



# Synthesis of antioxidant for natural rubber using new heterogeneous catalytic system

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## Abstract

In this paper, a new type of heterogeneous catalytic system was devised for the synthesis of 4,4'-bis-(2,6-di-*t*-butylphenol), (hereinafter referred to as bisphenol-VN). The properties of the catalytic system were studied using SEM–EDS and transmission electron microscope methods. The results have demonstrated the presence of hydrophobic phenolate layer on the surface of the catalytic system, which provides high catalytic activity in the synthesis of bisphenol-VN. The bisphenol-VN obtained was taken for structural analysis by SEM, IR and MS–HPLC methods to prove the purity of the product. Simultaneously, the bisphenol-VN was also tested in natural rubber to enhance the physical–mechanical properties. The use of bisphenol-VN extends the oxidation induction time of natural rubber by three times in the comparison with the commercial antioxidant 6PPD.

**Keywords** Natural rubber · Antioxidant · Composite · Synthesis · Catalyst

## Introduction

Natural rubber (NR) is widely applied in many fields due to its valuable properties such as: high mechanical strength and elasticity, easy to work, etc. (Kohjiya and Ikeda 2014; Kurian and Mathew 2011; Azahar et al. 2016). However, because of its high degree of unsaturation (each recurring unit contains one double bond in its structure), it is less resistant to oxidation, impacts of ozone, weathering, various chemicals, and solvents in comparison to other synthetic rubbers (Mohapatra and Nando 2013; Sari et al.

2017). Therefore, chemical modification of NR is essential to overcome some of its disadvantages. The addition of antioxidants is an expedient technique used to improve the aging properties of rubbers (Zakir Hossain et al. 2010; Klinpituksa et al. 2011, 2014; Sulekha et al. 2004). Antioxidants protect the rubber goods from attack by air, heat, light and even ozone in the atmosphere. Commercial antioxidants are generally either of the amine type or of the phenolic type such as 4-aminodiphenylamine, 2,6-di-*tert*-butyl-4-vinylphenol, *N*-(4-hydroxyphenyl)-maleimide, etc.

One of the promising phenolic antioxidants for industrial application is the 4,4'-bis (2,6-di-*t*-butylphenol), (bisphenol-VN), which has all the positive properties necessary for its widespread use in the stabilization of various plastics, rubbers and also fuels and oils (Akhmadullin 2015). In accordance with the specifications of the GOST 12.1.007-76 (GOST 12.1.007-76 1977), the stabilizer of bisphenol-VN belongs to the class of low-hazardous substances and it can be used in polymers which can get into contact with food and biological media.

However, the cost of bisphenol-VN in the world market is quite high, so it is difficult to use in industrial technologies. To reduce the cost, a research team from R&D Center Ahmadullin has studied the synthesis of bisphenol-VN from simple, cheap substances using different catalysts

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(Akhmadullin et al. 2012, 2014). However, the weak point is the nature and efficiency of catalysts that have a short operation life, technologically difficult to separate from the reaction products; moreover, some catalysts can cause fire and exhibit explosion hazard in synthesis technology.

The purpose of this work was to elaborate environment friendly and economical methods for the synthesis of bisphenol-VN based on the development of new effective heterogeneous catalytic system. Moreover, the present work dealt with the application of bisphenol-VN in processing natural rubber.

## Experimental

### Materials

Natural rubber latex (60% total solids content) and technical rubbers were supplied by Do Kim Thanh Trading Service Co., Ltd, Viet Nam. Other solvents and reagents, such as decane, KOH, 2,6-di-*tert*-butylphenol, diphenol-quinone, toluene, TiO<sub>2</sub> were supplied by Sigma-Aldrich Co. and were used directly without further purification.

### Analytical techniques used

The heterogeneous catalytic system was analyzed for surface properties by the SEM–EDS method on the ZEISS EVO50 XVP system and by transmission electron microscope technique using Electron-Microscope “Emma-4”.

Bisphenol-VN was analyzed for physical–chemical properties by different methods: SEM, FTIR, MS–HPLC on the ZEISS EVO50 XVP system, IR Fourier spectrometer of Bruker Vector 22 and MS–HPLC chromatograph by Spectra-Physics: column 250 × 4.0 mm; Nucleosil-C1810; pressure—0.1 MPa; UV detector, 258 nm.

### Synthesis of heterogeneous catalytic system (HCS)

The heterogeneous catalytic system was prepared in a batch reaction apparatus under atmospheric pressure.

At first, 50 ml of decane and 10 g of solid KOH were put into round-bottom flask. The reaction mixture was stirred at a speed of 1400 rpm on a magnetic stirrer by increasing the solution temperature to 120 °C. Once the required temperature was reached, 5 g of the monophenol was added. The reaction took place in 30 min. The catalyst was obtained in solid form, then, it was filtered and dried for use in bisphenol-VN synthesis.

### Synthesis of bisphenol-VN under pressure

In a cylindrical steel tank, 50 ml of toluene and 0.125 g of heterogeneous catalytic system were measured. Then, 7.5 g of monophenol and 10.0 g of diphenol-quinone as raw materials were added. The reactor was closed, and the mixture was heated and stirred slightly. When the required temperature was reached (170 °C), the stirring was increased to 1400 rpm. The reaction was carried out at the desired temperature for the specified reaction time under continuous stirring. The pressure was adjusted not to exceed 0.5 MPa. After 120 min, the reaction was stopped, the mixture was cooled down, and the reaction products were crystallized and recovered. Bisphenol-VN was taken for physical–chemical investigations by SEM, FTIR, and MS–HPLC methods.

### Determination of the activity of bisphenol-VN in rubber

Laboratory-type internal mixer of 2-l capacity and two-roll mixing mill (Haake PolyLab OS Rheodrive 7) were used subsequently for preparing the rubber compound formulations, which were designed to replace the traditional antioxidants with bisphenol-VN. The vulcanization system of natural rubber is a conventional type system using elemental sulfur. The natural rubber latex (NRL) of 60% TSC content had to be diluted to 50% TSC by adding 1.5% dilute ammonia solution. After the addition of stabilizer and sensitizer, the stirring was continued for 3 h before the latex was dried heating in an oven at 100 °C for 1 h. All prepared compound formulations are given in Table 1.

The oxidation induction time of natural rubber samples was determined in accordance with ISO 11357-1:2009 by differential scanning calorimetry (DSC) method using Perkin–Elmer DSC 7 software. Samples were kept for 5 min at 60 °C in a nitrogen stream (50 ml/min). Then, the temperature was increased from 60 to 150 °C at a rate of 20 °C/min. After that, nitrogen was replaced by oxygen (flow rate of 50 ml/min).

Tensile tests were conducted using Shimadzu Rubber Auto according to standard of ISO 37 at temperature of 25 °C. Tensile test pieces were divided into unaged sample and aged sample which pre-conditionally were prepared in oven of 70 °C for 70 h.

Hardness in general is a measurement of compound stiffness. In this research, the hardness test was conducted as specified in Bareissdigi test method and the instrument was supplied by Bareiss Prufergeratebau GmbH for normal IRHD. The test was carried out according to BS ISO 48 and ASTM D1415 standard.

**Table 1** Rubber compound formulations

Samples	Comp. (phr)								
	PP-0	PP-1	PP-2	PP-3	PP-4	PP-5	PP-6	PP-7	PP-8
NR	100	100	100	100	100	100	100	100	100
Zinc oxide	3	3	3	3	3	3	3	3	3
Stearic acid	3	3	3	3	3	3	3	3	3
Zeosil 1165 MP	75	75	75	75	75	75	75	75	75
Nytex 4700	20	20	20	20	20	20	20	20	20
Irganox 1010	–	0.1	–	–	–	–	–	–	–
BHT	–	–	0.1	–	–	–	–	–	–
2,6-DBVP	–	–	–	0.1	–	–	–	–	–
Bisphenol-5	–	–	–	–	0.1	–	–	–	–
6PPD	–	–	–	–	–	0.1	–	–	–
Irganox 1098	–	–	–	–	–	–	0.1	–	–
Irganox HP2215	–	–	–	–	–	–	–	0.1	–
Irganox B215	–	–	–	–	–	–	–	–	0.1
DPQ	1	1	1	1	1	1	1	1	1
Sulfur	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
TBBS	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1

Ozone-resistance test was determined according to ISO 1431-1:2012. The parameters were as follows: thickness of the sample was 2 mm, operating time was 20 h at 55 °C, and ozone concentration was 5 ppm.

## Results and discussion

### The activity of heterogeneous catalytic system in the synthesis of bisphenol-VN

The study of HCS by transmission electron microscopy showed the structural formation of solid potassium hydroxide particles coated with a presumably thin film of the hydrophobic phenolate layer. As can be seen in Fig. 1, HCS is a pseudo-globular shape particle with a size of about 150 nm edged with a semitransparent clarified surface layer.

The SEM–EDS method was used to verify the presence of the surface hydrophobic phenolate layer. Figure 2 shows the surface of HCS using the SEM method, and it is clear that the surface of HCS is covered by a thin film. The composition of this thin film was analyzed by the EDS method. The following results were obtained: C = 47.73%, K = 12.35%, O<sub>2</sub> = 39.15% and impurity inclusions = 0.77% by weight. The appearance of a significant amount of carbon on the surface of HCS proves the presence of hydrocarbon layer.

The formation of the outer coating layer of HCS can be described as given in Scheme 1.

It is known that the oxidation rate of monophenol to bisphenol-VN increased in the presence of potassium hydroxide (Akhmadullin 2015). The advantage of the synthesized heterogeneous catalytic system is its ability to enhance the rate



**Fig. 1** The image of HCS by transmission electron microscopy method

of the bisphenol-VN synthesis. The bisphenol-VN is in solid state, and can easily be separated from the reaction mixture, as a result of this the obtained product has high purity.

The oxidation rate induced by HCS in the synthesis of bisphenol-VN is compared with the rate induced by potassium hydroxide (KOH) and the rate of non-catalyzed oxidation reaction (Fig. 3). The experimental results indicate that HCS exhibited high activity in the oxidation of monophenol to bisphenol-VN. Specifically, the synthesis of bisphenol-VN achieved 100% efficiency after 80 min reaction time, while in the presence of KOH or without catalyst the reaction efficiency is 57% and 25%, respectively.

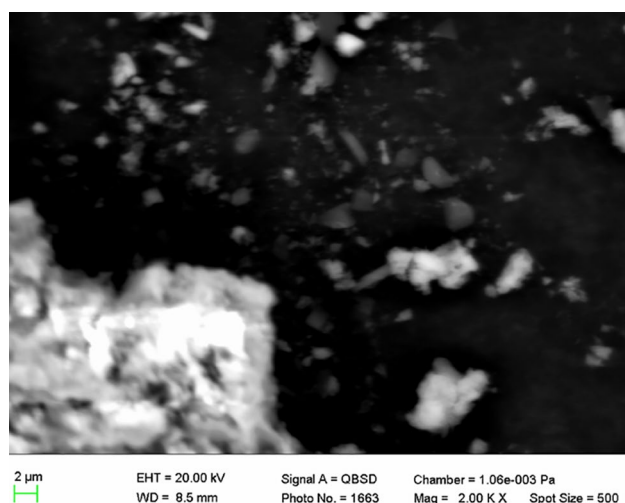


Fig. 2 The surface of HCS obtained by SEM method

### Properties of synthesized bisphenol-VN

The FTIR spectrum of bisphenol-VN (Fig. 4) shows some important absorption bands as follows:  $3631\text{ cm}^{-1}$  (phenolic  $\text{-OH}$  group),  $2968\text{--}2870\text{ cm}^{-1}$  (aliphatic  $\text{C-H}$  stretching),  $1761$  and  $1597\text{ cm}^{-1}$  (aliphatic  $\text{C=C}$  stretching),  $1484$  and  $1389\text{ cm}^{-1}$  ( $\text{C-H}$  bending vibration),  $1225\text{ cm}^{-1}$  ( $\text{C-C}$  stretching), and  $803\text{ cm}^{-1}$  ( $=\text{C-H}$  bending vibration).

The obtained product has light yellow color and melting temperature of  $260\text{ }^{\circ}\text{C}$ . The  $^1\text{H-NMR}$  spectrum shows full signals of 42 protons. Therein 36 protons in the high field with an interaction constant  $\delta_{\text{H}} = 1.48\text{ ppm}$  belong to 12  $\text{-CH}_3$  groups. The high field signal at  $\delta_{\text{H}} = 7.29\text{ ppm}$  corresponds to 4 protons linked to the aromatic nucleus (4H, s, H-2, H-6, H-2', H-6'). The signal at  $\delta_{\text{H}} = 5.16\text{ ppm}$  is that of the 2 protons of the  $\text{-OH}$  group. The  $^{13}\text{C-NMR}$  spectrum has resonance signals of 28 C-atoms of bisphenol-VN. In that signal at  $\delta_{\text{C}} = 30.38\text{ ppm}$  corresponds to 12 C-atoms of  $\text{-CH}_3$  groups, signals of 4 C-atoms of the *tert*-butyl group resonate at  $\delta_{\text{C}} = 34.45\text{ ppm}$ ,

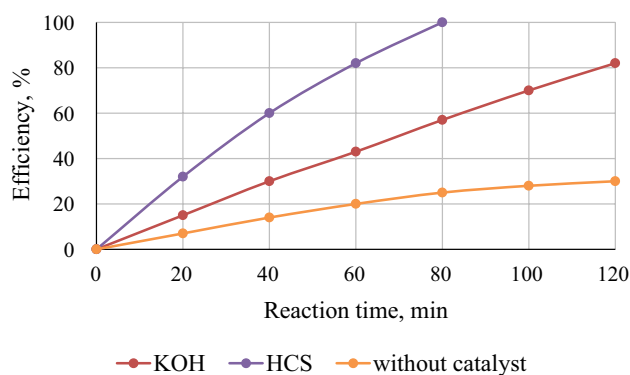


Fig. 3 Activity of heterogeneous catalytic system in the synthesis of bisphenol-VN in comparison with the non-catalytic reaction

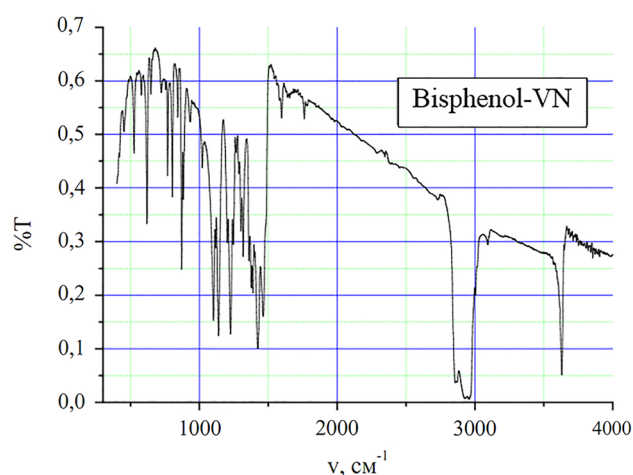
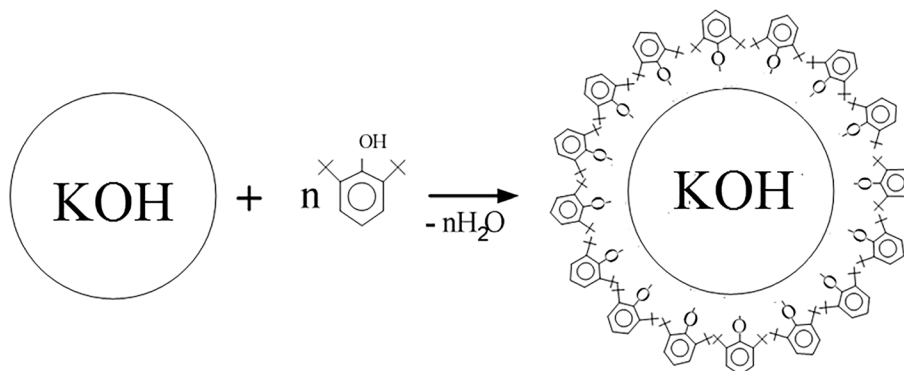


Fig. 4 FTIR spectrum of bisphenol-VN

signals of 4 C-atoms (C-2, C-6, C-2', C-6') resonate at  $\delta_{\text{C}} = 124.06\text{ ppm}$ , signals of 2 C-atoms (C-1, C-1') resonate at  $\delta_{\text{C}} = 133.94\text{ ppm}$ , signals of 4 C-atoms (C-3, C-5, C-3', C-5') resonate at  $\delta_{\text{C}} = 135.99\text{ ppm}$ ; and at last signals of 2 C-atoms (C-4, C-4') resonate at  $\delta_{\text{C}} = 152.81\text{ ppm}$  (Fig. 5).

Scheme 1 Formation of the outer coating layer of HCS



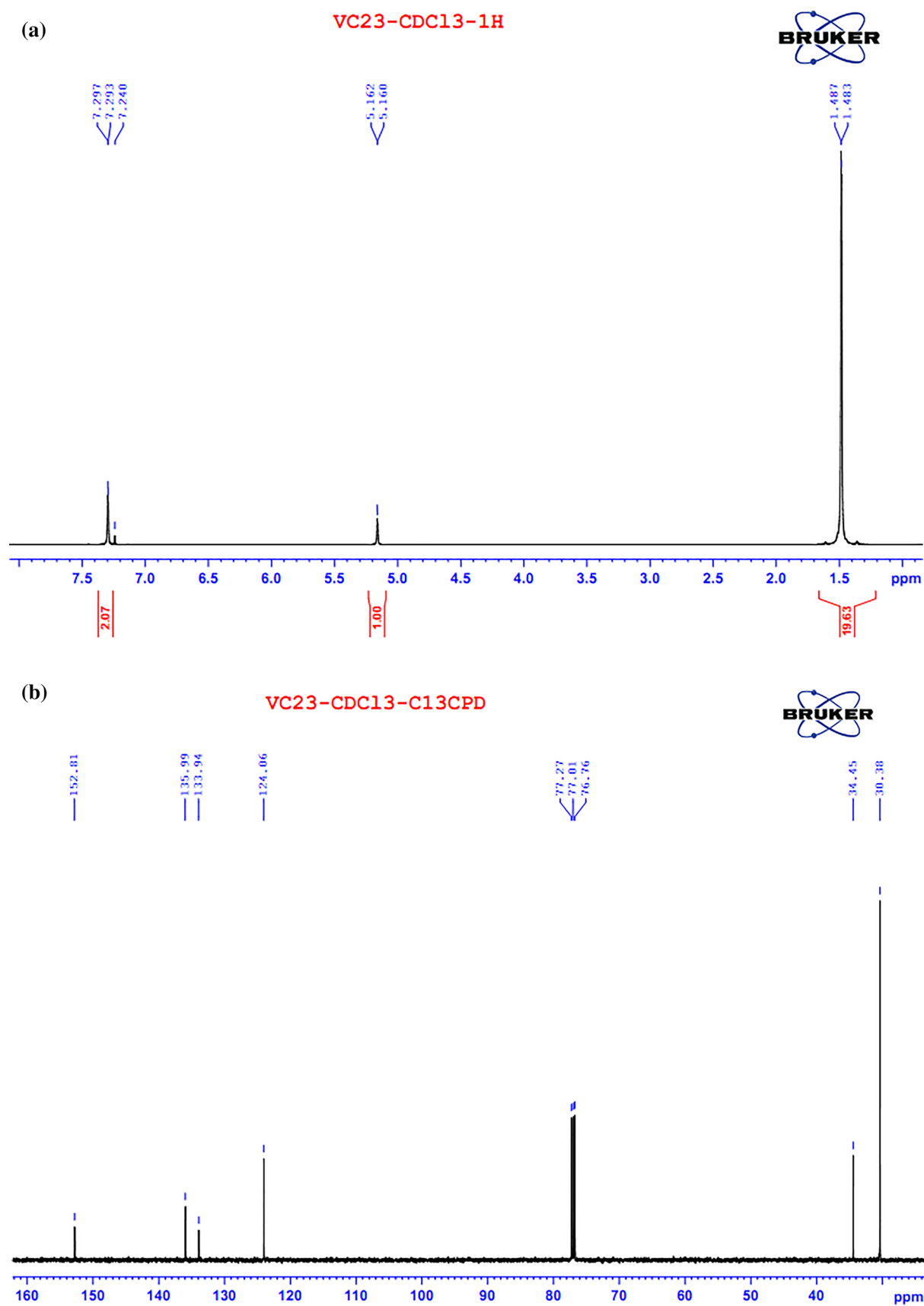


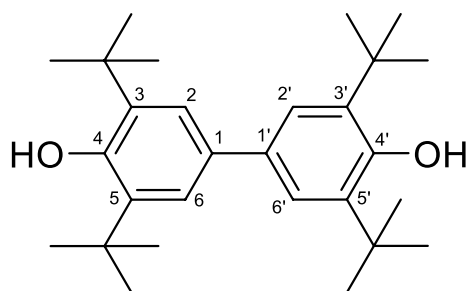
Fig. 5  $^1\text{H}$  (a) and  $^{13}\text{C}$  (b) NMR spectrum of bisphenol-VN

On the basis of the NMR and IR spectra, it can be concluded that the obtained product has the structure as shown in Scheme 2.

The MS-HPLC profile of obtained product reveals that there is only one peak corresponding to bisphenol-VN ( $m/z$  411), and peaks of other trace impurities cannot be observed (Fig. 6).

### The activity of bisphenol-VN in rubber

The oxidation induction time (OIT) is a standardized test performed in a differential scanning calorimeter (DSC) which measures the level of thermal stabilization of the material tested. The oxidation induction times of natural rubber in the absence or in the presence of antioxidants are given in Fig. 7 and Table 2.



**Scheme 2** Structure of the product

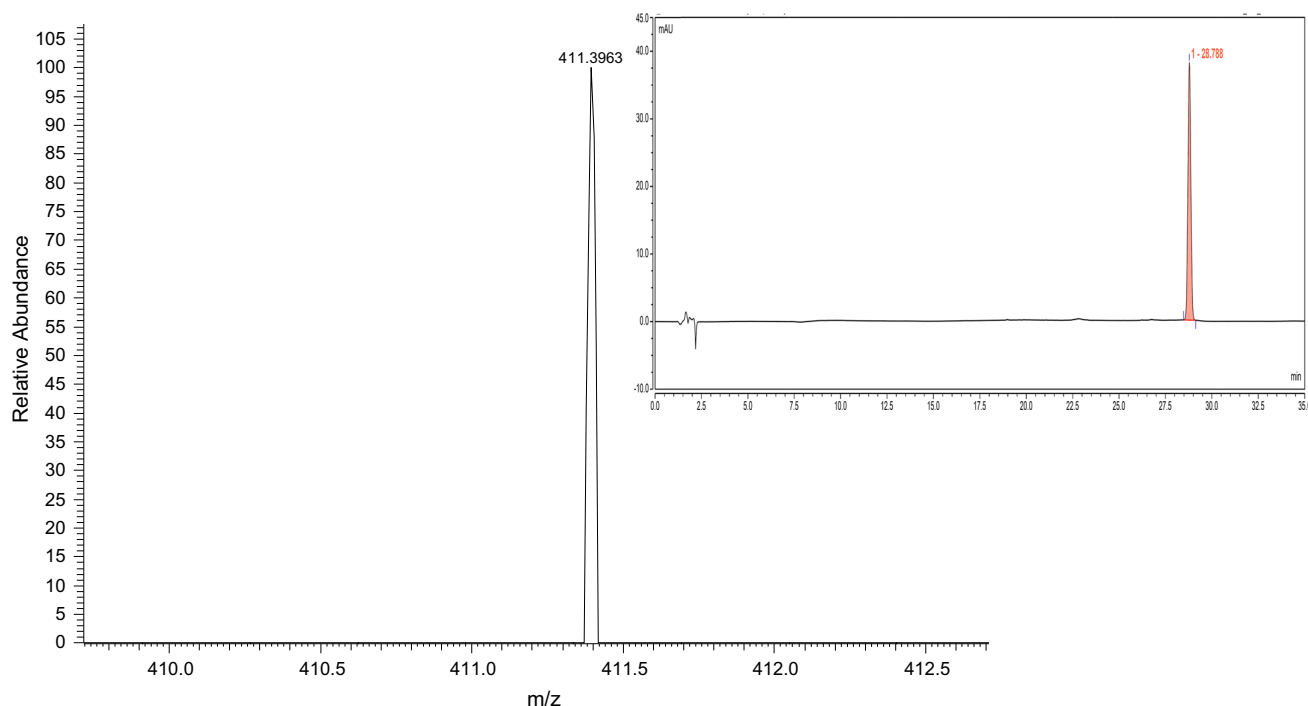
The resistance of natural rubber to oxidative decomposition in the presence of bisphenol-VN was compared with that of commercial antioxidants such as Irganox 1010, BHT, 2,6-DBVP, 6PPD, Irganox 1098, Irganox HP2215, and Irganox B215. Results showed that natural rubber is immediately oxidized in the absence of antioxidants, and commercial antioxidants protect natural rubber against the oxidation weakly, while bisphenol-VN is capable of extending the oxidation induction time to 21.4 min.

Physical-mechanical properties of natural rubber in the presence of bisphenol-VN were also compared with 6PPD randomly. Experimental results showed that natural rubber mixed with bisphenol-VN has better physical-mechanical properties than in case of using 6PPD before and after aging (Table 3).

Ozone testing is an accelerated test method used primarily for evaluating the resistance of rubber products to cracking during service life. The tester adopts the ultraviolet radiation absorption principle and it is based on the Beer-Lambert law to monitor the ozone concentration without the use of chemicals. The samples of NR 99.9% and bisphenol-VN 0.1% under ozone impact after 72 h were not cracked.

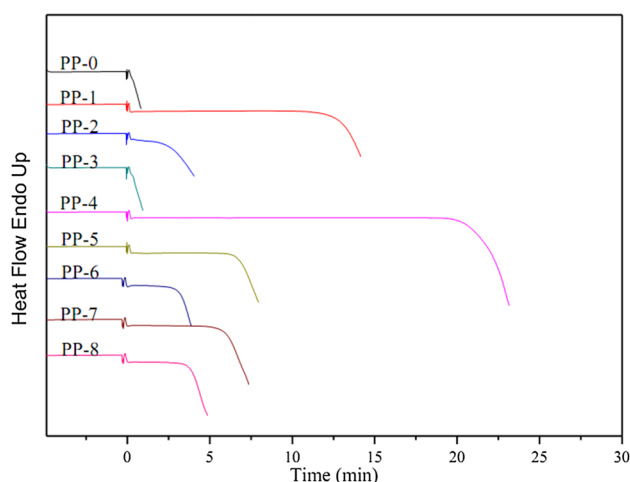
### Conclusions

Natural rubber has many valuable properties but low resistant to oxidation; therefore, the mixing of antioxidants into natural rubber to improve some of its properties is needed.



**Fig. 6** The MS-HPLC spectrum of bisphenol-VN





**Fig. 7** The oxidation induction time (OIT). PP-0: without antioxidants; PP-1: with Irganox 1010; PP-2 with BHT; PP-3: with 2,6-DBVP; PP-4: with bisphenol-VN; PP-5: with 6PPD; PP-6: with Irganox 1098; PP-7: with Irganox HP2215; PP-8: with Irganox B215

**Table 2** The oxidation induction time (OIT) of natural rubber (NR) under model conditions of accelerated aging at 150 °C temperature

Samples	Antioxidants (AO)	The oxidation induction time (OIT) (min)
PP-0	Without AO	0
PP-1	Irganox 1010	13.1
PP-2	BHT	2.5
PP-3	2,6-DBVP	1.5
PP-4	Bisphenol-VN	21.4
PP-5	6PPD	7.2
PP-6	Irganox 1098	3.5
PP-7	Irganox HP2215	6.3
PP-8	Irganox B215	4.2

**Table 3** Physical–mechanical properties of natural rubber in the presence of various antioxidants

	NR 99.9% + bisphenol-VN 0.1%		NR 99.9% + 6PPD 0.1%	
	Before aging	After aging	Before aging	After aging
Tensile strength (MPa)	19	17	15	13
100% tensile modulus (MPa)	2.89	2.23	2.80	2.24
Elongation at break (%)	336	433	291	381
Hardness	76	80	71	73

New heterogeneous catalytic system was prepared and used in the synthesis of bisphenol-VN. The experimental results have proven the presence of hydrophobic phenolate layer on

the surface of the catalytic system, which enhances the rate of the synthesis of bisphenol-VN. The oxidation product has high purity due to the fact that the catalyst can be easily separated from the reaction mixture. Bisphenol-VN increases the oxidation induction time and physical–mechanical properties of natural rubber, thus, it can be used to replace commercial antioxidants.

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## Compliance with ethical standards

**Conflict of interest** The authors declare no competing interests.

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