Solution Styrene-Butadiene Rubber (S-SBR)

WHAT IS SBR?

SBR stands for Styrene – Butadiene Rubber, that is a random copolymer from the aforesaid monomers. There are two major types of SBR, Emulsion SBR (E-SBR) and Solution SBR (S-SBR), based on the different manufacturing process. The peculiar nature of the insertion of butadiene on the growing chain, ie the 1,4 and 1,2 additions, together with the two possible 1,4 addition isomers, cis and trans, suggests that it would be more appropriate to refer to SBR as a four-monomer copolymer. This remark acquires a particular meaning if we consider the physical and rheological characteristics of the finished polymer. The balance between the structural unit content of styrene, 1,4 and 1,2 butadiene along the chain is the most important parameter affecting the Tg of the material. Most interestingly, the concentration of 1,4 trans units has a strong influence on the strain induced crystallization of the rubber, which means a reinforcing effect on the tensile ultimate properties: in this sense, natural rubber shows a strain induced crystallization behavior. Moreover, the relative concentration of 1,4 and 1,2 units may influence the thermal stability of the polymer. The oxidative degradation of the rubber starts from the addition of oxygen on a double bond: if the double bond id part of the main chain, as in the case of 1,4 units, the reaction will lead to a chain scission.

THE DEVELOPMENT OF NEW POLYMERS FOR TIRE INDUSTRY

Some of the requirements which have to be met during the development of a new polymer / formulation for tire production are:

- Processability
- Green strength, tack strength
- Low hysteresis
- Skid resistance, abrasion resistance, rolling efficiency
- Thermo-oxidative stability
- Low cut growth rate
- Low cost.

In recent years, because of the interest in fuel savings, technological efforts developed in tire rubbers showing the lowest dissipation of energy, namely, the lowest rolling resistance, highest traction during braking and highest wear resistance (low abrasion).

The present, most important trends in the study and development of SBR rubbers (especially Solution SBRs, because of their high synthetic flexibility, in comparison with Emulsion SBR) for tire applications are:

Modification of the macrostructure (ie width of the Molecular Weight Distribution (MWD); presence, concentration and distribution of Long Chain Branching (LCB)) and of the microstructure (ie monomer composition ratio, control of the addition of butadiene units)

Research of suitable functionalization agents, in order to achieve specific chemical interactions with the filler (carbon black and/or silica). Moreover, it is worth mentioning that a functionalized rubber may show an improved adhesion onto certain substrates, namely the steel cords of the tire carcass.
In both cases, the goal is to improve the rheological behavior of the polymer in all the various phases of its "service life", namely:

The preparation of the compound, searching for the best possible compromise between the quality of mixing and the mixing time. In this sense the flow characteristics of the rubber are of the utmost importance and the macrostructural features are the practical tools by means of which the rheological parameters are controlled (ie pseudoplasticity, extensional viscosity, swelling, etc.). Also the interaction with the filler plays an important role. Moreover, We must mention the search for additives / modifiers that can be added to SBR at the compound stage to improve properties.

The ease of processing, which could be defined as the facility, for a certain material, to be melted, conveyed and shaped even into complex items, without an excessive consumption of energy and time and without any significant change in its final characteristics (ie degradation). The vulcanization process is crucial in SBR manufacturing and must be considered as part of the overall processing cycle

The end use behavior of the manufactured. In case of tires and, in particular, of the treads, We are talking about the "solid state properties"; in this sense, the most important characteristics are the dynamic properties showed in the different service situations, the mechanical characteristics (ie tensile strength, elongation at break) and the resistance to abrasion. The polymer microstructure (via the Tg), together with the homogeneity and quality of the vulcanized compound, influences the dynamic properties and the resistance to abrasion, while the mechanical behavior is strongly related to the polymer macrostructure (molecular weight distribution - MWD, long chain branching - LCB) and to the final result of the vulcanization.

It would be correct to add to the former points the efforts to modify the S-SBRs from the point of view of the process itself: the tendency is to increase progressively the monomer / solvent ratio in order to reduce the cost for the solvent recovery and treatment and to cut the emission of low molecular weight hydrocarbons (ie n-hexane, cyclohexane, traces of the residual monomers) into the environment. The logical target would be to develop a solvent-free, mass polymerization of styrene and butadiene, based upon anionic initiators. A processing machine like the extruder (or something resembling it) seems to be the better answer to the problems associated to mass polymerization, that is run-away reactions, the conveying of fluids whose viscosity changes of several orders of magnitude during the polymerization reaction and the recovery or residual monomers.

E-SBR COMPARED TO S-SBR.

There is a growing competition between E-SBR and S-SBR grades. And the very beginning of their development, S-SBRs suffered from processing problems, due to their narrow MWD. As the matter of fact, the main problem for S-SBR to overcome has always been the non – interchangeability with the E-SBRs commonly used by the tire producers: the limited number of grades coming from the emulsion process makes it easier to switch from a supplier to the other, without any re-configuration of the processing machines and procedures. So one of the main efforts of the S-SBR producers has been the search for a better processability, which is obtained by modifying the polymer macrostructure (ie MWD and LCB). In this sense, the use of coupling agents like $SiCl_4$ and $SnCl_4$ in the batch anionic synthesis provided a way to broaden the MWD adding a star-shaped structure at the same time.

In order to maximize market share, automotive companies have continuously developed vehicles with superior performance and durability (increased mileage). This has resulted in increasingly stringent tire performance specifications. These have been partly met by redesigning the structure components (ie tread patterns and reformulating compounds). In spite of their resistance, tire producers have found no alternative to S-SBR grades for highly specified tire components for high performance tires. The need for reducing fuel consumption led to the definition of specifications also for the rolling resistance of the tread material: in the U.S. the CAFE (Corporate Average Fuel Economy) regulations are gradually pushing in this direction. The market is getting more and more demanding in the aforesaid specifications, and such performances improvements cannot be achieved with E-SBR, making a gradual trend toward the use of S-SBR inevitable.

PLANT SCHEMES

The production of emulsion and solution SBR can be carried out by means of two fundamental process configurations: the batch process and the continuous process.

Typically, the E-SBR process is continuous, while S-SBR facilities are both continuous and batch.

The batch process allows a better and easier “fine tuning” of the reaction conditions and, therefore, of the polymer characteristics

Solution SBR is made by termination-free, anionic “living” polymerization initiated by alkyl lithium compounds, usually n-butyl lithium (NBL). The use of alkyl lithium compounds is due the solubility of this class of organometallics in the hydrocarbon solvents (n-hexane and cyclohexane) used in this process.

Thanks to the characteristics of “living” anionic solution polymerization, the final practical conversion of the reaction is 100 %, so there is no need for a residual monomer recovery step, as it is the case in the emulsion radical process (~ 70 % end conversion for oil extended grades).

Due to the broad range of possible micro and macrostructures, it is difficult to define a typical recipe for a S-SBR: the following table represents a general scheme, showing some of the most important features of the recipe for a 25% styrene S-SBR (the styrene content of the commercial products varies typically from 10 to 40%).