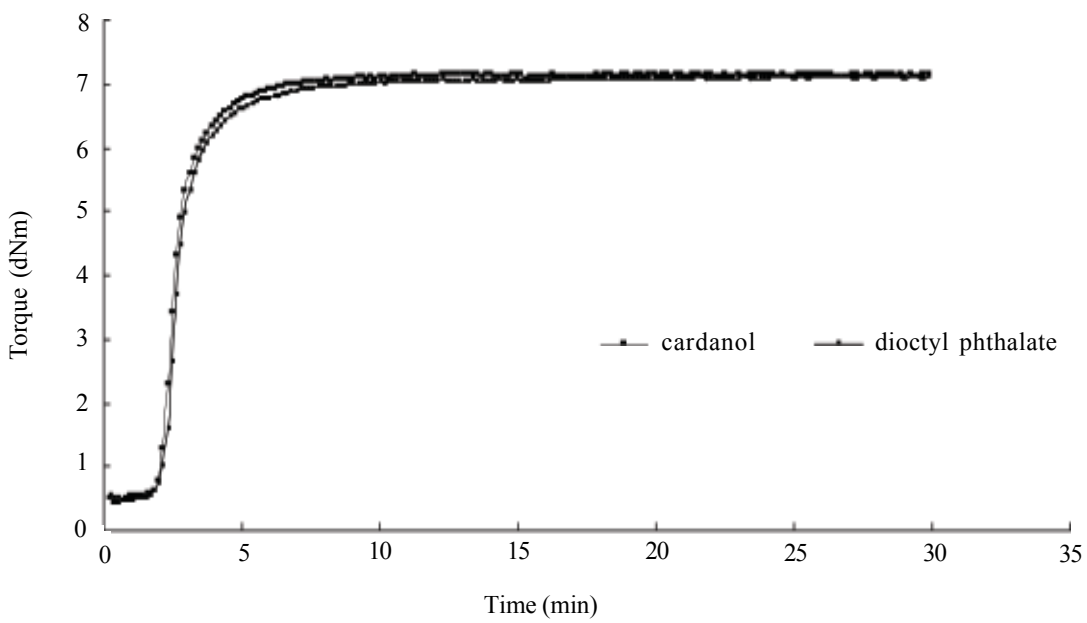

Figure 3. Cure curves for both cardanol and DOP-based samples with 30 p.h.r. HAF-black loading.

of the viscosity of the compound, were similar for both plasticisers. Hence both these substances were comparable in their plasticising action.

Figure 4 shows the tensile behavior of specimens containing varying amounts of HAF-black for both plasticisers. The shapes of the curves were similar. The tensile strength was a maximum at 40 p.h.r. HAF-black in the case of cardanol falling to lower values at higher filler contents. This effect is well known[20] and can be attributed to poor wetting of the reinforcement particles at filler contents above the optimum. However, cardanol gave a slightly higher tensile strength at this filler content compared to DOP. Also comparative data (not shown here) on the effect of filler content on elongation at break versus filler content and 300% modulus versus filler content show equivalent performance by both plasticisers.

The tear strength of samples employing both plasticisers has also been measured as a function of HAF black filler content (*Figure 5*). As in the case of tensile strength, the tear strength of the cardanol-based samples were 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 DOP. Abrasion loss, surface hardness and resilience curves for both plasticisers for different filler contents show remarkable similarity and are not reproduced here.

Figure 6 – 9 indicate the ageing properties of samples based on both plasticisers in terms of some mechanical properties. Tensile strength, tear strength and elongation at break (%) decreased after the first day of ageing. Tear strength values (*Figure 7*) were slightly higher for cardanol-based samples for most of the ageing period. Modulus at 100% elongation (*Figure 9*), on the other hand, remained lower for cardanol-based samples during the ageing period. This must be examined in the light of results of extraction studies on aged samples to be presented later. Higher modulus of DOP-based samples is probably the result of loss of plasticiser on ageing due to chemical decomposition or blooming. Since fairly rigorous conditions have been employed for ageing the thermal age resistance of the cardanol-based samples is remarkably good. The fall in properties after the first day of ageing may be the result of chemical reactions that had taken place between cardanol and sulphur during the curing process[6]. Many vulcanised vegetable oils (factices) customarily used for rubber processing are known to be unstable at temperatures normally employed for rubber vulcanisation[21]. It can be hypothesised that the sulphur liberated by decomposition of this product is utilised 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. A similar behavior is observed in the case of natural rubber plasticised by cardanol[6]. Variation of free sulphur estimated at various stages of ageing shown in *Figure 10* is supportive of this. Initially free sulphur content of the cardanol-based sample is much less than the DOP 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 utilised by nitrile 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.

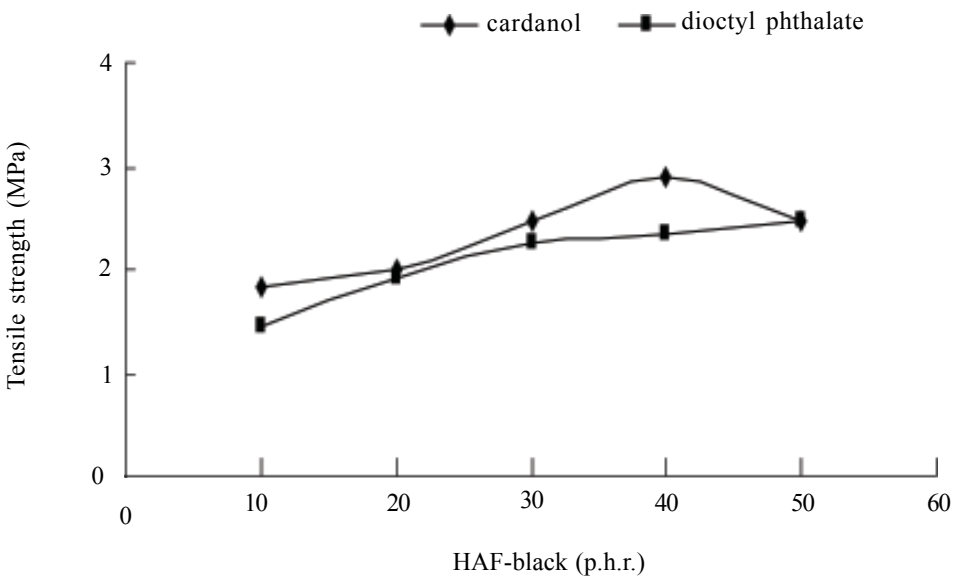

Figure 4. Variation of tensile strength (MPa) with HAF-black loading (p.h.r.).

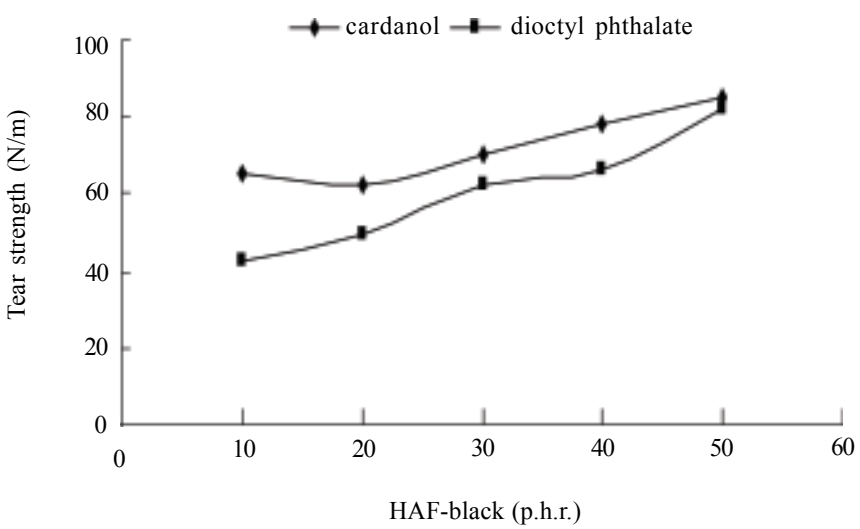

Figure 5. Variation of tear strength (N/mm) with HAF-black loading (p.h.r.).

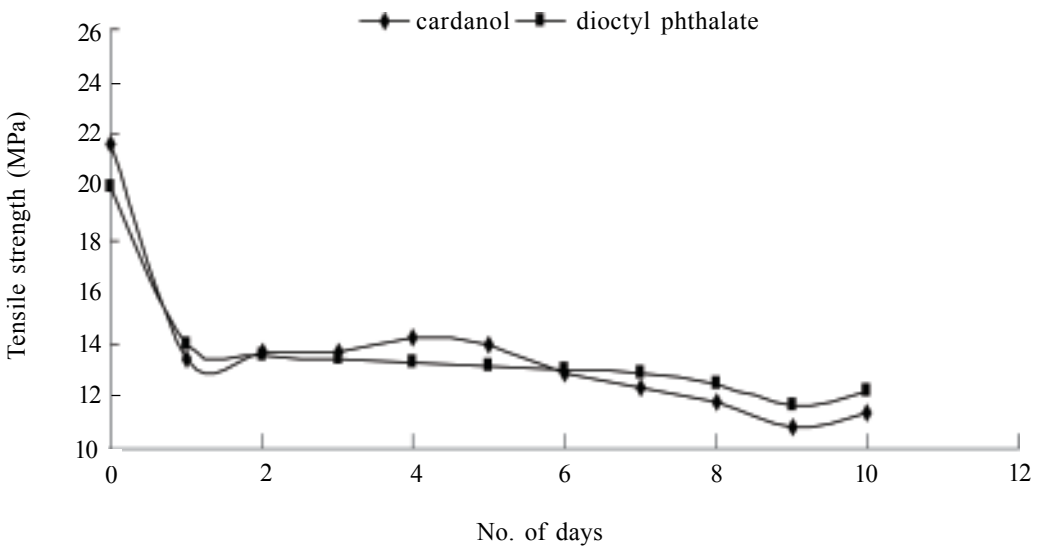

Figure 6. Ageing at 100 ˚C: Variation of tensile strength (MPa) of 30 p.h.r. carbon black.

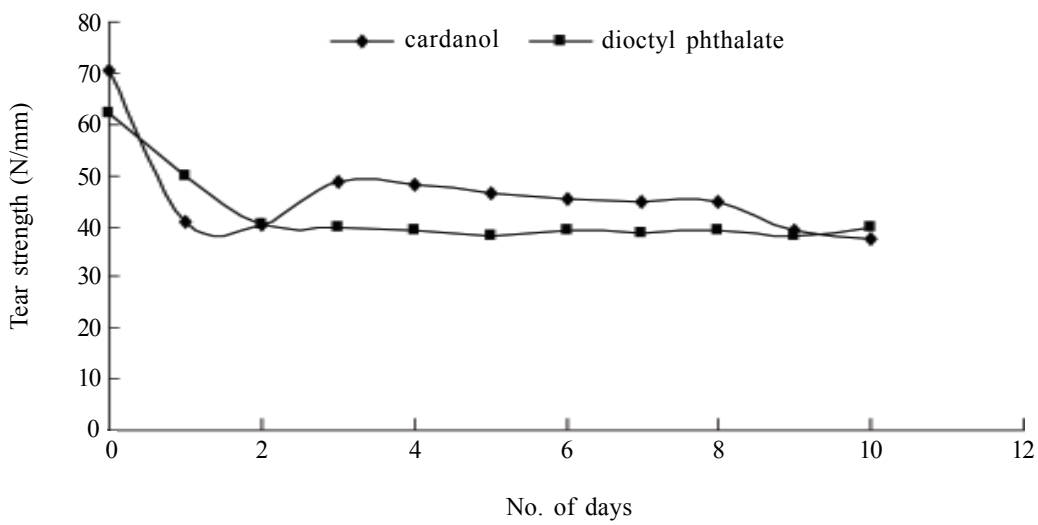

Figure 7. Ageing at 100˚C ; Variation of tear strength (N/m) of 30 p.h.r. HAF-black filled vulcanisate with number of days.

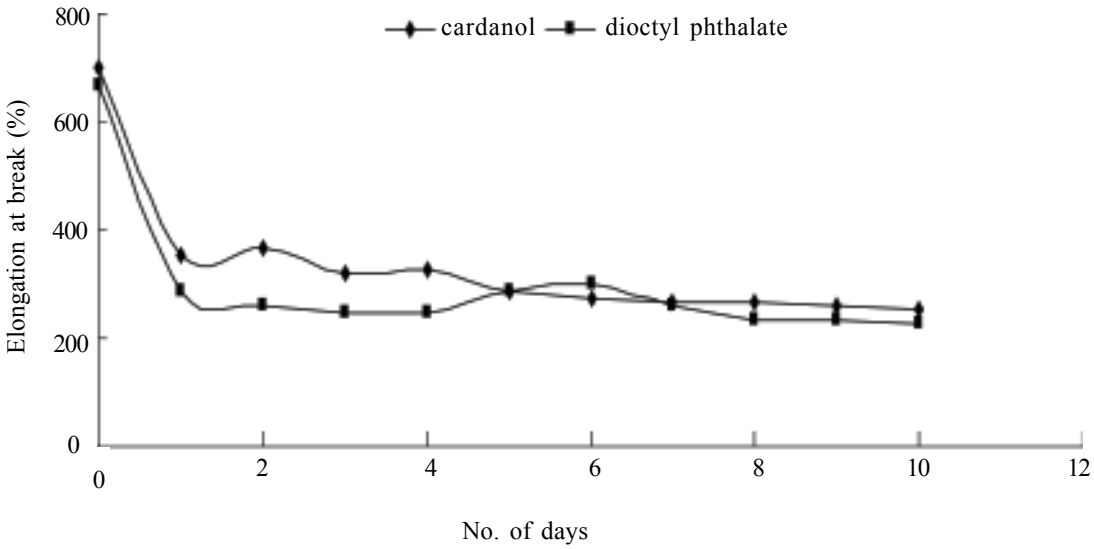

Figure 8. Ageing at 100°C. Variation of elongation at break (%) of 30 p.h.r. HAF-black filled vulcanisate with number of days.

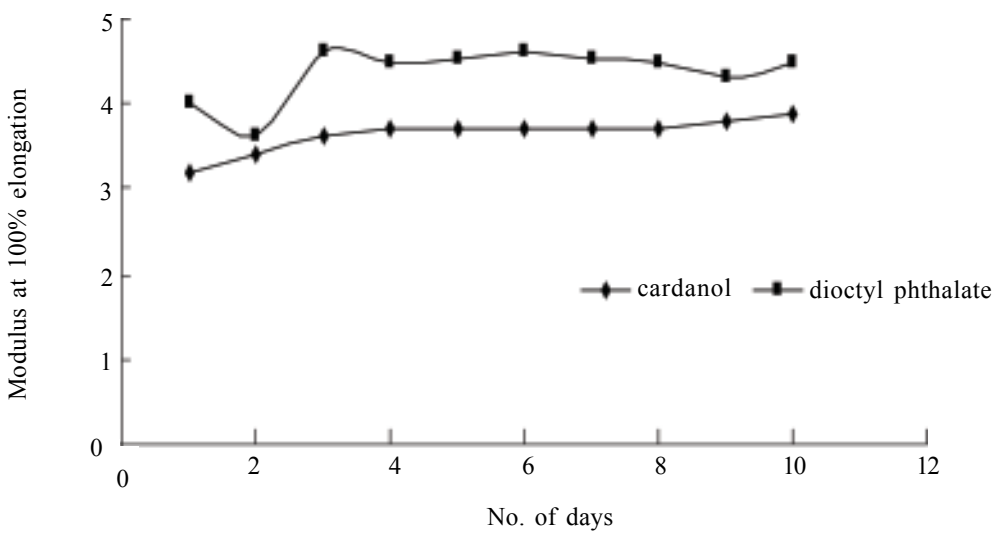

Figure 9. Ageing at 100°C. Variation of 300% modulus of 30 p.h.r. HAF-black filled vulcanisate with number of days.

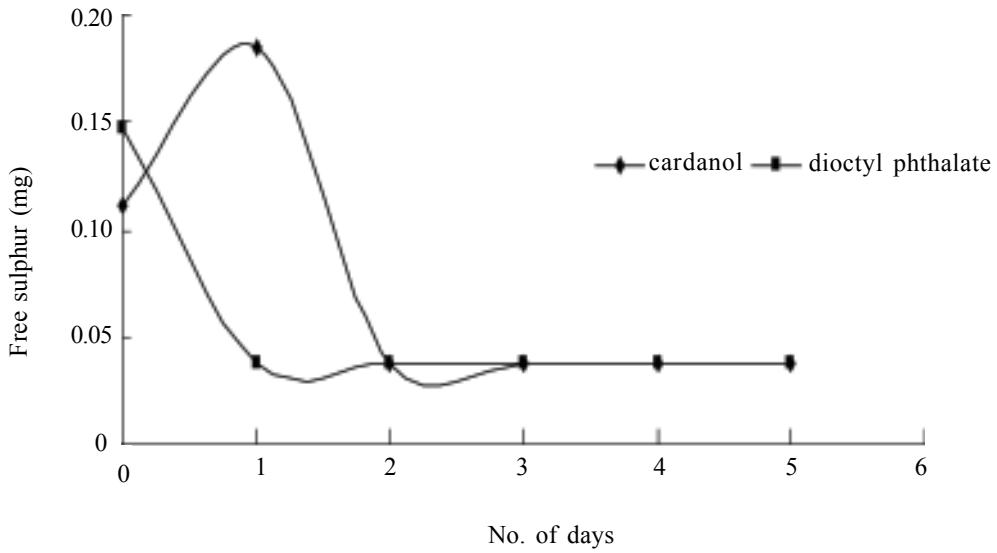

Figure 10. Results of free sulphur analysis of HAF-black loaded (30 p.h.r.) vulcanisate.

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 three days. Even after ageing for three days, the cardanol-based samples give almost the original value. This is noticeably contrasted by the DOP based sample. Any changes undergone by the cardanol-sulphur reaction product during ageing presumably 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 vulcanisate respectively. A comparison of the two shows no sign of cardanol in the extract, as the –OH absorption of cardanol observed at 3360 cm^{-1} is absent in the spectrum of the extract. This shows that in the case of cardanol, loss of plasticiser during service is not likely. It is likely that cardanol has undergone a vulcanisation type reaction with sulphur forming products that are stable at ordinary temperatures[6].

Figure 14 is a plot of crosslink density of both samples at various stages of ageing. Crosslink density is similar for both cardanol and DOP-based samples. The presence of cardanol molecules has led to a lower extent of crosslinking between the rubber chains. The reason can be the utilisation of sulphur by cardanol. Later when the sulphur is liberated, degrees of crosslinking become similar in both cases.

CONCLUSIONS

The mechanical properties, in general, show that cardanol is not inferior to DOP for plasticising nitrile rubber reinforced with various percentages of HAF black. Cardanol

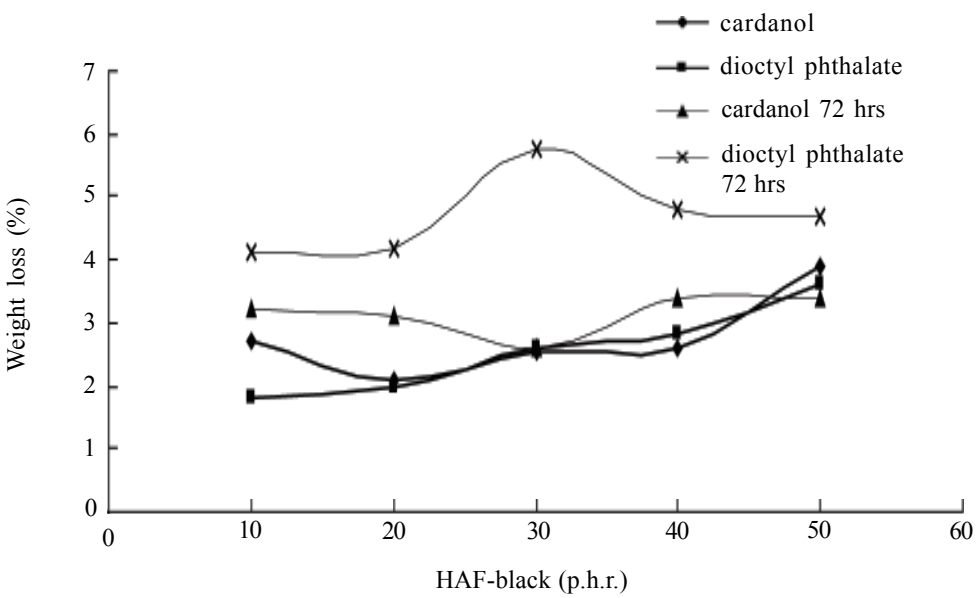

Figure 11. Results of Soxhlet extraction of 30 p.h.r. HAF-black loaded samples using toluene as solvent.

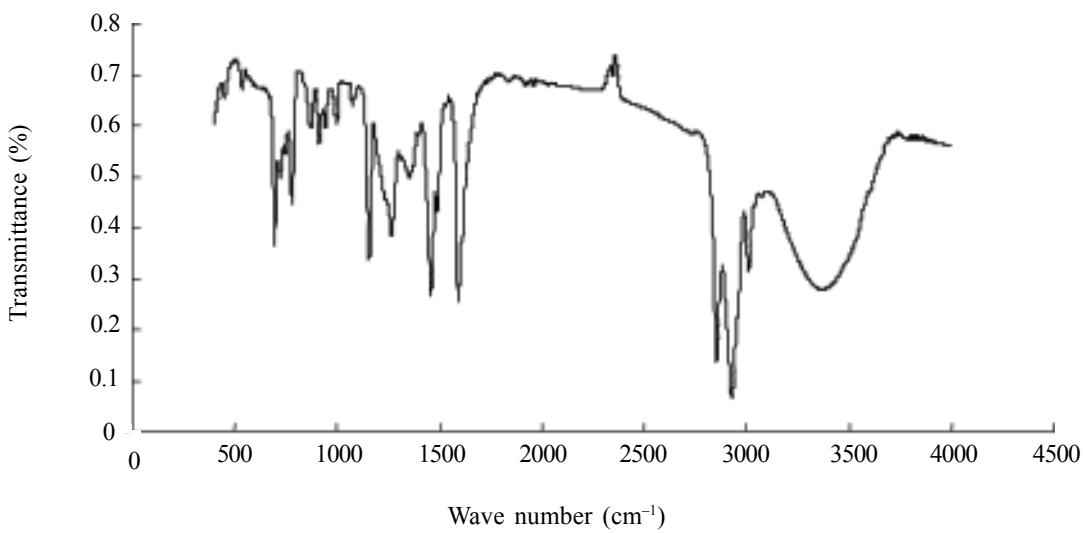

Figure 12. FT-IR spectrum of cardanol.

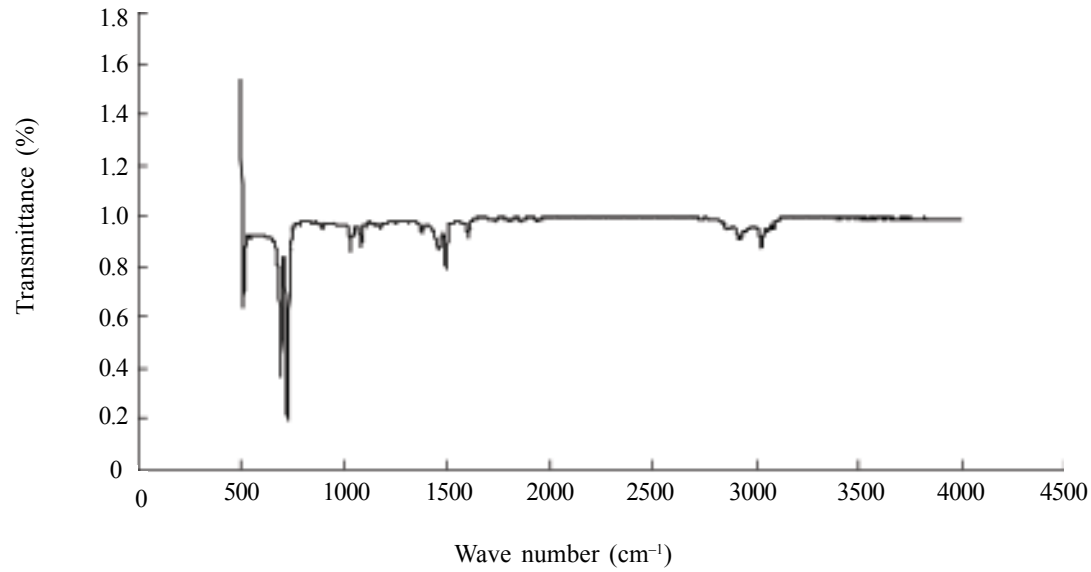

Figure 13. FT-IR spectrum of the extract of cardanol based vulcanizate (30 p.h.r. HAF-black filled) in toluene.

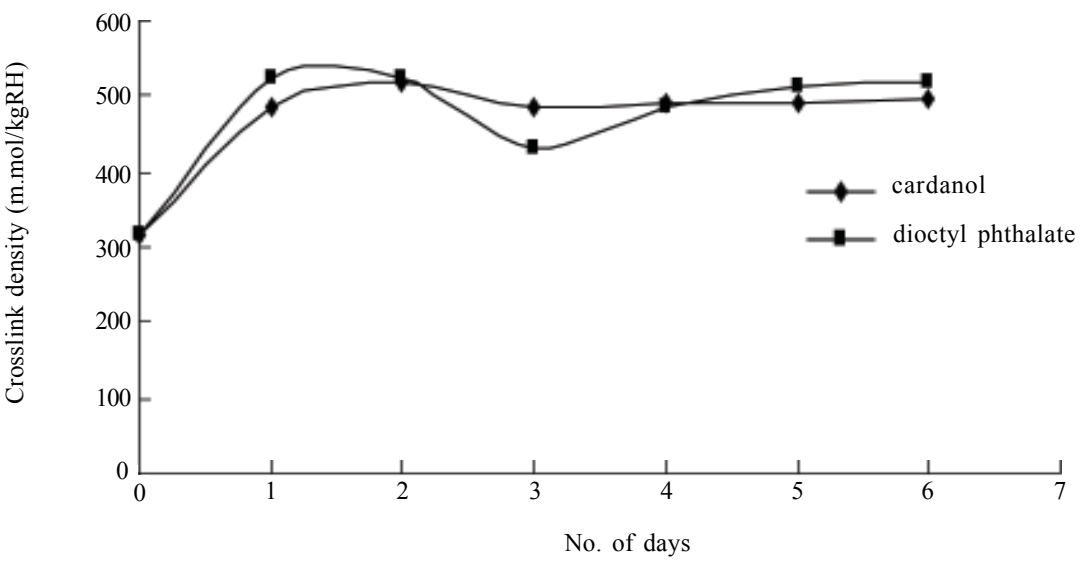

Figure 14. Variation of crosslink density (mmol/kgRH) of 30 p.h.r. HAF-black loaded vulcanisate on ageing.

has a definite superiority in the case of tear strength when reinforced with the same extent of filler. Ageing studies in both cases establish that cardanol leads to a vulcanisate of similar thermal stability indicated by comparable mechanical properties at various stages of ageing. Since cardanol does not get extracted by toluene from the cured NBR, there is no likelihood of plasticiser loss during the service period. Thus, cardanol has some superiority over DOP for plasticising NBR containing HAF-black.

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