

## PERP Program – New Report Alert

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Nexant's ChemSystems Process Evaluation/Research Planning program has published a new report, *Styrene Butadiene Rubber/Butadiene Rubber (02/03S1)*.

### Background

Styrene butadiene rubber (SBR) was the first major synthetic rubber to be produced globally. Early commercial grades (Buna S) produced in Germany and in the United States by Standard Oil Company/The Rubber Reserve Company during the Second World War were based on the emulsion polymerization technology developed by I.G. Farbenindustrie AG of Germany.

During the 1960s the first solution-polymerized random SBR grades were produced commercially by Firestone and Phillips. The original aim was to produce SBR with a lower styrene content than achievable by emulsion polymerization to counteract the increase in styrene price. Standard solution SBR (sSBR) grades now have comparable styrene content to emulsion types. These grades have superior mechanical properties to emulsion SBR (eSBR).

This report addresses the process technologies and developments in the production of SBR and PBR (polybutadiene rubber). The largest end use for both compounds is in tires, where they compete between themselves and with natural rubber. The basic production technology is well established, and much of the intellectual property development has been in chemical modification, by tire manufacturers seeking to improve tire performance and costs.

### Production Technology

#### SBR

There are three conventional routes used in producing solid SBR:

- Hot emulsion polymerization
- Cold emulsion polymerization
- Solution polymerization.

Each process produces SBR grades with different properties:

- Hot emulsion polymerization is the original SBR process. The major characteristic of this process is that these grades have exceptional processing characteristics in terms of low mill shrinkage, good dimensional stability, and good extrusion characteristics. However, high levels of microgels are also produced so there is a trend toward using cold emulsion grades

in many applications. However, they are still used in applications such as adhesives and flow modifiers for other elastomers where good flow properties are required.

- Cold emulsion polymerization produces SBR grades with superior mechanical properties, especially tensile strength and abrasion resistance, compared to grades produced by the hot emulsion polymerization route. This process has largely replaced hot emulsion polymerization for the production of eSBR grades.
- Typical eSBRs contain 18 percent cis, 65 percent trans, and 17 percent vinyl butadiene forms.

Solution SBR grades have superior mechanical properties, particularly tensile strength, low rolling resistance, and handling (encompasses traction under a variety of conditions and performance at different speeds, when cornering etc), when used in tire applications. The ratio of butadiene configurations varies. Generally speaking, sSBR grades have a lower trans and vinyl and a higher cis butadiene content than eSBR grades.

Solution SBR (sSBR) is of particular importance because of the improved performance and flexibility of grade ranges. It is a preferred component, with silica filler, in so-called “green tires” which exhibit low rolling resistance and therefore improved fuel economy.

In initially making sSBR grades producers attempted to replicate the stereochemistry of eSBR grades. However, solution polymerization differs from emulsion polymerization due to its flexibility and enables SBR grades with varying styrene/butadiene ratios and cis, trans, and vinyl contents to be produced by varying the catalyst and monomer ratios and process conditions. This enables sSBR producers to produce grades specifically tailored for individual applications.

Most sSBR producers have issued patents relating to various aspects of sSBR production. However, there are basically two major commercial process types used to produce conventional solution SBRs:

- Commercial Phillips processes are batch (although Phillips technology patents cover both continuous and batch polymerization) and produce a branched polymer with comparatively narrow molecular weight distribution. Phillips is no longer in the SBR business, but this process is being utilized by a number of European producers including Repsol, Petrochim and Dow in Italy. The process has been licensed by Petrofina in Belgium in the 1990s.
- The Firestone process is continuous, producing sSBR grades with more or less linear chains and a comparatively broad molecular weight distribution.

The basic principles of the Phillips and Firestone processes are the same. Solution SBR is made by termination-free, anionic (live) polymerization initiated by alkyl lithium compounds. Other lithium compounds are suitable (e.g. aryl, alkaryl, aralkyl, tolyl, xylyl lithium, and  $\alpha/\beta$ -naphthyl lithium as well as blends), but alkyl lithium compounds are the most commonly used commercially. The absence of a spontaneous termination step enables the synthesis of polymers possessing a very narrow molecular weight distribution and less chain branching.

Carbon dioxide, water, oxygen, alcohols, mercaptans, and primary/secondary amines interfere with the activity of alkyl lithium catalysts, so the polymerization must be carried out in clean, near-anhydrous conditions. Stirred bed or agitated stainless steel reactors are widely used commercially.

Polymerization is carried out in a solution of inert aliphatic or aromatic solvent. The polymerization rate of butadiene in the presence of lithium-based catalysts is lower than styrene. However, when butadiene and styrene are mixed, the rate of polymerization is reversed, resulting in block copolymer production with a high proportion of butadiene blocks. Block formation must be suppressed since the property requirements of traditional SBR markets cannot be met by block copolymers. Random copolymerization is encouraged by incorporating into the solution "randomizing" agents such as dialkyl and heterocyclic ethers, which act as a Lewis base on the catalyst, or by controlled monomer charging (i.e. some of the styrene is added later in the polymerization cycle).

The resulting copolymer is precipitated, separated, dried, and baled.

## PBR

The polymerization of butadiene results in the formation of a number of stereo isomers. The most important commercial isomer is cis 1,4, whose configuration is similar to that of natural rubber. Natural rubber has properties of high tack and high green (unvulcanized) strength which are hard to replicate in synthetic rubbers. Five main catalyst types are used to produce BR, and the catalyst type affects the proportion produced of cis 1,4.

**Table 1 Typical Composition of Polybutadiene: Different Catalyst Systems**

<b>Catalyst Type</b>	<b>Cis 1,4 (percent)</b>	<b>Trans 1,4 (percent)</b>	<b>Vinyl (percent)</b>
Neodymium	98	1	1
Cobalt	96	2	2
Nickel	96	3	1
Titanium	93	3	4
Lithium	36	52	12

High Cis-BR is required for tire production.

Commercially, Ziegler Natta catalyst systems based on transition metal compositions and on the rare earth neodymium are used to manufacture high cis types due to their selectivity in promoting polymerization of this type of stereo-regularity. High cis 1,4 polymer has a very low glass transition temperature (T<sub>g</sub>), leading to high resilience, good low-temperature properties, and low heat build up

on repeated deformation. High cis rubber (i.e. four percent or less of 1,2 vinyl) does not crosslink readily and withstands high temperatures without increase in melt viscosity, making it preferred for tires where significant heat build can take place. High cis BR is used widely in tires, where its properties are of benefit in sidewalls, carcass stocks, and tire treads. However, the high cis BR has poor wet grip performance to counter the advantages of the low rolling resistance and high abrasion resistance. Blending with other polymers such as SBR is typically used to achieve the desired mix of properties in the tire tread.

The properties of high cis BR vary between catalyst systems and even for one catalyst system. Products with unbranched chains and narrow molar mass distributions tend to provide high strength but are difficult to process. Long linear chains tend also to be subject to greater "cold flow", which is when green rubber flows and distorts in storage. Polymers made with neodymium catalyst systems are highly linear with broad molar mass distribution, giving good properties except for extrudability and cold flow. Nickel systems tend to produce rather more highly branched products, with better processability but lower tensile strength and fatigue resistance. Titanium and cobalt based products are between these two extremes, and the degree of branching can in any case be varied in the cobalt catalyzed system. Branching can be intentionally introduced into high cis BR by post-polymerization reactions such as with sulfur dichloride.

High molar mass BR has improved tensile strength, abrasion resistance and fatigue resistance. However, mixing and processing is more difficult with high molar mass product. Oil extension with naphthenic or aromatic oil is used to make this material more easily processed.

Low Cis BR is primarily used as a modifier for polystyrene.

## **Technical Developments**

In recent years, SBR developments have been predominantly initiated by the tire industry. This is not surprising when several of the SBR producers have put their assets up for sale in recent times such as Polimeri in Europe, DSM in the United States and others. This is partly due to the commoditization of SBR and also to butadiene price rises which are difficult to pass on to the tire producers. This has created severe pressure on margins for SBR producers. Therefore the majority of recent developments have been undertaken by the tire companies themselves rather than the SBR producers who were more active in the past. Property optimization of SBR has been achieved, to some extent, by conventional sSBR technology. By modifying the way in which monomers are added, the polymerization conditions, and the use of cocatalysts and randomizing agents, the proportion of cis and vinyl isomers and the chain structure of the resulting "tailored" polymer can be altered. Nevertheless, the overall properties of "tailored" sSBR sometimes fall short of expected tire industry requirements.

The automotive industry is under continued pressure to improve the environmental performance and useful life of automotive components. Solution SBR producers are responding by modifying conventional sSBR technology to develop SBR grades with optimum combination of rolling resistance, wear resistance, blow-out resistance, chipping/chunking resistance, road traction under a variety of weather conditions, handling, noise transmission, and other performance properties for different tire applications.

There are a number of ways in which these improvements are being achieved:

- Reformulating compounds and using high-performance additives in conjunction with "tailored" sSBR grades
- Developing novel additives/modifiers that can be added to the SBR at the compound stage
- Further modification of polymerization conditions to enable both block and random copolymerization
- Introduction of post-polymerization steps to enable better control of copolymer end group structure, thus significantly altering the properties of the resulting SBR
- Introduction of post-polymerization steps to facilitate better interaction with the reinforcement system. This is one of the most radical developments affecting the rubber industry, since it enables silica to significantly displace carbon black as the favored reinforcement for tire applications.

This report reviews recent developments of novel compound additives, developments in sSBR polymerization, and in-reactor, post-polymerization technology.

## Markets

With global demand at around 3.7 million tons per year, SBR is the most important synthetic elastomer. However, demand for natural rubber is still around double this at 7.2 million tons per year. Globally nearly 70 percent of SBR is consumed by the automobile industry for tires and tire products where it is most widely used in the manufacture of the tread.

PBR is the second largest commodity synthetic elastomer by volume, with global consumption estimated at around 2.1 million tons per year. As with SBR, the major application for PBR is tires. PBR is generally consumed in the side-walls of tires due to its low susceptibility to flex-cracking and high weather resistance. PBR is also consumed in tread compounds due to high abrasion resistance and low rolling resistance.

The second single most important area for PBR consumption is impact modification of polystyrene to produce high impact polystyrene (HIPS). Generally the low-cis product is favored, although there is some inter-material competition.

## Supply

Globally SBR is a fragmented industry with little leadership. The situation in sSBR is better than eSBR, where there is generally more market discipline and technology is harder to obtain. Global overcapacity in eSBR has led to a flood of low cost exports from Eastern and Central Europe and Asia into North America and Western Europe, which has depressed prices and production in the home markets. The situation in PBR is better with the top three producers representing a third of the market.

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