



HNBR – CHARACTERISTICS & GENERAL COMPOUNDING – AN OVERVIEW

HNBR – HYDROGENATED ACRYLONITRILE BUTADIENE RUBBER

Modern automotive engineering demands elastomers that can withstand high temperatures and aggressive substances and can meet the particular requirements of fuel-saving engine and carbody designs. The demands in the oil exploration industry are just as stringent. Here, elastomers must weather aggressive environments and high mechanical stresses. Standards were set in these fields over 25 years ago with the invention of **HNBR (Hydrogenated Acrylonitrile-Butadiene Rubber)**.

HNBR polymers are high temperature and oil resistant elastomers. HNBR compounds are formulated to meet demanding applications and environments with a wide operational temperature range.

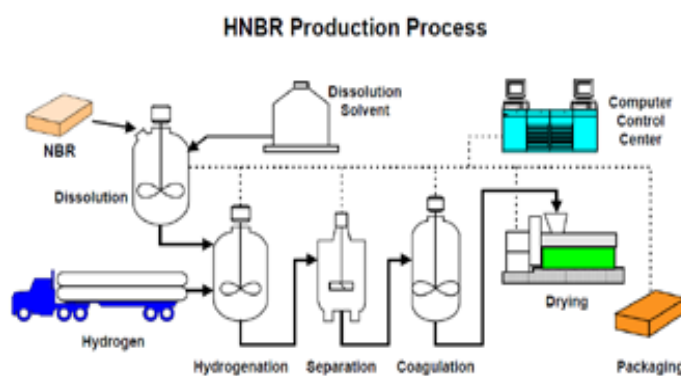
CHEMISTRY AND MANUFACTURING PROCESS

The material itself is a derivative of nitrile rubber, which is hydrogenated in solution using precious metal catalysts. The basic structure of an HNBR elastomer is provided in Figure 1. As outlined below, the process begins with the production of an emulsion-polymerized NBR. This polymer is then dissolved in an appropriate solvent. After the dissolution process is complete, the addition of hydrogen gas, in conjunction with a precious

metal catalyst at a designated temperature and pressure, brings about a selective hydrogenation to produce HNBR.

The nitrile groups are unaffected during the process, but the carbon-carbon double bonds in nitrile rubber are converted into more stable single bonds. Different grades can be made by precise control of the proportion of unconverted double bonds in the material - 10% is considered to be an upper limit, but grades containing 4-8% (partially hydrogenated) or virtually no double bonds (fully hydrogenated) are used in most cases.

Partially hydrogenated materials can be cross-linked using both sulphur and peroxide cure systems, and the fully hydrogenated grades can be cross-linked with peroxides only. This further expands the range of grades and opens up more applications for these HNBR materials.



Properties of HNBR

- High mechanical strength (up to 30 MPa) at RT.
- Good mechanical properties even at elevated temperature
- Excellent resistance to lubricants with extremely aggressive additives in engine oils, ATF, power steering fluid and coolants

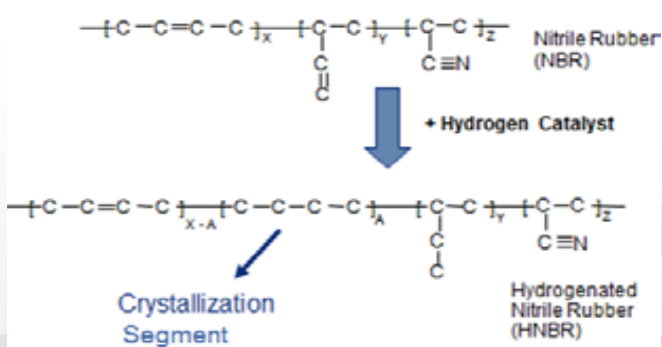


Figure 1

- Very good hot air and steam Resistance.
- Very good low temperature flexibility.
- Excellent resistance to many modern fuels including biodiesel
- Low permeability to volatiles and gases
- Good resistance to crude oil even in the presence of hydrogen sulfide, amines, alkaline corrosion inhibitors and Oxidizing media.
- Good ozone resistance
- very good abrasion resistance (DIN abrasion: 30 - 50 mm³)
- Excellent Chemical Resistance
- Low compression set even at high temperature
- Good resistance to high energy radiation
- Low noise/vibration transmission

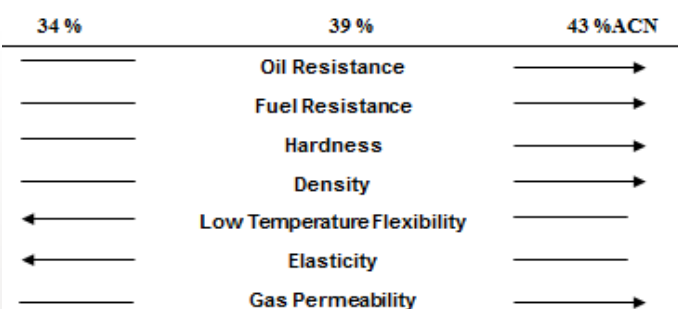
Selection Criteria for HNBR

When selecting a HNBR polymer for a specific application, three criteria to consider

1. Acrylonitrile content: fluid resistance as well as low temperature properties
2. Hydrogenation level: influences heat, chemical and ozone resistance
3. Polymer Mooney Viscosity: influences the processing of the compound and also the physical properties of the final article.

a. Effect of Acrylonitrile Content

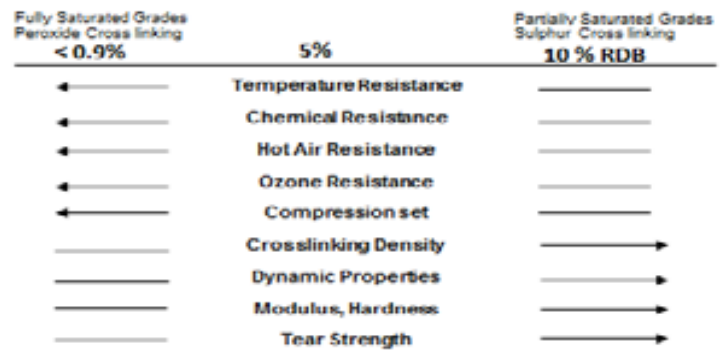
1. The nitrile group, coming from incorporated acrylonitrile monomers (ACN) strongly influences the oil resistance and low temperature flexibility.
2. Higher ACN content means better oil resistance, fuel resistance and gas permeability.
3. Higher ACN content means poorer low temperature flexibility



HNBR - Influence of Acrylonitrile Content

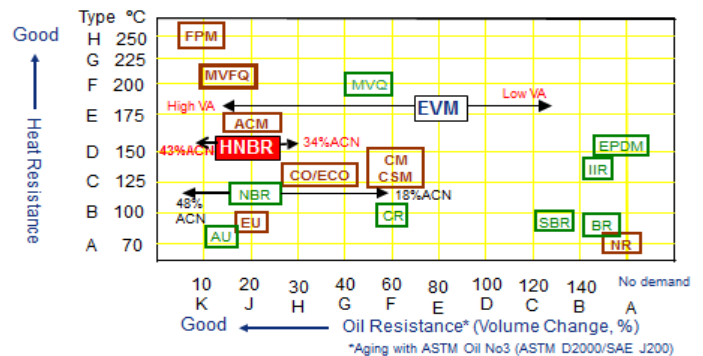
b. Effect of RDB Content

1. By controlled hydrogenation of NBR a HNBR, with different amounts of RDB (residual double bond) contents can be produced.
1. HNBR with high RDB can be cross-linked using sulfur and Peroxide
1. High RDB increases crosslinking density
1. High RDB increases the compression set and reduces the ageing stability of the material



Influence on RDB Content

Comparison of HNBR with other Polymers in term of Heat and Oil resistance



Comparison of Various Polymers in terms of Heat and Oil resistance

BASIC Compounding and Processing

- a. **Selection of Grade:** There are a wide variety of acrylonitrile (ACN) content polymers available in the HNBR today. They range from approximately 17 to 50% ACN. The ACN content not only controls fluid resistance but also impacts the low-temperature performance. If the ACN content of the polymer is increased, the volume swell of the associated compound will decrease while the low-temperature flexibility will become poorer. Alternatively, if one decreases the ACN level of the polymer, the associated compound will have higher volume swell and improved low-temperature flexibility.

Likewise, as RDB% lower, better is Heat resistance, Ozone resistance, Compression set and Chemical resistance where as higher RDB % will improve Dynamic properties, Hardness, Modulus and Crosslinking density.

Lastly, the wide range of Mooney viscosities grades available permits the compounder to choose a product which best suits their specific method of manufacturing (e.g., compression, transfer, or injection molding vs. extrusion). Today, HNBRs range in Mooney viscosity from 50 to approximately 100 when measured at ML(1+4)@100°C., with special grades having Mooney around 40.

A typical recipe of HNBR is listed in Table below

Ingredients	Phr
HNBR	100
Metal oxides	0 - 5
Antidegradents	1.5 - 3
Process Aid	0 - 3
Filler	40 - 100
Plasticizer	0 - 20
Curatives	3 - 10
Co-agents	0 - 5

- b. **Metal Oxides:** 2 - 10 Phr of ZnO/MgO recommended for Sulphur cure whereas 2 Phr of ZnO/MgO is recommended for Peroxide cure compounds, in combination with stearic acid.
- c. **Antidegradents:** Many antioxidants like Phenolic type interfere with peroxide crosslinking, affecting properties such as modulus and compression set resistance. A combination of 0.4 phr of zinc methylmercaptobenzimidazole and 1.1 phr substituted or styrenated diphenyl amine (SDPA) provides the best balance of protection together with minimum effect on vulcanizate properties, in the case of peroxide cure. For sulfur cure systems, levels of 1 phr zinc methylmercaptobenzimidazole and 2 phr SDPA are best.

Antiozonants are not needed.

- d. **Process Aids:** Process improvement additives can be incorporated in high-viscosity

formulations at nominal 2.0 phr levels, to facilitate mold flow and reduce cycle times. Generally Zinc salts of high molecular weight fatty acids are effective process aids, M C Wax like R A Wax 1080 also improves processing.

- e. **Fillers - Carbon Black:** The physical properties of HNBR compounds reinforced with carbon black depend on the particle size and structure of the black. Mostly FEF black is generally recommended to get optimum properties. Highly reinforcing black increases stiffness of compound permitting low doses. By increasing particle size of carbon black (FEF, GPF and MT) Resistance to compression set and heat resistance improve whereas tensile strength, tear resistance, and abrasion resistance are reduced.
- f. **Mineral fillers:** Precipitated silica provides the highest level of reinforcement; however, it yields very stiff, high viscosity compounds. Precipitated silicas generally improve the heat resistance of HNBR vulcanizates. Silane coupling agent improves rubber filler interaction.
- French powder (talc) is much easier to incorporate and yields comparatively similar modulus and hardness values as with silica. Blends of silica and talc are often utilized for balancing vulcanizate properties with processing characteristics.
- g. **Plasticizer:** Selection of Plasticizer is most important criteria of HNBR compounds. Plasticizers used to improve low temperature flexibility, to optimize physical properties and processing characteristics with low volatility at approx. temperature 150°C (302°F) and also resistance to extraction in oils and fuels. Generally Trimellitate plasticizers Like TOTM, TIOTM is being used. Sebacates, adipates can also be utilized but affects slightly high temperature ageing.
- h. **Vulcanization:** HNBR with less than 1% residual double bonds must be vulcanized with peroxide or high-energy radiation, as there is insufficient unsaturation to obtain a practical state of cure with sulfur systems. EV (efficient vulcanization) and semi-EV

sulfur cure systems can be used effectively with partially saturated grades to achieve improved adhesion to reinforcing substrates and to obtain favorable properties in dynamic applications.

HNBR elastomers are typically cured with either peroxide or sulfur/sulfur-donor cure systems. Comparisons of sulfur/sulfur-donor and peroxide cured HNBR compounds indicate that peroxide curing provides better compression set and heat resistance. Because HNBR has fewer highly reactive allyl position hydrogens versus other diene-based elastomers, it is necessary to add 50-100% more peroxide in order to produce excellent curing characteristics. Many kinds of peroxides are available for curing HNBR. However, it is important to select one that is the most suitable based on the process and cure temperature that will be utilized to produce the finished parts.

Since peroxides have different molecular weights and decomposition temperatures, it is imperative to select the correct one based on the criteria noted above or one can greatly affect the processability and cost-effectiveness of producing the finished goods in question.

- i. **Coagents:** Resistance to heat and compression set can be maximized by incorporating selected coagents with peroxides to increase the state of cure. Triallyl isocyanurate improves compression set properties, liquid 1,2-polybutadiene, N,N'-m-phenylene dimaleimide effective at low temperature, and trimethylolpropane trimethacrylate (TMPTMA) can be used as effective Coagents.

j. **Processing of HNBR**

All of the commercially available HNBRs can be mixed either on a two-roll mill or with an internal mixer. Most HNBRs are mixed by the use of internal mixing equipment. This is done to improve the quality of the finished compound while also significantly reducing the typical mix times.

Typically, HNBRs are two-pass mixed in an internal mixer where the first pass through the mixer without the cure chemicals and is typically dropped out of the mixer at

approximately 140°C. This master batch is then run through the mixer a second time adding the cure chemicals and again dropped from the mixer at approximately 100-110°C.

HNBR polymers generate more heat during compounding in internal mixers or on open mills than NBR polymers; however, this can improve processing due to the thermoplastic nature of the polymers.

Subsequent processing steps (extrusion, preform, moulding) should be carried out at the highest practical temperature to take advantage of the thermoplastic characteristics of the compound. This aspect of HNBR polymers is of particular importance for high-hardness formulations. Extrusion and Calendaring requires higher temperature as compare to NBR.

Application of HNBR

- 1 **Automotive:** Gaskets, Seals, Diaphragms, Boots, Timing Belts, Shaft Seals.

With the continued trend to ever decreasing space in the engine bay, temperatures continue to rise, placing ever more demanding requirements on the components operating in this environment. One consequence of this is the need for Elastomers capable of ever-greater long-term high-temperature resistance. Today's elastomer must withstand harsh environments in the engine compartment. Higher operating temperatures have resulted in the development of more aggressive automotive fluids and lubricants, further necessitating the use of specialty elastomers combining both greater heat and fluid resistance. The automotive industry seeks a



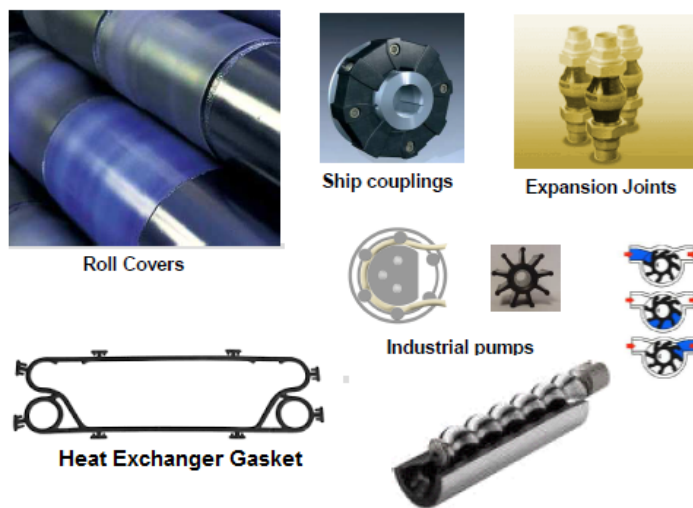
tough elastomer with improved resistance to chemical, fuel and heat. HNBR polymers offer a unique combination of resistance to coolants, fuels and oils used in today's automobiles while providing excellent compression set resistance.

2. Oil Industry: Stators, Packers, Drill Bit seals, Blow out preventors

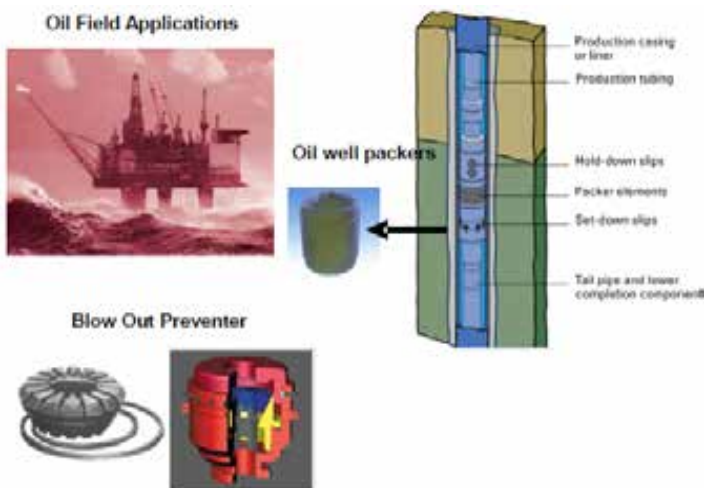
HNBR compounds meet the extreme demands in oilfield applications which require excellent properties in the harsh conditions like resistance to corrosion inhibitor, Hydrogen sulfide / Sour gas, Resistance to crude and drilling fluids, High Tear and Abrasion resistance, Low water swell. Low compression set and most importantly very good resistance to Extrusions and Explosive Decompression (Rapid Gas Decompression) seen with today's oilfield industry. While HNBR polymer can withstand the harsh abuse encountered in drilling operations, these compounds are also able to stand up to the high temperatures and pressures encountered in the well. Coupled with the excellent resistance to the various fluids such as crude oil, gases, acids and alkalis HNBR compounds can meet the demands required for application in these harsh environments.

3 Industrial and other Application: Rollers for Printing, Textile, Heat Exchanger Gaskets, Expansion jointing's, Pumps and Couplings, Textile applications like Spinning cots and Aprons etc.

Due to the ethylene content of HNBR polymers, they are resistant to many chemicals used in the roll industry offering excellent heat and steam resistance, for plate heat exchanger for Fat/Oil application, it provides high temperature resistance and low compression set at high temperature including FDA. It is also being used as expansion joint, Industrial pumps, Couplings etc for very good dynamic properties and heat resistance.



Note: For the requirement of HNBR, kindly contact us.



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BRANCHES

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|----------------|---------------------------------------|-----------|------------------------|
| Tamil Nadu | : Chennai, Hosur, Madurai, Coimbatore | Kerala | : Trissur, Ernakulam |
| Andhra Pradesh | : Hyderabad | Karnataka | : Bangalore, Belgaum |
| West Bengal | : Kolkata | NCR | : Faridabad, Ghaziabad |
| Maharashtra | : Mumbai | | |