

BUTADIENE-STYRENE RUBBER (SBR)

Introduction

- The butadiene-styrene rubbers whose abbreviation is SBR (Styrene Butadiene Rubber), are today the most consumed elastomers in the world.
- The first butadiene-styrene copolymers were produced in Germany in 1937, in the laboratories of the company IG Farbenindustrie, using the emulsion process. Researchers Bock and Tschunker named this product Buna S. This same process later resulted in the butadiene-acrylonitrile copolymer, which became commercially known as Buna N.

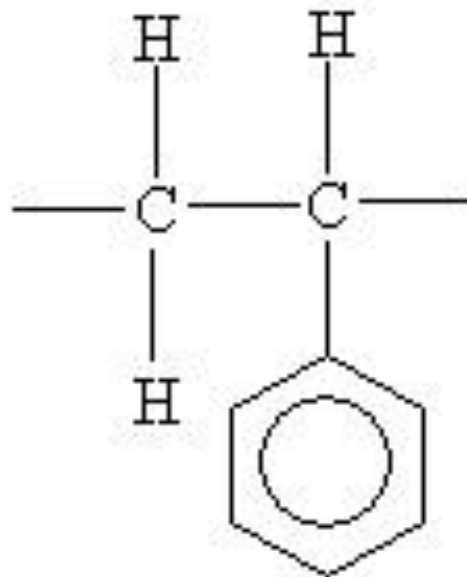
Introduction

- The product produced in Germany had poor properties when compared to natural rubber. During the 2nd world war, the United States improved the technology and arrived, in 1942, to the production of the so-called rubber GR-S (styrene), later called SBR. At the end of the 2nd war, the United States had 15 SBR plants, 16 butadiene plants and 5 styrene plants, later sold to the private sector, between 1946-1955.

Introduction

- The first butadiene-styrene copolymers were produced by emulsion polymerization, with persulfate polymerization initiators, at a temperature of 50°C. With the introduction of redox polymerization catalysts, the production temperature became 5°C; to differentiate the types produced at one temperature or another, the first ones are called hot SBR (hot SBR) and those obtained at 5°C, cold SBR (cold SBR). The application of ionic polymerization techniques allowed the production of styrene-butadiene rubbers in solution; to differentiate them from the previous ones, the abbreviations E-SBR and S-SBR were proposed for SBR polymerized in emulsion and solution, respectively.

Introduction



E-SBR. Structure and commercial types

- Among the E-SBR, the cold polymerized types are practically the only ones used in the rubber industry today. The main reason for this is that, with redox-type polymerization at 5°C, the tendency to branching during polymer chain formation is considerably reduced; This trend is very much observed in polymerizations at 50°C, which can even lead to chain cross-linking and consequent gel formation, limiting its molecular weight to 90,000.

E-SBR. Structure and commercial types

- In polymerization at 5°C, the chains maintain a predominantly linear structure, allowing molecular weights of around 250,000 to be obtained; this process can lead to obtaining molecular weights of 800,000, corresponding to vulcanized rubbers with better mechanical resistance, but which, due to their high molecular weight, are practically unprocessable in conventional rubber equipment. This problem is solved by introducing extender oils during the polymerization process, when an oil emulsion is added mineral, naphthenic or aromatic, in the proportions of 25, 37.5 or 50 parts (phr). In these oilextended SBRs (OESBR - extended SBR), the presence of the plasticizer makes mixing in conventional rubber equipment possible, however, there is a decrease in mechanical strength; but, as it starts from a very high level, the end result is a rubber with resistance comparable to that of non-extended types and with a lower price, as the plasticiser is cheaper than the rubber.

E-SBR. Structure and commercial types

- To obtain an optimal dispersion of fillers, a dispersion of carbon black is introduced into the latex phase of some SBRs and then coagulation is carried out. These SBRs, known as masterbatches, reduce or avoid carbon black handling, which also increases production capacity by ensuring correct and uniform carbon black dispersion.

E-SBR. Structure and commercial types

- Regardless of the trade name of each product, the International Institute of Synthetic Rubber Producers (IISRP) assigns a number to each type of SBR. The hundred from 1000 to 1099 are reserved for hot cured SBRs; from 1100 to 1199 to masterbatches of these with carbon black (whose commercial production does not currently exist); from 1500 to 1599 the cold SBRs; from 1600 to 1699 with masterbatches of these with carbon black; from 1700 to 1799 SBRs extended in oil and from 1800 to 1899 OESBR masterbatches with carbon black.

E-SBR. Structure and commercial types

- Within each group, the characteristics that differentiate one type from the other and those that we must consider to select the most suitable SBR for a given application are:
- **Staining or non-staining factor** of the antioxidant incorporated into the rubber during its manufacturing process. This is the only difference between an SBR 1500 (with staining antioxidant) and an SBR 1502 (with non-staining antioxidant);
- **The type of soap used as an emulsifier:** we basically use two types of soap - fatty acid soap and rosin soap (also known as rosin soap). SBRs made in fatty acid soap have better vulcanization speed; however, those made with rosin soap have better stickiness; although there are some types with combinations of the two soaps, their effects can easily be compensated in the formulation;
- **The combined styrene content:** most types of SBR have 23.5% styrene, however, there are types with a different content - from 9.5% in SBR 1505 to 40% in SBR 1513, 1519 and 1516.

E-SBR. Structure and commercial types

- **Mooney viscosity:** is related to molecular mass and molecular weight distribution; in most types it is 50 ± 5 Mooney units, but there are also types with lower viscosity, such as SBR 1510 (viscosity 32), suitable for the production of expanded artifacts; there are others with higher viscosity, such as SBR 1570 (viscosity 117), especially indicated for formulations with a large amount of fillers and plasticizers.

E-SBR. Structure and commercial types

- **The type of coagulation system**, with acid or salts. This characteristic only affects electrical insulation; for example, SBR 1509 coagulated with aluminum sulphate, is especially suitable for cable insulation.

Formulation and Processing

- Like natural rubber, SBR can be vulcanized by sulfur and accelerators, by peroxides and by other special vulcanizing agents, the first system being the most used.
- Because it has less unsaturation, it needs smaller doses of sulfur, around 1.5-2.0 phr; on the other hand, the lower chemical reactivity of the double bond, derived from butadiene, when compared to isoprene from NR or IR, requires higher activation energy, which means the use of faster accelerators or higher doses of conventional accelerators. In the case of OESBR, the proportion of vulcanizing agents is calculated on the rubber portion, excluding the incorporated oil. The lower reactivity of the double bond reduces the pre_x0002_vulcanization tendency, but as this is related to the accelerator system, in some cases it is advisable to use a retarder.

Formulation and Processing

- Compared to NR, SBR is less prone to oxidation, partly because it has an antioxidant incorporated into the manufacturing process, and partly because of the lower reactivity of the double bond. It is recommended to add 1-2 parts of an antioxidant to the compound, as well as to use EV and semi-EV vulcanization systems. The use of peroxides or special systems, such as isocyanates, are also indicated to obtain better heat resistance. The double bond in SBR makes it sensitive to ozone; therefore, if the SBR must be exposed to ozone, the use of a chemical antiozonant or waxes is recommended.

Formulation and Processing

- The differences between SBR and natural rubbers are predominantly in load acceptance. As with all rubbers that do not crystallize under stress (the rule for most synthetic rubbers), unfilled SBR has very low mechanical strength, but with the addition of reinforcing or semi-reinforcing fillers, a level of mechanical strength is achieved. Inert fillers can be used to reduce the cost of the compound, but they should always be added as a complement to a reinforcing filler, not in its place.

Formulation and Processing

- The SBR is not as sensitive to hot mechanical chewing in the presence of peptizers as is the NR; thus, plasticizers play an important role in adjusting the viscosity of compounds; but, fortunately, as most synthetic rubbers have a standardized viscosity, a standardized viscosity can be used to make a compound. SBR does not have particular compatibility problems with plasticizers. As it does not have natural tackiness, it is recommended to use tack agents, such as rosin resins, coumarone-indene, pine tar, etc., to increase tackiness, for example, in tire covers.

Formulation and Processing

- The preparation of the compounds can be done either in a cylinder mixer or in an internal mixer. For mixing in cylinders, a temperature of 45-55°C is used, and the addition of fillers must be done quickly so that the compound is smooth and homogeneous. During the mixing generates more heat than NR, which requires good cooling to maintain shear forces that ensure good dispersion of ingredients. In closed mixers, the cycles must be shorter compared to the NR, and the power consumption is about 20% higher. In the case of mixers with tangential motors, with the OESBR it is recommended to carry out the mixing in two stages:
 - - 1st. Step: high-speed preparation - 150-165°C discharge - of the masterbatch with rubber, fillers and plasticizers;
 - - 2nd. Step: after the compost has cooled down, it is finished preparing at a lower speed.
- With the new interpenetrating mixers the compost can be prepared in a single step

Formulation and Processing

- In the remaining operations, such as molding, extrusion, etc., we must follow the same procedures used in NR. These steps must be taken into account:
- The lower resistance to tearing can damage the parts when removed from the mold;
- In extrusion and calendering, generally the processing temperatures are lower than those of NR.

Formulation and Processing

- Hot polymerized SBRs provide higher extrusion speed, followed by cold polymerized SBR and equal to NR in OESBR.
- Swelling at the extruder nozzle is minimal with cold cured SBRs; it is medium with OESBR and maximum with hot cured SBRs.
- For complicated profiles with sharp edges, the most recommended types are cold polymerized SBRs, which give smoother and more regular surfaces; hot cured SBRs give brighter, more irregular surfaces. OESBR have opaque and rough surfaces.

E-SBR Properties and Applications

- With the use of reinforcing fillers, SBR have superior abrasion resistance than NR, with a more competitive price. Due to this, the SBRs replaced the NR in the manufacture of small tread parts (bicycles, motorcycles, passenger cars and light trucks), in conveyor belts, in footwear and many technical artifacts.

E-SBR Properties and Applications

- SBR rubber is inferior to NR rubber in terms of resilience and hysteresis, absorbing (and transforming into heat) a greater amount of imposed energy. The need to use greater amounts of reinforcing loads makes this difference more pronounced. Therefore, in larger tires (trucks, tractors, etc.), where the tread is thicker, it is more difficult to dissipate the heat generated; in particularly severe services (airplanes and competition cars), due to the heat generated by their higher speed, NR also continues to be used. NR generates less heat and maintains a better level of mechanical properties at moderately high temperatures.

E-SBR Properties and Applications

- With regard to behavior against dynamic fatigue, in the appearance of cracks due to fatigue or mechanical laceration, SBRs are better than NR; however, once the crack is generated, it propagates quickly. Its resistance to heat and oxidation is better than NR.

E-SBR Properties and Applications

- As for your applications;
- 70% is used in the tire sector, 13% is consumed in the form of latex (mainly for foams) and the rest is used in a wide variety of applications, including: conveyor belts, shoes, hoses, moldings, etc.

Solution Polymerized SBR (S-SBR)

- The polymerization of this type of SBR occurs with the monomers dissolved in an organic solvent, which in turn dissolves the polymer produced; polymerization occurs with the use of butyl-lithium type catalysts. Unlike emulsion polymerization, latex is not obtained, but rubber dissolved in a solvent, which, after evaporation, separates the rubber from the residual monomers.

Solution Polymerized SBR (S-SBR)

- Its main advantage is to allow certain control of the resulting polymer, varying the polymerization conditions, such as catalyst concentration, type of solvent, presence or absence of polar compounds, the order of addition of monomers, etc.; within certain limits, it is possible to easily modify the molecular characteristics of the resulting rubber, and, as a consequence, its technical properties

Solution Polymerized SBR (S-SBR)

- In the SBR emulsion synthesis and due to the reactivity ratio of styrene and butadiene being close to unity, the entry of both in the chain is random; as a consequence, the structure of the copolymer is also random in terms of the distribution of monomers. On the contrary, in ionic solution polymerization, the reactivity of butadiene is greater than that of styrene to the point that, if we load a mixture of the two monomers in equal parts, the polymerization of butadiene will continue to grow in a linear chain until all the monomer is exhausted. ; only then will the polymerization of the styrene begin, which will give rise to a polystyrene block; this process taken to the extreme is the basis of styrenic thermoplastic elastomers (SBS). One

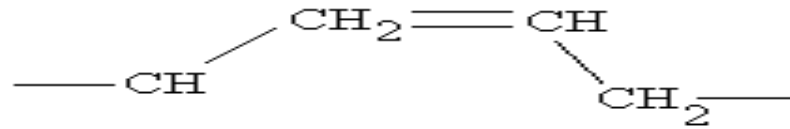
Solution Polymerized SBR (S-SBR)

- Another peculiarity is that the growing chain acts like a living polymer, that is, it is capable of continuing to grow when more monomer is added. The addition of a polar compound, such as diethyl ether, tetrahydrofuran or tertiary amines at the beginning of polymerization, tends to equalize the reactivity of the monomers in the butyllithium-induced polymerization, leading to an S-SBR with a random structure.

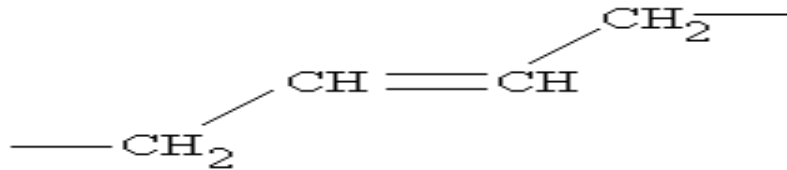
Solution Polymerized SBR (S-SBR)

- It is also possible to regulate the molecular weight of the chains, the distribution of molecular weights, the proportion of cis-1,4, trans-1,4 and 1,2 (vinyl) additions of the butadiene molecules that enter the chain, the degree branching, etc
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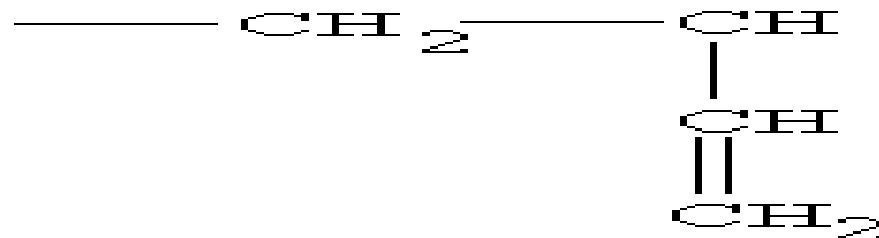
Solution Polymerized SBR (S-SBR)



Cis 1,4



Trans 1,4



Vinyl

Solution Polymerized SBR (S-SBR)

- As the initial problem was not having enough knowledge of how these molecular characteristics would translate into technological properties; numerous studies have been done in order to:
- 1st: improve process control to obtain the desired characteristics;
- 1st: improve process control to obtain the desired characteristics;
- 2nd: to improve the understanding of the influence of these characteristics on the properties of vulcanizates.

Solution Polymerized SBR (S-SBR)

- Solution polymerization provides a molecular weight distribution and structure predominantly linear, with few branches; thus, the S-SBR have greater resistance to abrasion and tearing, compared to E-SBR, as well as better dynamic properties, in favors less fatigue cracking and less hysteresis heat generation

Solution Polymerized SBR (S-SBR)

- The absence of low molecular weight fractions, which in E-SBR and other emulsion-polymerized synthetic rubbers, which act as internal plasticizers and which do not have “nerves”, makes mixing in a cylinder mixer difficult, as the band tends to detach and the compound, to be glued to the rear cylinder. When using this equipment, a low friction ratio, smaller volume and greater cooling must be used in the front cylinder, keeping it at a temperature of 45-55°C and in the rear cylinder at 70-80°C. In internal mixers, increase the load factor by 10-15%, compared to NR or E-SBR, as the power consumed is lower and the increase in the mixture size increases the machine's performance.

Solution Polymerized SBR (S-SBR)

- The second important group of solution-polymerized SBRs are those with a block structure. The grouping of styrene units in blocks increases thermoplasticity, especially useful in extrusion and calendering operations with higher speeds and smaller deformations (swelling at the extruder nozzle or at the exit of the cylinders and their subsequent contraction). Another effect of polystyrene blocks is to provide vulcanizates with higher hardness, when compared to a random SBR; this is important in the manufacture of high hardness artifacts, such as shoes.

Solution Polymerized SBR (S-SBR)

- On the other hand, polybutadiene blocks improve low temperature resistance, as well as resistance to abrasion and bending, when compared to vulcanizates of similar hardness based on random SBR.
- With regard to the preparation of SBR compounds with a block structure, the same recommendations made for the random types are valid: it is advisable to add stearic acid quickly as it acts more as a peptizer than as an activator, and to increase the load factor on internal mixer. When preparing in cylinder mixers, it is only recommended to raise 10°C at the recommended temperatures.
- S-SBR with block structure are used in the footwear industry and in the manufacture of extruded and calendered artifacts. They are widely used in blends with natural and synthetic rubber to improve extrusion and calendering characteristics.

Referências

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