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Cardanol: A green substitute for aromatic oil as plasticizer in natural rubber

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Abstract

Grafting of cardanol on to natural rubber in the latex stage was carried out successfully at room temperature using cumene hydroperoxide and tetraethylene pentamine. The grafted natural rubber was characterized by FTIR, NMR and GPC. Grafting of cardanol on to natural rubber has resulted 45.6 % increment in the molecular weight without affecting the molecular weight distribution. Taguchi method was used to optimize the grafting conditions to achieve maximum yield in terms of percent grafting and grafting efficiency. The optimal parameter combination was found to be initiator concentration 2 phr, cardanol concentration of 10 phr, reaction temperature of 35 °C and reaction time of 10 hours. The percent grafting was found to be 8.25% and grafting efficiency was 82.5 % for the optimum parameter combination. Analysis of variance method was used to evaluate the percentage contribution of different control factors on percent grafting and grafting efficiency. Cardanol concentration was found to be the most dominant parameter on grafting efficiency while initiator concentration was found to play the dominant role on the percent grafting. The cardanol grafted natural rubber (CGNR) was found to have higher molecular weight, lower Mooney viscosity, lower Wallace plasticity number and higher cure rate as compared to the unmodified natural rubber. The physico-mechanical properties of the CGNR vulcanizates were at par with or even better than the gum natural rubber vulcanizates. The rheological characteristics exhibit better flow behavior as compared to the unmodified natural rubber. Differential scanning calorimetry and dynamic mechanical analysis exhibit lowering of the glass transition temperature of the CGNR as compared to the raw natural rubber. This confirms the plasticization effect of the cardanol when grafted onto the natural rubber.

Key words: cardanol, natural rubber latex, plasticization, grafting, Taguchi method

Introduction

Aromatic oils are still predominating as the plasticizers and process aids in the rubber industry despite its carcinogenic effect due to presence of polycyclic aromatic hydrocarbons within it. However, because of growing concerns on environmental and health protection related issues, one has to look for alternate sources of plasticizers mostly from renewable resources. Thus, it is appropriate to search for an environmental friendly substitute to these hazardous aromatic oils. Cardanol, chemically known as m-pentadecenyl phenol, obtained by double vacuum distillation of cashew nut shell liquid (CNSL) is an agricultural renewable resource and a by-product of the cashew industry. In the last few decades, CNSL has been found to be a very desirable substitute for the commercial phenolic compounds, in the resin industry especially because of its sustainability, low cost, large availability and biodegradability.

The phenolic moiety of cardanol along with the aliphatic side chain containing 15 carbon atoms in the *meta* position to the hydroxyl group, renders it amenable to a variety of chemical reactions. Moreover, the long aliphatic side chain which may vary its functionality, by being a saturated hydrocarbon, a monoene, diene or triene (non-conjugated) as shown in Figure 1. Cardanol and its derivatives have wide range of applications in the form of brake linings, surface coatings, paints, and varnishes because of its bifunctional moiety and high chemical reactivity. Recently it has been used in the polymer and rubber industries as a multifunctional additive. It has been reported that, cardanol may be used along with lignin based compounds for the synthesis of polyurethanes that exhibit good thermal and mechanical properties.[1] Calo et al. [2] have reported a novel benzoxazine prepolymer derived from cardanol which is employed in the synthesis of phenolic resins that exhibit good thermal properties and flame retardant characteristics empowered with improved mechanical properties and greater molecular design flexibility.

Ravichandran et al. [3] have reported the synthesis of polycardanol in aqueous media, which is a non-toxic, low-leaching, non-halogenated fire retardant polymer. Bai et al. [4] have also reported preparation of polycardanol by solvent free grinding polymerization technique which has higher thermal stability with degradation commencing at 360 °C. The oxidative polymerization of cardanol using a fungal peroxidase from *Coprinus cinereus* (CiP), produced an oil soluble polymer, and this polymer may be used as a glossy coating material.[5] Applications of CNSL, along with its major constituents cardanol and their hydrogenated derivatives has also been explored as new green larvicides [6] and these may be considered as a new alternative to combat spreading of dengue. Vasapollo et al. [7] have presented an overview of the developments in olefin metathesis involving cardanol or cardanol-derivatives for the preparation of new cardanol based olefins and hybrid materials, combined with porphyrins, phthalocyanines and fullerenes. More et al. [8-10] have reported synthesis of processable polyamides, aromatic polyazomethines and poly amidesimides having pendant pentadecyl chains which were synthesized from cardanol. The presence of an alkyl side chain and flexibilizing ether linkage in the polymer backbone imparts greater segmental mobility to the polymer and enhances its solubility. It also lowers down the glass transition temperature marginally.

Since cardanol is an important natural renewable resource containing a phenolic group, it possesses fairly antioxidant properties. Derivatives of cardanol also shown equal promise as anti-oxidants in the stabilization of gasoline.[11] Maria et al. [12] have studied the antioxidant properties of phosphorated cardanol on mineral oils NH10 and NH20. Lomonaco et al.[13] have reported that CNSL as well as its main components i.e. cardanol and cardol and their thiophosphorylated derivatives[14] have good antioxidant activity up on Polymethylmethacrylate in concentration as low as 1%. Mazzetto et al.[15] have also reported the synthesis and characterization of four phosphorylated esters derived from hydrogenated cardanol and their applications as antiwear additives for diesel and as antioxidant additives for mineral oils. They have also reported about the synthesis of phosphorylated compounds[16] from cardanol and proposed their application as antioxidants for biodiesel which are comparable with butylated hydroxytoluene (BHT). Rios et al. [17] have explored the thermal behavior of phosphorylated derivatives of hydrogenated cardanol and butylated cardanol and suggested the possibility of application of these compounds as antioxidants for petrochemical products, like lubricant oils.

Menon et al.[18] have reported that natural rubber (NR) modified with phosphorylated cardanol as a plasticizer are superior to those obtained with di-ethyl-hexyl-phthalate as a plasticizer in terms of higher tensile properties, better flame retardancy and resistance to thermo-oxidative degradation. Also, phosphorylated cardanol has been established as an effective plasticizer for ethylene-propylene diene rubber[19] , polychloroprene and polybutadiene rubber[20], natural rubber/EPDM tercopolymer blends[21] and LLDPE/EVA copolymer blends.[22] Greco et al.[23, 24] have also used cardanol acetate and epoxidated cardanol acetate, the esterified derivatives of cardanol as efficient plasticizers for PVC.

Natural rubber is a well-known renewable resource and is obtained from the tree *Hevea brasiliensis* in the form of a milky white fluid. Because of its high unsaturation (each repeat unit contains one double bond in its structure) it is less resistant to oxidation, ozone, weathering, various chemicals and solvents in comparison with other synthetic rubbers. Also processability for good surface finish and dimensional stability are poor. Hence, chemical modification of NR is essential to overcome some of its drawbacks. Graft copolymerization is one such technique used to modify natural rubber.

Menon et al. [25] have established that cardanol and its derivatives act as good plasticizers in NR. They have confirmed the multifunctional activity of cardanol in NR. They have also reported that cardanol and its derivatives incorporated into the rubber act as a plasticizer, process aid, cure promoter, antioxidant and tackifier.[26] However, incorporation of cardanol and its phosphorylated derivative which are highly viscous, is tedious and a time consuming process. Besides, it causes cure-retardation due to absorption of activators by this additive and thus needs additional doses of ZnO to compensate for the loss.[26] In order to overcome this problem, Vikram and Nando [27] have accomplished grafting of cardanol onto NR backbone by solution technique. They established that cardanol and its derivatives act a better non-mineral plasticizer than the aromatic oils not only by better processability but also by imparting better tensile properties, higher thermal stability, flame retardancy and age resistance properties.[28]

NR in the latex stage would be a more viable option both technically and commercially. Hence, the present work has been focused on grafting in the latex stage. Grafting is usually conducted using free-radical emulsion polymerization, in which the initiator utilized in the polymerization is either a redox initiator or thermal initiator.[29-31] Arayapranee et al. [32] have reported that redox initiation system consisting of organic hydroperoxide and tetraethylene pentamine (TEPA) are insensitive to oxygen and can work well at high pH. Hence, it is more suitable for carrying out reactions involving NR latex with ammonia added for preservation purposes. Moreover, redox initiators can work at low temperatures, which is advantageous in terms of lower energy consumption and prevention of thermally induced termination or depolymerization process.[33] Kochthongrasamee et al.[31] have reported that, cumene hydroperoxide (CHP)/tetraethylene pentamine (TEPA) initiator is the best redox system as compared to other redox initiators (i.e., TBHPO–TEPA and $K_2S_2O_8$–$Na_2S_2O_3$ initiators), for the graft copolymerization of methyl methacrylate onto NR latex because of the highest solubility in the oil phase of CHP, which gives the highest grafting efficiency.

In our previous work, grafting of cardanol on to natural rubber in the latex stage was undertaken successfully using the redox initiator system potassium persulfate/ sodium thiosulfate [34] and the optimum conditions for grafting was found to be at a higher temperature of 65 °C. The present study focuses on the grafting of cardanol on to natural rubber in the latex stage using cumene hydroperoxide (CHP)/ tetraethylene pentammine (TEPA) with the objective of lowering the temperature of the reaction. Moreover, the present paper emphasizes on the optimization of the grafting parameters by an economic and viable experimental strategy based on Taguchi's parameters design.[35] The effect of grafting of cardanol on to the natural rubber backbone has been evaluated by studying its processability characteristics, physico-mechanical properties and thermal characteristics of its vulcanizates as compared to natural rubber vulcanizates prior to grafting.

Experimental

Materials

Natural rubber latex (60.02% dry rubber content) was supplied in kind by The Rubber Board, Kottayam, India. Cardanol was procured from M/S Satya Cashew Chemicals Limited, Chennai, India. The initiator cumene hydroperoxide (CHP) was procured from E-Merck, India and tetraethylene pentamine (TEPA) was obtained from Sigma-Aldrich, India. Sodium dodecyl sulfate, the anionic surfactant was obtained from E-Merck, India. Zinc oxide, stearic acid, N-(1,3-dimethylbutyl)-N'-phenyl-P-phenylenediamine (6-PPD), 2-Mercapto benzothiazole disulfide (MBTS), Tetra methyl thiuram disulfide (TMTD) and sulfur were of the commercially available grades. Other solvents and reagents from E-Merck were used directly without further purification.

Grafting of cardanol onto natural rubber latex

The grafting was carried out by following the process described in an earlier publication of the authors.[34] In a three-necked flask natural rubber latex (5 g, DRC 60.02%) was taken. Then 10 mL of 10 wt % of potassium hydroxide solution and sodium dodecyl sulfate (1 phr) as an emulsifier was added and the mixture was stirred. The cardanol was made into an emulsion by mixing mechanically with 10 % aqueous solution of sodium dodecyl sulfate. The cardanol emulsion thus prepared was added to the natural rubber latex mixture and stirred for at least one hour with nitrogen purged for 15-20 minutes. Then the initiator cumene hydroperoxide was added followed by tetraethylene pentamine after an interval of 15 minutes (the ratio of CHP/TEPA was 1:1). The reaction was carried out at different temperature, for different time with constant stirring at 300 rpm. After the reaction was over, the cardanol grafted natural rubber latex was coagulated and washed with distilled water several times and dried under vacuum at 70 °C till a constant weight. Then the dried coagulum was soxhlet extracted with methanol to remove any unbound cardanol present in the rubber coagulum. Grafting parameters such as percentage grafting and grafting efficiency were calculated gravimetrically using equations (1) and (2).

$$\text{Percent Grafting (PG \%)} = \frac{\text{Weight of cardanol grafted}}{\text{Weight of NR taken}} \times 100 \qquad (1)$$

$$\text{Grafting Efficiency (GE \%)} = \frac{\text{Weight of cardanol grafted}}{\text{Weight of cardanol taken}} \times 100 \qquad (2)$$

Preparation of rubber vulcanizates

The formulation used for preparation of the rubber vulcanizates is given in Table 1. All ingredients, except the curatives were mixed with rubber in a Haake Rheomix OS (Germany) for four minutes at a set temperature of 120 °C and rotor speed of 60 rpm. Then the curatives were added to it on a two-roll mixing mill and mixed for 4 minutes at room temperature. The cure characteristics of the rubber compounds were determined at 150 °C by a rheometer

(Monsanto R100) as per ASTM D-2084-11. Then, the rubber compounds were compression molded into sheets at 150 °C using hydraulic hot press (model David Bridge) according to their respective optimum cure times.

Characterization methods

Characterization of the raw NR and CGNR

IR spectroscopy of natural rubber (NR) and cardanol grafted natural rubber (CGNR) was studied using the FTIR-spectrophotometer (model spectrum RX-I, PerkinElmer Life and Analytical Sciences, Massachusett, USA) in the range of 700-4000 cm^{-1}. The samples were dissolved in chloroform and then a film was cast on the KBr disk. ^1H NMR spectra of natural rubber (NR) and cardanol grafted natural rubber (CGNR) was recorded on a Bruker 500 MHz NMR Spectrometer using $CDCl_3$ as solvent and tetramethyl silane as an internal standard.

The molecular weight of the natural rubber (NR) and cardanol grafted natural rubber (CGNR) was determined by Gel permeation chromatography (GPC) (Agilient 1260 Infinity GPC instrument) using THF as eluent at a flow rate of $1\ mL\ min^{-1}$ and narrow disperse polystyrene as calibration standard. The polymer solutions were passed through three PLgel 10 μm Mixed-B columns (300X7.5 mm) connected in series, which were preceded by a PLgel 10 μm guard column (50X75 mm). The RI detector was used to record the signal. Before injecting the polymer solution to the GPC instrument, it was thoroughly filtered by using regenerated cellulose filter of pore size 0.2 μm. Intrinsic viscosity measurements of the rubbers were carried out using an Ostwald viscometer with benzene as the solvent at 30 °C.

Mooney viscosity and Mooney scorch time (t_5) were determined as per ASTM D-1646-07, by using a Mooney viscometer (MK 3, Negretti Automation Aylesbury, England). The plasticity number was determined by Wallace rapid plastimeter MK-II.

The viscoelastic properties of the raw cardanol grafted natural rubber and the ungrafted rubber were studied using a Rubber Process Analyzer (RPA 2000, Alpha Technologies, Ohio, USA).The dynamic frequency sweep test was carried out at strain of 6.98 % (0.5° of arc) and temperature of 100 °C in the frequency range of 0.30–33 Hz. The dynamic strain sweeps of the samples were studied at a frequency of 0.33 Hz and at a temperature of 100 °C in the strain range of 0.7–1256 %.

The glass transition temperature of the rubbers were measured by Differential scanning calorimeter (TA instruments, DSC Q100) in the temperature range -100 °C to +100 °C at a heating rate of 10 °C/min. Thermogravimetry analysis was carried out by Thermogravimetry Analyzer (TA instruments, TGA Q50) from ambient to 600 °C at a heating rate of 10 °C/min.

Characterization of the NR and CGNR vulcanizates

Tensile properties were measured with the help of Hounsfield Universal testing machine (model H10KS), at a cross head speed of 500 mm/min as per ASTM D-412-06 (method A). Tear strength of the specimens were determined as per ASTM D-624-00. Hardness was measured as per ASTM D-2240-05, using an indentation hardness tester (Type shore A). Compression set at constant strain was carried out according to ASTM D-395-03 (method B). The rebound resilience was measured using a Dunlop tripsometer as per BS 903: part A8. Heat build-up test of the specimens was measured using a Goodrich flexometer (Ferry machine co. Kent, Ohio, USA) at 50 °C, as per ASTM D-623-07. The abrasion resistance was determined by using a DuPont abrader as per ISO 4649:2010 (method A). The fatigue life of the rubber vulcanizates were with the help of a Monsanto Fatigue-to-Failure Tester (FTFT) as per ASTM D4482-11 at an extension ratio of 2.0.

The crosslink density was measured by equilibrium swelling method using benzene as the solvent. Flory-Rehner equation[36] was employed to calculate crosslink density as given in equation (3).

$$-\ln(1-v_r)-v_r-\chi v_r^2=2v_s\eta(v_r^{1/3}-2v_r/f) \qquad (3)$$

Where, v_r is the volume fraction of the rubber in the swollen sample, v_s is the molar volume of solvent, χ is the rubber-solvent interaction parameter, η is the crosslink density of rubber (mol/cm^3) and f is functionality of the crosslinks (being 4 for sulfur curing system).

Dynamic mechanical properties of the vulcanizates were determined with the help of a Dynamic Mechanical Analyzer DMA Q800 (TA Instruments, Lukens Drive, Newcastle, Delaware). The measurements were done under tension mode in the temperature range from -100 °C to +100 °C at a heating rate of 3 °C/min with 0.1% strain and 1 Hz frequency.

Taguchi method

Taguchi method is an experimentally established technique in the design of experiments for achieving optimum conditions to improve quality performance based on a mathematical approach.[35] It is highly effective in studying the effects of the multiple factors on the deliverables with minimum number of experiments. It also determines the factors which have greater influence than the others, by using analysis of variance technique.

Taguchi method drastically reduces the number of experiments that are required to model the response function compared with the full factorial design of experiments. Hence, it is a technique for designing experiments to investigate processes where the output depends on many factors (variables or inputs) without resorting to all possible combinations of values which are tedious and uneconomical in the process. Scheme 1 represents the major steps of implementing the Taguchi method. [35]

In Taguchi method, the result of experiments are analyzed to achieve the following objectives: (1) to find out the best or optimal condition for the product or process, (2) to identify the contribution of individual factors and (3) to estimate the response under optimal conditions.[37]

In the present work, Taguchi method has been employed to study the effect of the four control parameters viz. initiator concentration (A), cardanol concentration (B), reaction time (C) and reaction temperature (D) each set at three different levels 1,2 and 3 as shown in Table 2. With four factors each at three levels, the full factorial design requires 3^4= 81 runs or experiments to be carried out. However, with the help of Taguchi method using the L9 orthogonal array only 9 runs/experiments need to be carried out as shown in Table 3. The response variables chosen are percent grafting and grafting efficiency.

Taguchi method employs a generic signal-to-noise (S/N) ratio which measures the effect of noise factors on performance characteristics. A larger S/N ratio represents better quality characteristics and less variation. There are primarily three categories of S/N ratios: “smaller-is-better”, “larger-is-better” and “nominal-is-best”. The selection principles of S/N ratio depend on the goal of the design.

In the present study, since both the response variables, the percent grafting and grafting efficiency are intended to be maximized, hence the "larger-is-better " approach is adopted for which the S/N ratio is calculated as follows: [35]

$$S/N = -10 \log \frac{1}{n}\left(\sum_{i=1}^{n} \frac{1}{y_i^2} \right) \qquad (4)$$

Where, y_i is the observed data and *n is* the number of observations.

RESULTS AND DISCUSSION

IR Spectroscopy study

The FTIR spectrum of natural rubber (Figure 2a) shows very important absorption peaks at 2960-2854 cm^{-1} due to aliphatic C-H stretching, 1634 cm^{-1} is due to aliphatic C=C stretching, 1448 and 1375 cm^{-1} peaks are due to C-H bending vibration, 1260 cm^{-1} is for C-C stretching and 801 cm^{-1} for =C-H bending vibration. However, the FTIR spectrum of cardanol grafted natural rubber (Figure 2b) shows an additional peak at 3446 cm^{-1} which has been attributed to the –OH stretching vibration of the phenolic moieties present in the cardanol. This infers that the double bonds present in the side chain of cardanol have taken part in the grafting reaction leaving behind the phenolic moiety intact. This observation is similar to the previous one of the authors reported earlier by using potassium persulfate/sodium thiosulfate as the initiator system [34] for the grafting reactions with NR.

NMR spectroscopy study

The ^1H NMR spectrum of NR (Figure 3a) shows a singlet resonance signal at 5.16 ppm corresponding to the unsaturated methyne proton. The signal at 2.08 ppm is attributed to the methylene protons and the singlet resonance signal at 1.71 ppm may be due to the methyl protons. The spectrum of CGNR (Figure 3b) shows signals at 1.73, 2.08 and 5.12 ppm corresponding to the NR backbone. In addition, it shows a multiplet at 6.70-7.18 corresponding to the aromatic protons due to the presence of phenolic moiety in cardanol that is absent in the ^1H NMR spectrum of NR. Hence, it may be presumed that the unsaturation present in the cardanol must have taken part in the grafting reaction leaving behind the phenolic moiety intact.

The grafting sites on the natural rubber backbone in a free radical reaction may be generated through two possible routes (Scheme 2) viz. abstraction of α-methylenic hydrogen (Route-A) or the addition to the double bond in the polyisoprene backbone (Route-B) that leads to formation of polyisoprene macro-radicals.[38] Bulky initiator radicals such as cumyloxyl radical (generated from cumene hydroperoxide) tend to favour abstraction of the α-methylenic hydrogen from the allylic carbon (5th carbon) as compared to the addition reaction. Moreover, addition of polymeric radicals to the trisubstituted double bonds on the polyisoprene is slow and hence, abstraction is more likely to be favoured than addition against the double bond.[39] Among the allylic protons present in the NR backbone, the most labile one is the $–CH_2–$ group present in the fifth position in comparison with the $–CH_3$ group present at the second position of the isoprene moiety because of the existence of maximum number of hyperconjugate structures for the radical which forms upon loss of a hydrogen atom. Hence, the preferred grafting site at the main chain backbone of natural rubber is the carbon which is at the fifth position. The probable mechanism of the grafting of cardanol on to natural rubber in the latex stage and the structure of CGNR are given in Scheme 3.

Optimization of the reaction conditions using Taguchi method

The response variables such as percent grafting and grafting efficiency are calculated by using equations (1)-(2) and the results are shown in Table 4. The signal-to-noise ratio (S/N) for each series of experiments has been calculated using equation (4) and the results are presented in Table 4. The response to each factor at its individual level has also been calculated by averaging the S/N ratios of all experiments at each level for each factor. In order to evaluate the influence of each factor on the yield, the S/N ratio for each factor is computed. The S/N ratio for a single factor can be determined from the average values of S/N ratios at different levels. For example, the mean S/N ratio for reaction temperature at level 1 can be calculated by averaging the S/N ratios for the experiments 1, 6 and 8. The mean S/N ratio for every factor at different levels has also been calculated similarly. Figures 4 and 5 represent the effect of four control factors on the percent grafting and grafting efficiency respectively. Monitoring the S/N ratios at the different levels of the control factors for higher values, led to a conclusion that the combination A2, B2, C1 and D3 of the factors yield maximum percent grafting while maximum grafting efficiency is achieved with the combination A2, B1, C1 and D3 of the control parameters.

The present work focuses on the grafting of cardanol on to NR by using CHP/TEPA system unlike the earlier published work[34] with the objective to carryout the reaction at ambient temperature which is usually 35 °C in the southern part of the country throughout the year. Both the initiating systems give similar results regarding the grafting yield and grafting efficiency. But the optimized reaction temperature for grafting was 65 °C in the earlier published work and for the current system it is 35 °C. This will be beneficial from commercial point of view when the grafting of NR latex would be carried out in large scale for use by the industries. It will save energy and reduce production cost significantly as no heating of the latex is required in this case.

Analysis of variance (ANOVA) results

The analysis of variance (ANOVA) has been performed to evaluate the influence of the relative control factors on the grafting reaction. From the analysis, it becomes easier to identify the effectiveness of the four control factors on the percent grafting and grafting efficiency. ANOVA has been established based on the sum of the square (SS), the degree of freedom (*D*), the variance (*V*), and the percentage of the contribution to the total variation (*P*) which can be calculated as follows [40, 41] :

The total sum of squares SS_T can be calculated as:

$$SS_T = \sum_{i}^{m} n_i^2 - \frac{1}{m}\left[\sum_{i=1}^{m} n_i\right]^2 \qquad (5)$$

Where, *m* is the total number of the experiments and n_i is the S/N ratio at the *i*th test.

$$SS_p = \sum_{j=1}^{t} \frac{\left(S_{nj}\right)^2}{t} - \frac{1}{m}\left(\sum_{i=1}^{m} n_i\right) \qquad (6)$$

Where, SS_p denotes the sum of squares for the tested factors, p represents one of the tested factors, *j* the level number of this specific factor p, *t* the repetition of each level of the factor p, and $S\eta j$ the sum of the S/N ratio involving this factor and level *j*.

$$V_p(\%) = \frac{SS_p}{D_p} \times 100 \qquad (7)$$

Where, V_p is the variance of the tested factors and D_p is the degree of freedom for each factor.

$$SS'_p = SS_p - D_p V_e \qquad (8)$$

$$P_p(\%) = \frac{SS'_p}{SS_T} \times 100 \qquad (9)$$

Where, P_p is the percentage of the contribution of each individual factor to the total variation.

The analysis of variance (ANOVA) for the response variables viz. percent grafting and grafting efficiency has been performed and the results are shown in Table 5 and Table 6 respectively. From Table 5, it is evident that the control factor such as initiator concentration stands as the most significant factor for the percent grafting with the percentage contribution of up to 45.1% followed by the reaction temperature which contributes up to 32.8 %. From Table 6, it may be inferred that, cardanol concentration is the most significant factor for the grafting efficiency which contributes up to 72.2 %. The percentage contributions due to all the four factors have been shown in Figure 6. Reaction time is found to be the least significant factor for both percent grafting and grafting efficiency. The order of the effect of the control factors for percent grafting is; initiator concentration, reaction temperature cardanol concentration, and reaction time as presented in the last column of Table 5. While as far as grafting efficiency is concerned, it is observed that cardanol concentration has the highest influence and reaction temperature has the minimum effect of up to only 1.4 % for overall grafting efficiency. Both initiator concentration and reaction temperature however have almost nominal effect on the grafting efficiency.

As per the ANOVA results, if the percentage error (P_e) contributes to lower than 15% of the total variance, there is no significant defect in the experimental design. On the other hand, if the percent contribution of the error exceeds 50%, then there is significant defect in the design of the experiment and it must be re-designed. As seen from Table 5 and 6, the percentage error (P_e) appears to be 0%. This implies that there is no significant factor that has been missed out from the experimental design and thus, the design of experiment is correct.

Confirmatory Test

A correlation between the input control factors and the yield such as percent grafting and grafting efficiency has been established by using the multiple linear regression analysis. Linear regression is performed with the help of “Minitab 15” software.

The regression equation for percent grafting is obtained as follows:

$$\text{Percent grafting (\%)} = 8.09 - 0.022 \times A + 0.107 \times B - 0.0362 \times C - 0.043 \times D \qquad (10)$$

The regression equation for grafting efficiency is obtained as follows:

$$\text{Grafting efficiency (\%)} = 143 - 1.28 \times A - 4.31 \times B - 0.471 \times C - 1.26 \times D \qquad (11)$$

Where A=initiator concentration (phr), B=cardanol concentration (phr), C=reaction temperature (^{o}C), D=reaction time (hours).

The final step in the Taguchi method is to confirm the experimental results. Once all the control factors have been optimized, then the experiment is performed at the optimum level of each of the control factors as shown in Table 7. The experiments were performed in duplicates and the results are recorded in the Table 8 for confirmation and for comparison with the theoretical values calculated by using the regression equations (10) and (11) for percent grafting and grafting efficiency respectively.

Moreover, it is observed (from Table 8) that, for cardanol concentration of 5 phr, percent grafting is less but grafting efficiency is more. However, when the cardanol concentration is increased to 10 phr, percent grafting increases and grafting efficiency decreases. Hence, considering both percent grafting and grafting efficiency, the optimum combination of parameters is determined as; cardanol concentration of 10 phr having all other control factors same as shown in Table 7.

From Table 8 it is observed that the error in the calculations may vary from 11.18 % to 14.09 % for percent grafting and from 0.62 % to 20.86 % for grafting efficiency. This establishes the fact that the multiple regression equation derived from equations 10 and 11 correlate with the percent grafting and grafting efficiency to a reasonable degree of approximation.

GPC analysis of NR and CGNR

The GPC trace before and after the grafting reaction is shown in figure 7. A marginal shift of the GPC trace for the CGNR towards the higher molecular weight region in comparison to NR is observed which indicates that there is increase in the molecular weight due to grafting of cardanol on to natural rubber backbone. The molecular weight (M_n) for NR is found to be 2.83×10^5 g mol^{-1}. The molecular weight of CGNR is found to be 4.12×10^5 g mol^{-1} which shows 45.6 % increase in the molecular weight as a result of grafting of cardanol on to NR. The PDI value for NR is 3.14 and that of CGNR is 2.90 which indicate that the molecular weight distribution for both NR and CGNR is almost same.

Processability characteristics

The processability characteristics of cardanol grafted natural rubber and the ungrafted natural rubber and the physicomechanical properties of their vulcanizates are given in Table 9. Intrinsic viscosity practically refers to the hydrodynamic volume of the macromolecules in the solvent.[42] The intrinsic viscosity of the grafted rubber is found to be higher than that of the unmodified rubber. This may be due to an increase in the hydrodynamic volume resulting from grafting of cardanol on to natural rubber backbone. The Mooney viscosity of virgin CGNR is found to be lower than that of NR which is a clear indication of plasticization effect of cardanol in NR because of the long aliphatic side chain of cardanol. CGNR shows higher plasticity than that of NR as indicated by its lower plasticity number.

Rheological measurements by Rubber process Analyzer

(a)Frequency sweep

Figure 8 shows the dependence of storage modulus (G') and complex viscosity (η^*) on the angular frequency resulting from the dynamic frequency sweep measurements. The G' value for CGNR is higher than that of NR which may be due to the higher hydrodynamic volume of CGNR resulting from grafting of cardanol on to the natural rubber backbone. The initial complex viscosity is higher for the grafted rubber (Figure 8b). With increase in frequency the complex viscosity gradually decreases for both the rubbers, however, the extent of decrease is more in case of CGNR and at very higher frequency both have almost the same complex viscosity. It may be due to the fact that at higher frequency disentanglements of polymer chains may have taken place and the extent of disentanglement is higher in the grafted rubber as a result of the plasticizing effect of the long aliphatic side chain present in the cardanol.

(b) Strain sweep

Figure 9 shows the dependence of storage modulus (G') and complex viscosity (η^*) on the strain amplitude in the dynamic sweep measurements. The plateau region of the dynamic strain sweep experiment where elastic modulus is independent of shear strain is termed as the linear viscoelastic region of the polymers. The magnitudes of storage modulus, G′ of all the polymers exhibit a linear region (Newtonian plateau) at low strains and nonlinear region (non-Newtonian plateau) at high strain amplitudes. At low strain (up to 28 % strain) the storage modulus and complex viscosity for CGNR are higher than that of NR which may be due to the increase in hydrodynamic volume imparted by the grafted cardanol on to the polymer chain as explained earlier. However, with increase in strain, there may be disentanglement of polymer chains from the scheduled coiled and twisted state which leads to decrease in storage modulus and in complex viscosity. It is seen that the extent of decrease is more in the grafted rubber as a result of the plasticizing effect of the long aliphatic side chain of cardanol in natural rubber.

Cure characteristics

The cure characteristics of the vulcanizates are listed in the Table 9. It is seen that CGNR shows higher cure rate than that of the NR vulcanizates. It may be due to the participation of the unsaturation present in the side chain of cardanol in the curing reaction[26]. The scorch time found to be lower for the CGNR vulcanizates.

Crosslink density

The crosslink density for the ungrafted and the cardanol grafted natural rubber vulcanizates have been found to be 7.61×10^{-5} mol/cm^3 and 8.36×10^{-5} mol/cm^3 respectively. The higher crosslink density in the CGNR vulcanizates has been explained as due to the active participation of the unsaturation present in the side chain of cardanol in the vulcanization reaction. This has been amply substantiated by Menon et al.[26] where phosphorylated cashew nutshell liquid added physically to NR was vulcanized by sulphur and accelerator.

Physico-mechanical properties

The physico-mechanical properties are listed in the Table 9. CGNR shows higher tensile and tear strength than that of NR vulcanizates. This may be due to the higher crosslink density in the CGNR vulcanizates which accounts for the enhancement in the tensile properties. The hardness of CGNR is lower than that of NR. This may be due to the plasticizing effect of cardanol which makes the grafted rubber softer. CGNR exhibits a compression set of 3.26 % which is 9.6% lower than that of the NR vulcanizates. This lower compression set may be because of the higher elastic behaviour of the cardanol grafted rubber which undergoes a fast recovery up on removal of the force. The CGNR vulcanizates show better rebound resilience than that of the NR vulcanizates. However, the heat buildup is revealed to be same in both the vulcanizates. The CGNR vulcanizates show better abrasion resistance than that of the NR vulcanizates. The resistance to fatigue and failure is enhanced in case of the CGNR vulcanizates. This may be due to the increase in flexibility imparted by cardanol as an internal plasticizer.

Differential scanning calorimetry (DSC)

Figure 10 shows the differential scanning calorimetry thermograms for the ungrafted and the cardanol grafted natural rubber. The glass transition temperature, T_g of ungrafted NR is found to be -62 °C while the T_g of CGNR is found to be -66 °C. The decrease in T_g of the grafted rubber confirms the plasticization effect of cardanol within NR inherently. It is well established that plasticizers increase the free volume due to facilitation of molecular mobility of the polymer chains. This leads the glass transition, T_g, towards lower temperature for the plasticized polymers.

Thermogravimetric Analysis (TGA)

The TGA thermograms of NR and CGNR are shown in Figure 11. The thermograms overlap on each other amply suggesting that there is no change in the thermal stability of NR on grafting with cardanol.

Dynamic Mechanical Analysis (DMA)

Figure 12 shows the effect of dynamic storage modulus (E') and loss factor (tan δ) as a function of temperature for NR and CGNR in the temperature range of -100 °C to +100 °C. The dynamic storage modulus (E') of CGNR is higher than NR below the T_g. Above the T_g, the difference is very small, and the trend is also reversed.

However, there is a marginal shift in the maximum loss tangent (tan δ_{max}) of CGNR towards the lower temperature (-46.2 °C) as compared to NR (-41.6 °C) which confirms the findings from DSC the plasticizing effect of cardanol in NR. In general, plasticizers lower the Tg by configuring between the polymer chains, thus altering polymer intermolecular interactions and enhancing chain mobility. The peak height is slightly increased for CGNR indicating marginally higher damping behaviour of CGNR. This may be due to an increase in the number of crosslinks in case of cardanol grafted natural rubber.

Conclusions

Grafting of cardanol on to natural rubber in the latex stage has been accomplished successfully by using the redox initiator system; the cumene hydroperoxide and tetraethylene pentammine. FTIR, NMR and GPC results confirm the grafting of cardanol on to natural rubber backbone. The grafting results in 45.6% increase in the molecular weight without affecting the molecular weight distribution. Taguchi method provides a simple, systematic and efficient tool to evaluate the effect of the four different control factors on the response variables of grafting; the percent grafting and grafting efficiency. The optimum combination of the parameters are found to be initiator concentration of 2 phr, cardanol concentration of 10 phr, reaction temperature of 35 °C and reaction time of 10 hours considering both percent grafting and grafting efficiency. The percent grafting is found to be 8.25 % and grafting efficiency is 82.5 % for the optimum parameter combination. The CHP/TEPA initiator system enables the grafting of cardanol on to natural rubber latex at much lower temperature (ambient temperature) in comparison with the earlier method reported. This method is expected to be techno-economically feasible and suitable from the scale-up perspective.

Analysis of variance technique provides the percent contribution of different control factors on percent grafting and grafting efficiency. Initiator concentration has the most dominant effect on the percent grafting to the extent of 45.13% while, cardanol concentration has the highest effect on the grafting efficiency to the extent of 72.25 %. The experimental results of percent grafting and grafting efficiency are found to be in good agreement with the predicted values as derived from regression analysis. The processability characteristics of the grafted rubber studied by a Rubber process analyzer exhibit higher complex viscosity and storage modulus at lower frequency and under lower strain in comparison to the ungrafted rubber. The physico-mechanical properties of the CGNR vulcanizates have an edge over those of the unmodified rubber because of higher crosslink density. Plasticizing effect of cardanol up on grafting on to NR has been confirmed from the DSC and DMA results. Thus cardanol grafting on to NR imparts inherent plasticizing effect to NR in addition to acting as a cure promoter.

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Fig. 1: Structure of cardanol
21x5mm (600 x 600 DPI)

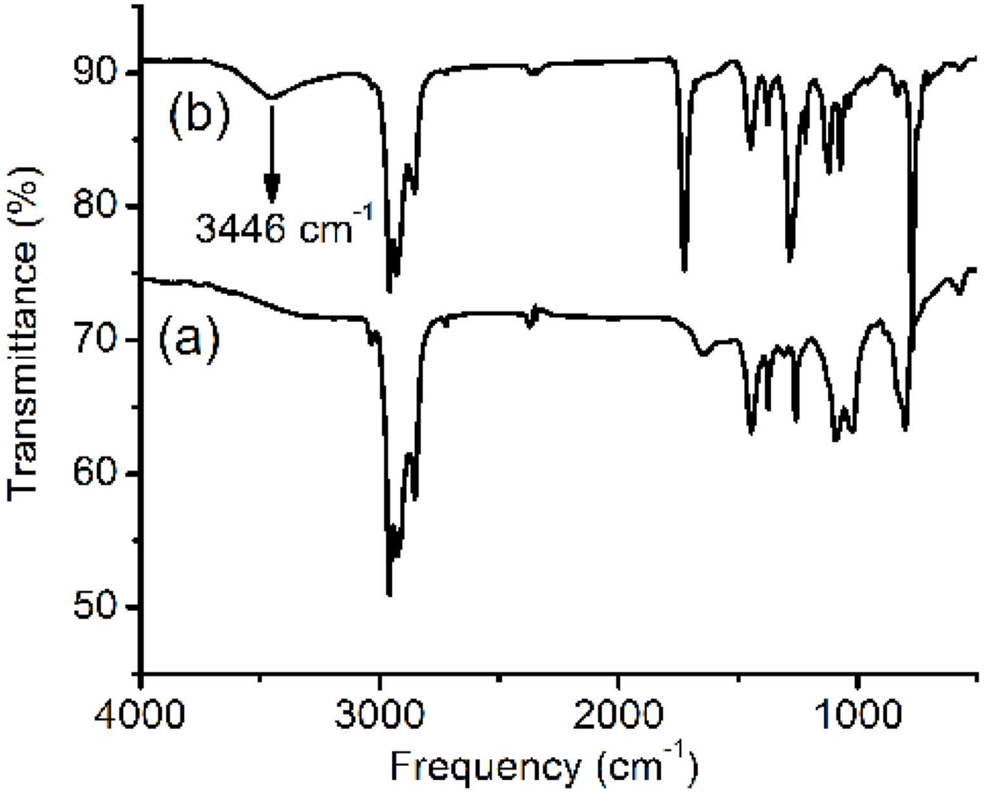


Fig. 2: IR spectrum of (a) NR and (b) CGNR
68x56mm (600 x 600 DPI)

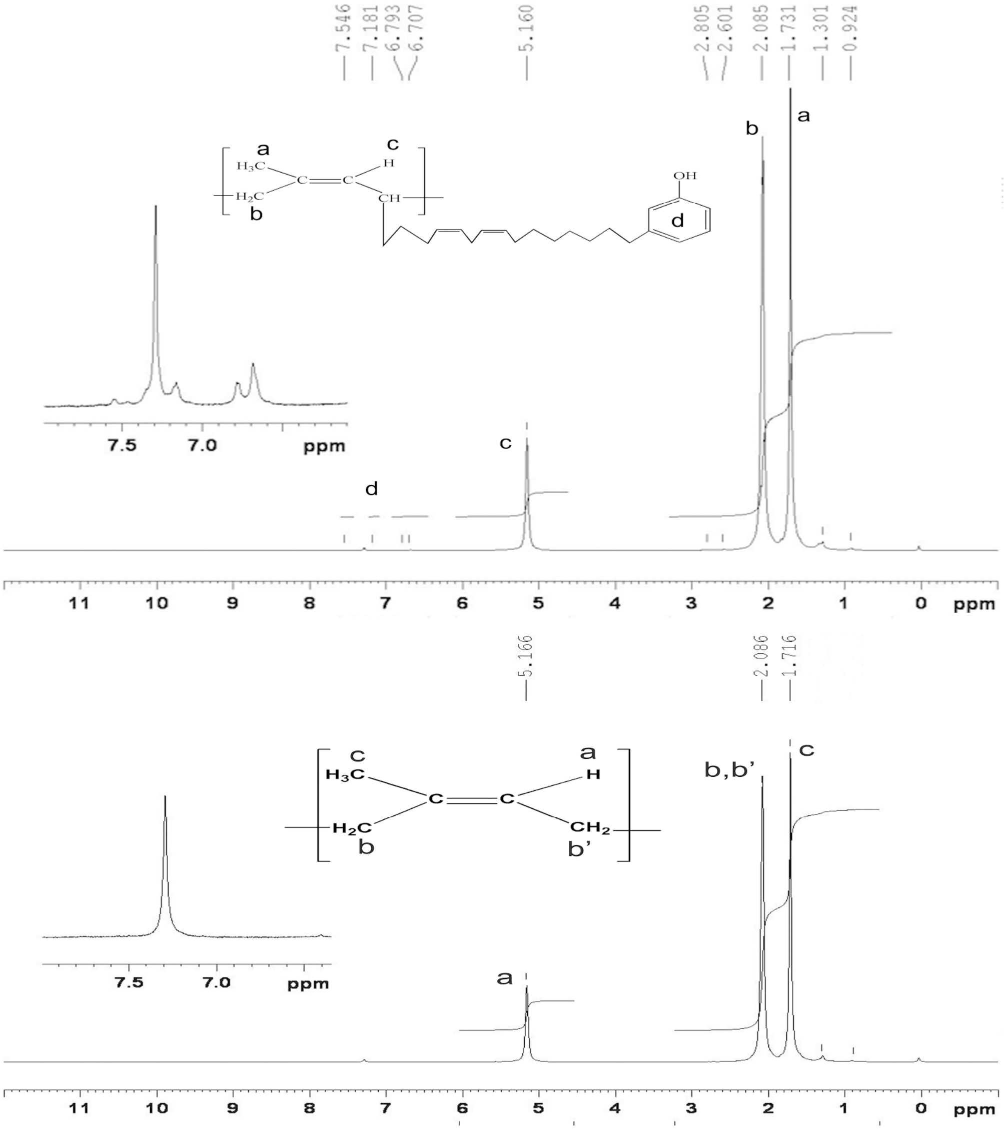


Fig. 3: 1H NMR spectrum of (a) NR and (b) CGNR

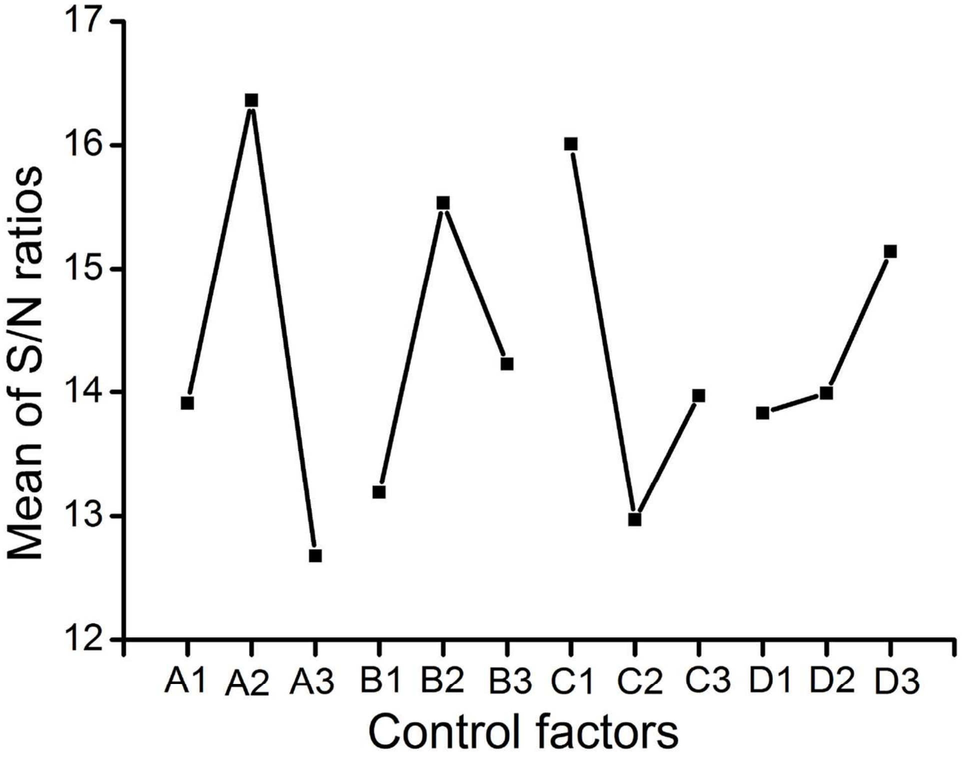


Fig. 4: Effect of control factors on percent grafting
66x53mm (600 x 600 DPI)

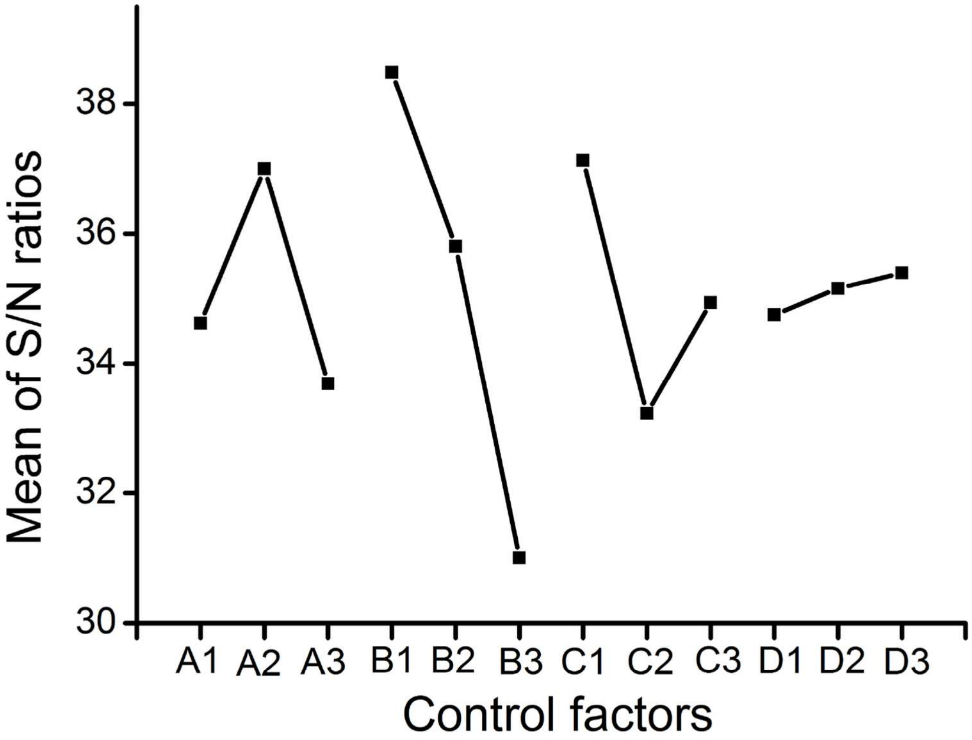
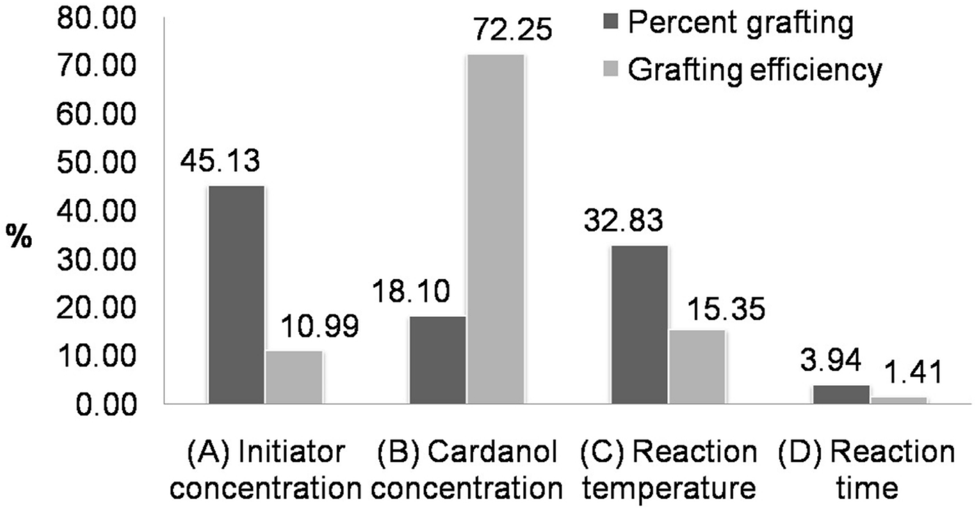


Fig. 5: Effect of control factors on grafting efficiency
64x49mm (600 x 600 DPI)



Percentage contribution of the control factors to percent grafting and grafting efficiency
50x30mm (600 x 600 DPI)

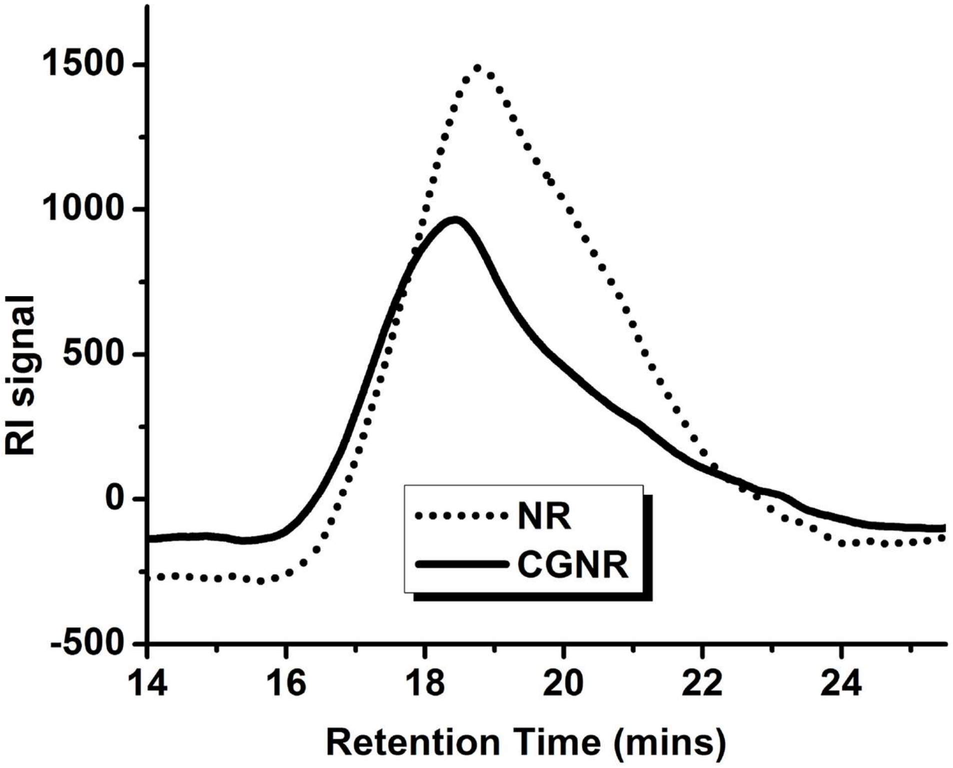


Fig. 7: GPC traces of NR and CGNR
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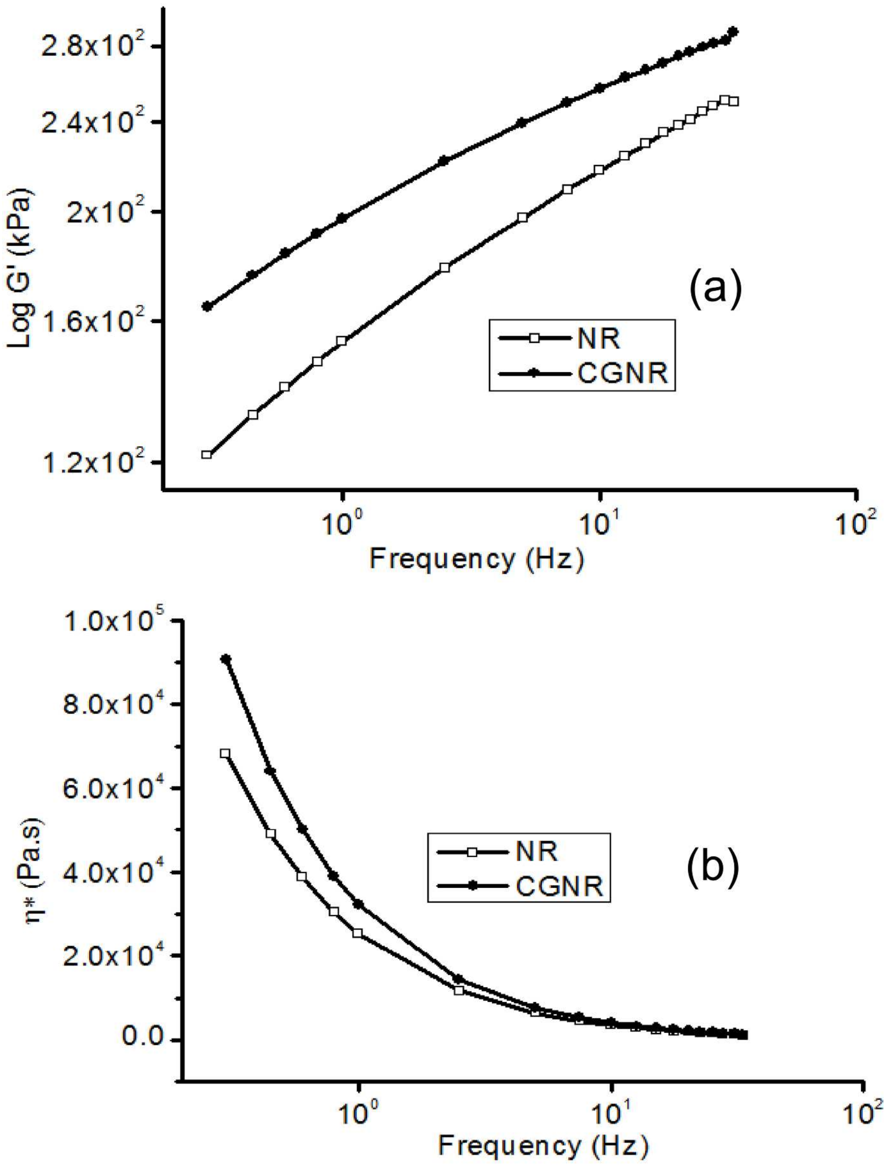

Fig. 8: Dynamic frequency sweep of (a) storage modulus, G’ (b) complex viscosity, η* of the raw cardanol grafted natural rubber and ungrafted natural rubber
111x150mm (600 x 600 DPI)

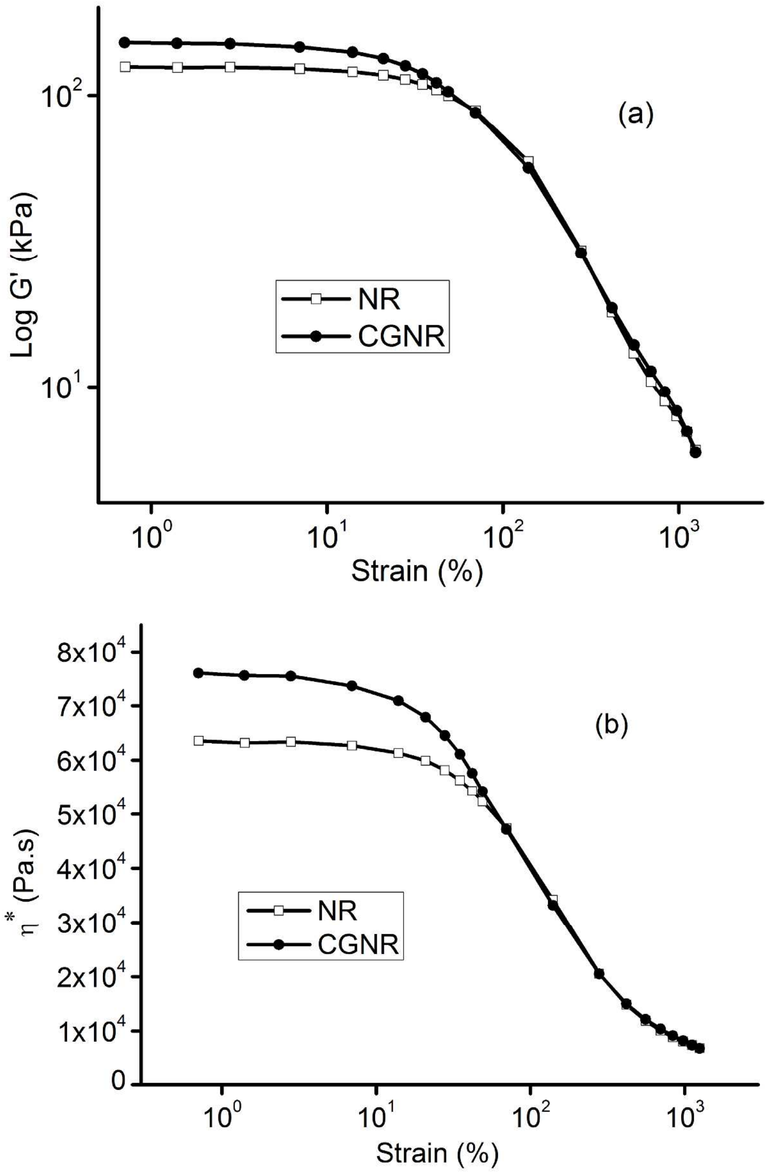

Fig. 9: Dynamic strain sweep of (a) storage modulus, G’ (b) complex viscosity, η* of the raw cardanol grafted natural rubber and ungrafted natural rubber
126x192mm (600 x 600 DPI)

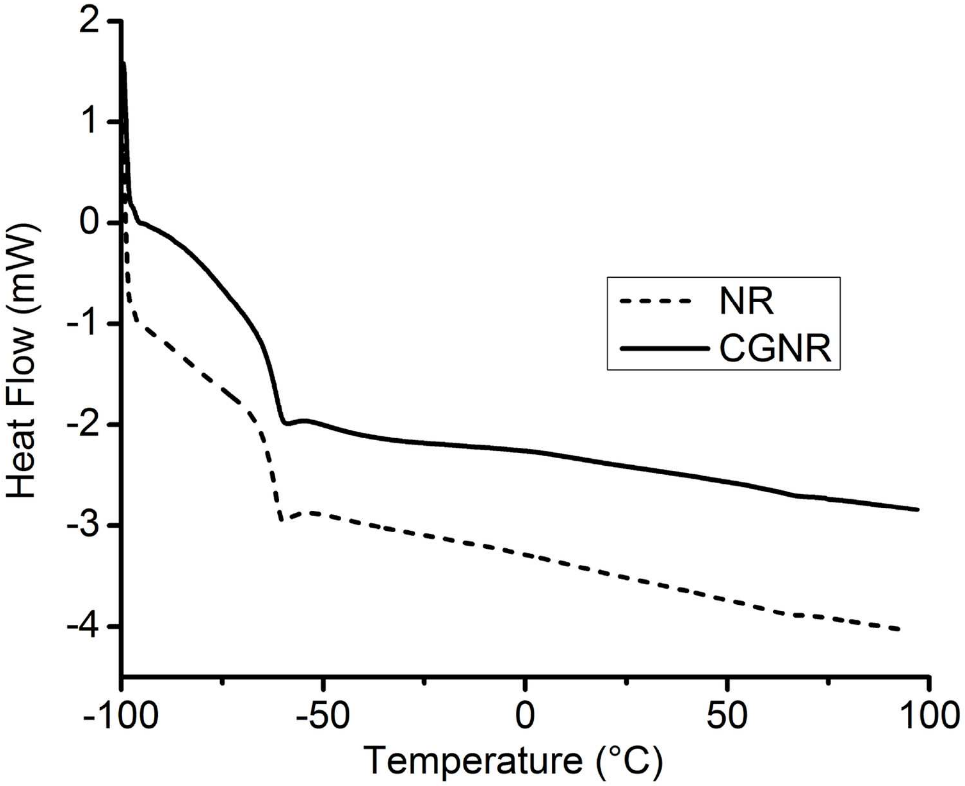

Fig. 10: DSC curve for cardanol grafted rubber and the ungrafted natural rubber
68x56mm (600 x 600 DPI)

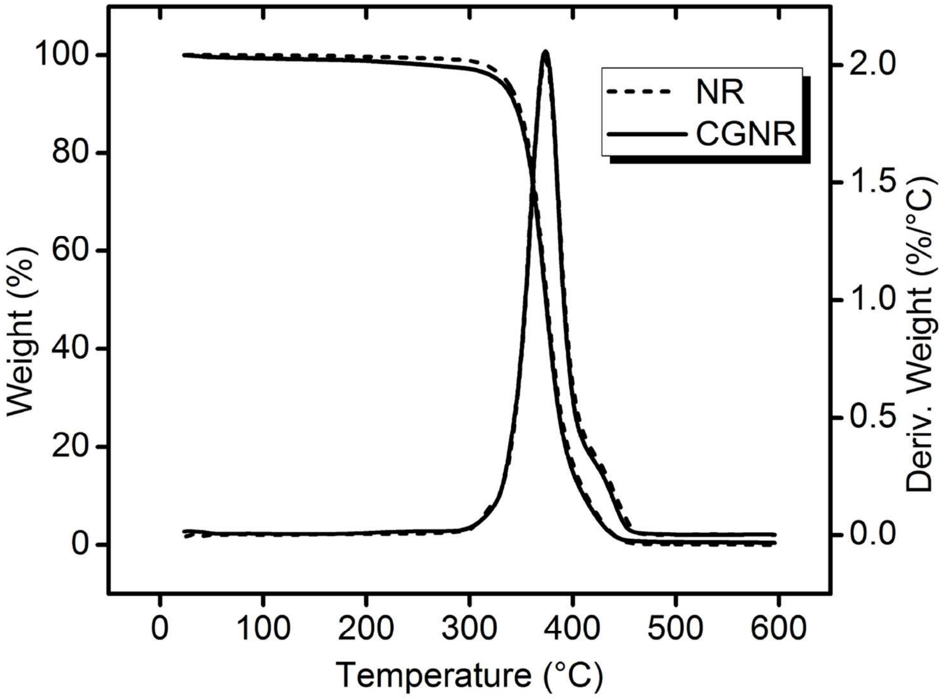

Fig. 11: Thermo-gravimetry analysis of cardanol grafted natural rubber and the ungrafted natural rubber
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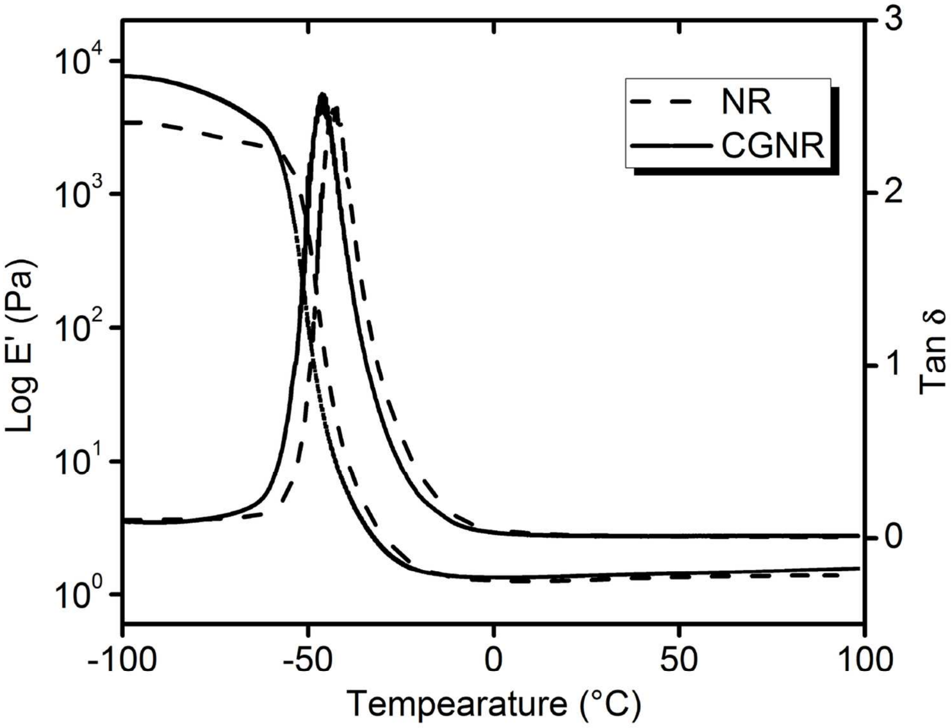
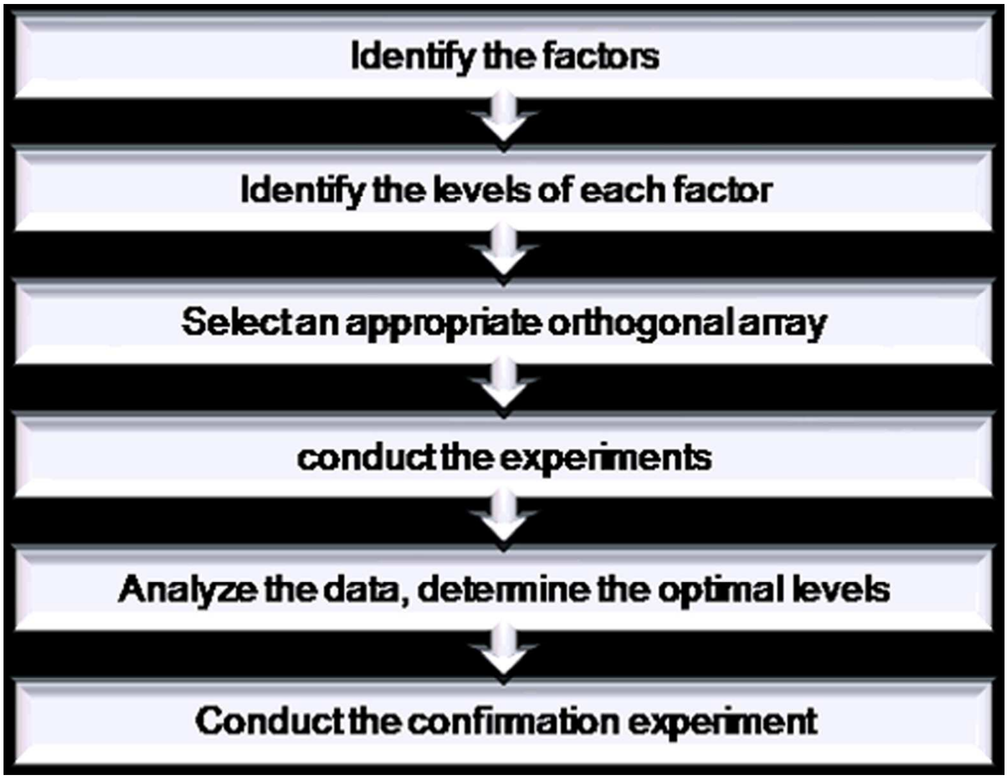


Fig. 12: Effect of dynamic storage modulus (E′) and loss factor (tan δ) as a function of test temperature for CGNR and NR vulcanizates

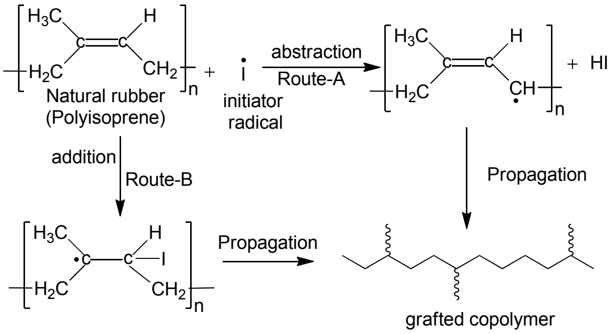
65x52mm (600 x 600 DPI)



Scheme 1: Scheme of the major steps of implementing Taguchi method
63x49mm (600 x 600 DPI)

RSC Author Templates - ChemDraw (CDX) - Single Column Artwork

All text and images must be placed within the frame.



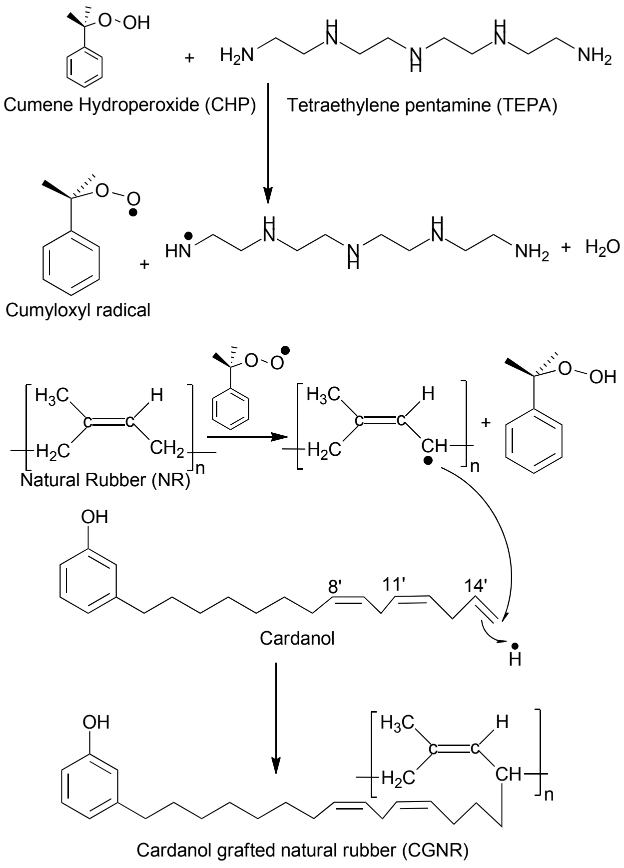

Cumene Hydroperoxide (CHP)
Tetraethylene pentamine (TEPA)
Cumyloxyl radical
H_2O
Natural Rubber (NR)
Cardanol
8'
11'
14'
Cardanol grafted natural rubber (CGNR)

Table 1

Formulations for preparation of the rubber vulcanizates

Sample code	Natural Rubber (coagulated from latex)	Cardanol grafted natural rubber	ZnO	Stearic acid	6-PPD	TMTD	MBTS	Sulfur
NR	100	-	5	2	1	0.2	0.8	2.5
CGNR	-	100	5	2	1	0.2	0.8	2.5

Table 2

Control factors and levels

Code	Control factors	levels 1	2	3
A	Initiator concentration (phr)	1	2	3
B	Cardanol concentration (phr)	5	10	15
C	Reaction temperature (^{o} C)	35	50	65
D	Reaction time (hours)	6	8	10

Table 3

Grafting conditions: Taguchi L_9 orthogonal array layout

Run No.	Initiator concentration (phr)	Cardanol concentration (phr)	Reaction temperature (^{o} C)	Reaction time (hours)
1	1	5	35	6
2	1	10	50	8
3	1	15	65	10
4	2	5	50	10
5	2	10	65	6
6	2	15	35	8
7	3	5	65	8
8	3	10	35	10
9	3	15	50	6

Table 4

Response variables and results for the S/N ratios

Run No.	Percent grafting (%)	Grafting efficiency (%)	S/N ratio for percent grafting	S/N ratio for grafting efficiency
1	5.01	96.36	13.99	39.68
2	4.70	47.39	13.45	33.51
3	5.19	34.11	14.30	30.66
4	5.44	87.21	14.71	38.81
5	6.87	72.39	16.74	37.19
6	7.61	56.18	17.63	34.99
7	3.50	70.55	10.88	36.97
8	6.61	68.60	16.40	36.73
9	3.45	23.36	10.75	27.37

Table 5

ANOVA table for percent grafting

Factors	Degree of freedom (D)	Sum of squares (SS)	Variance (V)	Corrected sum of squares (SS’)	Percentage contribution (P, %)	Rank
Initiator concentration (A)	2	501.12	250.56	501.12	11.0	3
Cardanol concentration (B)	2	3293.3	1646.66	3293.31	72.2	1
Reaction temperature (C)	2	699.77	349.89	699.77	15.4	2
Reaction time (D)	2	64.28	32.14	64.28	1.4	4
Error	0	0		0		
Cor Total	8	4558.48	569.81	4558.48	100.00	

Table 6
ANOVA table for grafting efficiency

Factors	Degree of freedom (D)	Sum of squares (SS)	Variance (V)	Corrected sum of squares (SS')	Percentage contribution (P, %)	Rank
Initiator concentration (A)	2	7.497	3.75	7.50	45.1	1
Cardanol concentration (B)	2	3.0075	1.50	3.01	18.1	3
Reaction temperature (C)	2	5.4542	2.73	5.45	32.8	2
Reaction time (D)	2	0.6537	0.33	0.65	3.9	4
Error	0	0		0		
Cor Total	8	16.61		16.61	100.00	

Table 7

Set of control factors for the confirmation tests

Test	Initiator concentration (phr)	Cardanol concentration (phr)	Reaction temperature (^{o} C)	Reaction time (hours)
1	2	5	35	10
2	2	10	35	10

Table 8

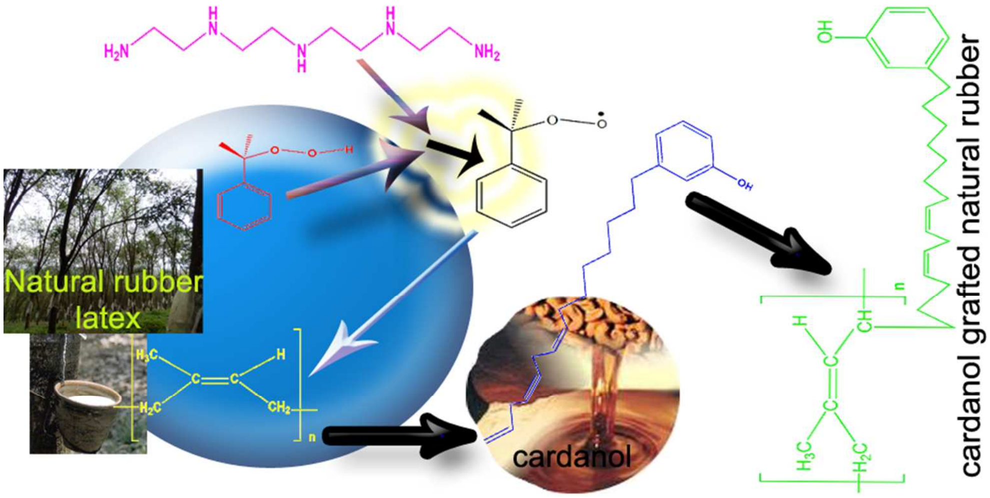
Confirmation tests and their comparison with regression model

Test	Percent grafting (%)			Grafting efficiency (%)		
	Experimental	Predicted	%Error	Experimental	Predicted	%Error
1	5.91	6.88	14.09	90.37	89.81	0.62
2	8.25	7.42	11.18	82.5	68.26	20.86

Table 9

Processability characteristics and Physico-mechanical properties of the vulcanizates

	Properties	NR	CGNR
1.	Intrinsic viscosity (dL/g)	0.845	0.971
2.	Mooney viscosity, ML(1+4)@100 °C	89	78
3.	Plasticity number	47	39
4.	Optimum cure time @ 150 °C, t_{90}	4 min 30 sec	3 min 37 sec
5.	Scorch time, t_2	2 min 45 sec	1min 45 sec
6.	Cure rate (s^{-1})	0.95	1.33
7.	Mooney scorch time @ 120 °C, t_5	11 min 30 sec	6 min 15 sec
8.	Tensile strength (MPa)	20.36	23.34
9.	Elongation at break (%)	998	1268
10.	Modulus at @100% elongation (MPa)	0.65	0.71
11.	Modulus at @200% elongation (MPa)	1.14	1.14
12.	Modulus at @300% elongation (MPa)	1.67	1.49
13.	Tear strength (N/mm)	30.20	34.64
14.	Hardness (Shore A)	39	34
15.	Compression set (%)	3.61	3.26
16.	Rebound resilience (%)	72.60	76.31
17.	Goodrich Heat buildup, ΔT, after 25 min (°C)	3	3
18.	Abrasion loss (cm^3/hr)	1.63	1.38
19.	Monsanto fatigue-to-failure (kC)	394	450



Cardanol grafted natural rubber, prepared at room temperature, as a potential green substitute for carcinogenic aromatic oil plasticized natural rubber

80x40mm (300 x 300 DPI)