STM JOURNALS

Journal of
Materials & Metallurgical Engineering

https://journals.stmjournals.com/jomme

ISSN: 2231-3818 (Online)
ISSN: 2321-4236 (Print)
Volume 15, Issue 2, 2025
May–August
DOI (Journal): 10.37591/JoMME

Research JoMME

Hydrogenated Nitrile Butadiene Rubber (HNBR): A Comprehensive Review

Sandeep Rai[1,*], Pradeep Uthale[2]

Abstract

HNBR is produced by the hydrogenation of nitrile rubber (NBR) using either a homogeneous or heterogeneous technique. NBR is a copolymer of butadiene and acrylonitrile monomers. The hydrogenation process involves adding hydrogen to the nitrile butadiene copolymer, which results in improved resistance to heat, oxidation, and chemicals compared to NBR. This process alters the molecular structure of the rubber, providing it with superior properties compared to its unmodified counterpart, NBR. Due to hydrogenation, the number of double bonds in NBR is reduced, and the polymer backbone becomes more stable, exhibiting enhanced performance properties in HNBR. HNBR possesses good resistance to heat and oil products. Because of these superior properties, Hydrogenated Nitrile Butadiene Rubber (HNBR) has found extensive applications across various industries such as automotive (engine seals, hoses), oil & gas (seals), aerospace (seals), medical (medical devices), and food processing (seals). Its exceptional properties include high thermal stability, chemical resistance, and mechanical strength. This article presents a comprehensive overview of HNBR, discussing its synthesis, properties, applications, and future prospects. It also explores the unique and superior characteristics that distinguish HNBR from other rubbers, making it more versatile and suitable for high-end engineering applications. The chemistry of manufacturing, along with a brief description of HNBR production via emulsion NBR and solution NBR techniques, is also presented. Due to its unique and superior properties, HNBR is projected to witness massive growth in the future, with increased usage in various high-performance applications, including the automotive, oil & gas, and industrial sectors.

Keywords: Nitrile butadiene rubber (NBR), hydrogenated nitrile butadiene rubber (HNBR), hydrogenation, automotive application, aerospace application

INTRODUCTION

Synthetic rubbers are integral materials in the production of industrial products that require flexibility, resilience, and durability under extreme conditions. Among the several types of synthetic rubbers available today, Hydrogenated Nitrile Butadiene Rubber (HNBR) stands out because of its superior thermal stability, enhanced chemical resistance, and excellent mechanical properties. These characteristics make HNBR a key material for niche applications in industries such as automotive, aerospace, oil and gas, and manufacturing.

***Author for Correspondence**
Sandeep Rai
E-mail: sadeep1964@yahoo.co.in

[1]General Manager R&D, Dyne Chemicals LLP, 3312/18, Chhatral GIDC, Phase-IV, Taluka - Kalol, District - Gandhinagar, Gujarat, India
[2]Application Manger, Dyne Chemicals LLP, 3312/18, Chhatral GIDC, Phase-IV, Taluka - Kalol, District - Gandhinagar, Gujarat, India

Received Date: March 04, 2025
Accepted Date: March 19, 2025
Published Date: April 10, 2025

Citation: Sandeep Rai, Pradeep Uthale. Hydrogenated Nitrile Butadiene Rubber (HNBR): A Comprehensive Review. Journal of Materials & Metallurgical Engineering. 2025; 15(2): 14–22p.

The growing demand for advanced, high-performance elastomeric materials with improved properties has propelled the development and usage of HNBR in critical applications where standard rubber would fail. These applications include oil seals, gaskets, and O-rings, where HNBR is

engineered to perform reliably under extreme conditions such as high temperatures, exposure to harsh reactive chemicals, and demanding mechanical stresses.

This article aims to explore the chemistry, manufacturing processes, and diverse applications of HNBR, along with the factors contributing to its growing prominence.

CHEMISTRY AND SYNTHESIS OF HNBR

Nitrile Butadiene Rubber

Before diving into HNBR chemistry, it is essential to understand chemistry of the base material, NBR, from which HNBR is derived. Using a well-known emulsion polymerization technique, butadiene and acrylonitrile are typically polymerized to create nitrile butadiene rubber, a copolymer. NBR is the only synthetic rubber which possess unique property, that is, oil resistance in addition to excellent chemical and thermal resistance properties.

However, NBR possess very poor ozone resistance. The ratio of butadiene to acrylonitrile affects the material's properties. In fact, bound acrylonitrile content (BACN) alters the properties significantly. Higher acrylonitrile content provides better oil and fuel resistance but can decrease the rubber's flexibility exhibits decent mechanical properties, low compression set, and resistance to oil, fuels, and solvents, making it a popular choice in automotive and industrial applications. However, its performance at higher temperatures and exposure to oxidation is limited, so overcoming these performance limitations led to the development of HNBR.

Hydrogenation Process

The hydrogenation of NBR involves treating the copolymer with hydrogen in the presence of a catalyst (usually a nickel or platinum catalyst). The butadiene units' double bonds are broken down into single bonds by the hydrogen atoms.

This process saturates the polymer, which reduces its susceptibility to oxidation and enhances its thermal stability (Figure 1). The extent (%) of hydrogenation of NBR can vary, resulting in different grades of HNBR with different characteristics. The degree of hydrogenation influences the material's performance in different environments. Typically, a higher degree of hydrogenation improves the polymer's resistance to heat, ozone, and chemical degradation (Figure 2).

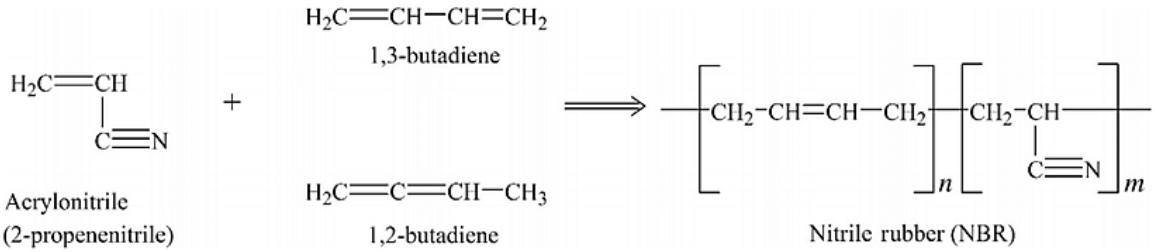

Figure 1. Chemical reaction to produce nitrile butadiene rubber (NBR).

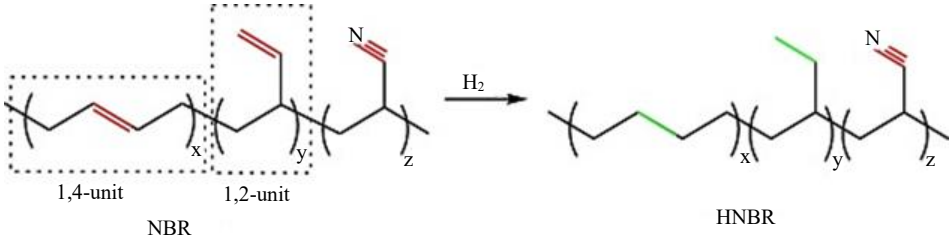

Figure 2. Chemical reaction to produce hydrogenated nitrile butadiene rubber (HNBR) from NBR by hydrogenation [1].

Methods for Production of HNBR

There are three ways to prepare HNBR, and the specifics of each are listed below:

Ethylene Acrylonitrile Copolymerization Method [2]

This process copolymerizes acrylonitrile and ethylene to create HNBR. But each monomer's reaction rate in the copolymerization reaction varies a lot (rAN = 0.04, rE = 0.8), making it very hard to control. The polymer's performance is also poor; thus the approach is still in the development stage as a tiny pilot research.

NBR Emulsion Hydrogenation [3]

Diimide, an efficient hydrogenation agent, is produced by the thermal breakdown of *p*-methyl sulfonyl hydrazide in the emulsion hydrogenation process of NBR. Wideman first described this process for creating an HNBR emulsion with diimide in 1984 [2, 3]. They discovered that NBR latex could produce HNBR directly when exposed to oxidants like hydrazine hydrate, oxygen, or hydrogen peroxide, as well as metal ion initiators like copper and iron. Additionally, the emulsion hydrogenation process for producing HNBR latex was reported by Parker and colleagues at Good Year Rubber & Tire Company in the United States. However, this approach is still in the development stage because of the sluggish hydrogenation reaction and high cost of the hydrogenated masterbatch (*p*-toluene sulfonyl hydrazide).

NBR Solution Hydrogenation [4]

NBR solution comprising hydrogen gas and the precious metals palladium, calcium, and rhodium as catalysts is used to hydrogenate NBR. The oil resistance of NBR is determined by the amount of bound acrylonitrile in its molecular chain. The side chain eyeball group -C≡N of the acrylonitrile unit is not hydrogenated during the hydrogenation of NBR; only the diene unit's double bond is selectively hydrogenated and transformed into saturated bonds. The two primary catalyst types used in this hydrogenation process are homogeneous coordination catalysts and non-homogeneous carrier catalysts. The Pd/C catalyst with carbon carrier is the first non-homogeneous carrier catalyst. It has a high selectivity and a hydrogenation rate of up to 95.6%. However, during the hydrogenation reaction, diene rubber's affinity for carbon black may be readily adsorbed on the carbon black's surface, and the carbon black can readily coagulate into lumps when stirred. This will negatively impact the vulcanization properties of HNBR. Pd/SiO_2 catalysts that use SiO_2 as the carrier have since been made available for purchase.

CATALYTIC HYDROGENATION OF NBR: CHEMICAL AND THERMAL RESISTANCE IMPROVEMENT

Acrylonitrile-butadiene rubber, a copolymer of acrylonitrile (ACN) and 1,3-butadiene in various ratios, is used to make hydrogenated NBR elastomer on a commercial basis. The double bonds of the butadiene monomer remain in the NBR main chain even after polymerization, and due to double bond, this polymer chain is susceptible to chemical attack, thermal degradation and oxidation. By using catalytic hydrogenation to change double bonds into stable single bonds and NBR into HNBR, this drawback can be removed.

HYDROGENATION OF NBR

The catalyst used in the quantitative hydrogenation of NBR must be highly active and selective in order to hydrogenate just the olefinic double bonds and not the nitrile groups. The optimum catalysts for the NBR hydrogenation process are heterogeneous palladium or homogeneous rhodium (I) catalysts.

Heterogeneously Catalyzed Hydrogenation of NBR [5]

On industrial scale, the heterogeneous hydrogenation of NBR is carried out using palladium (Pd) as the active metal as catalyst. Palladium ranging from 0.01 to 1.0 weight percent is used to achieve complete hydrogenation. In order to accomplish full hydrogenation with a lesser quantity of palladium, Group 1 to 6 metals, such as calcium, titanium, zirconium, or vanadium, are also utilized as promotors

with Pd. In polymer solutions containing 10 weight percent NBR rubber, the reaction between NBR and HNBR typically occurs at 50°C and 50 bar of hydrogen pressure. After the reaction is finished, the catalyst is removed by centrifugation or filtration. After removing the catalyst and assessing its activity, it can be utilized again [6].

Homogeneously Catalyzed Hydrogenation [7]

Only Wilkinson's catalyst (chloridoids(triphenylphosphine)-rhodium(I)) and hydridotetrakis(triphenylphosphine)rhodium(I){$HRh[P(C_6H_5)_3]_4$} are used for homogeneously catalyzed NBR hydrogenation. Without reducing the nitrile groups, both catalysts are successful in quantitatively hydrogenating the C=C double bonds.

The temperature range for this reaction is 100°C to 150°C, while the pressure range is 30 to 85 bars. Complete hydrogenation was found to take over 10 hours at reduced pressure. As the pressure increases, the reaction time decreases by a few hours. Homogeneous catalysts are inert after recovery and cannot be utilized again without undergoing chemical regeneration treatment (Figures 3 and 4).

Heterogeneous Hydrogenation of NBR [8]

Reaction of Hydrogenation of NBR for HNBR Production

It is produced through a two-step process: emulsion polymerization followed by selective hydrogenation.

1. *Emulsion Polymerization of NBR:* The process begins with the emulsion polymerization of acrylonitrile (ACN) and butadiene to form nitrile butadiene rubber (NBR). This occurs in an aqueous medium with the help of surfactants and initiators (typically peroxides or redox systems). The acrylonitrile content can be varied depending on the desired properties like oil resistance and flexibility.
2. *Hydrogenation:* The unsaturated double bonds in the butadiene segments of NBR are then selectively hydrogenated using a catalytic hydrogenation process (usually with homogeneous catalysts like Wilkinson's catalyst or heterogeneous ones like palladium on carbon). This step saturates the double bonds, significantly improving the rubber's resistance to thermal and oxidative degradation.

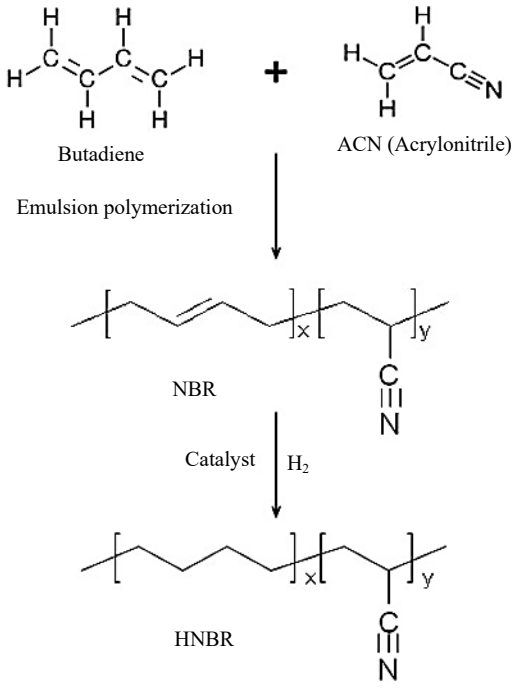

Figure 3. Industrial process for production of hydrogenated nitrile butadiene rubber (HNBR) [9].

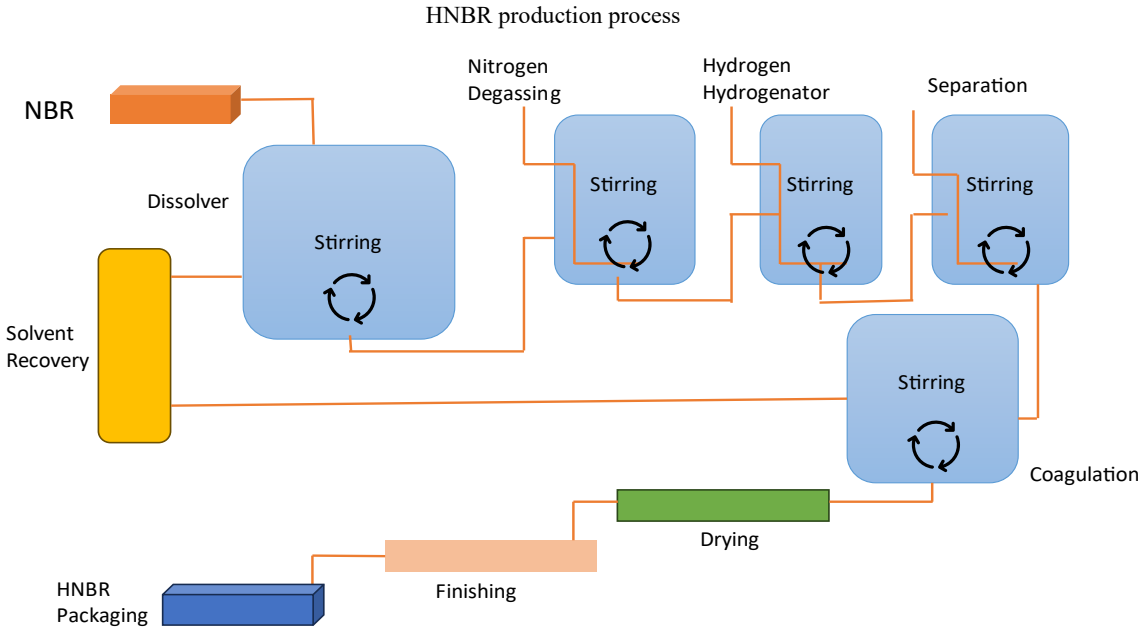

Figure 4. Overview of hydrogenated nitrile butadiene rubber (HNBR) production plant [10].

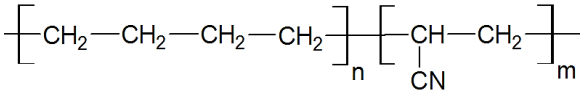

Figure 5. Chemical structure of hydrogenated nitrile butadiene rubber (HNBR).

Structure of HNBR

The molecular structure of HNBR consists of alternating butadiene and acrylonitrile units, with the butadiene component is fully hydrogenated. The hydrogenation of NBR results in a modified polymer with saturated carbon-carbon bonds, which is more stable and resistant to oxidative and thermal degradation than the unmodified unsaturated NBR (Figure 5).

This modification makes HNBR a more versatile material, capable of withstanding harsher environmental conditions and maintaining its mechanical properties even under such harsh conditions during applications.

PROPERTIES OF HNBR

The properties of HNBR are largely determined by its molecular structure, which has been optimized for high performance. These properties enable HNBR to outperform many other rubbers, especially in extreme conditions.

Thermal Stability [11–13]

One of the key advantages of HNBR over NBR and other types of rubber is its exceptional thermal stability. HNBR can withstand temperatures ranging from –40°C to 170°C (–40°F to 338°F), and in some formulations, it can endure even higher temperatures without significant degradation. This makes it ideal for use in automotive engines, oil refineries, and other applications where high temperatures are prevalent.

Chemical Resistance [14]

Oils, fuels, acids, alkalis, and solvents are just a few of the many substances to which HNBR has exceptional resistance. This resistance is particularly useful in industries such as oil and gas, where materials must be exposed to harsh chemicals over extended periods. HNBR's chemical resistance is significantly better than that of NBR, which makes it a superior choice for sealing and gasketing applications where exposure to aggressive chemicals is common.

Mechanical Properties [15, 16]

HNBR possesses high tensile strength, excellent elongation at break, and superior resilience. These mechanical properties make it suitable for demanding sealing applications, where the rubber must maintain its integrity under pressure, while also providing flexibility and elasticity.

Aging and Ozone Resistance [17]

The hydrogenation process reduces the presence of double bonds in the polymer structure, which in turn minimizes the susceptibility of the material to ozone and oxidative aging. As a result, HNBR has improved resistance to degradation from environmental factors like sunlight, oxygen, and ozone. This gives HNBR a much longer service life compared to non-hydrogenated rubbers.

Swelling and Compression Set Resistance [18]

HNBR shows excellent resistance to swelling in contact with oils and fuels. It also exhibits a low compression set, meaning that it can maintain its original shape and performance even after being subjected to long-term compression. These features make HNBR a reliable choice for sealing and gasket applications where dimensional stability is critical.

APPLICATIONS OF HNBR [19]

Its qualities make it essential for a wide range of high-performance applications in many different industries. Here are a few of the industries that use HNBR most frequently.

Automotive Industry [20]

In the automotive sector, HNBR is used in a variety of applications due to its high resistance to heat, oil, and fuel. These include:

- *O-rings and seals* [21]: HNBR's resistance to high temperatures and chemical exposure makes it ideal for seals in engine compartments, including gaskets, O-rings, and fluid seals.
- *Timing belts and hoses* [22]*:* HNBR is often used in the manufacture of belts and hoses that need to resist high temperatures and exposure to automotive fluids.
- *Fuel systems:* Its superior fuel resistance makes it a perfect material for sealing components in fuel systems and ensuring the longevity and safety of automotive parts.

Oil and Gas Industry [23]

Materials that can tolerate high temperatures, high pressures, and exposure to harsh chemicals are required by the oil and gas sector. HNBR's chemical resistance and ability to function in harsh environments make it the go-to material for the following applications:

- *Seals and gaskets:* HNBR is used extensively in seals for drilling, exploration, and production equipment. It is the perfect option for subsea and offshore applications because to its resilience to high temperatures and oil.
- *Downhole tools [24]:* HNBR is often used in downhole drilling tools, including packers and sealing elements, which are exposed to oil, gas, and extreme temperatures.

Aerospace and Aviation [25]

In the aerospace industry, materials are required to perform reliably in extreme conditions, including fluctuations in temperature, exposure to oils, and high-pressure environments. HNBR's high thermal stability and resistance to oils make it suitable for applications such as:

- *Seals for hydraulic systems:* HNBR is used in hydraulic systems of aircraft where it can withstand high temperatures and pressures.
- *O-rings and gaskets:* Its reliability in sealing systems that operate under high mechanical stresses makes HNBR a preferred choice.

Industrial Applications [26]

HNBR's mechanical strength, chemical resistance, and durability make it an excellent choice for industrial seals, gaskets, and hoses used in a variety of manufacturing processes. This includes:

- *Gasket material* [27]: HNBR gaskets are used in applications where exposure to extreme chemicals and temperatures occurs, such as in the chemical and power generation industries.
- *Pumps and compressors* [28]: HNBR's ability to resist degradation in aggressive environments makes it ideal for use in pumps, compressors, and other machinery that handle harsh fluids.

Medical and Food Processing [29]

HNBR's resistance to oils and chemicals also extends to medical applications, where it is used in seals, gaskets, and diaphragms. Its non-toxic properties and ability to withstand sterilization processes make it a viable material for medical devices and food processing equipment.

FUTURE TRENDS AND INNOVATIONS

As industries evolve and demand for higher-performance materials increases, HNBR is likely to remain a central material for high-stress applications. Some trends and innovations in HNBR include:

Enhanced Hydrogenation Techniques [30]

Ongoing research is focused on improving the hydrogenation process to achieve even higher degrees of saturation. This could improve the rubber's tolerance to high temperatures and increase its use in more specialized applications, among other benefits.

Sustainability and Recycling [30]

As industries look for more sustainable solutions, there is an increasing emphasis on recycling and reusing materials. HNBR's resistance to chemical degradation might offer new pathways for recycling and reusing scrap material in applications where high-performance rubber is needed.

Smart HNBR

Emerging technologies such as the integration of smart sensors into elastomers could create "smart" HNBR materials. These rubbers could have self-monitoring capabilities that can signal when they are reaching the end of their service life, improving safety and reliability in high-risk applications.

CONCLUSION

HNBR represents a significant advancement in the field of synthetic elastomers, offering a unique combination of properties that make it a critical material for numerous high-performance applications. Its superior thermal stability, chemical resistance, and mechanical strength set it apart from other rubbers, making it indispensable in industries such as automotive, oil and gas, aerospace, and manufacturing. As technological advancements continue and new manufacturing techniques emerge, the role of HNBR in critical applications is set to expand. Whether through further improvements in its hydrogenation process, developments in sustainability, or the potential integration of smart technology, HNBR's future remains promising. In industries that require materials to withstand extreme conditions, HNBR will likely continue to be the material of choice for decades to come.

REFERENCES

1. Ai C, Li J, Gong G, Zhao X, Liu P. Preparation of hydrogenated nitrile-butadiene rubber (H-NBR) with controllable molecular weight with heterogeneous catalytic hydrogenation after degradation via olefin cross metathesis. Reactive Funct Polym. 2018; 129: 53–57. doi: 10.1016/j.react functpolym.2017.12.016.
2. Chaudry RA. Investigation of Degradation of NBR and HNBR Elastomers by Light Scattering Rheology and Molecular Dynamics Techniques. Master's Thesis. Dharan, Saudi Arabia: King Fahd University of Petroleum and Minerals; 2008.

3. Wang X, Zhang L, Han Y, Shi X, Wang W, Yue D. New method for hydrogenating NBR latex. J Appl Polym Sci. 2013; 127 (6): 4764–4768. doi: 10.1002/APP.38009.
4. Zhou S, Bai H, Wang J. Hydrogenation of acrylonitrile–butadiene rubber latexes. J Appl Polym Sci. 2004; 91 (4): 2072–2078.
5. Rempel GL. Catalytic hydrogenation of nitrile butadiene rubber. Abstr Papers Am Chem Soc. 2000; 220: U247.
6. Liu M. Hydrogenation of Nitrile and Olefinic Groups in Butadiene Rubbers. PhD Thesis. Waterloo, Ontario, Canada: University of Waterloo; 2014.
7. Yin Y, Cheng T, Bao X, Yuan P. Deactivation and regeneration of heterogeneous catalysts for hydrogenation of nitrile butadiene rubber. CIESC J. 2019; 70 (7): 2528–2539.
8. Wang H, Yang L, Rempel GL. Homogeneous hydrogenation art of nitrile butadiene rubber: a review. Polym Rev. 2013; 53 (2): 192–239. doi: 10.1080/15583724.2013.776586.
9. Goettler LA. Handbook of Elastomers. New York, NY, USA: Marcel Dekker; 1988. pp. 215–244.
10. Nakagawa T, Toya T, Oyama M. Ozone resistance of highly saturated nitrile rubber (HNBR). J Elastomers Plast. 1992; 24 (3): 240–261.
11. Wrana C, Reinartz K, Winkelbach HR. Therban®–the high performance elastomer for the new millennium. Macromol Mater Eng. 2001; 286 (11): 657–662.
12. Chen X, Krejci M, Drake A, Salem H, Mozisek T. Chemical resistance of HNBR and NBR in propylene. Rubber Chem Technol. 2025; 98 (1): 169–185.
13. Chang X, Yin H, Lyu Y, Shi X, Hoch M. HNBR-based composite for seals used in coolant fluids: swelling related to different silicates at high temperature. Polymer. 2019; 178: 121691.
14. Alcock B, Jørgensen JK. The mechanical properties of a model hydrogenated nitrile butadiene rubber (HNBR) following simulated sweet oil exposure at elevated temperature and pressure. Polym Testing. 2015; 46: 50–58.
15. Mengistu T, Pazur RJ. The thermal oxidation of hydrogenated acrylonitrile-co-butadiene rubber from ambient to 150 C. Polym Degrad Stabil. 2021; 188: 109574.
16. Han Y, Nie J, Zhu Z, Yin H, Shi L, Wang S, Liu X, He Q. Investigation of mechanical properties and oil resistance of hydrogenated-butadiene-acrylonitrile-rubber-based composites across various temperatures. Polymers. 2024; 16 (23): 3294.
17. Chen L, Lin W, Han Y, Ai Z, Kuang Y, Yang C. Simulation and experimental study of a new structural rubber seal for the roller-cone bit under high temperature. Adv Mech Eng. 2020; 12 (12): 1687814020985622.
18. Sexsmith FH. Rubber-to-metal bonding. In: Bhowmick AK, Hall MH, Benarey HA, editors. Rubber Products Manufacturing Technology. New York, NY, USA: Routledge; 2018. pp. 449–472.
19. Nasreddine V, Pazur RJ. HNBR: Fulfilling requirements of auto and heavy duty vehicle applications. Rubber World. 2008; 238 (1): 31–38.
20. Hassani F, Faisal NH, Nish R, Rothnie S, Njuguna J. The impact of thermal ageing on sealing performance of HNBR packing elements in downhole installations in oilfield wellhead applications. J Petrol Sci Eng. 2022; 208: 109200.
21. Qiao Z, Guo Y, Zhang Z, Wang D. Comparative study of reciprocating sliding wear of HNBR on the effects of temperature. J Phys Conf Ser. 2024; 2680 (1): 012047.
22. Jiang X, Wang C, Liu S, Wang H, Yu J, Liu G. Influence of aviation hydraulic oil swelling on the mechanical properties of HNBR/EPDM vulcanizates reinforced by carbon black. J Appl Polym Sci. 2023; 140 (9): e53549.
23. Psarras GC, Sofos GA, Vradis A, Anastassopoulos DL, Georga SN, Krontiras CA, Karger-Kocsis J. HNBR and its MWCNT reinforced nanocomposites: crystalline morphology and electrical response. Eur Polym J. 2014; 54: 190–199.
24. de Ruijter PQ, de Bittencourt Ribeiro E, Zanzi MD, de Souza EL, Goes Oliveira JL, Paiva KV, Benedet Dutra G. HNBR and NBR gasket rubbers for plate heat exchangers: thermo-oxidative aging and service lifetime prediction. J Appl Polym Sci. 2024; 141 (10): e55055.
25. Balasooriya W, Schrittesser B, Wang C, Hausberger A, Pinter G, Schwarz T. Tribological behavior of HNBR in oil and gas field applications. Lubricants. 2018; 6 (1): 20.

26. Grob K. The role of the European Food Safety Authority (EFSA) in a better European regulation of food contact materials – some proposals. Food Addit Contaminants Part A. 2019; 36 (12): 1895–1902.
27. Alarifi IM. A comprehensive review on advancements of elastomers for engineering applications. Adv Indus Eng Polym Res. 2023; 6 (4): 451–464.
28. Wang H, Yang L, Rempel GL. Homogeneous hydrogenation art of nitrile butadiene rubber: a review. Polym Rev. 2013; 53 (2): 192–239.
29. Zhao G, Wang Z, Liu T, Zhang X. Recycling of used hydrogenated nitrile butadiene rubber through powder modification by trans-polyoctylene rubber. Ann Chim Sci Matériaux. 2019; 43 (6): 383–388.
30. Saha S, Bhowmick AK. Smart thermoplastic elastomers with high extensibility from poly (vinylidene fluoride) and hydrogenated nitrile rubber: processing–structure–property relationship. Rubber Chem Technol. 2018; 91 (1): 268–295.

