

ACRYLONITRILE-BUTADIENE RUBBER (NBR)

Properties and Applications

Nitrile Rubber (NBR) is commonly considered the workhorse of the industrial and automotive rubber products industries. NBR is actually a complex family of unsaturated copolymers of acrylonitrile and butadiene. By selecting an elastomer with the appropriate acrylonitrile content in balance with other properties, the rubber compounder can use NBR in a wide variety of application areas requiring oil, fuel, and chemical resistance. In the automotive area, NBR is used in fuel and oil handling hose, seals and grommets, and water handling applications. With a temperature range of -40°C to $+125^{\circ}\text{C}$, NBR materials can withstand all but the most severe automotive applications. On the industrial side NBR finds uses in roll covers, hydraulic hoses, conveyor belting, graphic arts, oil field packers, and seals for all kinds of plumbing and appliance applications. Worldwide consumption of NBR is expected to reach 368,000 metric tons annually by the year 2005[1].

Like most unsaturated thermoset elastomers, NBR requires formulating with added ingredients, and further processing to make useful articles. Additional ingredients typically include reinforcement fillers, plasticizers, protectants, and vulcanization packages. Processing includes mixing, pre-forming to required shape, application to substrates, extrusion, and vulcanization to make the finished rubber article. Mixing and processing are typically performed on open mills, internal mixers, extruders, and calenders. Finished products are found in the marketplace as injection or transfer molded products (seals and grommets), extruded hose or tubing, calendered sheet goods (floor mats and industrial belting), or various sponge articles. Figure 1 shows some typical molded and extruded rubber products.

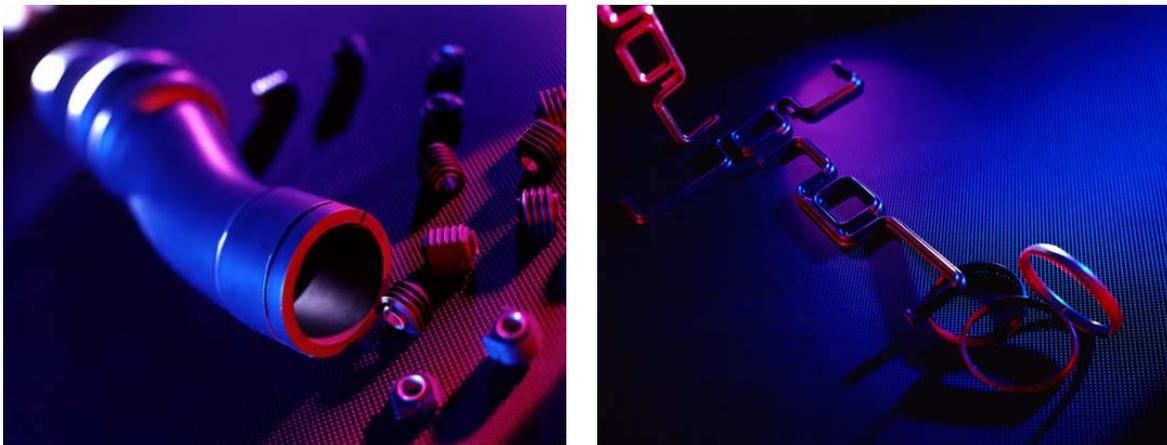


Figure 1: Typical Finished Rubber Articles

Chemistry and Manufacturing Process

NBR is produced in an emulsion polymerization system. The water, emulsifier/soap, monomers (butadiene and acrylonitrile), radical generating activator, and other ingredients are introduced into the polymerization vessels. The emulsion process yields a polymer latex that is coagulated using various materials (e.g. calcium chloride, aluminum sulfate) to form crumb rubber that is dried and compressed into bales. Some specialty products are packaged in the crumb form. Most NBR manufacturers make at least 20 conventional elastomer variations, with one global manufacturer now offering more than 100 grades from which to choose[2]. NBR producers vary polymerization temperatures to make "hot" and "cold" polymers. Acrylonitrile (ACN) and butadiene (BD) ratios are varied for specific oil and fuel resistance and low temperature requirements. Specialty NBR polymers which contain a third monomer (e.g. divinyl benzene, methacrylic acid) are also offered[3,4]. Some NBR elastomers are hydrogenated[5] to reduce the chemical reactivity of the polymer backbone, significantly improving heat resistance (see HNBR product summary). Each modification contributes uniquely different properties. Figure 2 shows the typical NBR manufacturing process.

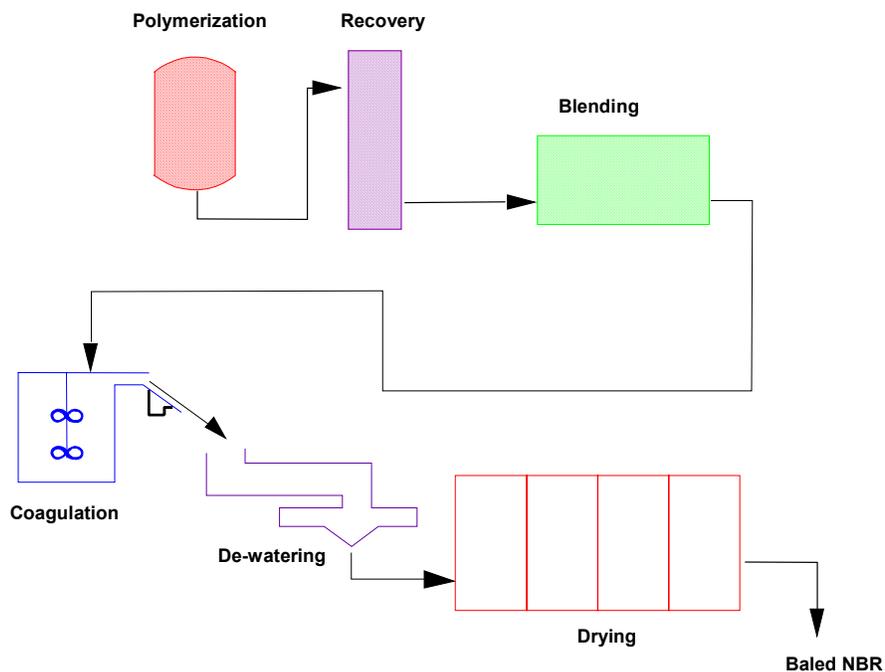


Figure 2: NBR Manufacturing Process

Acrylonitrile (ACN) Content

The ACN content is one of two primary criteria defining each specific NBR grade. The ACN level, by reason of polarity, determines several basic properties, such as oil and solvent resistance[6,7], low-temperature flexibility/glass transition temperature, and abrasion resistance. Higher ACN content provides improved solvent, oil and abrasion resistance, along with higher glass transition temperature. Table 1 below summarizes most of the common properties for conventional NBR polymers. The direction of the arrows signifies an increase/improvement in the values.

Table 1: NBR Properties – Relationship to Acrylonitrile Content [8]

<u>NBR with Lower Acrylonitrile Content</u>	<u>NBR with Higher Acrylonitrile Content</u>
	Processability →
	Cure Rate w/Sulfur Cure System →
	Oil/Fuel Resistance →
	Compatibility w/Polar Polymers →
	Air/Gas Impermeability →
	Tensile Strength →
	Abrasion Resistance →
	Heat-Aging →
←	Cure Rate w/Peroxide Cure System
←	Compression Set
←	Resilience
←	Hysteresis
←	Low Temperature Flexibility

Mooney Viscosity and Polymer Architecture

Mooney viscosity is the other commonly cited criterion for defining NBR. The Mooney test is reported in arbitrary units and is the current standard measurement of the polymer's collective architectural and chemical composition. The Mooney viscosity provides data measured under narrowly defined conditions, with a specific instrument that is fixed at one shear rate. Mooney viscosity of polymers will normally relate to how they will be processed. Lower Mooney viscosity materials (30 to 50) will be used in injection molding, while higher Mooney products (60 to 80) can be more highly extended and used in extrusion and compression molding. More definitive polymer characterization can now be achieved using newer instruments and techniques that measure properties at shear rates pertinent to specific processing requirements. Using these newer instruments, such as the RPA2000, MDR2000, Capillary Die Rheometer and the newer Mooney machines, it is now possible to rheologically measure elastic, as well as viscous characteristics. The RPA2000 and MDR2000 also measure cure rates and cure states.

General Types of NBR

Cold NBR

The current generation of cold NBR's spans a wide variety of compositions. Acrylonitrile content ranges from 15% to 51%. Mooney values range from a very tough 110, to pourable liquids, with 20-25 as the lowest practical limit for solid material. They are made with a wide array of emulsifier systems, coagulants, stabilizers, molecular weight modifiers, and chemical compositions. Third monomers are added to the polymer backbone to provide advanced performance. Each variation provides a specific function.

Cold polymers are polymerized at a temperature range of 5 to 15°C[9], depending on the balance of linear-to-branched configuration desired. The lower polymerization temperatures yield more-linear polymer chains. Reactions are conducted in processes universally known as continuous, semi-continuous and batch polymerization. Figure 3 shows the chemical structure of NBR, indicating the three possible isomeric structures for the butadiene segments.

Nitrile Rubber (NBR)

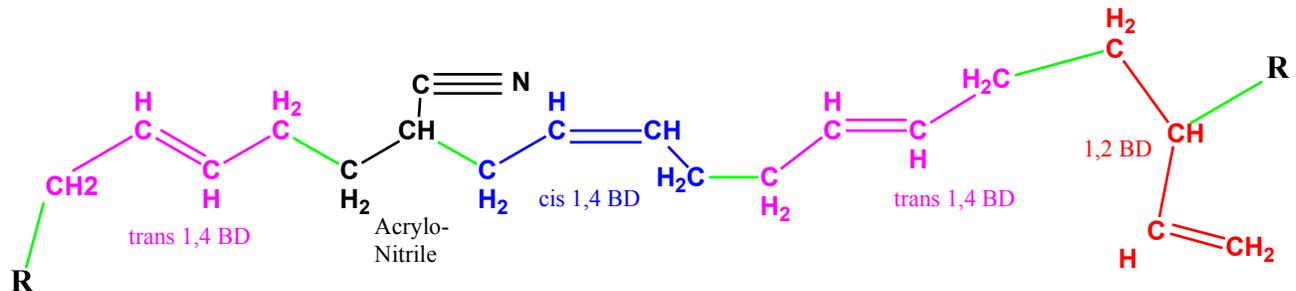


Figure 3: NBR Structure

Hot NBR

Hot NBR polymers are polymerized at the temperature range of 30 to 40°C[9]. This process yields highly branched polymers. Branching supports good tack and a strong bond in adhesive applications. The physically entangled structure of this kind of polymer also provides a significant improvement in hot tear strength compared with a cold-polymerized counterpart. The hot polymers' natural resistance to flow makes them excellent candidates for compression molding and sponge. Other applications are thin-walled or complex extrusions where shape retention is important

Crosslinked Hot NBR

Crosslinked hot NBR's are branched polymers that are further cross-linked by the addition of a di-functional monomer. These products are typically used in molded parts to provide sufficient molding forces, or back pressure, to eliminate trapped air. Another use is to provide increased dimensional stability or shape retention for extruded goods and calendered goods. This leads to more efficient extruding and vulcanization of intricate shaped parts as well as improved release from calender rolls. These NBR's also add dimensional stability, impact resistance, and flexibility for PVC modification.

Carboxylated Nitrile (XNBR)

Addition of carboxylic acid groups to the NBR polymer's backbone significantly alters processing and cured properties[10]. The result is a polymer matrix with significantly increased strength, measured by improved tensile, tear, modulus and abrasion resistance. The negative effects include reduction in compression set, water resistance, resilience and some low-temperature properties.

Bound Antioxidant NBR

Nitrile rubbers are available with an antioxidant polymerized into the polymer chain[11,12]. The purpose is to provide additional protection for the NBR during prolonged fluid service or in cyclic fluid and air exposure. When compounding with highly reinforcing furnace carbon black the chemical reactivity between the polymer and the pigment can limit hot air aging capability. Abrasion resistance is improved when compared with conventional NBR, especially at elevated temperatures. They have also been found to exhibit excellent dynamic properties.

Major Producers

The major producers of NBR include:

Company	Production Locations
Bayer	Canada; France
Girsa	Mexico
Hyundai	South Korea
JSR Corporation	Japan
Kumho	South Korea
Nantex	Taiwan
Nitriflex	Brazil
PetroChina	China
Petroflex	Brazil
Polimeri Europa	Italy
Zeon Chemicals	USA
Zeon Chemicals Europe	UK
Zeon Corporation	Japan

Conclusion

NBR is and will continue to be a complex family of workhorse elastomers. The unique balance of oil, chemical, heat and cold resistance allows it to work well in a wide variety of automotive and industrial applications. The family is well differentiated to include general purpose types for cost sensitive applications and specialty products (XNBR, Hot-Crosslinked NBR, HNBR) for more demanding service conditions.

References

1. Table 2, Worldwide Long Term New Rubber Consumption Forecast by Elastomer Type, *IISRP Worldwide Rubber Statistics* (2001).
2. Table 14, Nitrile Dry Rubber (NBR), *IISRP Synthetic Rubber Manual, 13th Edition*, (1995).
3. *Op. cit.*, Table 21, Nitrile Carboxylated Rubber (XNBR).
4. *Op. cit.*, Table 14.
5. *Op. cit.*, Table 46, Highly Saturated Nitrile Rubber (HNBR).
6. Mackey, D. and Jorgensen, A.H., *Elastomers, Synthetic (Nitrile Rubber)*, Kirk-Othmer Concise Encyclopedia of Chemical Technology, 4th Edition, 687-688 (1999).
7. Hofmann, W., *NITRILE RUBBER*, Rubber Chemistry and Technology, A RUBBER REVIEW for 1963, 154-160 (1964).
8. *Ibid.*, 71.
9. Semon, W.L., *NITRILE RUBBER, SYNTHETIC RUBBER*, Division of Chemistry, American Chemical Society, 802-3 (1954).
10. Technical Brochure, *CHEMIGUM[®] NX775*, No. 439500-10/91 GOODYEAR CHEMICAL DIVISION (1991).
11. Kline, R. *Polymerizable Antioxidants in Elastomers*, Presented at Rubber Division Meeting, ACS, Toronto, Canada (1974).
12. Horvath, J.W., Paper No. 18, *Dynamic Properties of Nitrile Rubbers*, Presented at Rubber Division Meeting, ACS, Las Vegas, Nevada (1990).