

# Synthesis and Characterization of Cardanol-Grafted Natural Rubber—The Solution Technique

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**ABSTRACT:** Cardanol, a by-product of the cashew industry, has been recently proven to be a multifunctional additive (MFA) in rubbers. It is expected that grafting of cardanol onto natural rubber (NR) would impart inherent MFA characteristics to the rubber. Grafting has been carried out in solution using toluene as the solvent and a peroxide initiator. Optimized conditions of grafting reaction could be arrived at using a statistical tool namely orthogonal array testing strategy, keeping the maximum percentage of grafting as the selection criteria. Further studies were conducted to study the influence of monomer concentration and initiator concentrations. The effect of the reaction temperature and reaction time were also investigated. Characterization of grafted rubber was carried out with the help of infrared spectroscopy, nuclear magnetic resonance spectroscopy and thermal analysis. IR spectrum of cardanol exhibited the characteristic peak of

cardanol at  $3356\text{ cm}^{-1}$ . Percent grafting (PG) of cardanol onto NR was determined by residual weight method. PG increased with increasing cardanol quantity reached an optimum and then decreased. The increase in reaction time and reaction temperature also caused increasing levels of the grafted cardanol. However, PG continuously increased with increasing initiator concentrations. Differential scanning calorimetry studies of the grafted NR showed a lower glass transition temperature than that of the raw NR, which is indicative of the plasticization effect of cardanol. The thermogravimetric analysis showed a higher thermo oxidative stability for cardanol-grafted NR. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1280–1288, 2007

**Key words:** elastomers; renewable resources; cardanol; grafting; infrared spectroscopy; thermogravimetric analysis; differential scanning calorimetry

## INTRODUCTION

Cardanol is a *m*-pentadecenyl phenol obtained by the double vacuum distillation of cashew nut shell liquid (CNSL), which in turn is a by-product of the cashew industry.<sup>1</sup> Various constituents of CNSL are given in Table I. Cardanol recovered from technical CNSL is a mixture of saturated, monoene, diene, and triene.<sup>2</sup> The quantitative determination of the olefinic composition of CNSL has been reported by Tyman<sup>3</sup> as early as 1975. The presence of these double bonds in the side chain adds more scope to the plethora of reactions possible in the chemistry of cardanol. The chemical structures of the various components of cardanol and its relative abundance in the CNSL are given in Figure 1. CNSL, due to the inherent advantages of its chemical structure, can function as more than one additive, such as plasticizer<sup>4</sup> and antioxidant,<sup>5,6</sup> when added to the rubber compound.

The multifunctional activity of the phosphorylated derivative of cardanol (PCP), when added to the natural rubber (NR) during the compounding, has already been established by Menon et al.<sup>7–17</sup> in their series of

publications. Grafting of cardanol onto the backbone of NR is a novel idea for the development of newer grades of NR that have inherent multifunctional additive activity. Grafting eliminates the problems like bleeding of the additive onto the surface of rubbers after compounding, leaching of cardanol into polar solvents, and difficulty in processing and handling on a two-roll mill encountered while adding cardanol physically during compounding.<sup>18</sup> Grafting of cardanol onto the backbone of NR not only overcomes all these difficulties mentioned above but also imparts multifunctional properties to the raw rubber itself. Grafting is feasible due to the presence of unsaturation in its  $C_{15}$  side chain. Literature is replete with examples of grafting of different monomers like maleic anhydride,<sup>19</sup> methyl methacrylate,<sup>20,21</sup> and acrylic acid<sup>21</sup> onto the NR backbone using the free radical initiators. Recently, Vikram et al.<sup>22</sup> have reported grafting of cardanol onto NR backbone by exposure to gamma radiation. The present study involves optimization of the grafting reaction conditions such as the initiator concentration, cardanol concentration, reaction temperature, and reaction time using the statistical tool orthogonal array testing strategy (OATS)<sup>23</sup> followed by the study of individual effect of the aforesaid parameters on the grafting reaction. Spectroscopic analysis and thermal characteristics of the cardanol-grafted NR also has been discussed in this publication.

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**TABLE I**  
Composition of CNSL

S. no.	Component	Cold extracted CNSL (%)	Hot-oil bath CNSL (%)
1.	Cardanol	1.6	63
2.	Cardol	14	11
3.	2-Methylcardol	2.6	2
4.	Anacardic acid	82	Nil
5.	Gallic acid	Traces	
6.	Polymer	23	

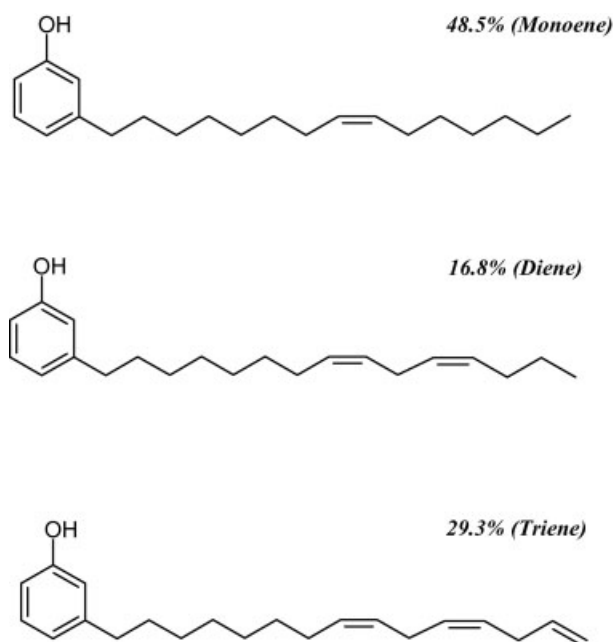
## EXPERIMENTAL

### Materials

The natural rubber (NR) used was Indian standard natural rubber, ISNR-5, supplied by the Rubber Board, Kottayam, India. Cardanol used to prepare the cardanol-grafted NR (CGNR) was supplied by Satya Cashew Chemicals, Chennai, India having the following specifications: Boiling point (°C): 228–235 (3.4 mmHg), Color (Lovibond, 1 cm Cell): Brownish-red (1.0–3.0), Acid value: 1.9–2.0, Iodine value (Wij's test): 210–235, Hydroxyl value: 180–200, Viscosity, 30°C (cp): 45–52. Benzoyl peroxide (BPO) used as initiator was manufactured by Merck (Mumbai, India). Toluene and methanol used were of AR grade manufactured by Merck.

### Synthesis of cardanol-grafted natural rubber (NR-g-C or CGNR)

Grafting of NR with cardanol was done in solution state. A solution of NR in toluene was prepared by



**Figure 1** Chemical structure of mono, di, and triene components of cardanol.

dissolving 5 g of ISNR-5 in 100 mL of toluene under constant stirring. Cardanol and the initiator BPO were added to the NR solution and stirred till a homogeneous mixture was obtained. The reaction was carried out at different temperatures and for different periods of time, under constant stirring, after which the contents of the reaction vessel were poured into methanol to precipitate the CGNR. Precipitated CGNR was washed thoroughly with methanol followed by drying in the vacuum oven at 70°C for 24 h to remove the residual solvent. The excess cardanol was extracted in a soxhlet apparatus using methanol as the solvent; to make sure that no free or physically bound cardanol was present.

Since initiator concentration, cardanol concentration, reaction temperature, and reaction time are the four parameters that control the grafting reaction and to arrive at the optimum combination of these parameters, the orthogonal array testing strategy (OATS), a statistical tool for the optimization of the reaction conditions, was utilized. Orthogonal arrays are two dimensional arrays of numbers, which possess an interesting quality: by choosing any two columns in the array, one receives an even distribution of all the pair-wise combinations of values in the array. It is a systematic and statistical way of testing the pair-wise interactions.<sup>24</sup> In this technique, the aforesaid four parameters were varied at three different levels by using L<sub>9</sub> orthogonal array table as constructed in Table II. The test set created by OATS has only nine test cases, yet tests all the pair-wise combinations. By making use of this technique, the number of experiments could be reduced to 9 from 81.

### Determination of percent grafting

After extraction of CGNR for 48 h with methanol in a soxhlet apparatus to remove any physically bound or entrapped cardanol from it, the grafted rubber was dried, in a vacuum oven at 70°C, till constant weight.

Percent grafting was calculated from the residual weight as given below:

**TABLE II**  
L<sub>9</sub> Orthogonal Array Table for Four Factors and Three Levels

Run no.	Initiator (wt %)	Cardanol concentration (phr)	Reaction temperature (°C)	Reaction time (h)
1	1	40	60	6
2	1	60	70	8
3	1	80	80	10
4	2	40	70	10
5	2	60	80	6
6	2	80	60	8
7	3	40	80	8
8	3	60	60	10
9	3	80	70	6

$$\text{Percent Grafting (PG \%)} = \frac{\text{Weight of cardanol grafted onto rubber} \times 100}{\text{Weight of grafted rubber}}$$

### Gel fraction

Gel fraction was determined as per ASTM D3616-95 (2000), using toluene as the solvent. The following formulae were used to determine the gel fraction.

$$\text{Gel fraction} = \frac{(C - B) \times 100}{C}$$

where  $B = 4 \times A$  = mass of total dried solvents,  $A$ : the amount of rubber present in 25 mL of the sol;  $C$ : the amount of rubber initially taken to make the rubber solution (100 ml).

### Infrared spectroscopy

IR spectroscopy of NR and CGNR was studied by using the Perkin-Elmer 843 spectrophotometer in the range of 600–4000  $\text{cm}^{-1}$ . The grafted rubber was dissolved in chloroform and then a film was cast on the KBr disk. Solvent was evaporated with the help of an infrared lamp.

### Nuclear magnetic resonance spectroscopy

The proton NMR spectroscopy of raw NR and CGNR was studied by using the Bruker MSL 300, 300 MHz instrument. The sample was dissolved in  $\text{CDCl}_3$  and a small quantity of the internal reference, tetra methyl silane, was added prior to testing. The spectrum was recorded using the continuous wave method by sweeping the magnetic field.

### Thermal analysis

Differential scanning calorimeter (DSC), model no: Q100, from TA instruments was used for the determination of glass transition temperature. Around 15 mg of the sample was placed in an aluminum crimple, sealed with the help of a sealing press prior to placing it on the sample platform in the instrument. A heating rate of 10°C/min was used to scan in the temperature range of –100 to 100°C, using dry nitrogen as the medium.

Thermogravimetric analysis (TGA) was carried out using Q50 thermal analyzer from TA instruments to study the thermo oxidative stability of CGNR in comparison with that of raw NR. All the TGA experiments were performed by heating the sample at a rate of 20°C/min, in oxygen atmosphere, from room temperature to 800°C.

## RESULTS AND DISCUSSION

### Percent grafting and grafting efficiency

In OATS strategy, more than one reaction parameter is changed at a time and the effect on the outcome is monitored. In the present case, the outcomes are the percent grafting and the grafting efficiency, which need to be optimized. The reaction parameters to be varied are initiator concentration (wt %), cardanol concentration (parts per hundred rubber), reaction temperature (°C), and reaction time (hrs), selected based on the existing literature on grafting reactions onto polymer backbone. In the present case, we have considered three levels of variations in each of the reaction parameter. Hence, 1, 2, 3, and 4% (by wt) of initiator concentration, 40, 60, and 80 phr of cardanol concentration, 60, 70, and 80°C of reaction temperature, and 6, 8, and 10 h of reaction time are used in the optimization using OATS. Table II summarizes the reaction conditions of the all nine experiments based on OATS. By using this optimization technique, the CGNR having percent grafting varying from 8 to 67% and grafting efficiency varying from 17 to 63% is obtained. The spread in percent grafting and grafting efficiency is wide as expected out of an optimization experiment based on OATS. Based on the result of percent grafting and grafting efficiency, the experimental conditions of run 5, where the grafting efficiency and percent grafting are maximum, has been identified as the optimum set of conditions. Thus the percent grafting of 60% and grafting efficiency of 63% have been achieved at the initiator concentration of 2 wt % of the peroxide, 60 phr of cardanol, at a temperature of 80°C and a reaction time of 6 h.

### IR spectroscopy

The IR spectrum of ISNR-5 and the CGNR are as shown in Figures 2 and 3, respectively. The spectrum of NR shows characteristic peaks at 1137, 1180, 1377, 1460, 1739, 2850, and 2918  $\text{cm}^{-1}$ . There is no peak beyond 3000  $\text{cm}^{-1}$  in NR, whereas the spectrum of CGNR showed an absorption band at 3356  $\text{cm}^{-1}$  in addition to all the characteristic peaks of NR. The additional peak at 3356  $\text{cm}^{-1}$  as shown in Figure 3 has been attributed to the –OH stretching vibration of the phenolic moieties of cardanol. A peak at 750  $\text{cm}^{-1}$  in the spectrum of CGNR is another characteristic peak of cardanol arising due to out of plane bending from the aromatic ring. This peak is absent in the spectrum of NR. Hence, it has been presumed that the

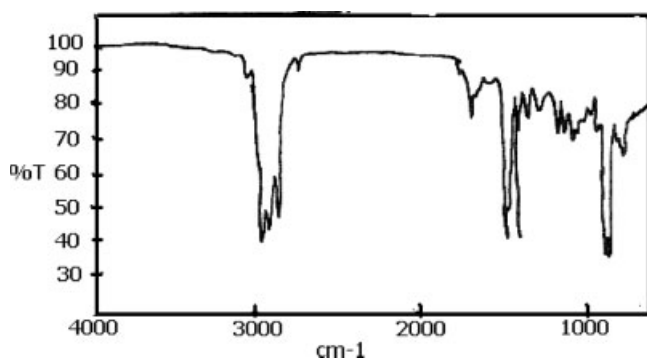


Figure 2 IR spectrum of ISNR-5.

grafting reaction takes place through the side chain of cardanol, leaving behind the phenolic moiety intact.

Thus the probable structure of the grafted NR is most likely to be a substitution product arising out of the allylic radical generated on NR main chain at the C1–C5 carbon atom and the unsaturated side chain of cardanol. It is well known that isoprene repeat units of NR contains highly labile allylic protons, which get knocked off easily by the initiators. Similarly, cardanol also contains several allylic protons in its side chain. Hence, the grafting reaction of NR with cardanol may result in two types of probable products. In one case, the NR macroradical may attack the unsaturated carbon atoms of cardanol side chain via 1,2-addition across the double bonds [Fig. 4(A)] and in the other case, the reaction between the allylic radical of NR and the allylic radicals of cardanol side chain, leaving the unsaturated component intact.

### Probable grafting mechanism

The proton NMR spectra of the CGNR as well as that of raw NR were compared to find out the change in the peak positions and also either the appearance or disappearance of certain peaks. The  $^1\text{H}$  NMR spectra of ISNR and CGNR are shown in Figures 5 and 6,

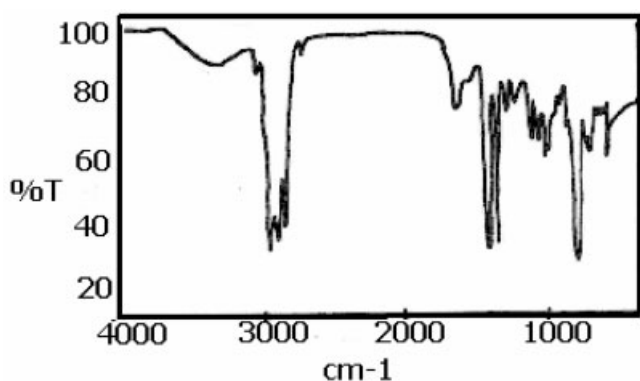


Figure 3 IR spectrum of CGNR.

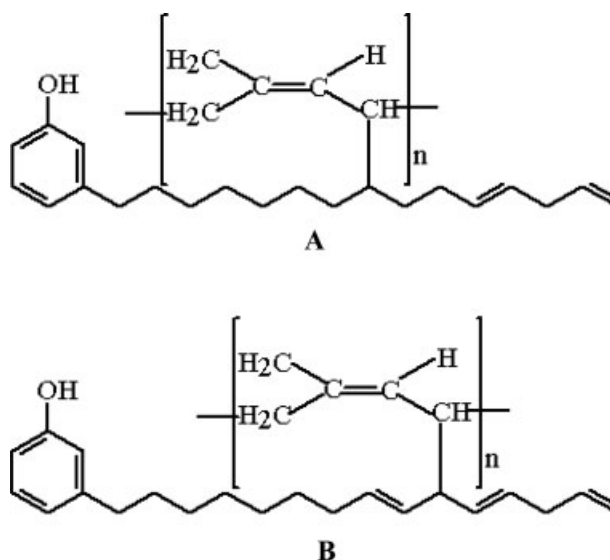


Figure 4 Plausible structures of CGNR based on (A) addition and (B) substitution mechanisms.

respectively. The peak positions and the identification of the corresponding protons are shown below:

NR:  $\delta\text{H}$  ( $\text{CDCl}_3$ ): 1.31 ( $-\text{C}(\text{CH}_3)=\text{CH}-$ , s), 1.68 ( $-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-$ , s), 4.67 ( $-\text{C}(\text{CH}_3)=\text{CH}-$ , s); CGNR:  $\delta\text{H}$  ( $\text{CDCl}_3$ ): 1.69 ( $-\text{C}(\text{CH}_3)=\text{CH}-$ , s), 2.05 ( $-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-$ , s), 5.11 ( $-\text{C}(\text{CH}_3=\text{CH}-$ , s), 7.25 (aromatic ring protons, meta-substituted, m).

The spectrum of NR shows strong signals at  $\delta$  4.67 corresponding to vinylic proton and at  $\delta$  1.31 and  $\delta$  1.68 corresponding to the allylic protons of *cis*-1,4-isoprene units. The spectrum of CGNR although shows signal similar to those of NR, there is a shift in signal position toward higher  $\delta$  values. This can be attributed to the through space deshielding effect of the polar groups such as  $-\text{OH}$  group of cardanol. In addition to this, a signal appears at  $\delta$  7.25 corresponding to the aromatic protons, which is not pres-

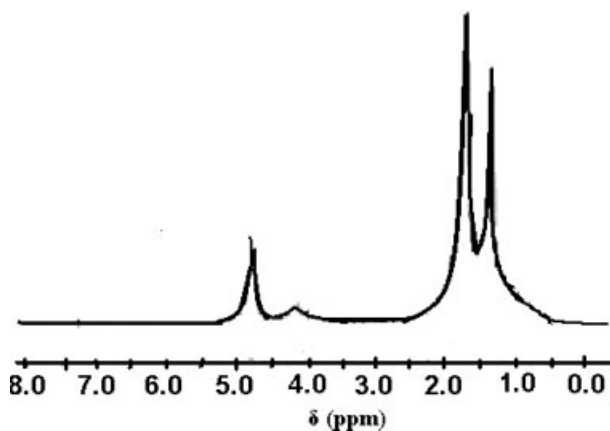


Figure 5  $^1\text{H}$  NMR spectrum of ISNR-5.



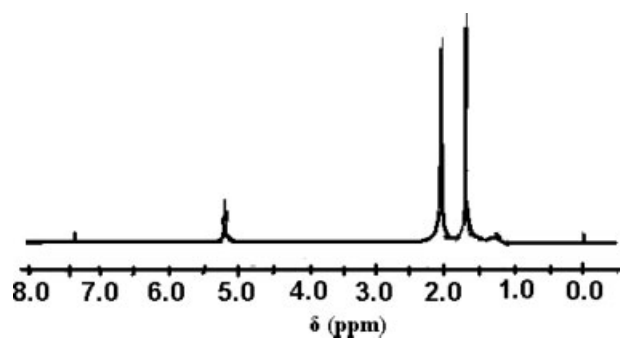


Figure 6  $^1\text{H}$  NMR spectrum of CGNR.

ent in the spectrum of NR. This additional peak corresponding to aromatic protons is due to the phenolic moiety of cardanol. Another important criterion, which proves that the cardanol is chemically bonded to NR at the allylic protons, is the reduction in the ratio of allylic to vinylic peaks in the spectrum of CGNR. Among the allylic protons, the most labile one is the  $-\text{CH}_2-$  in comparison to the  $-\text{CH}_3$  due to the existence of the maximum number of hyperconjugative structures for the radical, which forms upon loss of the proton. Hence, the preferred grafting site is the carbon attached to the most labile proton. It is evident from the reversal of the peak heights corresponding to the  $-\text{CH}_2-$  and  $-\text{CH}_3$  protons of the isoprene unit. From the above analysis, a plausible mechanism of the grafting reaction has been presented in Figure 7.

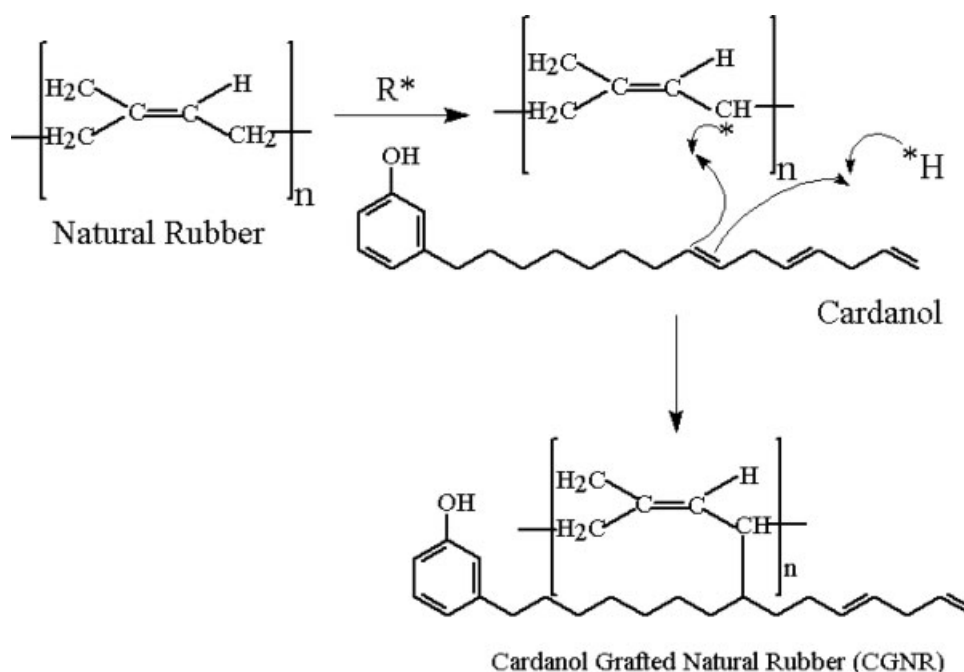


Figure 7 Probable mechanism of grafting.

#### Effect of the initiator concentration

The effect of the initiator concentration on the percent grafting and grafting efficiencies has been investigated. The concentration of the initiator has been changed from 0.5 to 3.0 parts per hundred parts of rubber (phr) keeping the monomer concentration the same at 60 phr, reaction temperature at  $80^\circ\text{C}$ , and reaction time of 6 h. Figure 8 shows an increase in percent grafting with increase in concentration of the free radical initiator. This has been attributed to an increase in the amount of free radicals that are capable of generating sites for grafting on the rubber main chain. A similar trend has been observed in case of the IR absorbance ratio [a ratio of stretching corresponding to  $\text{O}-\text{H}$  group in cardanol ( $3356\text{ cm}^{-1}$ ) to the  $\text{C}-\text{H}$  stretching of  $\text{C}=\text{C}-\text{H}$  in *cis*-1,4-polyisoprene ( $835\text{ cm}^{-1}$ )], which steadily increases with concentration of the initiator free radical. Very high percent grafting such as 63% has been achieved at higher concentration of the initiator i.e., at 3.0 phr because of the generation of abundant free radicals, which immediately react with cardanol present in the system.

#### Effect of the cardanol concentration

To see the effect of the cardanol concentration on percent grafting and grafting efficiency, the proportion of cardanol in the reaction mixture has been varied from 30 to 80 phr. From Figure 9, it is evident that the grafting efficiency increases continuously up to 60 phr and then decreases. This has been attrib-

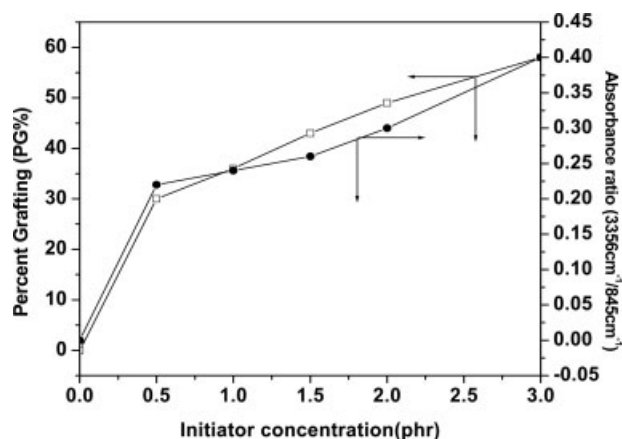


Figure 8 Effect of initiator concentration on percent grafting.

uted to the availability of cardanol for the grafting reaction. Higher amounts of cardanol in the system favors higher grafting reaction and hence the grafting efficiency goes on increasing. But, at very high dosages of cardanol such as 70 and 80 phr, the other competitive side reactions commence such as the chain transfer to monomer, which predominates, leading to reduced efficiency of grafting.

The change in the percent grafting is monitored by changing the dose of cardanol from 30 to 80 phr keeping the initiator concentration at 3 phr, temperature at 80°C, and a reaction time of 6 h. The IR absorbance ratio, which is an indicator of the amount of grafting, exhibited the same trend as those obtained from the residual weight method adopted to calculate the percent grafting. The grafting percentage increases up to 60 phr of cardanol after which it falls down upon increasing the cardanol concentration in the reaction mixture (Fig. 10). This trend has been attributed to the

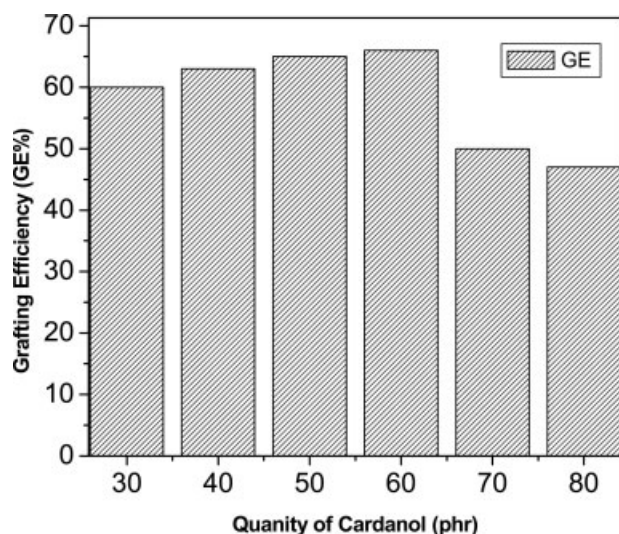


Figure 9 Effect of cardanol concentration on grafting efficiency.

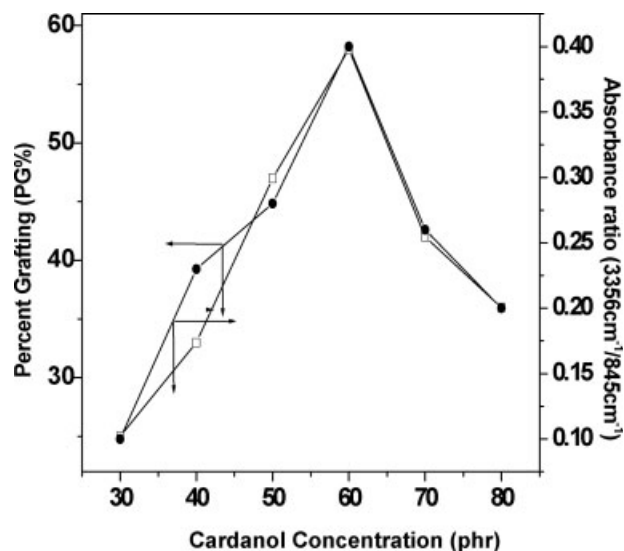


Figure 10 Effect of cardanol concentration on percent grafting.

increasing side reactions such as chain transfer to cardanol as mentioned above in the system. As the side reactions dominate, which is observed in cases of 70 and 80 phr of cardanol, the percent grafting falls down. The percent grafting and grafting efficiency show almost similar trend. Hence, 60 phr of cardanol may be considered as the optimum dose to obtain maximum percent grafting and grafting efficiency.

#### Effect of the reaction temperature

The effect of temperature on the levels of grafting has been studied by changing the temperature of the reaction from 60 to 100°C, maintaining cardanol concentration at 60 phr, initiator concentration at 3 phr, and reaction time of 6 h. The percent grafting is calculated based on the residual weight method and plotted against the reaction temperature as shown in the Figure 11. It is observed from the figure that the reaction

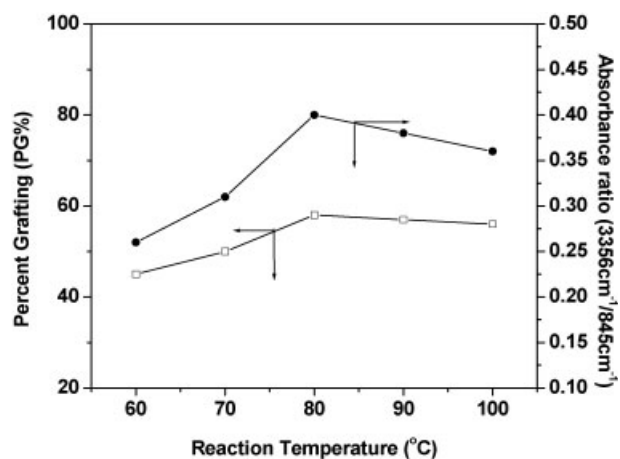


Figure 11 Effect of reaction temperature on percent grafting.

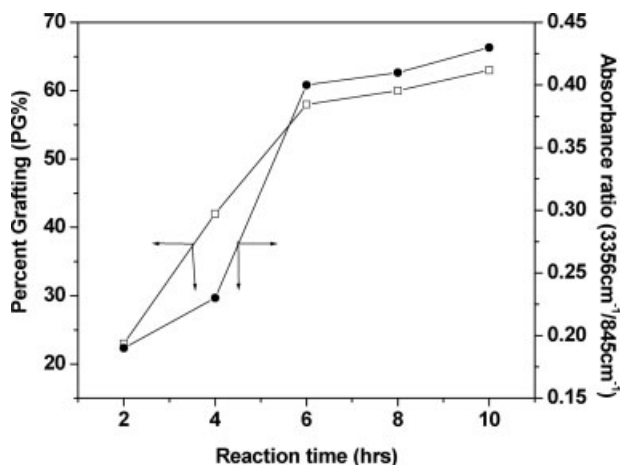


Figure 12 Effect of reaction time on percent grafting.

temperature has a significant influence on the percent grafting of cardanol. Continuous increment in percent grafting is quite evident as the reaction temperature increases from 60 to 80°C. This may be attributed to the increased decomposition and lower half-life periods of the initiator at high temperatures, giving rise to release of higher initiator free radicals in the reaction mixture. Higher amounts of initiator free radicals cause an increase in the number of sites for grafting reaction on the NR backbone. Hence, the percent grafting increases significantly upon increasing the temperature. However, upon further increase in temperature to 90°C and to 100°C, a fall in the percent grafting is observed. Probably at higher temperatures such as 90 or 100°C, the initiator decomposes at a faster rate and hence gives rise to an excess generation of free radicals. In such a scenario, the chances of recombination of the free radicals are very high, leading to inactive initiator fragments or it may be due to

reactive sites attached with initiator fragments or free radicals only. Hence, the number of free radicals present in the system drastically falls, which in turn results in the reduction percentage of grafting. In addition to this, at higher temperatures, the reaction between the highly reactive sites of the NR becomes pronounced and hence the grafting reaction is hampered. Thus, the percent grafting falls down at higher temperatures.

#### Effect of the reaction time

The role of the reaction time has been investigated by changing the time from 2 to 10 h, keeping the initiator concentration constant at 3 phr, cardanol concentration at 60 phr, and the reaction temperature at 80°C. Figure 12 presents the plot of percent grafting with respect to reaction time. From Figure 12, a drastic increase in percent grafting is evident as the reaction time is increased from 2 to 6 h. However, for longer durations such as 8 and 10 h of the reaction time, only a marginal increase in percent grafting is observed. Similar trend has also been observed for absorbance ratio against the reaction time (Fig. 12). At longer reaction times, the grafting reaction attains a saturation level at which most of the reactive sites on NR backbone are expected to be used up either due to grafting reaction or due to crosslinking reaction. It has also been observed that longer durations of reaction time results in predominance of the crosslinking reaction over grafting reaction. A higher gel content of 55 and 58% has been recorded in case of CGNR synthesized by varying the reaction time to 8 and 10 h, respectively, whereas the gel content of CGNR vary from 37% to 40, 42, and 45%, respectively, at reaction times 0, 2, 4, and 6 h. A drastic

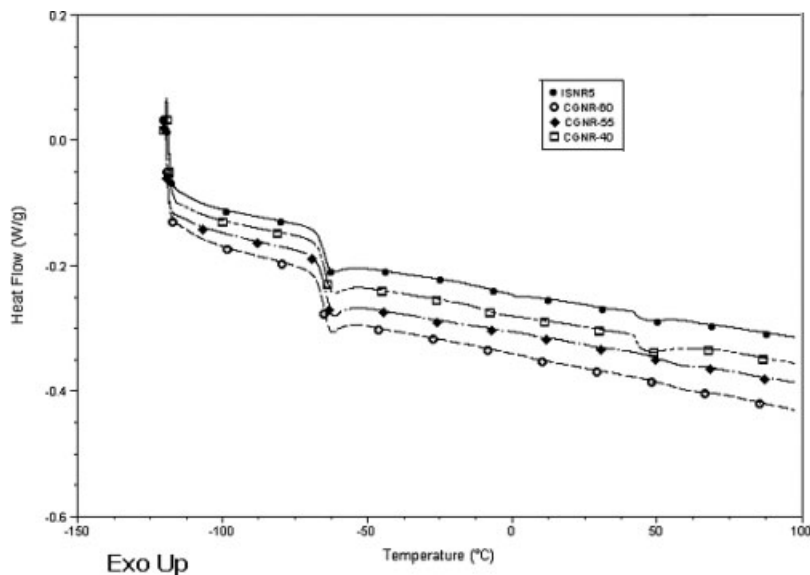


Figure 13 DSC thermograms of raw NR and CGNR with varying percent grafting.

**TABLE III**  
 $T_g$  of Raw NR and Various Grades of CGNR  
 as Measured from Differential Scanning  
 Calorimetric Analysis

Sample designation	Glass-transition temperature, $T_g$ ( $^{\circ}\text{C}$ )
ISNR-5	-64.5
CGNR-40	-66
CGNR-55	-67
CGNR-60	-68.5

increase in the gel content in CGNR for 6 and 8 h of reaction may be attributed to the predominance of the crosslinking reaction over grafting reaction.

#### Differential scanning calorimetric analysis

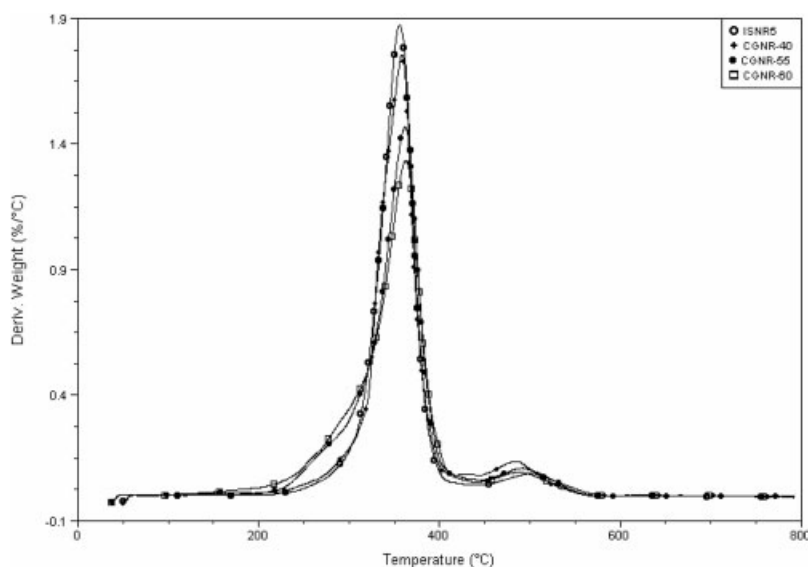
DSC study of the NR and the grafted NR show a major secondary transition below  $-50^{\circ}\text{C}$ ; indicative of the  $T_g$  of the polymer. The glass transition temperatures of the raw NR and CGNR at various percent of grafting such as 40, 55, and 60% show a lowering of the  $T_g$  values as the percent grafting increases from  $-64.5^{\circ}\text{C}$  to  $-66$ ,  $-67$ , and  $-68.5^{\circ}\text{C}$  respectively, as shown in Figure 13. The  $T_g$  values are compiled in Table III. It may be noted from the figure that  $T_g$  of all the grades of CGNR are lower than that of raw NR. CGNR-60 shows a decrease by  $4^{\circ}\text{C}$  in the  $T_g$ , as compared to raw NR. This may be due to the plasticizing effect of cardanol upon grafting onto the NR backbone. Because of the presence of both aromatic and aliphatic segments in the structure of cardanol, it acts as a highly compatible plasticizer and as it has been chemically grafted onto the rubber, the NR inherently possesses this property. The

lowering of  $T_g$  of the CGNR is an indicative of the plasticization behavior of cardanol.

#### Thermogravimetric analysis

Comparative studies on the thermo oxidative degradation of raw NR, CGNR-40, CGNR-55, and CGNR-60 are shown in the DTG thermograms (Fig. 14). Table IV summarizes the results of TGA experiments. From the DTG traces, two peaks are prominent; one in the temperature range of  $250$ – $400^{\circ}\text{C}$  and the other in the range of  $400$ – $550^{\circ}\text{C}$ . The first degradation may be attributed to the NR and the second to the thermally stable products formed during decomposition. It may be easily observed that the  $T_{\text{max}}$  shifts toward a higher temperature in case of CGNR. Such a shift in the temperature curve is an indication of improved thermo oxidative stability of CGNR. In case of CGNR-60, a  $7^{\circ}\text{C}$  raise in the  $T_{\text{max}}$  value is observed with respect to that with ISNR-5.

The extent of decomposition in the temperature range  $250$ – $400^{\circ}\text{C}$  also indicates that the thermo oxidative stability of CGNR is better than that of ISNR-5. ISNR-5 has a weight loss of 89% in the first phase of degradation, whereas all the other grades of CGNR showed a reduction in weight loss. A 5% reduction in weight loss is significant in case of CGNR-60. Similarly, an increase in the weight loss in the region  $400$ – $550^{\circ}\text{C}$  and a reduction in weight loss at lower temperature range of the grafted product indicate an improvement in thermo oxidative stability. This may be attributed to the formation of higher amounts of thermally stable intermediates after first phase of degradation. ISNR-5 has only a 9% weight loss in the second phase, whereas CGNR-60 has 13% weight loss.



**Figure 14** DTG thermograms for raw and grafted NR in oxygen atmosphere.



TABLE IV  
Oxidative Degradation Temperatures of Raw NR and CGNR as Measured  
from Thermogravimetric Analysis

Sample designation	$T_i$ (°C)	$T_f$ (°C)	$T_{max}$ (°C)	% Weight loss in the range 250–400°C	% Weight loss in the range 400–550°C
ISNR-5	331	373	355	89	9
CGNR-40	330	375	358	86	12
CGNR-55	327	377	361	85	12.5
CGNR-60	327	381	362	84	13

## CONCLUSIONS

Grafting of cardanol onto NR backbone has been carried out in solution state. Percent grafting was estimated using the residual weight method. The optimization of the conditions of grafting was performed using OATS. Effect of individual parameters such as initiator concentration, dose of cardanol, reaction temperature, and reaction time were studied. It was found that increasing the initiator concentration and reaction time increases the percent grafting. However, increasing the cardanol doses up to 60 phr increases the percent grafting and any further increase in dose results in decrease in percent grafting. Similar trend has been recorded in case of increase in reaction temperature. Percent grafting increases up to 80°C, after which it falls down. The glass transition temperature, as determined from the DSC thermogram, is lower for CGNR as compared to ISNR-5. All the grades of CGNR exhibited an improvement in thermo oxidative stability.

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