Kirk-Othmer Encyclopedia of Chemical Technology.

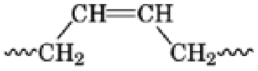
NITRILE RUBBER

Nitrile rubber is a synthetic polymer made from 1,3-butadiene and acrylonitrile using emulsion polymerization techniques. The ASTM designation (D1418) for nitrile rubber is NBR and the Chemical Abstracts Service (CAS) registry number for poly(acrylonitrile-*co*-1,3-butadiene) is [9003-18-3]. Nitrile rubber was first developed in Germany during the early 1930s (1). Domestic production of NBR started during the 1940s. Nitrile rubber is classified as a specialty rubber and is well known for its resistance to various oils, fuels, and chemicals. After mixing with other ingredients (fillers, plasticizers, antidegradants, curatives) and curing, NBR compounds commonly see use in various seals, gaskets, hose, and roll applications. Nitrile rubber has been chemically modified by a solution hydrogenation process in order to extend its high temperature performance. Hydrogenated nitrile rubber (HNBR) [88254-10-8] was developed and commercialized during the early 1980s. The saturated backbone of the HNBR polymer leads to improved heat resistance of the rubber, while retaining excellent oil/chemical resistance.

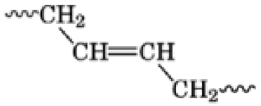
1. Chemical Properties

Nitrile rubbers are high molecular-weight amorphous copolymers of 1,3-butadiene [106-99-0], $CH_2{=}CH{-}CH{=}CH_2$, and acrylonitrile [107-13-1], $CH_2{=}CH{-}CN$. Average molecular weights of commercial products have been reported to be between 250,000 and 600,000, with a wide distribution around the average in any single product (2). Structure of the polymer can vary widely from largely linear to highly branched to cross-linked, depending on the conditions of polymerization (3).

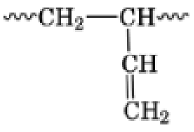
Distribution of the monomer units in the polymer is dictated by the reactivity ratios of the two monomers. In emulsion polymerization, which is the only commercially significant process, reactivity ratios have been reported (4). If M_1 = butadiene and M_2 = acrylonitrile, then $r_1 = 0.28$, and $r_2 = 0.02$ at 5°C. At 50°C, $r_1 = 0.42$ and $r_2 = 0.04$. As would be expected for a combination where r_1r_2 = near zero, this monomer pair has a strong tendency toward alternation. The degree of alternation of the two monomers increases as the composition of the polymer approaches the 50/50 molar ratio that alternation dictates (5, 6). Another complicating factor in defining chemical structure is the fact that butadiene can enter the polymer chains in the cis **(1)**, trans **(2)**, or vinyl(1, 2) **(3)** configuration:



(1)



(2)



$$\sim\!\!\sim CH_2-\underset{\underset{\displaystyle CH_2}{\|}}{\underset{\displaystyle CH}{|}}{CH}\sim\!\!\sim$$

(3)

In a copolymer of 33% acrylonitrile, the most common composition for commercial products, the butadiene occurs in the approximate ratio of 90% trans, 8% vinyl, and 2% cis. At higher acrylonitrile content the cis configuration disappears, and at lower levels it increases to about 5%; the vinyl configuration remains approximately constant (6, 7). Since actual compositions of commercial nitrile rubbers are between 15 and 50% acrylonitrile, they also vary somewhat in sequence distribution and in the content of the three isomeric butadiene configurations.

This combination of monomers is unique in that the two are very different chemically, and in their character in a polymer. Polybutadiene homopolymer has a low glass-transition temperature, remaining rubbery as low as $-85^{\circ}C$, and is a very nonpolar substance with little resistance to hydrocarbon fluids such as oil or gasoline. Polyacrylonitrile, on the other hand, has a glass temperature of about $110^{\circ}C$, and is very polar and resistant to hydrocarbon fluids (see Acrylonitrile polymers). As a result, copolymerization of the two monomers at different ratios provides a wide choice of combinations of properties. In addition to providing the rubbery nature to the copolymer, butadiene also provides residual unsaturation, both in the main chain in the case of 1,4, or in a side chain in the case of 1,2 polymerization. This residual unsaturation is useful as a cure site for vulcanization by sulfur or by peroxides, but is also a weak point for chemical attack, such as oxidation, especially at elevated temperatures. As a result, all commercial NBR products contain small amounts ($\sim$0.5 – 2.5%) of antioxidant to protect the polymer during its manufacture, storage, and use.

Chemically modified nitrile rubbers are also produced commercially with the objective of changing their chemistry in such a way that specific properties are enhanced (8). The oldest of the chemically modified NBRs are the carboxylated varieties, made by copolymerizing methacrylic or acrylic acid with the butadiene and acrylonitrile. The resultant products, which typically contain 2–6% by weight of the acid monomer, can be vulcanized with polyvalent metals in addition to the normal sulfur or peroxide cure systems (9). The most outstanding result of this modification is a large improvement in abrasion resistance. Another chemical modification currently in use is the copolymerization of a monomer which causes an antioxidant structure to be attached to the polymer (10). The result is improved resistance to oxidation, particularly after the rubber has been exposed to a hydrocarbon fluid that would normally extract a conventional antioxidant from the polymer, leaving it unprotected. The most recent and potentially the most important chemical modification is hydrogenation of the polymer so that little of the unsaturation remains (11–15). This results in a product with much improved resistance to oxidation and weathering, but with little or no sacrifice in other useful properties. The usual procedure is to hydrogenate in a solution process until just enough unsaturation is left to provide sites for curing, using catalysts based on ruthenium, rhodium, or palladium. A latex reduction process has been reported using hydrazine and an oxidizer such as hydrogen peroxide (16, 17). Other chemical modifications such as attachment of isocyanate or hydroxyl functionality have been reported (18), but have not become commercially significant.

Table 1. Physical Properties of Nitrile Rubber

Property	Acrylonitrile content, %	Value
specific gravity	15	0.94
	20	0.95
	35	0.99
	45	1.02
	50	1.03
T_g, °C	15	−49
	22	−40
	30	−30
	40	−19
	50	−9
thermal conductivity[a], kJ/(m·h·°C)[b]	28	0.90
	33	0.90
	38	0.92
thermal expansion coefficient[a] $\times 10^6/{}^\circ\mathrm{C}$	28	175
	33	170
	38	150
specific heat[a], J/(g·°C)[b]	40	$0.00283T + 1.126$

[a] Ref. 4.

[b] To convert J to cal, divide by 4.184.

2. Physical Properties

Nitrile rubbers are produced over a wide range of monomer ratios and molecular weights, so their physical constants and basic polymer properties also cover a range of values. Some of the more widely used properties are listed in Table 1.

3. Manufacturing

Virtually all nitrile elastomers are manufactured by emulsion polymerization, according to technology that evolved from efforts in Germany in the 1930s and in the United States in the 1940s to find a substitute for natural rubber. The primary steps in the process include polymerization into a latex form, coagulation of the latex into a wet crumb, and then drying into a final product. In practice, latex is usually collected in large blend tanks where it is sampled and tested before "finishing" to a dry product. As a result, a description of the manufacturing of nitrile rubber can be conveniently divided into two areas: polymerization and finishing.

3.1. Polymerization

The two different methods of carrying out emulsion polymerization on a commercial scale are shown in Figures 1 and 2. In the batch process, each reactor operates independently to carry out a complete polymerization reaction. Raw materials are charged to each reactor and the polymerization proceeds to the desired end point in each reactor, where it is either stopped or dropped to a "blowdown" tank and stopped. When large quantities of a single product are being made, many individual polymerizations are carried out, and the latices from them are blended together. In the continuous process, a number of reactors are connected in series, usually three or more. Raw materials are charged to the first reactor where polymerization is started. The reacting mass then

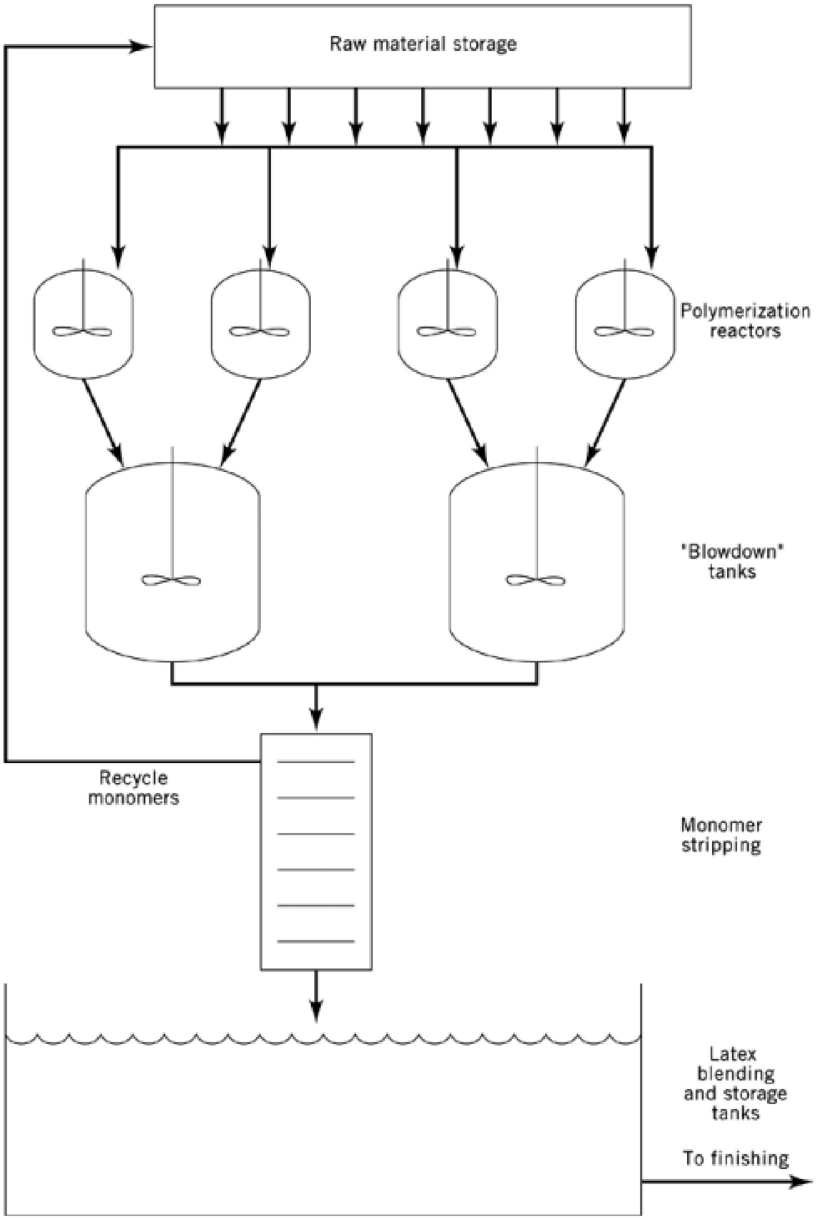


Fig. 1. Nitrile rubber polymerization, batch process.

flows from one reactor to the next continuously, until it reaches the desired end point where polymerization is stopped.

The batch process is most useful when relatively short runs of a large number of products are planned. A number of products can be made simultaneously and collected in separate storage tanks for testing and later finishing. The continuous process is more efficient when large quantities of a few products are desired. Reactors remain in operation a larger fraction of the time because no time is lost for emptying and recharging such as

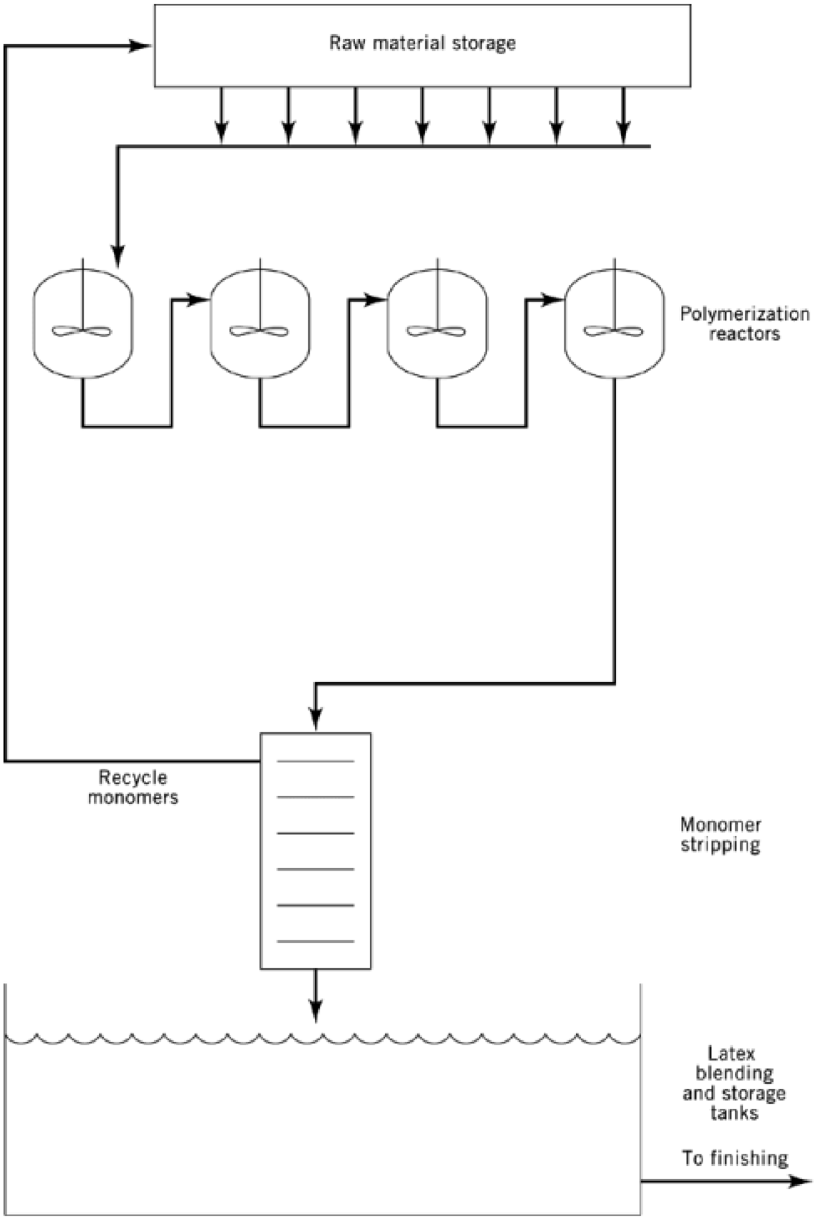


Fig. 2. Nitrile rubber polymerization, continuous process.

in the batch mode. In both cases, the progress of polymerization is closely monitored to follow the conversion of monomer to polymer. The conversion is important for two reasons: some recipes call for additions of ingredients at specific points during polymerization, and all recipes have a specific final conversion at which they must be stopped so that desired product properties are achieved.

Simplified nitrile rubber polymerization recipes are shown in Table 2 for “cold” and “hot” polymerization. Typically, cold polymerization is carried out at 5°C and hot at 30°C. The original technology for emulsion

Table 2. Typical Nitrile Rubber Polymerization Recipes

	Recipe, parts by weight, active	
Materials	5°C Polymerization	30°C Polymerization
soft or demineralized water	200	200
butadiene	67	67
acrylonitrile	33	33
primary emulsifier	2.5	2.5
secondary emulsifier	0.5	0.5
electrolyte	0.3	0.3
modifier (mol wt regulator)	0.4	0.4
iron chelate	0.005	
reducing agent	0.03	
hydroperoxide	0.04	
potassium persulfate		0.25
oxygen scavenger (if needed)	0.01	0.01
shortstop (at desired final conversion)	0.2	0.2

polymerization was similar to the 30°C recipe, and the redox initiator system that allowed polymerization at lower temperature was developed shortly after World War II. The latter uses a reducing agent to activate the hydroperoxide initiator and soluble iron to reactivate the system by a reduction–oxidation mechanism as the iron cycles between its ferrous and ferric states.

In the recipes shown in Table 2, the amount of water can vary widely, depending on the available heat-transfer capacity of the reactor and the rate of polymerization. Each of the monomers has a heat of polymerization of about 75 kJ/mol (18 kcal/mol), so removing the heat of polymerization to control temperature is often the limiting factor on rate of polymerization.

The ratio of monomers can be varied from zero acrylonitrile up to approximately 60% to produce copolymers of zero to about 50% acrylonitrile. This is, of course, a crucial factor in determining the properties of the final material. Rubbers with low acrylonitrile content have extremely low glass temperatures but little resistance to solvents and oils. The opposite is true at high acrylonitrile levels.

The choice of emulsifiers is dependent on cost to some degree, but is also chosen on the basis of ease of coagulation in the finishing process and on the influence of residual emulsifier in the product on properties such as water sensitivity and cure rate. Ideally, an emulsifier is chosen which is inexpensive, results in latex that is very stable to shear during stripping and pumping, easy to coagulate, and inert in the final product. All the practical polymerization recipes use an anionic primary emulsifier such as fatty soaps or synthetic detergents like sodium alkyl benzenesulfonate. The secondary emulsifier, when used, can be a nonionic or a wetting agent like sodium naphthalenesulfonate.

Electrolyte is added to the recipe to help control particle size of the latex produced. Materials like sodium carbonate or trisodium phosphate are commonly used.

One of the most important ingredients is the modifier added to control molecular weight. These operate by stopping the polymerization of a growing polymer chain and transferring the free radical to start a new copolymer molecule. For that reason, they are also called chain-transfer agents. Without this control, emulsion polymerized butadiene copolymers would be extremely high in molecular weight and would be highly branched. They would be almost impossible to process in subsequent mixing, extrusion, and molding operations. The most commonly used modifiers are alkyl mercaptans, especially *tert*-dodecyl mercaptan.

The initiator ingredients are designed to generate free radicals at a moderate rate at the temperature of the polymerization. Sodium, potassium, or ammonium persulfate are commonly used for hot polymers. The initiator ingredients in a cold recipe are more complex and a wide variety of materials can be used. The iron is usually added in a chelated form so it is soluble, but not as reactive as free ions in solution. A typical reducing agent is sodium formaldehyde sulfoxylate and *p*-menthane hydroperoxide is often used to provide the necessary free-radical source. Usually, a high acrylonitrile recipe requires less initiator than a low acrylonitrile recipe. All of these systems are sensitive to oxygen, so in many cases a small amount of a material like sodium hydrosulfite is used in case purging of air before polymerization was incomplete.

The choice of initiator system depends on the polymerization temperature, which is an important factor in determining final product properties. Cold polymers are generally easier to process than hot polymers and in conventional cured rubber parts have superior properties. The hot polymers are more highly branched and have some advantages in solution applications such as adhesives, where the branching results in lower solution viscosity and better cohesion in the final adhesive bond.

All ingredients in the polymerization recipe are not always added at the beginning of the process. For example, better latex stability can sometimes be achieved by starting with only part of the emulsifier, saving the rest for later addition. Sometimes a portion of the modifier is held out for late addition to allow higher final conversion without premature consumption of all of it. Occasionally, if a low acrylonitrile product is the objective, part of the acrylonitrile monomer will be saved for late addition so that a chemically more uniform copolymer is produced, which can sometimes enhance properties in critical applications.

A shortstop is necessary to control the final conversion of monomer to polymer. If allowed to run to very high conversion ($>95\%$), the resultant product is difficult to process, usually because the modifier has been consumed, and because free radicals begin to react with polymer instead of additional monomer, which at high conversion is in short supply. Uncontrolled molecular weight and branching begin to occur. In practice, a high conversion nitrile rubber polymerization is allowed to run to about 90% conversion and results in a product with excellent physical properties, but is difficult for the user to mix and mold. A low conversion polymer is shortstopped at 65–80% conversion and is much easier to process in later operations. Effective shortstops are destroyers of free radicals and include materials that liberate free hydroxylamine, hydroquinone and its derivatives, and carbamates such as sodium diethyldithiocarbamate [148-18-5].

After polymerization is complete, especially in the case of low conversion products, residual monomer must be removed and recovered for recycling. Butadiene can be removed by warming the latex under vacuum, since it boils at a very low temperature. The acrylonitrile and remaining small amount of butadiene monomer are usually removed by steam stripping in a column. This process requires that the latex be mechanically stable to avoid loss of product and consequent fouling of the stripping equipment. For reasons of cost, environmental concern, and product safety, the stripping process must be designed to remove residual monomer down to low ppm levels.

Polymerizer design variables such as length/diameter ratio of the polymerizer, type and speed of agitation, and materials of construction, have important effects on operation of the process but little effect on the product itself. Polymerization reactors are usually jacketed or contain cooling coils (or both) for temperature control. Stainless steel is common in modern reactors and agitation is usually designed for low shear and high pumping rates, the objective being to allow good heat transfer while avoiding the production of small particle size latex.

3.2. Finishing

After manufacturing a polymer in latex form by either batch or continuous polymerization, it is collected in large tanks for further processing to a dry rubber form. The most common finishing process involves addition of stabilizer to the latex, coagulation of the latex to form a slurry of rubber crumb in water, washing of the wet material, and dewatering and drying to a finished product. A typical finishing process is described in Figure 3. In modern facilities this is always a continuous process, although it could be carried out in a batch mode.

Because nitrile rubber is an unsaturated copolymer it is sensitive to oxidative attack and addition of an antioxidant is necessary. The most common practice is to add an emulsion or dispersion of antioxidant or stabilizer to the latex before coagulation. This is sometimes done batchwise to the latex in the blend tank,

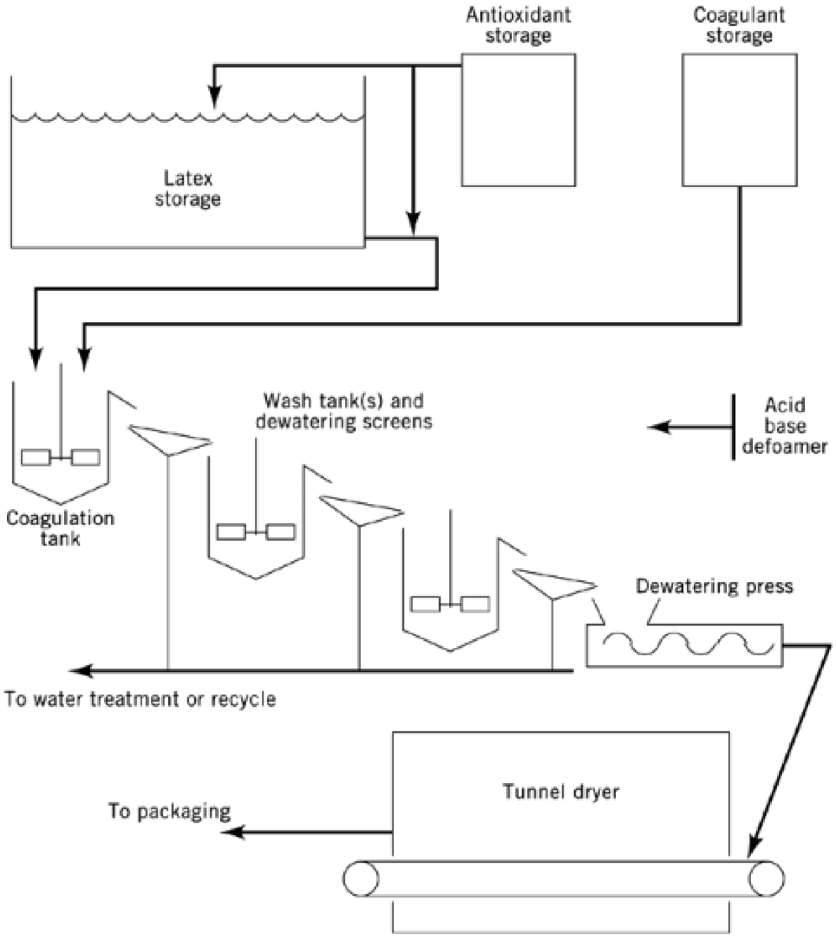


Fig. 3. Typical nitrile rubber finishing process.

and sometimes is added continuously to the latex as it is pumped toward further processing. Phenolic, amine, and organic phosphite materials are used. Examples are di-*tert*-butylcatechol, octylated diphenylamine, and tris(nonylphenyl) phosphite [26523-78-4]. All are meant to protect the product from oxidation during drying at elevated temperature and during storage until final use. Most rubber processors add additional antioxidant to their compounds when the NBR is mixed with fillers and curatives in order to extend the life of the final rubber part.

The choice of coagulant for breaking of the emulsion at the start of the finishing process is dependent on many factors. Salts such as calcium chloride, aluminum sulfate, and sodium chloride are often used. Frequently, pH and temperature must be controlled to ensure efficient coagulation. The objectives are to leave no uncoagulated latex, to produce a crumb that can easily be dewatered, to avoid fines that could be lost, and to control the residual materials left in the product so that damage to properties is kept at a minimum. For example, if a significant amount of a hydrophilic emulsifier residue is left in the polymer, water resistance of final product suffers, and if the residue left is acidic in nature, it usually contributes to slow cure rate.

Once the latex is coagulated, the resultant slurry is filtered through a screen and sent to a washing tank or tanks. The purpose is to remove water-soluble solids, sometimes at controlled pH, by addition of fresh water.

Table 3. Worldwide Nitrile Rubber Production History[a]

Year	Production, 10^3 t
1982	175
1983	189
1984	238
1985	213
1986	214
1987	231
1988	262
1989	243
1990	246
1991	244

[a] Ref. 19; includes latex and dry rubber.

Whether this is carried out in one tank or in two steps in series, water is usually recycled, and screens are used for separating the wet rubber crumb from the free water. The final operation in the washing process in modern plants is to dewater the crumb in a press. These are commonly extruder presses in which the screw forces the wet material through a restriction, and which have a slotted barrel to allow free water to drain away. Coagulated crumb of NBR is typically about 60% by weight water when fed to an extruder press, and is dewatered to about 10% moisture by this process. The benefits are that a minimum of water has to be removed by evaporation in the dryer (an energy savings), and that the water squeezed out carries much of the remaining soluble impurities with it.

After dewatering the crumb it is fed to the drying process which is usually carried out in a continuous tunnel dryer. The crumb is spread on a perforated stainless steel bed through which hot air is passed to evaporate the remaining water. Typically, in the first portion of the dryer, air at 110–140°C is used, with lower temperatures being used as the product approaches dryness. A typical target for final moisture content is 0.5% or less. At the exit of the dryer the product is cooled and conveyed to a baler which shapes it into bales for packaging and shipment.

For special products or product forms, NBR is sometimes finished by other methods. A powdered form can be produced by feeding latex directly to a spray dryer, where it is atomized and dried in a hot air stream. An anticaking material such as talc must be added to preserve the powder form during storage and shipment. Some products are ground to particulates of various sizes; they are carried out of the tunnel dryer to a grinding process where size is reduced and anticake is added. Finally, low molecular-weight NBR is a molasses-like liquid and is produced largely for use as a plasticizer for other polymers. It must be dried in an evaporator under vacuum and packaged in drums.

4. Economic Aspects

Late 1992 pricing for NBR was approximately $2.2/kg, with specialty grades slightly higher. Nitrile rubber is generally considered a mature product and growth of production and sales have been relatively low as reflected in the production history and long-term consumption forecast figures provided by the International Institute of Synthetic Rubber Producers (IISRP) (Tables 3 and 4) (19).

There are five nitrile rubber producers in North America. Details of production facilities for nitrile rubber as provided by the IISRP are shown in Table 5.

Table 4. Long-Term Rubber Consumption Forecast by Area[a], 10^3 t

Geographic area	1992	1996
North America	108	111
Western Europe	87	92
Asia	75	87
Latin America	12	15
Africa/Middle East	4	4
Total	*286*	*309*[b]

[a] Ref. 19; includes latex and dry rubber.
[b] +8.0%

Table 5. World Production Facilities for Nitrile Rubber

Producer	Plant location	Trade name	Capacity, 10^3 t
	North America		
Zeon Chemicals	Louisville, Ky.	Nipol	35
Goodyear Tire & Rubber	Houston, Tex.	Chemigum	28
Uniroyal Chemical Co.	Painesville, Ohio	Paracril	20
Polysar/Bayer	Sarnia, Ontario	Krynac	20
Copolymer Rubber/DSM	Baton Rouge, La.	Nysyn	10
Total North America			*113*
	Western Europe		
Bayer	Germany	Perbunan	35
Polysar/Bayer	France	Krynac	33
Enichem Elastomeri	Italy	Europrene N	30
Goodyear Chemicals Europe	France	Chemigum	11
Zeon Chemicals Europe	South Wales	Breon	10
Buna A.G.	Germany		5
Total Western Europe			*124*
	Asia		
Japan Synthetic Rubber	Japan	JSR N	40
Nippon Zeon	Japan	Nipol	20
Nantex	Taiwan	Nancar	12
Korea Kumho	Korea		10
Synthetics and Chemicals	India		2
Takeda Chemical	Japan		1
Total Asia			*85*
	Latin America		
Nitriflex	Brazil	Nitriflex	11
Hules Mexicanos	Mexico	Humex	6
Pasa	Argentina	Arnipol	2
Total Latin America			*19*
Total global capacity			*341*

5. Grades of Nitrile Rubber

There are many grades of nitrile rubber available on the market today; for example, Zeon Chemicals offers approximately 75 different grades of NBR. The principal variables that are commonly changed include the following:

5.0.0.1. Acrylonitrile Content. Standard grades available in the market contain between 15 to 50% acrylonitrile. The acrylonitrile content of nitrile rubber has a significant effect on two properties: chemical resistance and low temperature performance. As the acrylonitrile content of the polymer is increased, the chemical resistance is improved whereas the low temperature properties are diminished.

5.0.0.2. Mooney Viscosity. This is a measurement of the viscosity of the polymer that is commonly used in the rubber industry. Mooney viscosity values typically range from 25 to 100. *Mooney viscosity* generally relates to polymer molecular weight, with the lower Mooney viscosity polymers providing improved flow and processing characteristics and the higher Mooney NBRs providing improved physical properties.

5.0.0.3. Emulsifier Type. The manufacturers of NBR use a variety of emulsifiers (most commonly anionic) for the emulsion polymerization of nitrile rubber. When the latex is coagulated and dried, some of the emulsifier and coagulant remains with the rubber and affects the properties attained with the rubber compound. Water resistance is one property in particular that is dependent on the type and amount of residual emulsifier. Residual emulsifer also affects the cure properties and mold fouling characteristics of the rubber.

5.0.0.4. Antioxidant Type. Producers of nitrile rubber add stabilizers to the nitrile rubber latex prior to coagulation and drying of the NBR. These antioxidants are required because the polymer contains residual double bonds that can be oxidized during the elevated temperature drying process. The mechanisms of oxidation of diene elastomers (including nitrile rubber) have been covered in a recent review (20). Many different types of antioxidants are used, including amine and phenolic derivatives. Of course these antioxidants affect the properties of the nitrile rubber in the final rubber compound. Choice of antioxidant is especially important when food contact is planned for the rubber. Grades of nitrile rubber are available to meet various regulations and requirements from the Food and Drug Administration (FDA) and the National Sanitation Foundation.

5.0.0.5. Third Monomers. In order to achieve certain property improvements, nitrile rubber producers add a third monomer to the emulsion polymerization process. When methacrylic acid is added to the polymer structure, a carboxylated nitrile rubber with greatly enhanced abrasion properties is achieved (9). Carboxylated nitrile rubber carries the ASTM designation of XNBR. Cross-linking monomers, eg, divinylbenzene or ethylene glycol dimethacrylate, produce precross-linked rubbers with low nerve and die swell. To avoid extraction losses of antioxidant as a result of contact with fluids during service, grades of NBR are available that have utilized a special third monomer that contains an antioxidant moiety (10). Finally, terpolymers prepared from 1,3-butadiene, acrylonitrile, and isoprene are also commercially available.

5.0.0.6. Preplasticized. A plasticizer can be incorporated into the rubber during the manufacturing process. By adding a phthalate plasticizer to the rubber latex prior to coagulation and drying, the NBR producer can prepare a rubber that is particularly well suited to low hardness applications such as rolls (21).

5.0.0.7. Blends with PVC. Nitrile rubber may be blended with poly(vinyl chloride) (PVC) by the polymer producer by two different techniques: (1) blending of NBR latex with PVC latex followed by co-coagulation and drying, or (2) physically mixing the solid NBR and PVC powder in mixing equipment such as an internal mixer. NBR–PVC polymer blends are well known for the good ozone resistance that is imparted by the PVC.

5.0.0.8. Masterbatches with Carbon Black. Two producers (Zeon Chemicals and Copolymer) offer nitrile rubber–carbon black masterbatches. These grades are prepared by mixing the carbon black with the rubber latex prior to the coagulation and drying process.

5.0.0.9. Physical Form. Nitrile rubber is available in several different forms, ie, solid bale, particulate/powder, and high viscosity liquid. The most common form is a 50-lb (22.7-kg) bale. Particulate and powder grades of nitrile rubber are produced by either grinding of the solid rubber or spray drying of the nitrile rubber latex. Liquid grades are produced by using high levels of mercaptan molecular-weight modifiers during the polymerization process to produce a relatively low molecular-weight/high viscosity liquid, eg, Brookfield viscosity of Nipol 1312LV is 13,000 mPa·s (=cP) at 50°C.

Storage of nitrile rubber is recommended in a cool, dry place away from direct light. Producers of nitrile rubber add an antioxidant to the rubber for stability during the rubber drying operation and subsequent warehouse storage. As such, assurances of one-year warehouse storage stability are typically provided. Special problems exist with the storage of powdered NBRs because they tend to agglomerate when stored for long periods of time at elevated temperatures.

6. Rubber Analysis and Quality Control Testing

The Rubber Manufacturer's Association (RMA) is a cooperative manufacturing trade association. Recently, the RMA has issued a technical bulletin to standardize the reporting of key analytical/quality control data on nitrile rubber (22). The various tests commonly run on nitrile rubber include raw polymer Mooney viscosity, $\mathrm{ML1}' + 4$ at 100°C, ASTM D1646; cure profile using ASTM D3187 compound, ASTM D2084; total volatile matter, total ash, and total extractables, ASTM D1416; and bound ACN.

7. Health and Safety Factors

Nitrile rubber presents no unusual hazards when processed and handled in areas with good housekeeping and ventilation. Like other elastomers, nitrile rubber emits fumes and vapors when heated to high temperatures during processing and curing. Acrylonitrile and 1,3-butadiene monomers are known or suspected carcinogens, thus producers of NBR must follow strict Occupational Safety and Health Administration (OSHA) standards that regulate permissible exposure of personnel to these materials during the nitrile rubber manufacturing process. In order to minimize the residual acrylonitrile and 1,3-butadiene in the final product, nitrile rubber producers physically strip or remove the unreacted monomers from the in-process latex prior to the coagulation and drying of the final product. As a result, typical acrylonitrile and 1, 3-butadiene residues in the final NBR are on the order of a few parts per million of each of the two monomers for most NBRs. This is important to minimize exposure of the consumer of the NBR to acrylonitrile and 1, 3-butadiene during the mixing, processing, and curing of any nitrile rubber article.

Acrylonitrile (qv), listed as a carcinogen by several government agencies, is covered by a specific OSHA standard (29CFR1910.1045) that regulates exposure to two parts acrylonitrile per million parts of air (2 ppm) as an 8-h time-weighted average. The regulation also states that no employee shall be exposed to an airborne concentration of acrylonitrile in excess of 10 ppm over any 15-min period (ceiling limit). The current permissible exposure limit for airborne 1,3-butadiene is 1000 ppm as an 8-h time-weighted average. However, in Aug. 1990 OSHA drafted a proposed rule that would lower the permissible exposure limit to 2 ppm as an 8-h time-weighted average. In Sept. 1991 a new risk assessment for 1,3-butadiene was submitted to OSHA by the National Institute for Occupational Safety and Health (NIOSH). This new risk assessment states that the cancer risk for workers exposed to 1, 3-butadiene is greater than believed when OSHA drafted its proposed rule. Thus NIOSH recommended that worker exposure to 1,3-butadiene be kept to the lowest feasible level.

8. Uses

Most nitrile rubber is consumed in applications utilizing vulcanized rubber compounds. Rubber compounds are mixed with a wide variety of ingredients, including various fillers, plasticizers, processing aids, stabilizers, and curatives (23). After mixing the rubber compound, various vulcanization techniques, such as compression molding, transfer molding, and injection molding, can be used to prepare the final cured rubber article. Common applications for nitrile rubber take advantage of the chemical resistance of the rubber and are as follows:

seals
O-rings
gaskets
oil field parts
diaphragms
printing supplies
gloves
pump stators
belts
wire and cable insulation
hose tubes/covers
rolls
weather stripping
footwear/shoe products
milking inflations
miscellaneous molded rubber goods

Nitrile rubber is also used in many applications that do not involve the mixing of a traditional rubber compound as described above. Some of these areas include the following:

8.0.0.10. Modification of Plastics. Many plastics, such as PVC, ABS, polypropylene, and nylon, are blended with nitrile rubber to improve flexibility, toughness, or appearance. An oil-resistant thermoplastic elastomer has been prepared by blending nitrile rubber and polypropylene (24).

8.0.0.11. Adhesives / Cements / Sealants / Coatings. Excellent adhesives of high strength and high oil resistance can be prepared using nitrile rubber (25). Many references have discussed the use of nitrile rubber–phenolic and nitrile rubber–epoxy adhesives for printed circuit boards.

8.0.0.12. Friction Materials. Nitrile rubber has been used as a modifier in various friction materials such as brake lining and clutch pads.

9. Hydrogenated Nitrile Rubber

Hydrogenated nitrile rubber is a high performance polymer with significantly better high temperature properties compared to nitrile rubber because of the largely saturated backbone of the rubber (11–15). Hydrogenated nitrile rubber was first developed during the late 1970s and commercialized during the early 1980s. It is produced by a solution process that leads to a selective hydrogenation of the butadiene unsaturation in the polymer. Late 1992 prices varied from approximately $22 to $31/kg. Estimates of production capacities for the two commercial producers of hydrogenated nitrile rubber in the world today are shown in Table 6.

Table 6. World Production Facilities for Hydrogenated Nitrile Rubber[a]

Producer	Plant location	Trade name	Capacity, 10^3 t
Zeon Chemicals	Bayport, Tex.	Zetpol	1500
Nippon Zeon	Japan	Zetpol	1800
Polysar/Bayer	Orange, Tex.	Tornac/Therban	1600

[a] Ref. 19.

As in nitrile rubber there are different grades of hydrogenated nitrile rubberthat vary in acrylonitrile content and Mooney viscosity. In addition, various grades with different extents of hydrogenation are available. Finally, grades of hydrogenated nitrile rubber are available containing zinc oxide and methacrylic acid. Extremely high tensile strength, up to 58 MPa (8400 psi), and excellent abrasion resistance have been reported for hydrogenated nitrile rubber compounds containing zinc oxide and methacrylic acid (26).

Applications for hydrogenated nitrile rubber are similar to those of nitrile rubber in that they take advantage of the excellent chemical and oil resistance of the polymer. However, the increased high temperature

Table 7. Applications for Hydrogenated Nitrile Rubber[a]

Oil-field applications	Automotive applications	Industrial applications
blowout preventers	rotating shaft seals	hydraulic hose
downhole packers	lip seals	hydraulic packings
drill pipe protectors	bearing/wheel seals	cable jacket for power station
mud pump pistons	O-rings	laminating rolls
well head seals	valve cover gaskets	printing rolls
O-rings	fuel pump diaphragm	textile rolls
valve seals	fuel pump isolators	paper mill rolls
cable jackets	fuel hose tubes	military components
drilling hoses	timing belts	chemical plant diaphragms
pressure accumulators	valve stem seals	
wipers	water pump seals	
swab cups		
pump stators		

[a] Refs. 27 and 28.

performance of the hydrogenated nitrile rubber makes it far superior to standard grades of nitrile rubber. Examples of applications for hydrogenated nitrile rubber are shown in Table 7 (27, 28).

BIBLIOGRAPHY

"Rubber, Synthetic" in *ECT* 1st ed., Vol. 11, pp. 827–852, by J. D. D'Ianni, The Goodyear Tire & Rubber Co.; "Elastomers, Synthetic" in *ECT* 2nd ed., Vol. 7, pp. 676–705, by W. M. Saltman, The Goodyear Tire & Rubber Co.; "Elastomers, Synthetic (Nitrile Rubber)" in *ECT* 3rd ed., Vol. 8, pp. 534–546, by H. W. Robinson, Uniroyal, Inc.

Cited Publications

1. Ger. Pat. 658,172 (Apr. 26, 1930); Brit. Pat. 360,821 (May 30, 1930); Fr. Pat. 710,901 (Feb. 4, 1931); U.S. Pat. 1,973,000 (Sept. 11, 1934), E. Konrad and E. Tschunkur (to I. G. Farbenindustrie A.G.).
2. D. A. Seil, "How New Nitrile Rubbers Improve Product Quality," *Rubber Plas. News* (Sept. 23, 1985).
3. N. Nakajima, E. R. Harrel, P. R. Kumler, D. A. Seil, and A. H. Jorgensen, *Adv. Polym. Technol.* **4**(3/4), 267 (1983).
4. W. Hoffmann, *Rubber Chem. Technol.* **37**(2), part 2 (April–June 1964).
5. D. F. Kates and H. B. Evans, in Clara D. Craver, ed., *Polymer Characterization: Interdisciplinary Approaches*, Plenum Press, New York, 1971, p. 213.
6. B. G. Willoughby, *Polym. Test.* **8**, 45 (1989).
7. R. Schmolke and W. Kimmer, *Plaste Kautschuk* **21**(9), 651 (1974).
8. P. W. Milner, *Dev. Rubber Technol.* **4**, 57 (1987).
9. P. H. Starmer, *Plast. Rubber Proc. Appl.* **9**(4), 209 (1988).
10. J. W. Horvath, "Bound Antioxidant Stabilized NBR in Automotive Applications", *Annual Meeting Proceedings of the IISRP*, Paper No. 11, 1979, p. 20.
11. S. Hayashi, M. Oyama, K. Hashimoto, and T. Nakagawa, "New Improved Low Temperature Hydrogenated Nitrile Rubber (HNBR)," paper presented at the *A.C.S. Rubber Division Meeting*, Detroit, Mich., Oct. 8–11, 1991.
12. K. Hashimoto and Y. Todani, in A. Bhownick and H. Stephens, eds., *Handbook of Elastomers*, Marcel Dekker, Inc., New York, 1988, Chapt. 24, p. 741.
13. R. C. Klingender, in M. Morton, ed., *Rubber Technology*, 3rd ed., Van Nostrand Reinhold, New York, 1987, p. 488.
14. N. A. Mohammadi and G. L. Rempel, *Macromolecules* **20**, 2362 (1987).
15. Y. Kubo, K. Hashimoto, and N. Watanabe, "Structure and Properties of Highly Saturated Nitrile Elastomers," paper presented at the *A.C.S. Rubber Division Meeting*, New York, Apr. 7–11, 1986.

16. Int. Pat. Appl. (PCT) 91/06579 (May 16, 1991), H. W. Schiessl and F. W. Migliaro (to Olin Corp.).
17. U.S. Pat. 4,452,950 (June 5, 1984), L. G. Wideman (to The Goodyear Tire & Rubber Co.).
18. D. K. Parker, H. A. Colvin, A. H. Weinstein, and S. L. Chen, *Rubber Chem. Technol.* **63**(4), 582 (1990).
19. *Worldwide Rubber Statistics 1992*, International Institute of Synthetic Rubber Producers Inc., Houston, Tex., 1992, pp. 10, 13, 68–70.
20. C. Adam, J. Lacoste, and J. Lemaire, *Actual. Chim.* (2), 85 (1991).
21. T. L. Jablonowski, *Rubber World* **200**(4), 25 (1989).
22. Rubber Manufacturers' Association, *RMA Form SP-241*, Washington, D.C., 1991.
23. H. L. Stephens, in Ref. 13, p. 20.
24. U.S. Pat. 4,409,365 (Oct. 11, 1983), A. Y. Coran and R. Patel (to Monsanto Co.).
25. D. E. Mackey and C. E. Weil, in Irving Skeist, ed., *The Handbook of Adhesives*, 3rd ed., Van Nostrand Reinhold, New York, 1990, p. 206.
26. Y. Saito, A. Fujino, and A. Ikeda, *High Strength Elastomers of Hydrogenated NBR Containing Zinc Oxide and Methacrylic Acid*, Society of Automotive Engineers (SAE) Technical Paper Series, No. 890359, Detroit, Mich., Feb. 27–Mar. 3, 1989.
27. K. Hashimoto, Y. Otawa and Y. Todani, "Applications for HSN Elastomers," *Autom. Polym. Des.* **8**(3) (Feb. 1989).
28. K. Hashimoto and co-workers, "Highly Saturated Nitrile Elastomer, A Review," paper presented at the *A.C.S. Energy Rubber Group*, Dallas, Tex., Jan. 19, 1989.

General References

29. J. R. Purdon, in J. R. Purdon, *The Vanderbilt Rubber Handook*, 13th ed., R. T. Vanderbilt Co., Inc., New York, 1990, p. 166.
30. D. A. Seil and F. R. Wolf, in Ref. 13, Chapt. 11, p. 332.
31. P. W. Milner, *Dev. Rubber Technol.* **4**, 57 (1987).
32. J. R. Dunn, *Kautsch. Gummi Kunstst.* **36**(11), 966 (1983).
33. H. H. Bertram, *Dev. Rubber Technol.* **2**, 51 (1981).
34. J. R. Dunn, *Rubber Chem. Technol.* **51**(3), 389 (1978).
35. A. H. Jorgensen, in J. McKetta and W. Cunningham, eds., *The Encyclopedia Chemical Processes and Design*, Vol. **1**, Marcel Dekker, New York, 1976, p. 439.
36. C. H. Lufter, "Vulcanization of Nitrile Rubber," in C. H. Lufter, "Vulcanization of Nitrile Rubber," *Vulcanization of Elastomers*, Reinhold Publishing Corp., New York, 1964.

DONALD MACKEY
AUGUST H. JORGENSEN
Zeon Chemicals, USA

Related Articles

Acrylonitrile; Butadiene; Sealants