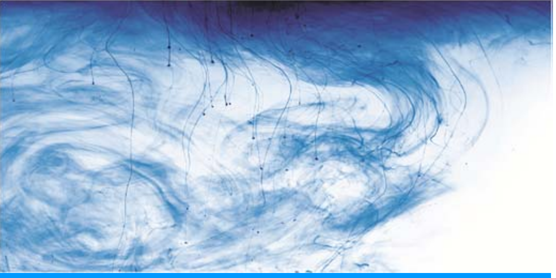

CHEMSYSTEMS
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“Green” Tires

PERP 2011S12

Report Abstract
May 2012

Nexant

"Green" Tires

May 2012

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The ChemSystems Process Evaluation/Research Planning (PERP) program is recognized globally as the industry standard source for information relevant to the chemical process and refining industries. PERP reports are available as a subscription program or on a report by report basis.

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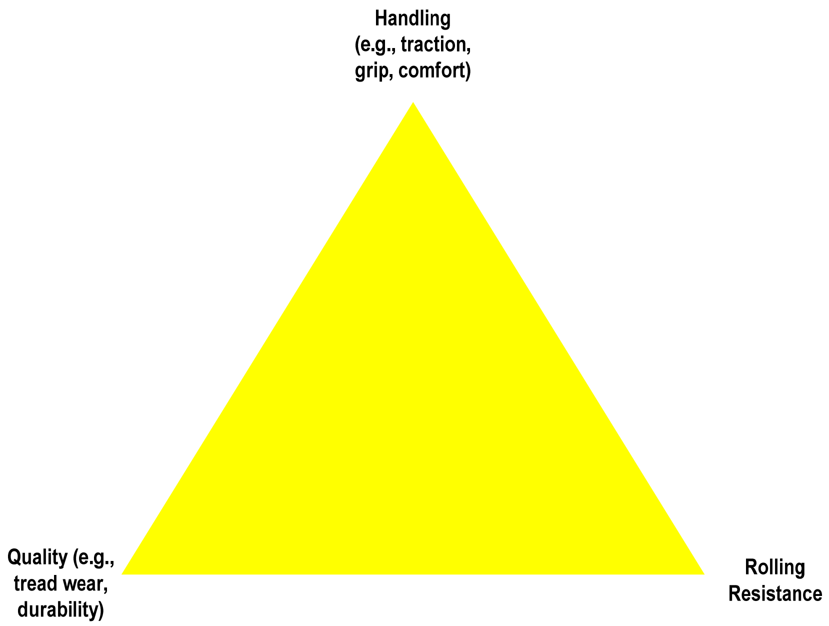
INTRODUCTION

Pneumatic tires (or tyres) are manufactured according to relatively standardized processes and machinery in around 450 tire factories in the world. With over one billion tires manufactured worldwide annually, the tire industry is the major consumer of natural rubber (virtually 100 percent *cis*-1,4 polyisoprene). There has been a strong emphasis over the past 20 years on reducing the use of petroleum ingredients in the manufacturing of tires. At the same time there is increasing pressure to improve the fuel consumption and reduce the carbon emissions from automobiles.

To reduce motorist’s fuel consumption and therefore carbon emissions, in the 1990s tire producers developed tires with reduced rolling resistance, the so-called “green” tire (available only in black). These “green tires” are so named for the environmental advantages of lower emissions and improved fuel economy. The discussion herein is not to be confused with the term green tire which refers to the uncured production step in the manufacturing of a tire.

The tire manufacturers are concerned with the “magic triangle of tire technology.” That is, the rolling resistance, quality and handling of a tire and it is the first of these, rolling resistance, which is a referred to when considering how green a tire is (re. Figure 1.1). Rolling resistance is a function of vehicle weight, silica tread, radialization, and natural rubber content. Handling considers traction (both wet and dry), grip and comfort. Quality considers durability, tread wear, endurance and cost.

Figure 1.1 Magic Triangle of Tire Technology



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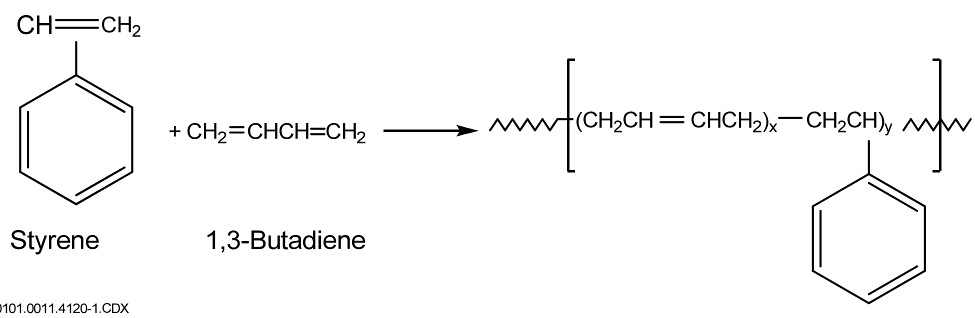
There are many aspects that make a tire "green". This report discusses one of the latest technologies that make tires green. Namely the use of high *cis* butadiene rubber produced through the use of neodymium catalyst.

COMMERCIAL TECHNOLOGY

Styrene Butadiene Rubber (SBR)

In the production of tires, SBR is principally used in tread applications, and its main advantages are its processability, uniform quality, low ageing by heat, and low frictional force resistance.

SBR is produced by the reaction of styrene with butadiene monomers as follows:



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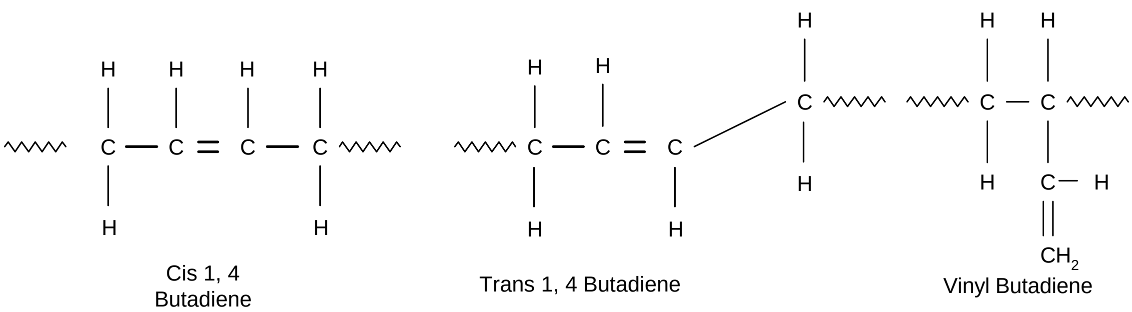
Once polymerized, each butadiene component in the SBR takes one of three forms. The ratio of these governs the properties of the rubber.



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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. Nonetheless, they are still used in applications such as adhesives and flow modifiers for other elastomers where good flow properties are required. In hot polymerized ESBR the typical microstructure of the butadiene portion is 65 percent *trans*-1,4, 18.5 percent *cis*-1,4, and 16.5 percent 1,2.

- 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. For cold ESBR polymerized at 4 to 10 °C, the typical microstructure of the butadiene portion is 72 percent *trans*-1,4, 12 percent *cis*-1,4, and 16 percent 1,2.
- 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.

Polybutadiene Rubber (PBR)

In the production of tires, PBR or simply BR (butadiene rubber) is generally used for the sidewalls, due to its low susceptibility to flex cracking and its high weather resistance. BR is also used for tread compounds because of its high abrasion resistance and low rolling resistance.

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 (re. Table 1.1).

Table 1.1 Typical Composition of Polybutadiene: Different Catalyst Systems
(Percent)

Catalyst Type	Cis 1,4	Trans 1,4	Vinyl
Neodymium	98	1	1
Cobalt	96	2	2
Nickel	96	3	1
Titanium	93	3	4
Lithium	36	52	12

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 (Tg), leading to high resilience, good low-temperature properties, and low heat buildup 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.

TECHNOLOGY DEVELOPMENTS

Tire makers across the board are getting really creative about how they are helping reduce the impact their product has on both consumer wallets and the environment. Section 4 provides short description of how some tire makers are using innovative materials such as sunflower oil, vegetable oil and orange peels to make a greener tire.

Another aspect of Green Tires is the use of renewable chemicals or non-petroleum-based chemicals. The use of renewable feeds allows products to be labeled and marketed as "green" not only because they are renewable but because of the smaller carbon footprint.

Goodyear has entered into a research collaboration with Genencor (now owned by DuPont), an industrial biotechnology company, to use engineered micro-organisms to produce BioIsoprene™, a chemical building block used to make synthetic rubber.

Polish rubber manufacturer Synthos S.A., and French biotech company Global Bioenergies have announced the signing of a partnership agreement to develop a new process for the conversion of renewable resources into butadiene.

Arzeda Corporation announced that it has been awarded a National Science Foundation (NSF) Small Business Innovation Research (SBIR) phase I grant for the computational design and experimental validation of an enzyme for the production of butadiene from plants and plant-derived materials rather than from petroleum.

Genomatica has announced its successful production of laboratory quantities of butadiene made from renewable feedstocks. This achievement confirms the technical viability of Genomatica's bio-based manufacturing process for the dedicated, on-purpose production of butadiene.

Lanxess, which has been developing a new family of nano rubber nanoparticles, trademarked as Nanoprene, aiming at expanding further the “magic triangle” by improving wet grip and abrasion resistance without affecting rolling resistance negatively.

A research group at Oregon State University led by Kaichang Li recently reported that microcellulose, or microcrystalline cellulose (a micrometer-sized type of crystalline cellulose with an extremely well-organized structure), which can be made from various plant fibers, provides a promising alternative to the energy intensive silica mineral fillers now being used to reduce tires' rolling resistance.

There are plants besides the rubber tree (Hevea brasiliensis) from which polyisoprene (natural rubber) can be extracted. Two of these, the guayule plant and the Russian dandelion, are discussed in Section 4.

BIOTECHNOLOGY

Tire makers across the board are getting really creative about how they are helping reduce the impact their product has on both consumer wallets and the environment. Included are short description of how some tire makers are using innovative materials such as sunflower oil, vegetable oil and orange peels to make a greener tire.

PROCESS ECONOMICS

The cost of production for both BR and SBR is dominated by the cost of raw materials, i.e., butadiene and styrene. Cost estimates for the production of the following rubber products is included:

- SBR (both solution and emulsion route)
- NdBR and NiBR

The above cost estimates highlight the different process performances as they are all compared on a same capacity and location basis. However, other regions reflect to a greater extent the developing industry based on planned new projects. Therefore, Nexant has also developed a regional analysis for the production of NdBR for the USGC, Japan, Western Europe, South Korea, Singapore, and the Middle East.

All cost tables given in this report include a breakdown of the cost of production in terms of raw materials, utilities direct and allocated fixed costs, by unit consumption and per metric ton and annually, as well as contribution of depreciation to arrive at a cost estimate (a simple nominal return on capital is also included)

COMMERCIAL ANALYSIS

SBR consumption is dominated by the automobile industry for tires and tire products where it is most widely used in the manufacture of the tread. BR is the second largest commodity synthetic rubber by volume after SBR. Its main application is in tires and other automotive applications.

- Global SBR and BR supply, demand and trade data are given and discussed.

- In addition, supply, demand and trade data is given and discussed according to key regions (i.e., United States, Western Europe, and Asia Pacific)
- A list of plants in each of the key regions above is given showing specific plant capacities, owning company, location and annual tonnage produced

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