

Antioxidant Activity of Cashew Nut Shell Liquid (CNSL) Derivatives on the Thermal Oxidation of Synthetic *cis*-1,4-Polyisoprene

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LCC (Líquido da Castanha de Caju), ou CNSL (Cashew Nut Shell Liquid), é uma mistura de *meta*-alquilfenóis, que variam no grau de insaturação do grupo ligado ao núcleo benzênico. A degradação térmica do poli(1,4-*cis*-isopreno) sintético a 140 °C foi estudada na presença do LCC técnico e de alguns derivados (cardanol, cardanol hidrogenado e cardanol hidrogenado e alquilado), através de FTIR. A quantidade de grupamentos OH/OOH e C=O formados e de C=C consumidos foi determinada durante a degradação. Todos os materiais aumentaram o tempo de indução e diminuíram as constantes aparentes de velocidade. Com base nos parâmetros cinéticos, a ordem de atividade antioxidante é: LCC >> cardanol ≈ cardanol hidrogenado e alquilado > cardanol hidrogenado. O efeito do LCC pode ser atribuído à contribuição extra de seus outros componentes, além do cardanol, e à insaturação na longa cadeia lateral. Essa maior atividade é importante, considerando que o LCC tem mais baixo custo do que seus derivados.

CNSL is a mixture of *meta*-alkylphenols with variable degree of unsaturation attached to the benzene ring. The kinetic study of the thermal degradation at 140 °C of synthetic *cis*-1,4-polyisoprene film, in the presence of technical CNSL and some derivatives (cardanol, hydrogenated cardanol and alkylated hydrogenated cardanol) was carried out by FTIR. The amount of OH/OOH and C=O formed and also of C=C consumed during the degradation was determined. All materials increase the induction period and decrease the apparent rate constants of thermal-oxidation. Based on kinetic parameters, the order of antioxidant activity was: CNSL >> cardanol ≈ hydrogenated and alkylated cardanol > hydrogenated cardanol. The effect of CNSL could be attributed to the extra contribution of the other components besides cardanol and to the unsaturation on the long side chain. This greater activity is important because CNSL is much more cost effective than its derivatives.

Keywords: CNSL, phenol, polyisoprene, thermal oxidation, antioxidant

Introduction

Cashew nut shell liquid (CNSL) is a unique natural source for unsaturated long-chain phenols. It is a cheap and renewable material, obtained as a by-product of the cashew industry. CNSL by itself is useful as insecticidal, fungicidal, anti-termite and medicinal applications.¹ It can be used as starting material for organic synthesis² and replaces phenol in many instances with equivalent or better results.¹ Resins derived from CNSL are widely employed in the field of friction materials, automobiles, surface

coating, adhesives, laminates, rubber compounding, and have several miscellaneous applications.¹ The most attractive consideration for CNSL use as an industrial product can be its low cost, abundant availability, and its chemically reactive nature.

On the basis of the mode of extraction from cashew nut shell, CNSL is classified into two types: solvent-extracted CNSL and technical CNSL. A typical solvent-extracted material contains anacardic acid (60-65%), cardol (15-20%), cardanol (10%), and traces of 2-methyl cardanol (Figure 1).³ Technical CNSL is obtained by roasting shell at 180-200 °C. The anacardic acid is thermally unstable and is easily decarboxylated during the extraction process

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by heating and then transformed into cardanol. Technical CNSL contains mainly cardanol (60-65%), cardol (15-20%), polymeric material (10%), and traces of 2-methyl cardol.³ Depending on the conditions of the roasting process, the composition of the technical CNSL can change and reach higher cardanol content (83-84%), less cardol (8-11%) and maintain polymeric material as 10% and 2-methyl cardol content as 2%.⁴

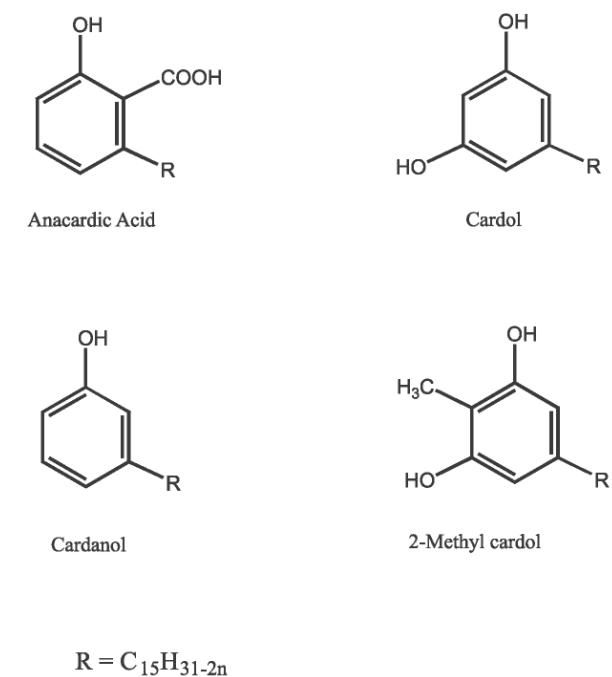


Figure 1. Structures of CNSL constituents.

The use of natural antioxidants is well established. Hindered phenolic compounds ($ArOH$) represent the major family of both natural and synthetic antioxidants.⁵ They are an excellent additive in polymers and lubricants.⁶ In general, efficient phenol antioxidants have substituents in *ortho*- and/or *para*-positions. The antioxidant effect is related to the electron donating nature and the steric effect of the substituent(s).⁷ The electron-donating effect can enhance the electron density at the oxygen of the phenol, resulting in a high radical-trapping rate. The steric effect prevents phenoxy radicals from coupling and to increase the number of trapped peroxy radicals.⁷ CNSL is a mixture of hindered phenols

with a long alkyl substitution at the *meta*-position. Despite not displaying substitution in the preferential *ortho* and/or *para*-position, the antioxidant activity of CNSL or its derivatives, in special phosphorylated, in natural rubber vulcanizates has been reported.⁸⁻¹³ The presence of phosphate group,¹² the formation of a network bound antioxidant¹¹ or the formation of phenolic sulfides *in situ* during the vulcanization¹³ have been used to explain the antioxidant activity of CNSL derivatives in natural rubber vulcanizates. The steric effect, due to long tail substituent, has been also reported as an important factor.¹⁴

The inexistence of studies about the effect of CNSL on the oxidation of natural rubber or synthetic polyisoprene during processes other than the vulcanization and the possibility of new uses of this material motivated the present work. Its objective is to determine the antioxidant activity of CNSL and some derivatives on the thermal oxidation of the synthetic *cis*-1,4-polyisoprene films at 140 °C. Technical CNSL, cardanol, hydrogenated cardanol and alkylated hydrogenated cardanol (Figure 2) were tested. The influence of long tail unsaturation, alkylation on *ortho*-position, and synergistic effect of these phenolic compounds on their antioxidant activity were examined.

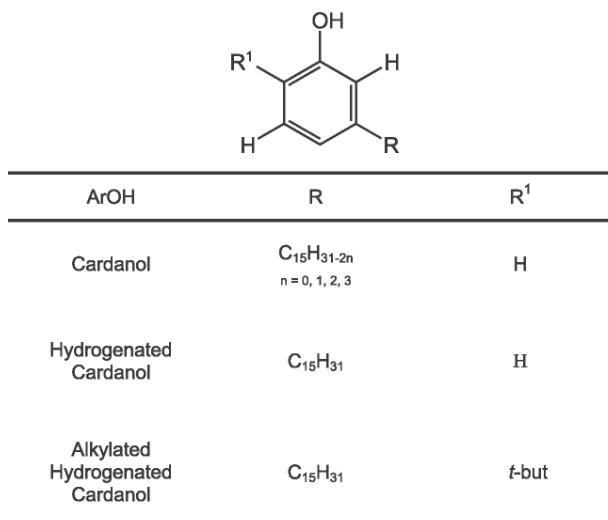


Figure 2. Structure of antioxidant species.

Experimental

Materials and methods

The synthetic *cis*-1,4-polyisoprene was provided by Aldrich Chemical Company and kept at low temperature (~ -10 °C). The cashew nut shell liquid derivatives, such as the hydrogenated cardanol (Hcardanol), and the alkylated hydrogenated cardanol (HALkcardanol) were supplied by PADETEC (Parque de Desenvolvimento

Tecnológico do Estado do Ceará). The technical CNSL was supplied by CIONE cashew industry. Cardanol was purified from the technical CNSL following the method described by Paramashivappa *et al.*¹⁵ Technical CNSL, cardanol, Hcardanol and HALkcardanol were tested with concentrations of 1, 2, 3 and 5% (m/m).

Film preparation

The films were prepared from *cis*-1,4-polyisoprene by successive casting and solvent evaporation from polymer solution (2 g dL⁻¹ in CHCl₃) on PTFE film (thickness of 0.10 mm) in the presence and in the absence of CNSL and its derivatives. Before being deposited over the PTFE film, the rubber solution was homogenized by stirring for approximately 12 h. Subsequently, CNSL and its derivatives were added directly into the polymer solution and stirred for further 12 h. The evaporation lasted for 24 h in order to assure that the solvent (CHCl₃) had been completely eliminated. The thickness of the films was in the range of 50-60 µm confirmed by absorbance at 1447 cm⁻¹, assigned to CH₂ deformation vibration and determined as directly proportional to film thickness up to 80 µm.

Film heating

The rubber films were heated both in the presence and in the absence of CNSL derivatives, using an oven Model-19 Thelco, in a constant temperature of 140 ± 1 °C in atmospheric air and pressure. Each film was heated during time intervals of 10 min followed by Fourier Transformed Infrared (FTIR) measurements. At least three films of each antioxidant concentration were heated and analyzed. The results are the average values of these replicates.

Infrared analysis

The FTIR spectra were obtained in a Shimadzu model 8300 spectrometer. Taking into account that polyisoprene degradation produces volatile materials, and thus reduces film thickness, a normalization procedure was adopted. The band at 1447 cm⁻¹ was used as an internal standard for the calculation of relative absorbance consider as a normalized value.¹⁶

Thermogravimetric analyses

Thermogravimetric analyses were performed in a Shimadzu TGA equipment, under N₂ atmosphere, at 50 mL min⁻¹ rate flow, and sample weight of 10 mg. An initial

heating at 10 °C min⁻¹ was applied until the temperature of 140 °C was reached. An isotherm curve was then obtained up to 300 minutes. Rubber film without antioxidant and with 5% (m/m) of CNSL and its derivatives were heated.

Results and Discussion

Effect of CNSL derivative structure

The FTIR spectrum for thermally-oxidized rubber presented three important bands, as verified in previous publications:¹⁶ at 835 cm⁻¹, assigned to out of plane bending of =C-H; at 3450 cm⁻¹, attributed to stretching of OH and/or OOH; and 1720 cm⁻¹, due to stretching of C=O. The presence of OH/OOH and C=O groups corresponds to products of degradation such as alcohols, carboxylic acid, hydroperoxides, aldehyde, ketone, ether or ester.¹⁷ Figure 3A shows the relative absorbance evolution, Abs_{rel}, of these bands for the polyisoprene oxidation without antioxidant. An initial region can be noticed, where changes in the Abs_{rel} do not occur. The subsequent region shows the formation of OH/OOH and C=O groups and a concomitant consumption of =C-H, and indirectly of C=C bonds of isoprene units. The band at 835 cm⁻¹ will be considered hereafter as related to the double bond.

The formation of OH/OOH and the consumption of C=C, in the beginning of thermal oxidation, obey a first order kinetics.¹⁸ The curve relative to the formation of C=O group shows an auto-acceleration feature and follows the parabolic law ([C=O] = kt²).¹⁸ The equations utilized for the determination of the induction period (τ_i) and the apparent rate constants (k), were reported in previous study.¹⁶

The presence of 5% (m/m) of technical CNSL displaces all curves for longer times of reaction (Figure 3B) in comparison with the curves in Figure 3A. This is indicative of a delay on the start of the thermal oxidation and an increase in the induction period when the CNSL is added. After the induction period, the process is faster and is similar to the one observed for pure polyisoprene. The effects of the addition of all CNSL derivatives (cardanol, Hcardanol and HALkcardanol) over the thermal oxidation of polyisoprene were similar to those observed with rubber in the presence of CNSL, but at different degree.

Table 1 shows the apparent rate constant and the induction period for polyisoprene in the absence and in the presence of 5% (m/m) of technical CNSL and its derivatives. Each value represents the average of at least three replicates. An average induction period was calculated from the individual induction period and represents the process as a whole. The addition of alkylated hydrogenated cardanol (HALkcardanol) for each measured

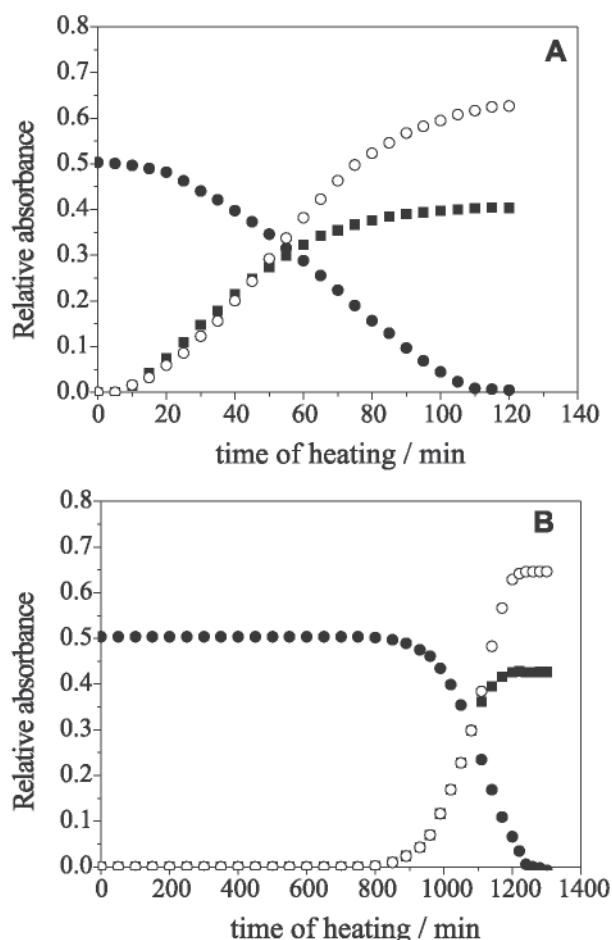


Figure 3. Kinetics of thermal-oxidation of polyisoprene film at 140 °C. (A) in absence of antioxidant; (B) in the presence of 5% of technical CNSL. Consumption of C=C (●) 835 cm⁻¹; formation of C=O (■) 1720 cm⁻¹; formation of OH/OOH (○) 3450 cm⁻¹.

phenol concentration caused higher induction periods and smaller apparent rate constants than the addition of hydrogenated cardanol (Hcardanol) at the same ArOH concentration. The antioxidant activity of HALkcardanol is greater than that of nonalkylated cardanol (Hcardanol).

The basic mechanism of autoxidation of polyisoprene (RH) includes four steps: initiation, propagation, chain branching and termination. One important reaction in the propagation step is the formation of RO₂[•]; also formed in chain branching step.¹⁹ Phenolic compounds (ArOH) are chain breaking antioxidants (interrupt the chain reaction)

well known as a radical scavengers that trap peroxy radicals (RO₂[•]). The manifested activity is due to their higher reactivity towards these radicals. While reducing the RO₂[•] radicals in reaction (1), phenols convert themselves into resonance-stabilized phenoxy radicals (ArO[•]). To be effective the phenoxy radical must also reacts slowly with substrate RH and rapidly with RO₂[•]. In the oxidation chain termination reaction (2), ArO[•] are generally consumed to produce non radical products:²⁰



In the HALkcardanol, a *tert*-butyl substituent was added in the *ortho* position of the ring (Figure 2). This electron donating substituent increases the electron density at the oxygen of the phenol and stabilizes the phenoxy radicals, resulting in a high radical-trapping rate.⁷ Additionally, an increase in the size of the *ortho* substituent causes a decrease in the O-H bond strength, thus improving phenol reactivity, and also leading to a more pronounced steric hindrance in the reaction of the peroxy radical with the functional center.²¹

The higher antioxidant activity of cardanol (higher τ_i and smaller k) compared with Heardanol, both added at 5% concentration (Table 1) indicates that the unsaturation on the long side chain could be an important factor. Recently, Ohkatsu *et al.*²² proposed that some phenols with allyl substituents could trap both alkyl and peroxy radicals, and increase antioxidant activity, taking into account that autoxidation includes these two radicals as chain carriers. The mechanism of trapping rubber radicals (R[•]) is suggested in Figure 4, similar to that proposed by the authors.²² To assure a better understanding of those mechanism, the long side chain of cardanol ($R = C_{15}\text{H}_{31-2n}$) was considered as having only one unsaturation ($n = 1$). Steps II and IV are probably difficult to occur considering the high molar mass of the rubber radical. Another contribution to lesser antioxidant activity of hydrogenated cardanol could be the remains of metal catalyst (Pd), used during the hydrogenation reaction. Metals are known to be pro-oxidant of polyolefins.²³

Table 1. Kinetic parameters for thermal oxidation at 140 °C of *cis*-polyisoprene in the absence and in the presence of 5% of antioxidant (ArOH) from cashew nut shell liquid

ArOH	Induction period, τ_i (min)			Average value	Apparent rate constant, k		
	OH/OOH	C=O	C=C		$k_{\text{OH/OOH}} \times 10^3$ (min ⁻¹)	$k_{\text{C=O}} \times 10^6$ (min ⁻²)	$k_{\text{C=C}} \times 10^3$ (min ⁻¹)
none	23	19	21	21 ± 2	21	113	20
CNSL	923	876	906	902 ± 17	4.2	0.47	4.1
cardanol	392	360	378	377 ± 11	5.4	2.6	5.3
Hcardanol	134	114	124	124 ± 7	8.4	9.3	7.4
HALkcardanol	260	249	251	253 ± 5	6.3	4.8	5.9

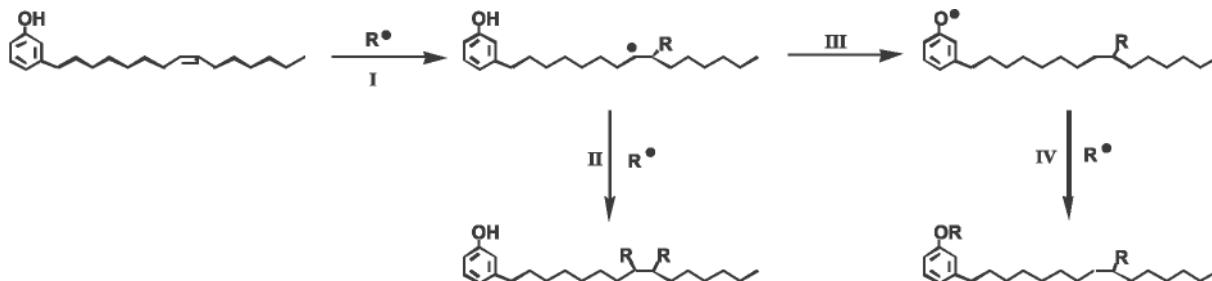


Figure 4. Suggested mechanism of cooperative action of hydroxyl and allyl groups in trapping rubber radicals (R[•]).

The positive effect of *ortho* substitution verified on HALkcardanol seems not to be strong enough to overcome the negative effects of elimination of the unsaturation on the long side chain of cardanol and the possible presence of metal from the remain catalyst.

Technical CNSL at 5% concentration was the material that presented the highest antioxidant activity over the thermal oxidation at 140 °C of synthetic polyisoprene. This could be due to the extra or synergistic contribution of others CNSL components besides cardanol (cardol, 2-methyl-cardol and polymerized material).^{3,4} Cardol is known to contribute more towards the antioxidant activity of CNSL than cardanol.¹³

One important parameter in the antioxidant activity is the molar mass. Low molar mass antioxidants are easily lost from polymer through migration, evaporation, and extraction. This physical loss of antioxidants constitutes a major concern in the long-term use of polymers or when high temperature is employed.²⁴ The new tendency to prevent this problem and guarantee their performance is the production of polymer-bound antioxidants.²⁴ The presence of about 10% of polymerized and compatible material, normally present in the technical CNSL,³ could decrease the migration of this antioxidant to the surface, reduce its volatilization and retain the antioxidant activity during heating.

Table 2 presents the mass loss of polyisoprene films in absence and in the presence of 5% of CNSL and its derivatives after isothermal heating at 140 °C by 150 and 300 minutes. Technical CNSL is the material more volatilized, especially after 300 min of heating. This means that part of the added CNSL migrates to the surface and is lost by volatilization. Even so, it presents the highest antioxidant activity. Difference in ArOH volatilization could not explain the higher activity of cardanol in comparison with HALkcardanol, once the mass loss of HALkcardanol is significantly smaller than that of cardanol.

Effect of antioxidant concentration on the induction period

Figure 5 shows the effect of ArOH concentration on the induction period (τ_i) of the thermal oxidation of

Table 2. Mass loss of polyisoprene films in the absence and in the presence of 5% of antioxidants during 150 and 300 minutes of heating at 140°C in atmosphere of nitrogen

ArOH	Mass loss (% m/m)	
	150 min	300 min
CNSL	0.48	0.83
cardanol	0.52	0.62
Heardanol	0.44	0.46
HALkcardanol	0.11	0.12

polyisoprene. The behavior observed for 5% of antioxidants happens in lower concentrations (1, 2 and 3%), but at a lower intensity.

Cibulková *et al.*²⁵ considered that a better estimation of the antioxidants activity can be obtained using the ratio of the induction period of stabilized polymer, $\tau_i(P+ArOH)$, and unstabilized polymer, $\tau_i(P)$, defined as the protection factor (PF).

$$PF = \frac{\tau_i(P+ArOH)}{\tau_i(P)} \quad (3)$$

To normalize the PF taking into account the molar mass, an effectiveness parameter was proposed: AEM.

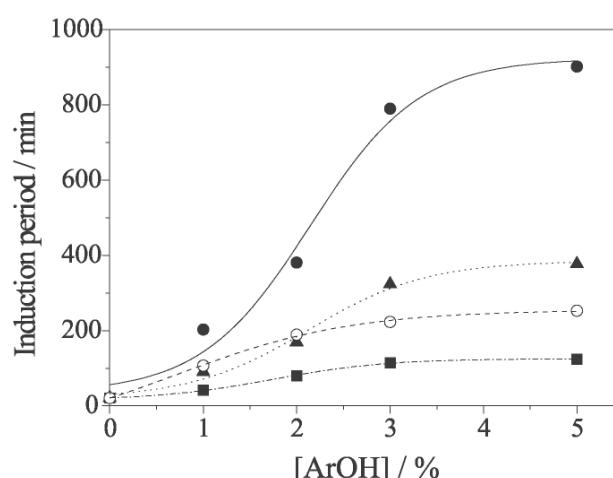


Figure 5. Effect of the antioxidant concentration on the induction period of the thermal oxidation of polyisoprene at 140 °C. Antioxidants: Heardanol (■); Cardanol (▲); HALkcardanol (○); Technical CNSL(●).

$$\text{AEM} = \frac{\text{PF}}{m} - 1 \quad (4)$$

where m is the concentration of antioxidant in the polymer matrix expressed in mol kg⁻¹.

Figure 6 shows the dependence of antioxidant effectiveness on the antioxidant concentration. Molar mass of cardanol, Hcardanol and HALkcardanol were considered as 0.302; 0.304 and 0.360 kg mol⁻¹. Molar mass of technical CNSL was determined based on its average composition as 0.306 kg mol⁻¹. CNSL and cardanol present a maximum AEM value at ArOH concentration around 3%. Above and below this concentration the antioxidant effectiveness decreases. Hcardanol also presents the same tendency, but in a smaller intensity. On the other hand, HALkcardanol shows a different behavior, with AEM value diminishing with increasing concentration and a tendency of stabilization at concentration higher than 5%.

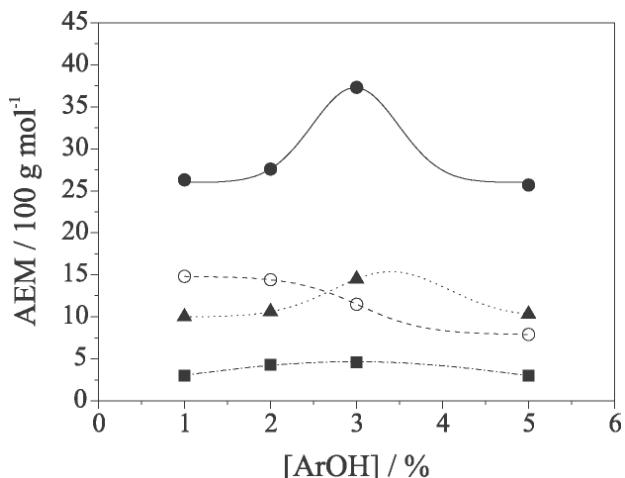


Figure 6. Effect of the antioxidant concentration on its effectiveness over thermal oxidation of polyisoprene at 140 °C. Antioxidants: Hcardanol (■); Cardanol (▲); HALkcardanol (○); Technical CNSL(●).

Decarboxylated CNSL, that is the technical CNSL, can protect natural rubber vulcanizates against autoxidation when used in 2%.¹³ Maximum antioxidant activity of phosphorylated CNSL (PCNSL) in polyethylene was observed in formulation containing 2% of this material.¹⁴ However, when PCNSL was added in vulcanization of natural rubber, the improved resistance to thermal oxidation ageing and decomposition was highest at the concentration of 20%.⁸

Effect of antioxidant concentration on the apparent rate constants

Figure 7 shows that the apparent rate constants of the thermal-oxidation of the polyisoprene, taken here as the rate constant of the consumption of carbon double bonds

($k_{\text{C}=\text{C}}$), is reduced when the concentration of each ArOH increases. This is indicative that as soon as the polyisoprene oxidation begins, after the induction period, it occurs at a lower rate in the presence of antioxidants than in their absence. The curves present a similar behavior for all studied antioxidants. The rate constant reduction decreases as more ArOH are added to polymer. There is a greater reduction for concentrations below 3%, while there was a tendency to stabilization for greater concentrations. Similar behavior was observed for the other rate constants ($k_{\text{OH}/\text{OOH}}$ and $k_{\text{C}=\text{O}}$) whose curves are not shown.

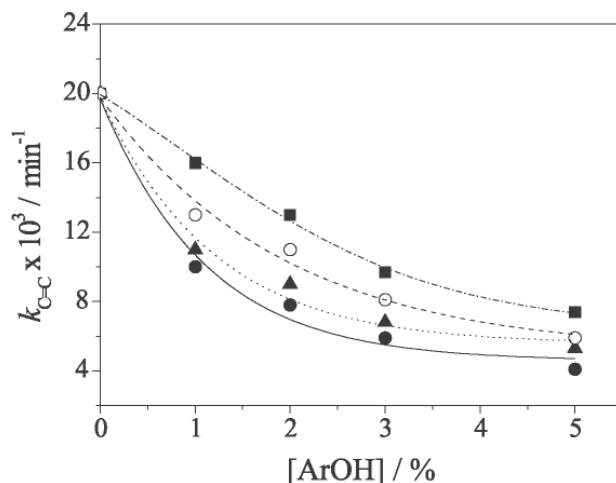


Figure 7. Effect of the antioxidant concentration on the apparent rate constant of C=C consumption during thermal oxidation of polyisoprene at 140 °C. Antioxidants: Hcardanol (■); Cardanol (▲); HALkcardanol (○); Technical CNSL(●).

The ability of hydrogenated cardanol in decreasing the rate of oxidation reactions is smaller than for the others antioxidants that have been studied. This material showed the least antioxidant effectiveness, based on induction period (Figure 6). Hcardanol was undoubtedly the CNSL derivative with lowest antioxidant activity among the tested materials. Technical CNSL, on the other hand, was the most effective antioxidant, based on induction period and rate constants. The difference between cardanol and HALkcardanol activity is small and could be within the range of experimental uncertainty.

Conclusions

The addition of technical CNSL, cardanol, Hcardanol and HALkcardanol to synthetic *cis*-1,4-polyisoprene caused an increase in the induction period and a decrease on the apparent rate constants of thermal oxidation at 140 °C. These effects augment with the concentration of added material. However, the antioxidant effectiveness is higher for the addition of 3% (m/m) of ArOH, except for

HAlkcardanol. This addition provoked an increase of approximately 6, 11, 15 and 38 times in the induction period in the Hcardanol, HAlkcardanol, cardanol and technical CNSL systems, respectively.

All tested material acted as antioxidant for polyisoprene and did not cause the formation of spots. Based on induction period and on apparent rate constants the order of antioxidant activity could be generalized as follows:

CNSL >> cardanol ≈ hydrogenated and alkylated cardanol > hydrogenated cardanol.

The more pronounced effect of CNSL could be attributed to the extra contribution of other CNSL components besides cardanol (cardol, 2-methyl-cardol and polymerized material). The higher antioxidant activity of CNSL and cardanol compared with Hcardanol, indicates that the unsaturation on the long side chain could be an important factor. The allyl substituents could trap both alkyl and peroxy radicals, and increase antioxidant activity. The effect of alkylated hydrogenated cardanol is greater than that of nonalkylated cardanol, as expected by the addition of a *tert*-butyl substituent in the *ortho* position of the ring.

The concentration of 3% (m/m) of CNSL and derivatives could be considered as too high to be used as an antioxidants. Fortunately, cashew nut shell liquid and derivatives have other useful properties as rubber additives, e.g. as plasticizers,²⁶ that in addition to the antioxidant characteristics make the use of CNSL more attractive and of great potential for industrial applications.

Acknowledgments

We thank the financial support from CAPES and CNPq.

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Received: August 1, 2005

Published on the web: February 6, 2006