

HYDROGENATED NITRILE BUTADIENE RUBBER (HNBR)

PROPERTIES AND APPLICATIONS

HNBR is widely known for its physical strength and retention of properties after long-term exposure to heat, oil, and chemicals. Depending on filler selection and loading, HNBR compounds typically have tensile strengths of 20 – 31 MPa when measured at 23°C. Compounding techniques allow for HNBR to be used over a broad temperature range, -40° to 165°C, with minimal degradation over long periods of time. For low-temperature performance, low ACN grades should be used; high-temperature performance can be obtained by using highly saturated HNBR grades with white fillers. As a group, HNBR elastomers have excellent resistance to common automotive fluids (e.g., engine oil, coolant, fuel, etc.) and many industrial chemicals. Like NBR, fluid and chemical resistance improves as the ACN content is increased.

The unique properties attributed to HNBR have resulted in wide adoption of HNBR in automotive, industrial, and assorted, performance-demanding applications. On a volume basis, the automotive market is the largest consumer, using HNBR for a host of dynamic and static seals, hoses, and belts. HNBR has also been widely employed in industrial sealing for oil field exploration and processing, as well as rolls for steel and paper mills. Common uses of HNBR include:

Automotive	Industrial	Specialized
A/C seals and hoses	Blow-out preventers	Hi-performance shoe soles
Engine seals, grommets, and gaskets	Chevron seals	
Fuel system seals and hoses	Heat exchanger gaskets	
Serpentine (multi-V) belts	Oil field packers	
Suspension seals	Paper mill rolls	
Synchronous (timing) belts Transmission system bonded piston seals	Rotary shaft seals Steel mill rolls	

CHEMISTRY AND MANUFACTURING PROCESS

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 a “highly saturated nitrile” (HSN) polymer. Even today, HNBR is still sometimes referred to as “HSN”.

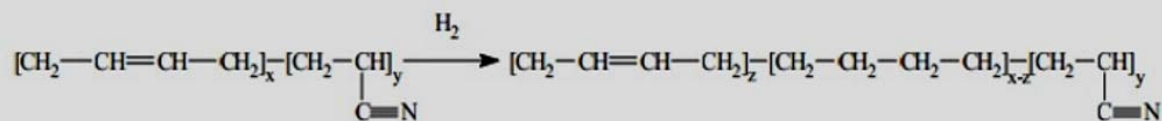
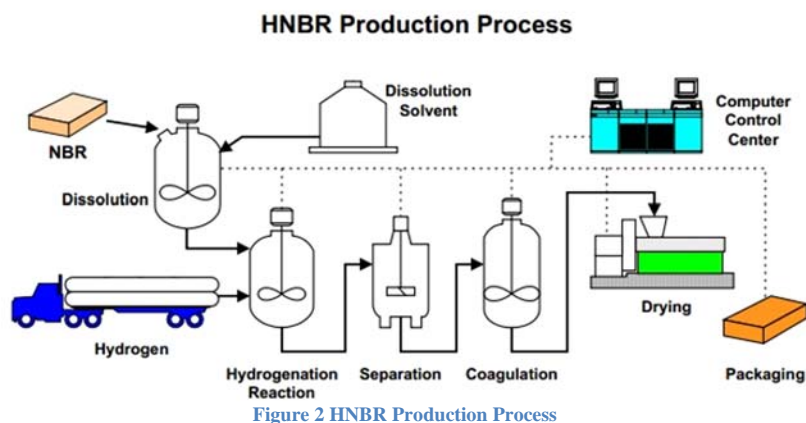


Figure 1 HNBR Structure



BASIC RECIPES

There are a wide variety of acrylonitrile (ACN) content polymers available in the HNBR market 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 the hydrogenation level is increased, the heat and ozone resistance improves but the dynamic hysteresis increases. If you decrease the hydrogenation level, the heat and ozone resistance is not as good but the dynamic hysteresis improves significantly. The other characteristic imparted by the hydrogenation level is the type or selection of the appropriate cure system.

Lastly, the wide range of Mooney viscosities 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 150 when measured at ML(1+4)@100°C. A typical HNBR recipe is listed in the table below.

Ingredients	Phr
Polymer Filler	100
Filler	40 – 100
Plasticizer	0 – 20
Metal Oxide	0 – 5
Anti-degradents	1.5 – 3
Process Aids	0 – 3
Coagent	0 – 10
Curative	5 – 12

PROCESSING AND VULCANIZATION

Mixing

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 incurred when done on a two-roll mill. Typically,

HNBRs are two-pass mixed in an internal mixer where the first pass through the mixer withholds the cure chemicals and is typically dropped out of the mixer at approximately 140°C. This masterbatch is then run through the mixer a second time adding the cure chemicals and again dropped from the mixer at approximately 100-110°C.

Milling

The milling of an HNBR compound is typically quite easy. HNBR compounds tend to build heat quickly; therefore, the use of full cooling capabilities is typically recommended. Normally one should start by setting the mill gap at approximately ¼". This ensures that you will get the shear action required to finish the mixing process while being thin enough to dissipate any excess heat generated during this process. One would normally drop the compound on the mill from an internal mixer from above or feed a stored compound one sheet at a time near the ends of the mill. After banding the compound on the mill, cross-cutting the compound 5 – 7 times from each end is usually adequate to complete this process. Batching off of the mill can easily be accomplished via automatic systems or by hand.

Vulcanization

HNBR elastomers are typically cured with either peroxide or sulfur/sulfur-donor cure systems. Laboratory 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, such as NBR and SBR, 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. As in all peroxide cured material, vulcanization in the presence of oxygen causes reversion and thus leaves a sticky surface on the cured part. Therefore, one must take care when using pressureless cures and purge the autoclave prior to pressuring up for curing.

When compared to SBR or NBR, the curing speed tends to be slower; therefore, to increase the curing speed a secondary accelerator should be employed in combination with the primary accelerator. Long curing times are required when thiazole based (MBTS) or sulfenamide-based (CBS, OBTS) primary accelerators are used. To speed up the curing process, a small quantity of guanidine-based (DPG) or thiuram-based (TMTM) secondary accelerator is used in combination with the primary accelerator. Even when using a thiuram-based (TMTD, TETD) primary accelerator, the addition of a thiazolebased (MBT) secondary accelerator will shorten the time required for curing. The use of dithiocarbamate (ZEDC) as the primary accelerator is undesirable since the scorch time will be shortened.

PRODUCERS

The hydrogenation of various diene-containing elastomers has been well known for many years. Berthelot began the earliest experiments in 1869, with many other workers carrying out numerous experiments under different conditions and with different catalyst systems. Pummerer et al., in the early 1920s and Staudinger about 1930 were notable contributors to the hydrogenation of polymer systems. Hydrogenated nitrile butadiene rubber or HNBR was first developed in the late '70s and early '80s. Though commercial production did not begin until 1984, there were numerous companies looking at the feasibility of producing this type of elastomer. Of those who chose to evaluate this polymer, three companies emerged: Bayer Corporation, Zeon Corporation, and Polysar. Of these three, Zeon Corporation was the first to commercialize HNBR in March of 1984 with Bayer and Polysar very close behind. Zeon Corporation's initial manufacturing site was in Takaoka, Japan. The other initial manufacturing site was Polysar's in Orange, Texas. However, Polysar eventually sold that business to Bayer Corporation (now Lanxess) who now owns and operates that facility.

CONCLUSION

HNBR has been the fastest growing specialty elastomer in the last decade. With its excellent cost-performance balance for the most demanding of applications; HNBR is the ideal choice for applications needing excellent physical properties, as well as oil, heat, and/or chemical resistance.