

Uses of Rubber and Rubber Mixtures-2: Special Purpose Elastomers

The worldwide production capacity for all elastomers is much more than 17,500 kilotons per year (kt/yr) and is split between natural rubber and synthetic elastomers. But the level of natural rubber being used has been decreasing due to the emergence of new solution-polymerized elastomers and special purpose polymers.

These synthetic elastomers occupy critical application areas principally because they have one or more unique attributes. This distinction in the attributes of the specialty elastomers and the structural features responsible for this distinction are illustrated in Table 1.

It is important to realize that specialty elastomers have a variety of components and structures that have been selected to provide key performance attributes. These compositions have been recognized by the ISO 1629

nomenclature procedures (Table 2) and have been commonly used to distinguish them.

For example, the word "rubber" is inserted after the name of the monomers from which the rubber was prepared and is applicable to elastomers that contain high levels of

Polybutadiene is thus denoted as BR and styrene-butadiene copolymer as SBR. Elastomers that have substituted carboxylic acid groups (UCOOH) on the polymer chain begin with an X. For example, carboxylated chloroprene rubber would be denoted XCR. Rubbers containing a halogen begin with the element employed. Bromobutyl rubber is therefore denoted as BIIR. Chlorobutyl rubber is described as CIIR. Table 3 presents the nomenclature for over 20 commercial elastomers

A notable example of this is the development of EPM elastomers, which contain both ethylene and propylene as the principal monomers. In these copolymers the absence of propylene would lead to crystalline polyethylene whereas the absence of ethylene would lead to thermally unstable polypropylene.

Therefore specialty elastomers typically consist of more than one monomer providing a combination of properties not available from a single monomer.

Elastomers with strong polarity are more resistant to polar organic fluids and oils than those that are composed entirely of hydrocarbons.

Table-1. Specialty elastomers-estimated volumes and key

Elastomer ^a	Key attribute	Structural feature	Estimated volume (kt/yr)
EPM, EPDM	Environmental resistance	Saturated backbone	1200
Plastomer	Environmental resistance; compatibility with iPP	Saturated backbone; higher α -olefin copolymer	1000
CR	Resistance to hydrocarbon solvents	Chlorination of isoprene rubber	310
CSM	Strong resistance to solvents	Ionic interactions and chlorinated backbone	280
EAM	Resistance to hydrocarbon solvents; heat resistance	Ethylene backbone with functionality	75
HNBR	Environmental resistance; oxidation resistance	Saturated backbone; nitrile groups by copolymerization	45
ACM	Oxidation resistance	Saturated backbone	8
Silicone (Q)	Wide temperature service	Stable silicon–oxygen bonds, low T_g for polymers	42
Polyether (O)	Excellent low-temperature properties	Ether linkage	11
Fluoroelastomers	Chemical resistance	Chemically unreactive carbon–fluorine bonds	8

^a EPM = ethylene-propylene copolymer; EPDM = ethylene-propylene-diene terpolymer; CR = chloroprene rubber; CSM = chlorosulfonated polyethylene; EAM = ethylene-vinyl acetate copolymer; HNBR = hydrogenated acrylonitrile-butadiene rubber; ACM = acrylic rubber; Q = polysiloxane rubber; O = oxygenated rubber.

Table-2. Generic nomenclature of Synthetic elastomers

M	Saturated polymethylene chain
N	Nitrogen on the polymer chain
O	Carbon and oxygen in the polymer chain
R	Unsaturated carbon chain
Q	Silicon and oxygen in the polymer chain
T	Carbon, oxygen, and sulfur in the polymer chain (polysulfide elastomers)
U	Carbon, nitrogen, and oxygen in polymer

Table 3 International Abbreviations for Elastomers

ACM	Copolymer of ethyl acrylate or other acrylate plus a low level of other unsaturated monomer for vulcanization
AU	Polyester polyurethane
BR	Butadiene rubber
BIIR	Bromo-isobutene-isoprene (bromobutyl) rubber
CFM	Polychlorotrifluoroethylene
CIIR	Chloro-isobutene-isoprene (chlorobutyl) rubber
CM	Chloropolyethylene
CR	Chloroprene rubber
CSM	Chlorosulfonyl polyethylene
EAM	Ethylene-vinyl acetate copolymer
EPDM	Terpolymer of ethylene, propylene, and a diene with unsaturation to facilitate vulcanization
EPM	Ethylene-propylene copolymer
EU	Polyether polyurethane
HNBR	Hydrogenated acrylonitrile-butadiene rubber
IIR	Isobutene-isoprene rubber (butyl rubber)
IM	Isobutene
IR	Polyisoprene (synthetic)
MQ	Silicone rubber with methyl groups on the polymer chain (e.g., dimethyl polysiloxane)
NBR	Acrylonitrile-butadiene rubber
E-SBR	Emulsion styrene-butadiene rubber
S-SBR	Solution styrene-butadiene rubber
XNBR	Carboxylated acrylonitrile-butadiene rubber
XSBR	Carboxylated styrene-butadiene rubber
YAU	Thermoplastic polyester polyurethane
YEU	Thermoplastic polyether polyurethane
YSBR	Block copolymer of styrene and butadiene
YSIR	Block copolymer of styrene and isoprene

NEED FOR SPECIALTY SYNTHETIC ELASTOMERS

Specialty elastomers are valued for particular properties or combinations of properties typically unavailable in the large-volume elastomers.

A wide variety of specialty synthetic elastomers have been developed to overcome some of the performance deficiencies of natural rubber (NR) and the larger volume general-purpose rubbers (GPRs) such as styrene-butadiene rubber (SBR) and butadiene rubber (BR). Some of these deficiencies are

1. Poor resistance to light, oxygen, and ozone weathering
2. Relatively poor heat resistance
3. Poor resistance to organic fluids

This property enhancement is performed by the polymer designer and they have considerable latitude in the selection of monomer(s) and polymer chain architecture as well as the process to be used for the synthesis.

There are six distinct and important tools employed in matching the structure of the synthetic specialty elastomer to its intended use:

1. The composition of the elastomer
2. The microstructure and orientation of the monomers
3. The use of a combination of monomers
4. Segregation of the different monomers into portions of a single chain (block copolymers)
5. The architecture of the elastomer as defined by distribution of composition and molecular weight

Two of the most important properties of an elastomer are its ability to resist weathering due to oxygen, ozone, and light and the ability to withstand organic fluids.

Elastomers with a saturated backbone are more resistant to weathering than those with unsaturated backbones. Thus EPM is significantly better than BR or NR. The ultimate weathering is for elastomers where the CUC backbone is replaced with the SiUOUSi

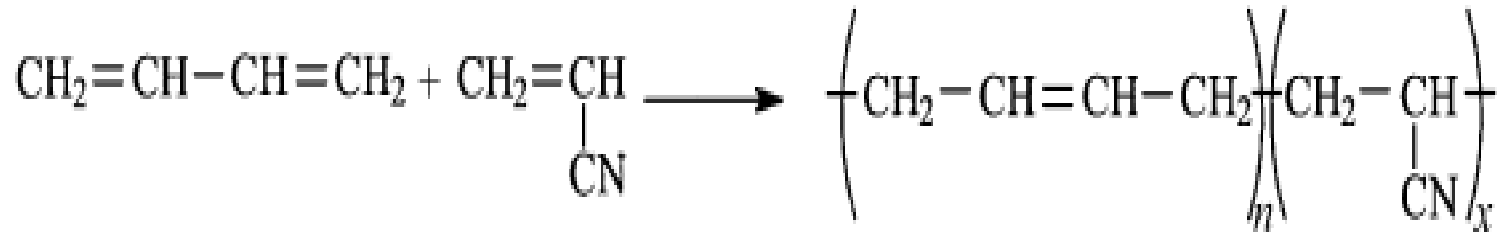
Thus nitrile (NBR), acrylic rubber (ACM), and fluorinated rubber (FKM) are more solvent-resistant than SBR, EPDM, or butyl rubber (IIR). Chlorinated polymers, such as polychloroprene (CR), which are intermediate in polarity, are intermediate between these extremes. The use of copolymers in specialty elastomers often leads to additional structural features such as intermolecular compositional differences by inducing differences in the comonomer distribution within the copolymer.

VENT-RESISTANT SPECIALTY ELASTOMERS

Solvents encompass a broad class of apolar organic fluids. This includes paraffins, aromatics, cycloalkanes, olefins, chlorinated hydrocarbons, and fatty acids and their esters but not small polar molecules such as methanol.

Vulcanizates of hydrocarbon elastomers easily swell in these solvents and lose most of their tensile strength, elongation, and resistance to set or abrasion. Thus specialty elastomers that resist hydrocarbon solvents are an important commercial development.

The polarity of acrylonitrile makes NBR resistant to common hydrocarbon solvents



NBR nitrile (acrylonitrile-butadiene copolymer).

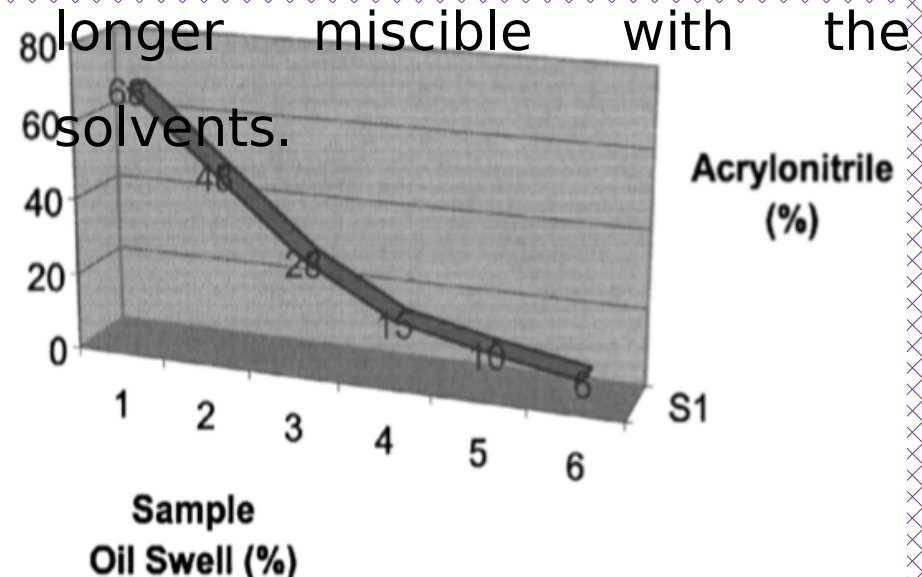
Increasing the acrylonitrile concentration of NBR improves its resistance to swelling in oil

However the trade-off is deterioration in crack resistance, elasticity, and low-temperature properties

However, NBR is an unsaturated elastomer and is easily degraded by weathering. Most of these shortcomings can be alleviated by hydrogenating the double bonds to form hydrogenated NBR (HNBR)

The class of solvent-resistant elastomers incorporates large amounts of strongly polarizing groups such as esters, nitriles, and halogens to raise the solubility parameter of the elastomer such that it is no

longer miscible with the solvents.



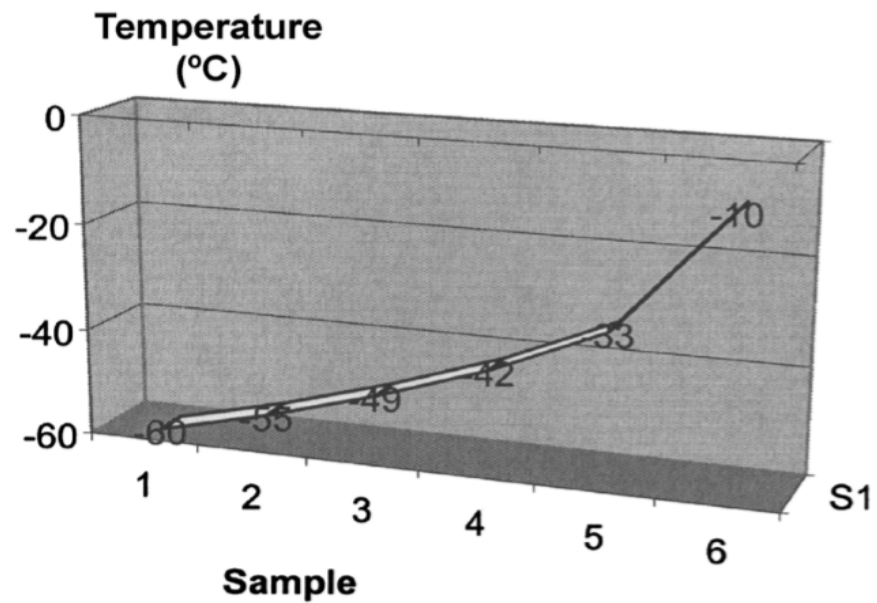


Figure 4 illustrates the effect of acrylonitrile on the brittle temperature of the elastomer.

Nitrile polymers are typically compounded with low-structure, large particle size carbon blacks such as N660 or N762.

In addition, a plasticizer is added along with stearic acid and zinc oxide for the cure system.

Table 4 displays a generic compound formulation suitable to serve as an inner tube of a high-pressure hydraulic hose.

Table 4 Generic NBR/SBR Hydraulic Hose Tube

Formula (phr)	
NBR (40% acrylonitrile)	80
E-SBR (1500)	20
N660	110
Stearic acid	1
Zinc oxide	5
Diocetyl phthalate	16
Sulfur	2
TBBS	1
TMTD	0.1
Typical property targets	
Tensile strength (MPa)	17.00
Ultimate elongation (%)	170.00
Volume swell (%) (ASTM #3 oil, aged 3 days at 70°C)	25

Source: Ref. 6.