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## Analyzing the Cross-Linking of HNBR Utilizing Peroxide and Triazine Compounds

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Investigated the role of polymer peroxide (1,4-bis-tret butyl peroxy isopropyl benzene) and triazine compounds (6-bis-trichloromethyl sym-triazine, 2-phenyl-4) under heating in hydrogenated butadiene nitrile rubber (HNBR) systems. The changes in HNBR's molecular structure when polymer peroxides and triazine compounds are present, as demonstrated by spectral, physical, and chemical methods of analysis: Decided the energy of yield and the rise of cross-connecting thickness of the matrix HNBR for each researched framework rely upon time. It is shown that cross connecting of the HNBR with peroxide polymers happens by an extreme sort. The study investigated the effects of polymer peroxides and triazine compounds on the molecular structure of hydrogenated butadiene nitrile rubber (HBNR) under heating, determined the kinetics of yield and the emergence of cross-linking density of the HBNR for each system studied, and showed that crosslinking occurs by a radical type.

**Keywords** Hydrogenated Butadiene Nitrile Rubber, Cross-Linking Polymers, Polymeric Peroxide, Triazine Compounds.

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## Introduction

Hydrogenated nitrile butadiene rubbers (HNBRs) are hydrogenated copolymers of acrylonitrile (AN) and butadiene (BD) that are frequently utilized in composites or polymer blends. NBR exhibits exceptional oil resistance and workability, while HNBR surpasses it with enhanced heat, chemical, oxidizing fuel, and ozone resistance due to its saturated backbone and acrylonitrile groups. When compared to traditional oil and heat resistant elastomers like acrylic and fluorocarbon elastomers, HNBR demonstrates superior tensile strength, flexibility, wear resistance, and resistance to fluids containing chemically aggressive additives, even in unfavorable conditions such as low temperatures. This is attributed to its relatively low glass transition temperature

#### $(T_g)$ [1-3].

These copolymers are typically cured with peroxides or vulcanized with sulfur to enhance their mechanical resistance and improve their chemical stability. However, the use of such cross-linking reagents can be problematic in high-quality systems because residual  $H_2O_2$  or sulfur can be harmful to the application [4]. Recently, there has been a growing focus on crosslinking highly saturated elastomers using different organic peroxides. Derivatives of aliphatic hydrocarbons are commonly utilized as crosslinking agents for hydrogenated butadiene nitrile rubber (HNBR). For instance, di-t-butyl peroxide and ditetrachloride-t-butyl peroxide [5].

Using the example of studying the effect of aromatic peroxides on the crosslinking of HNBR, it was shown early on that aromatic peroxides have high structureforming properties [6]. The presence of a small amount of chains with residual unsaturation in the rubber allows for the control of the rubber properties, depending on the structuring groups and the conditions of the structuring process.

The selection of curing agents, such as aromatic peroxides, not only impacts the cross-link density and mechanical characteristics of the rubber but also plays a crucial role in determining the solubility behavior and distribution of the cross-linking agents within the rubber blends. These factors can further influence the overall performance and durability of the HNBR materials in specific applications. To gain a comprehensive understanding of the influence of aromatic peroxides on HNBR cross-linking, it is essential to delve into the kinetics of the curing process, the distribution of crosslinks within the polymer network, and the resulting changes in mechanical and thermal properties. Additionally, given the demand for high-performance rubber materials in industries such as automotive, aerospace, and oil and gas, a more profound comprehension of the impact of aromatic peroxides on HNBR cross-linking can facilitate the way for the development of customized materials designed to fulfill the specific requirements of these sectors [7-9].

A series of peroxide-containing carboxylic acids have been described in the literature [10], especially with a view their use of tem in the vulcanization of saturated rubbers. Due to their lower decomposition temperatures, these products in this series cannot be used in technical applications. On the other hand, the peroxide compound 1,4-bis-benzene tret-butyl peroxy isopropyl has a very long half-life and is involved in crosslinking even in the presence of other crosslinking systems. When HNBR is cross-linked with a polymer peroxide (PP), only a low degree of crosslinking is usually achieved. Obtaining elastomers is an important task that requires a complex set of technical and rheological properties. To date, there are no data in the literature regarding the introduction of symmetric triazine compounds to crosslink HNBR with polymeric peroxides.

Although more detailed data on this topic is not available, this data has scientific and technological importance in studying the effects of lattice structural changes and the rheological properties of HNBR [11]. Moreover, to address the technical challenges encountered in elastomeric materials within the petroleum processing industry and mechanical engineering sectors, it is advised to incorporate specific additives. Specifically, it is recommended to include 6.0 parts by weight of triallyl cyanurate, 3 parts of stearic acid, 5 parts of zinc oxide, and 50 parts of carbon P324 [12]. A disadvantage of the known structural system is that the vulcanization has to be carried out in two stages, or at high temperatures above 426 K, which significantly increases the rate of destruction. Statistical tests in the compression process have shown that the accumulation level of residual strains in elastomers increases. Due to high drilling rates and depths, high operating pressures of equipment, and high temperatures in the development and exploration of oil and gas fields, as well as the increasing demands on components, they must be extremely durable. According to an investigation [13,14], the annual growth rate of

consumption of elastomers in the oil and gas industry is projected to increase significantly over the next decade.

The molecular structure of HNBR in the presence of triazine compounds is investigated in this work using solgel analysis, along with physical, chemical, and spectral methods. The structural characteristics of the peroxide elastomer grid are also elucidated.

## I. Experimental Part

## 1.1. Materials

The study focused on utilizing commercially available synthetic Hydrogenated Nitrile Butadiene Rubber (THERBAN 3467, Germany), characterized by an acrylonitrile content of 34%, a double bond content of 0.9%, and a Mooney viscosity ML1+4/100°C of 39±4 MU. Aromatic polymeric peroxide (PP), specifically 1,4-Bis(tert-butyl peroxy isopropyl) benzene (BIPB), served as an organic peroxide initiator, free radical crosslinking agent, and curing agent. The utilization of symmetric aromatic triazine compounds (ATC). particularly 2-phenyl-4,6-bis(trichloromethyl)-1,3,5triazine (PBTCMST), facilitated achieving a significant level of cross-linking. All co-agents were sourced from Sigma-Aldrich, USA, and the characteristics of the utilized compounds summarized in Table 1. All solvents and chemical reagents were of pure grade and were further purified, if necessary, by distillation. Other rubber ingredients were those customarily used in rubber industries.

## 1.2. Preparation of blends

HNBR-based blends were formulated using a laboratory two-roll mill equipped with rolls measuring 200 mm in diameter and 450 mm in length. The rolls were maintained at a temperature range of 20 - 25°C. The front roll operated at a speed of 20 rpm, with a friction ratio of 1 : 2. Initially, the rubber was plasticized for 1 minute. Subsequently, all components listed in Table 2 were added. The blend was mixed for 2 minutes before being transferred and stored in foils at room temperature.

For vulcanization, the prepared blends were subjected to an electrically heated hydraulic press under the following parameters: temperature – 423 K, pressure – 200 bars, and time – 40 minutes.

## 1.3. Methods of testing

## 1.3.1. Rheological measurements

The rheography of the mixtures and their curing characteristics were obtained at 170°C as per ASTM D 5289-17 using a Monsanto Rheometer R-100.

The nature of the action of the polymeric peroxide (PP) and triazine compounds on altering the characteristic viscosity can be determined using a standard approach. In this method, the characteristic viscosity  $[\eta]$  of cross-linking polymer systems in toluene at 20°C is estimated. The Mark-Houwink equation is utilized for this calculation, which is represented as (1):

$$[\eta] = KM^a \tag{1}$$

Where,  $[\eta]$  is the viscosity of the solution, M is the

Characteristics of the used compounds

#### Table 1.

|  | M. w. | M. w. Melting Density Elem |                   |      | Elemen | ntal composition |      |    |
|--|-------|----------------------------|-------------------|------|--------|------------------|------|----|
| Structure of compounds   | g/mol | point °C                   | g/cm <sup>3</sup> | С    | Н      | Ν                | Cl   | pН |
| $H_{3}C \xrightarrow{H_{3}C} H_{3}C \xrightarrow{H_{3}C} H_{3$ | 338   | 80-82                      | 0.87              | 76   | 8.4    | -                | -    | 8  |
|  | 394   | 88-90                      | 0.93              | 64.2 | 6.4    | 11.3             | 18.1 | Π  |

Table 2.

#### Compounding recipe of rubber

| Components   | Parts per 100 parts of rubber by weight |     |     |  |
|--|---|-----|-----|--|
| HNBR   | 100                                     | 100 | 100 |  |
| 1,4-Bis(tert-butyl peroxy isopropyl) benzene (PP)      | 8.0                                     | 8.0 | 8.0 |  |
| 2-phenyl-4,6-bis(trichloromethyl)-1,3,5-triazine (ATC) | -                                       | 6.0 | 6.0 |  |
| Zinc Oxide   | 5.0                                     | 5.0 | 5.0 |  |
| Epoxy Resin  | 6.0                                     | 6.0 | 6.0 |  |
| Carbon Black (P324)                                    | -                                       | -   | 50  |  |

molecular weight of the polymer. For toluene at 20°C,  $\alpha = 0.64$  and  $K = 4.9 \cdot 10^4$  as constants.

Cross-link density was determined by measurements of equilibrium solvent swelling in toluene at room temperature. A circular piece with a thickness of 2 mm was prepared to swell in toluene for about 72 hours to ensure that the swelling had reached equilibrium and then dried in an oven for 24 hours until a constant mass was obtained. The masses of the original, swollen and dried samples were measured using an analytical balance. The crosslink density value (v) was calculated using the modified Flory–Rehner equation [15].

## **1.3.2.** Fourier Transform Infrared (FT-IR) and EPR Spectroscopy

Infrared spectra were measured using an FT-IR Alpha (Bruker, Germany) spectrometer in the range of wavenumber 4000–600 cm<sup>-1</sup>. Samples in film form were determined without any additives. At this time, the error in the value of the wave number corresponding to the absorption band was  $\pm 2$  cm<sup>-1</sup>. The spectra were interpreted in accordance with correlation tables and guidelines [16].

EPR measurements were carried out on a Bruker EMX microX spectrometer operating in the X-frequency range, with a modulation frequency of  $9.8 \cdot 10^9$  Hz, ( $\lambda = 3$  cm). Samples for analysis were placed in sealed quartz ampoules with a diameter of 3 mm and a length of 15–20 cm, and then the ampoules were placed in the apparatus for research. The concentration of paramagnetic centers and g factors were determined by the method described in reference [17].

#### **1.3.3.** Mechanical properties

The mechanical properties: yield stress 100%, 200% and 300%, tensile strength and elongation at break were tested using the ZwickRoell 1435 universal testing machine (ZwickRoell, Germany). The tests were carried out in accordance with PN-ISO 37:2007. Cured samples with smooth surfaces were used to measure indentation hardness using a Shore-A hardness tester according to ASTM D 2240.

## **II. Results and Discussion**

All studies have demonstrated that the extension of the duration of cross-linking (vulcanization) results in an elevation in the molecular mass in both systems (Table 3).

| Table   | <u>: 3.</u> |
|---|-------------|
| Changing the molecular weight of HNBR systems           |             |
| HNRR $\perp$ PP and HNRR $\perp$ PP $\perp$ $\Delta$ TC |             |

| Cross linking | Time, min                                  |     |     |     |  |  |
|---------------|--|-----|-----|-----|--|--|
| system, phr   | 30 60 90 120                               |     |     |     |  |  |
|               | The characteristic viscosity $\eta_{char}$ |     |     |     |  |  |
| HNBR+PP       | 0.2  | 0.4 | 0.5 | 0.6 |  |  |
| HNBR+PP+ATC   | 0.4  | 0.5 | 0.7 | 0.9 |  |  |

For a system denoted as HNBR+PP at a time of 120 minutes, the characteristic viscosity is measured to be 0.6. Conversely, for the system when the presence of ATC is taken into account, the viscosity increases to a higher value of 0.9. The observed increase in viscosity within the time range of 30-120 minutes can potentially be attributed to the

generation of spatial structures as a result of intermolecular cross-linking with polymeric peroxide. Fig. 1. a shows the molecular mass distribution of masticated HNBR based blends as a function of mastication time. As evident from the curve, the molecular mass distribution peak occurred at the higher molecular mass range for the HNBR with ATC and PP blends.



**Fig. 1.** Kinetics of structuring the HNBR at 423 K; 1- without cross-linking agents; 2- in the presence of PP; 3- in the presence of ATC.

Additionally, the rate of increase is observed over time in both systems. It is noted that at 130 minutes, the quantity of chains present in the grid system HNBR+PP and HNBR+PP+ATC is 4.2 and  $6.3 \cdot 10^5$  mol/sm<sup>3</sup>, respectively. To assess the processes of structuring that take place during the expansion of samples in HNBR+PP and HBR+PP+ATC solutions, the structural characteristics of the elastomer mesh were determined through sol-gel analysis after a 50-hour extraction with cold acetone. The results are presented in Fig. 2.

It is evident that the presence of PP has a significant impact on the structural properties of the elastomer. The partial cross-linking of HNBR is associated with a limited degree of unsaturation in the rubber. Analysis of the structural data suggests that, in the presence of PP, the rate of cross-linking is greater compared to when PP is absent, and this difference becomes most pronounced when ATC is introduced into the system. A comparative examination of the cross-linking of HNBR reveals that the formation of cross-links and cross-linked molecules occurs at a slow rate within 30 minutes. Furthermore, the number of crosslinked molecules is found to be 0.98 and  $1.25 \cdot 10^5$  mol/sm<sup>3</sup> in the respective systems (Fig. 2).



**Fig. 2.** The kinetics of formation of cross-linked molecules, 1- HNBR (V3850) at 423K in systems HNBR; 2- HNBR+ PP; 3- PP+ HNBR + ATC.

The system HBR+PP+ATC exhibits a high sensitivity to cross-linking, which can be attributed to the structural characteristics of the low molecular symmetric triazine compound and the combined effect of polymeric peroxide on the density of the grid elastomer. The increase in the maximum concentration of chain grid  $(1/M_c)$  and cross-linked molecules  $(1/Mn_\tau)$  indicates that cross-linking in the system leads to the formation of new active centers. The short chains have higher polymer chain segment mobility and were more favorable for radical induced chemical reactions.

The formation of saturated peroxy radicals leads to an increase in cross-linking and density of elastomers grid. The reaction between the low molecular ATC and rubber, as well as the decomposition of PP to radicals in the chemical reaction, promote the formation of C-C structures in the rubber macromolecule.

FTIR spectroscopy serves as a crucial analytical tool for investigating the chemical structures of compounds, including polymers like Nitrile Butadiene Rubber (NBR) and cross-linking agents such as 1,4-Bis(tert-butyl peroxy isopropyl) benzene (PP) and 2-phenyl-4,6bis(trichloromethyl)-1,3,5-triazine (ATC). In the system of HNBR-PP, the interaction between the two polymers is primarily governed by the polar groups of C=N and C-O, exhibiting reactivity under thermal conditions.



Fig. 3. FTIR spectra of the HNBR-PP (a) and HNBR-PP-ATC (b) composites.

The FTIR spectra of HNBR-PP and HNBR-PP-ATC composites exhibit distinctive features. Intense absorption peaks at 2923 cm<sup>-1</sup> and 2864 cm<sup>-1</sup> correspond to asymmetric and symmetric stretching vibrations of carbon-hydrogen (C-H) bonds in methyl (-CH<sub>3</sub>) and methylene (-CH<sub>2</sub>-) groups, present in both HNBR and PP chains. Additionally, an absorption peak at 2236 cm<sup>-1</sup> is attributed to stretching vibrations of the C≡N groups in the acrylonitrile units of HNBR. The double band observed in the range of 1704–1654 cm<sup>-1</sup> corresponds to double bonds >C=C<, which can include vinyl, trans, and cis bonds, both substituted and unsubstituted. In the range of 1463-1445 cm<sup>-1</sup>, overlapping bands of asymmetric scissoring vibrations of methyl groups and symmetric scissoring vibrations of methylene groups are observed, along with inplane –C–H deformation in methylene groups.

Cross-linking of HNBR is believed to occur through the attachment of polymeric peroxide to double bonds (C=C) after heating for 120 minutes. Spectral bands at 1805 cm<sup>-1</sup> and 1765 cm<sup>-1</sup> indicate the involvement of -CO-RO-CO- and -COO bonds in cross-linking. The absorption peak at 967 cm<sup>-1</sup>, attributed to out-of-plane -CH=CH- deformations in trans-butadiene units, decreases in intensity in HNBR-PP-ATC vulcanizate spectra, indicating the participation of >C=C< trans bonds in interelastomer reactions with ATC during heating in the presence of PP. Moreover, strong absorption peaks in the range of 600–650 cm<sup>-1</sup> likely correspond to vibrations of C--Cl groups, confirming the presence of chlorine atoms in the HNBR-PP-ATC blend and its cross-linking product. It is well-established that the cross linking of diene rubbers, such as through the use of peroxide, does not solely occur as a first-order reaction. Unlike sulfur compounds, the flow of the cross linking agent (peroxide) is directly proportional to the number of formed cross-linking sites. This leads us to believe that the decomposition of peroxide proceeds through a hemolytic pathway, resulting in the formation of radical cleavage products. Furthermore, cross linking takes place through a radical mechanism without significant involvement of side reactions. These transformations are commonly observed during the cross linking of HNBR, as it is of interest to detect the radicals formed by the decomposition of polymeric peroxide.

Prior to conducting our research, we examined the EPR spectra of HNBR before and after heating. When pure HNBR is heated, it decomposes into radicals, as evidenced by the

EPR spectra which consist of three components (Fig. 4a).

The g-factor of these components corresponds to g = 2.0084, with a line width of  $\Delta H = 0.46$  mTl.

The EPR spectra observed for a mixture of HNBR and PP is typical for systems containing polymeric peroxide. It displays a narrow singlet line with an unchanged g-factor of  $\Delta H = 1.1 \text{ mTl}$  (figure 4b). However, when systems containing HNBR+ PP + ATC are heated, a different number of paramagnetic centers are observed and there is a significant reduction in the spectrum (figure 4c). The width of the band in this case is  $\Delta H = 0.7 \text{ mTl}$ .

Therefore, the concentration of radicals decreases by 1.5 times in the presence of HNBR+ PP + ATC compared to the HNBR+ PP system (Fig. 4b). By studying the behavior of polymeric peroxide in an elastic environment, we can draw conclusions about the microstructure of the molecular chains of the elastomer. Based on experimental and literature data [18], we can infer that the emergence of a radical without excess fine structure is due to the fact that, initially, the peroxide cross linking polymer mainly decomposes into two radicals R-O-O-R $\rightarrow$ 2R-O<sup>•</sup>. These radicals are then stabilized in the presence of hydrocarbon polymers. They dehydrogenate the polymer chain and keep it in a radical state:

$$- \overset{|}{\underset{l}{\operatorname{C}}} + \operatorname{RO}^{\bullet} - \overset{|}{\underset{l}{\operatorname{C}}}^{\bullet} + \operatorname{ROH}$$

Cross-links may created when the resultant hydrocarbon radical reacts with another radical.

 $-\overset{l}{\overset{\phantom{a}}_{\overset{\phantom{a}}}}\overset{l}{\overset{\phantom{a}}}\overset{l}{\overset{\phantom{a}}}\overset{\phantom{a}}{\overset{\phantom{a}}}}\overset{\phantom{a}}{\overset{\phantom{a}}}\overset{\phantom{a}}{\overset{\phantom{a}}}\overset{\phantom{a}}{\overset{\phantom{a}}}\overset{\phantom{a}}{\overset{\phantom{a}}}\overset{\phantom{a}}{\overset{\phantom{a}}}\overset{\phantom{a}}}\overset{\phantom{a}}{\overset{\phantom{a}}}\overset{\phantom{a}}}\overset{\phantom{a}}{\overset{\phantom{a}}}\overset{\phantom{a}}{\overset{\phantom{a}}}\overset{\phantom{a}}}\overset{\phantom{a}}{\overset{\phantom{a}}}\overset{\phantom{a}}}\overset{\phantom{a}}{\overset{\phantom{a}}}\overset{\phantom{a}}}\overset{\phantom{a}}{\overset{\phantom{a}}}\overset{\phantom{a}}}\overset{\phantom{a}}}\overset{\phantom{a}}{\overset{\phantom{a}}}\overset$ 

Based on the obtained experimental data, we can conclude that the lateral nitrile group in the main chain of saturated hydrocarbon units, as well as unsaturated butadiene units (within 2%), allows for the cross-linking of hydrogenated natural rubber in the presence of polymeric peroxides (1,4-bis-tert-butyl peroxy isopropyl benzene). It easily decomposes at 423K with satisfactory yields in the macromolecule cross-links and cross-linked molecules within the time range of 30-120 minutes. To achieve a higher degree of cross-linking, enhanced triazine compounds (2-phenyl-4, 6-bis(trichloromethyl)-symtriazine) should be introduced. However, the role of the ATC in causing the observed changes of the properties of HBNR is subject to further study.



 $\Delta H = 1,3 \text{ mTl} \qquad \Delta H = 1,1 \text{mTl} \qquad \Delta H = 0,7 \text{ mTl}$ Fig. 4. The EPR spectra following 423K heating.

In Table 3, the results of physical-mechanical tests of mixtures are presented. The results indicate that the process of structuring HBNR with polymeric peroxide without carbon black is slow, and the degree of cross-linking is low.

In the presence of ATC (8 parts per 100 parts of rubber by weight) and carbon black, the rate of cross-linking in the macromolecule at 423 K practically does not decrease compared to without carbon black (CB). This is clearly seen from the kinetic curves showing the change in viscosity of the mixture at 423K (Fig. 5).

The acceleration of cross-linking may be related to the dissociation of peroxide and triazine groups around the carbon black particles, as well as the presence of more polarized bonds (C-C) in the allyl group, since molecules of polymeric peroxide and ATC are highly polar.

Considering a filled polymer as a colloidal system in which the polymer is the dispersed phase, it appears that during cross-linking of HBNR with polymeric peroxide, carbon black acts as the dispersed phase [19,20]. This hypothesis can be extended to the study presented in this paper on the system HBNR+ATC+PP+P324.

Therefore, the introduction of metal oxide and an epoxy resin (ED-40) significantly affects the cross-linking

during heat treatment (Table 4).

To determine the effect of temperature and operational conditions on the performance of elastomeric materials (EM), comparative tests were conducted on the vulcanizate HBNR at 423 K in a hostile environment (Table 7), where seals, swivels, pumps, and other units of the oil industry operate. These data indicate that the experimental elastomers containing ATC and a metal oxide in their structure exhibit less swelling and accumulation of residual compressive strain. Tensile strength after contact with the medium for vulcanizates 1 and 2 was lower compared to vulcanizates 3.

Thus, the analysis of the study results suggests that elastomeric materials based on HBNR and obtained in the presence of cross-linking polymer peroxide agent (PP), ATC, and epoxy compounds are superior to sulfuric and dicumil peroxide elastomers in resistance to thermal aging and dynamic endurance during repeated stretching in corrosive environments. All studied compounds are recommended for use in the formulations of sealing manufacturing for EM parts of drilling equipment.

The utilization of these research results in the creation of stable elastomeric materials for drilling technology reduces the downtime of pumps and swivels in the drilling

Table 4.

| Compositon       | Duration of<br>structuring,<br>t,min | The number of cross-linking, Nv·10 <sup>-19</sup> , cm <sup>3</sup> | Resistance at<br>break, f, MPa | Elongation,<br>ε, % | Hardness by<br>HM, mm |
|------------------|--------------------------------------|---|--------------------------------|---------------------|-----------------------|
| HNBR+PP+ATC      | 20<br>60                             | 1.9<br>4.1  | 8<br>10                        | 820<br>790          | 20<br>35              |
|                  | 120                                  | 5.3   | 12                             | 710                 | 40                    |
|                  | 20                                   | 3.8   | 12                             | 770                 | 30                    |
| $\Pi NDK+FF+AIC$ | 60                                   | 6.4   | 14                             | 640                 | 40                    |
| P 524            | 120                                  | 11.0  | 17                             | 600                 | 50                    |

Physical-mechanical properties of HNBR-based compositions depending on structuring duration



Fig. 5. The kinetics of the change of Mooney viscosity of mixtures based on HNBR with and without CB.

Table 5.

The yield concentration of effective cross-linking (n'c) of peroxide and sulfuric vulcanizates of HNBR

| Vulcenizing system         | Type of       | Mooney viscosity | Amount of cross |
|----------------------------|---------------|------------------|-----------------|
| vulcanizing system         | chemical bond | (MU)             | linking, (n`c)  |
| 1 HNBR+S+kaptax+ZnO [21]   | C-S-C         | 55               | 5.4             |
| 2 HNBR+DCP*+PPR**+ZnO [22] | C-C           | 61               | 6.2             |
| 3 HNBR+PP+ATC+ED+ZnO       | C-C           | 72               | 8.9             |

DCP\* - dicumilperoxide

PPR\*\*- phenol phormaldehyde resin

Comparative characteristics of filled HBNR vulcanizates

#### Table 6.

|   | Vulcanization |      |      |  |
|---|---------------|------|------|--|
| Parameters  | 1             | 2    | 3    |  |
|   | C-S-C         | C-C  | C-C  |  |
| Resistance at break, f, MPa   | 18            | 15   | 21   |  |
| Elongation,%  | 550           | 570  | 480  |  |
| Hardness(by TM-2), c.u.   | 57            | 55   | 64   |  |
| Compression set (20%,423K,72h)  | 70            | 62   | 5    |  |
| Coefficient of thermal aging, 423K, 150h  | 0.61          | 0.53 | 0.85 |  |
| Change of mass due swelling in a mix of gasoline-<br>benzene (3:1) (353K, 24h), % | 54            | 48   | 35   |  |

#### Table 7.

Comparative information on the filled EM based on various saturated HBNR after use in sea water (1), oil-bearing solutions (2) and mud solutions (3).

| <b>e</b> , , ,                          | Vulcanization |      |      |  |
|---|---------------|------|------|--|
| Parameters                              | 1             | 2    | 3    |  |
|   | C-S-C         | C-C  | C-C  |  |
| Tensile strength, MPa                   |               |      |      |  |
| 1                                       | 10            | 9    | 14   |  |
| 2                                       | 13            | 11   | 15   |  |
| 3                                       | 15            | 13   | 16   |  |
| Coefficient of thermal aging, (I,II)    | 0.61          | 0.53 | 0.85 |  |
| By heat, (f <sub>p</sub> )              |               |      |      |  |
| By conduc. $(\varepsilon_p)$            |               |      |      |  |
| Change of mass due swelling, % (weight) | 54            | 48   | 35   |  |
| 1                                       | 235           | 198  | 125  |  |
| 2                                       | 98            | 104  | 88   |  |
| 3                                       | 71            | 83   | 59   |  |

process and ensures continuous operation of the plant.

## Conclusions

This study investigated the impact of polymeric peroxide (PP) on the cross-linking process of HNBR, with the addition of symmetrical triazine compounds (ATC) to enhance cross-linking efficiency. Capillary viscometry revealed that the characteristic viscosity of HNBR + PP and HNBR + PP + ATC initially increased up to 120 minutes, indicating higher molecular weight due to intermolecular cross-linking. However, viscosity began to decrease beyond 120 minutes, suggesting polymer chain breakdown. Sol-gel analysis showed a significant increase in the number of mesh and cross-linking density within the 30-120 minute range for both systems, indicating efficient cross-linking. IR Fourier spectroscopy confirmed the involvement of both -CO-RO-CO- and -COO groups in the cross-linking process, highlighting the role of HNBR structure alongside unsaturation in cross-linking kinetics.

ESR spectra analysis demonstrated radical formation during the PP-HNBR reaction, further stabilized by carbon polymers to facilitate cross-link formation. Laboratory tests at elevated temperature and corrosive conditions showed consistent performance of the elastomer, indicating its suitability for various applications. Overall, this research provides valuable insights into the effect of polymeric peroxide and symmetric triazine compounds on the cross-linking process of HNBR, shedding light on the factors influencing the rate of cross-linking and the performance of the elastomer under different conditions.

Mammadov A. Kh. – Phd candidate; Khankishiyeva R. F. – Doctor of Philosophy in Radiation materials science,; Akhundzada H. N. – Doctor of Philosophy in Nuclear chemistry;

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A. Kh. Mammadov, *Thermal and radiation effects on the cross-linking and mechanical properties of HNBR elastomers*, Journal of Thermoplastic Composite Materials, (2024); <u>https://doi.org/10.1177/08927057241305535</u>.
J. G. Speight, Handbook of Industrial Hydrocarbon Processes (Gulf Professional Publishing, Germany, 2020).

<sup>[3]</sup> H. Zou, Y. Jing, J. Tu, X. Shi, J. Kadlcak, Z. Yong, S. Liu, & G. Liu, *Investigation on the mechanical properties* 

<sup>[5]</sup> H. Zou, T. Jing, J. Tu, X. Shi, J. Kaucak, Z. Fong, S. Elu, & G. Elu, *Investigation on the mechanical properties and oil resistance of sulfur cured nitrile rubber/hydrogenated nitrile butadiene rubber blends*, Polymer Eng., Sci., 61(12), 3050-3059 (2021); <u>https://doi.org/10.1002/pen.25817.</u>

- [4] L.Gonzalez, A. Rodriguez, A. Del Campo & A. Marcos-Fernandez, Effect of heterogeneities on the physical properties of elastomers derived from butadiene cured with dicumyl peroxide, Polymer International, 53(7), 1009 (2004); https://doi.org/10.1002/pi.1393.
- [5] J. L.Valentín, A. Rodríguez, A. Marcos-Fernández & L. González, *Dicumyl peroxide cross-linking of nitrile rubbers with different content in acrylonitrile*, Journal of Applied Polymer Science, 96, 1-5 (2005); https://doi.org/10.1002/app.20615.
- [6] R. Khankishiyeva, H. Akhundzada, *The improvement of physical and mechanical properties of sealers based on nitrile-butadiene rubber and combination of nano-metal oxides*, Proceedings of Oil Gas Scientific Research Projects Institute SOCAR, 3, 174–182 (2020); <u>https://doi.org/10.5510/ogp20200300459</u>.
- [7] Sh.M. Mammadov, H.N. Akhundzada, R.F. Khankishiyeva, J.S. Mammadov, G.A. Mammadova, P.I. Ismayilova, A.Kh. Mammadov, A.I. Azadaliyev, M.N. Mirzayev. *Effect of gamma irradiation on the crosslinking process of nitrile-butadiene rubber with triazine and maleic compounds*, Journal of Optoelectronics and Biomedical Materials, 3, 81-87, (2020) (https://doi.org/10.15251/jobm.2020.123.81)
- [8] Sh. Mammadov, G. Azizova, R. Khankishiyeva, F. Amirov, G. Mammadova, I. Movlayev, & J. Mammadov. Investigation of the rheological structural parameters of a network of NBR-based vulcanizates with the participation of chlorine-containing, J. New Technol. Mater., 13(1), 70 (2023); https://www.asjp.cerist.dz/en/article/227655.
- [9] N. Osaka, M. Kato, & H. Saito, Mechanical properties and network structure of phenol resin crosslinked hydrogenated acrylonitrile-butadiene rubber, J. Appl. Polym. Sci., 129(6), 3396 (2013); https://doi.org/10.1002/app.39010.
- [10] Z. Cui, X. Li, W. Feng, L. Wei, Y. Liu, & A. Du, Effect of crosslinking agent dosage on the morphology and properties of thermoplastic vulcanizates based on hydrogenated acrylonitrile butadiene rubber and thermoplastic polyester elastomer, Polym., 287, 126420 (2023); <u>https://doi.org/10.3390/ma17040863.</u>
- [11] M. Pingot, T. Pingot, M. Zaborski, Nanostructured Metal Oxide and Unsaturated Acid as a New Co-agent in Peroxide Cross-Linking of Hydrogenated Butadiene-Acrylonitrile Rubber, Trends in Colloid and Interface Science XXIV. Progress in Colloid and Polymer Science, vol 138. Springer, Berlin, Heidelberg (2011); https://doi.org/10.1007/978-3-642-19038-4\_26.
- [12] B. Alcock, T. Peters, A.Tiwari, *The effect of hot air exposure on the mechanical properties and carbon dioxide permeability of hydrogenated nitrile butadiene rubber (HNBR) with varying CB content*, Polymer Test., 106273 (2019); <u>https://doi.org/10.1016/j.polymertesting.2019.106273</u>.
- [13] J. Kruželák, A. Kvasničáková, & I. Hudec, Peroxide curing systems applied for cross-linking of rubber compounds based on SBR, Adv. Ind. Eng. Polym. Res., 3(3), 120 (2020); https://doi.org/10.1016/j.aiepr.2020.05.001.
- [14] J. Kruželák, R. Sýkora, R. Dosoudil, & I. Hudec, Relationship between the cross-link structure and properties of peroxide and sulfur-cured magnetic composites based on NR and NBR, J. Elastomers & Plast., 49(6), 459 (2017); https://doi.org/10.1177/0095244316672094.
- [15] P. J. Flory, & J. Rehner, Statistical theory of chain configuration and physical properties of high polymers, Ann. New York Acad. Sci., 44, 419 (1943).
- [16] O. Keefe, F. Jerome, Identification of polymers by IR spectroscopy (Rubber World, 2004).
- [17] P. R. Dluzneski, *Peroxide vulcanization of elastomers*, Rubber Chem. Technol., 74(3), 451 (2001); https://doi.org/10.5254/1.3547647.
- [18] G. Heideman Reduced zinc oxide levels in sulphur vulcanisation of rubber compounds; mechanistic aspects of the role of activators and multifunctional additives, (Ed. Ipskamp, Netherlands, 2004).
- [19] A. Thitithammawong, C. Nakason, K. Sahakaro, & J. Noordermeer Effect of different types of peroxides on rheological, mechanical, and morphological properties of thermoplastic vulcanizates based on natural rubber/polypropylene blends, Polymer Testing, (2007). <u>https://doi.org/10.1016/j.polymertesting.2007.02.002.</u>
- [20] Y. Changjie, Q. Zhang, G. Junwei, Z. Junping, S. Youqiang, & W. Yuhang, Cure characteristics and mechanical properties of styrene-butadiene rubber/hydrogenated acrylonitrile-butadiene rubber/silica composites, Journal of Polymer Research, 18, 2487 (2011); https://doi.org/10.1590/0104-1428.2206.
- [21] C. Sheng, Z. Hu, H. Martin, Y. Duan, & J. Zhang, Effect of a small amount of sulfur on the physical and mechanical properties of peroxide-cured fully saturated HNBR compounds, Journal of Applied Polymer Science, 132(10) (2015); <u>https://doi.org/10.1002/app.41612.</u>
- [22] L.D. Loan, Mechanism of Peroxide Vulcanization of Elastomers, Rubber Chemistry and Technology, 40(1), 149 (1967); <u>https://doi.org/10.5254/1.3539040.</u>

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## Аналіз перехресних зв'язків HNBR із використанням пероксидних та триазинових сполук

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Досліджено роль пероксиду полімеру (1,4-біс-трет бутилперокси ізопропілбензол) та триазинових сполук (6-біс-трихлорметил сим-тріазин, 2-феніл-4) при нагріванні в системах гідрогенізованого бутадієннітрильного каучуку (HNBR). Зміни в молекулярній структурі HNBR за наявності полімерних пероксидів і триазинових сполук виявлено спектральними, фізичними та хімічними методами аналізу. Запропоновано, що енергія текучості та збільшення товщини перехресного зв'язку матриці HNBR для кожного досліджуваного каркасу залежать від часу. Показано, що перехресне зв'язування HNBR з пероксидними полімерами відбувається екстремальним типом. У статті досліджено вплив полімерних пероксидів і триазинових сполук на молекулярну структуру гідрогенізованого бутадієннітрильного каучуку (HBNR) при нагріванні, визначено кінетику виходу та виникнення щільності зшивання HBNR для кожної досліджуваної системи та показано, що зшивання відбувається за радикальним типом.

Ключові слова: Гідрогенізований бутадієн-нітрильний каучук, зшиті полімери, полімерний пероксид, триазинові сполуки.