

EMULSION STYRENE-BUTADIENE RUBBER (E-SBR)

INTRODUCTION

Emulsion polymerized styrene-butadiene rubber (E-SBR) is one of the most widely used polymers in the world today. The purpose of this article is to briefly review the history, production, chemistry, properties, and uses of E-SBR. Emulsion SBR is employed in many demanding applications, which enhance the quality of life and contribute significantly to our economy and standards of living.

HISTORY

In the 1930's, the first emulsion polymerized SBR known as Buna S was prepared by I. G. Farbenindustrie in Germany. The U. S. Government in 1940 established the Rubber Reserve Company to start a stockpile of natural rubber and a synthetic rubber program. These programs were expanded when the United States entered World War II. The synthetic rubber efforts were initially focused on a hot polymerized (41° C) E-SBR. Production of a 23.5% styrene and 76.5% butadiene copolymer began in 1942. Cold polymerized E-SBR (5°C), that has significantly better physical properties than hot polymerized SBR, was developed in 1947. Between 1946 and 1955 the synthetic rubber plants owned by the US Government were sold to the private industry or closed.

CHEMISTRY AND PRODUCTION

The emulsion polymerization process has several advantages. It is normally used under mild reaction conditions that are tolerant to water and requires only the absence of oxygen. The process is relatively robust to impurities and amenable to using a range of functionalized and non-functionalized monomers. Additional benefits include the fact that emulsion polymerization gives high solids contents with low reaction viscosity and is a cost-effective process. The physical state of the emulsion (colloidal) system makes it easy to control the process. Thermal and viscosity problems are much less significant than in bulk polymerization.

Table 1 shows the raw materials required in the polymerization of E-SBR and Table 2 shows a typical recipe which includes monomers (styrene and butadiene), water, emulsifier, initiator system, modifier, shortstop and a stabilizer system. The original polymerization reactions were charged out in batch reactors in which all the ingredients were loaded to the reactor and the reaction was shortstopped after it had reached the desired conversion. Current commercial productions are run continuously by feeding reactants and polymerizing through a chain of reactors before shortstopping at the desired monomers conversion. Figure 1 is a schematic of a typical continuous emulsion polymerization plant.

Table 1
Components of E-SBR

Styrene
Butadiene
Water
Emulsifier (Fa, RA, MA)
Dodecyl mercaptan
Cumene hydroperoxide
FeSO₄
EDTA
Na₄P₂O₇·10H₂O
Potassium persulfate
SFS
Stabilizer

Continuous Polymerization of E-SBR

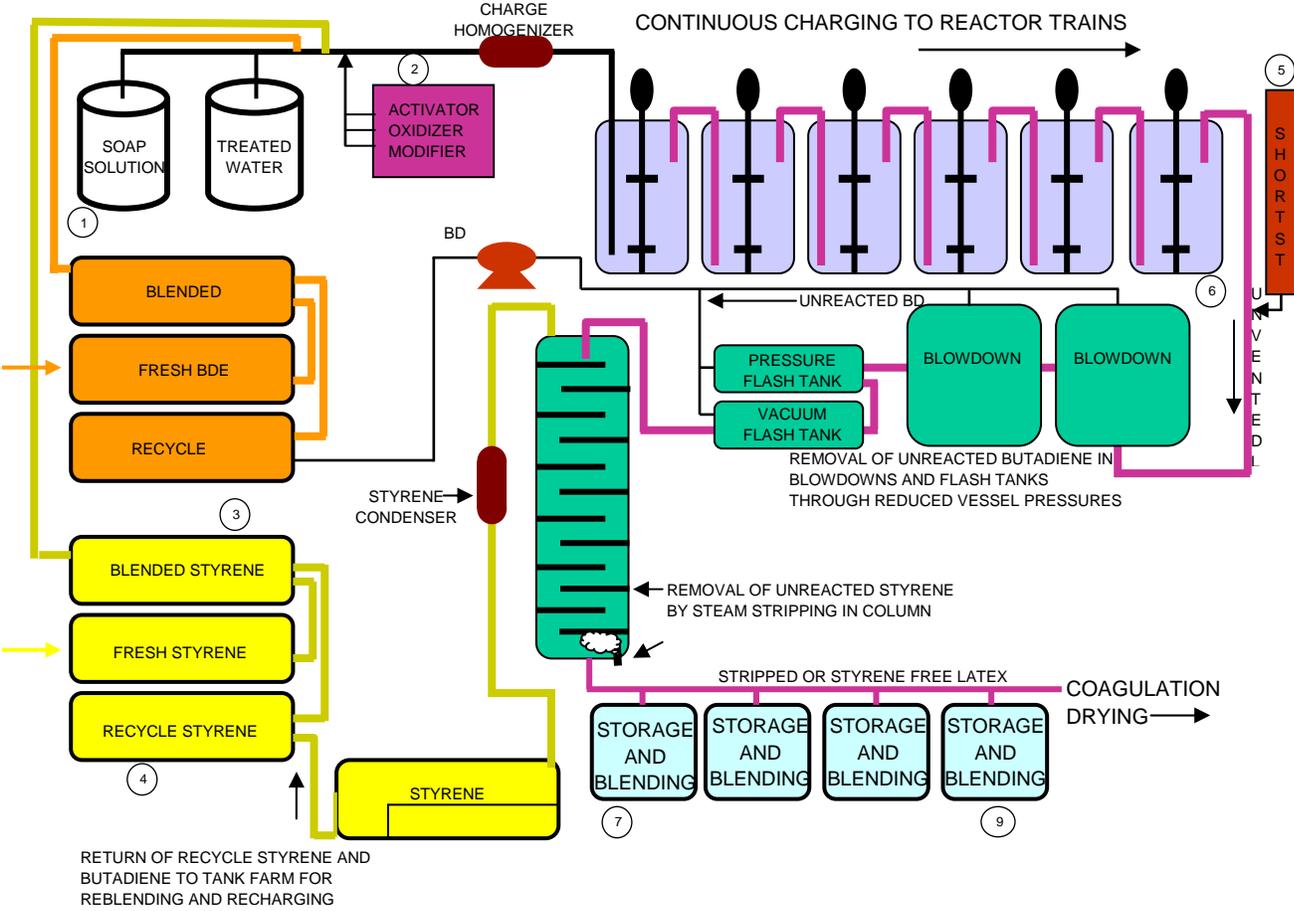
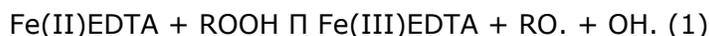


Figure 1 Continuous Polymerization of E-SBR



The monomers are continuously metered into the reactor chains and emulsified with the emulsifiers and catalyst agents. In cold polymerization, the most widely used initiator system is the redox reaction between chelated iron and organic peroxide using sodium formaldehyde sulfoxide (SFS) as reducing agent (see reactions 1 and 2 above). In hot polymerization, potassium peroxydisulfate is used as an initiator.

Mercaptan is added to furnish free radicals and to control the molecular weight distribution by terminating existing growing chains while initiating a new chain. The thiol group acts as a chain transfer agent to prevent the molecular weight from attaining the excessively high values possible in emulsion systems. The sulfur-hydrogen bond in the thiol group is extremely susceptible to attack by the growing polymer radical and thus loses a hydrogen atom by reacting with polymer radicals, equation (3). The RS \cdot formed will continue to initiate the growth of a new chain as shown in equation (4) below. The thiol prevents gel formation and improves the processability of the rubber.

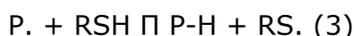


TABLE 2 Typical Recipe for SBR Emulsion Polymerization

Component	Parts by Weight	
	Cold	Hot
Styrene	25	25
Butadiene	75	75
Water	180	180
Emulsifier (FA,RA, MA)	5	5
Dodecyl mercaptan	0.2	0.8
Cumene hydroperoxide	0.17	-
FeSO ₄	0.017	-
EDTA	0.06	-
Na ₄ P ₂ O ₇ ·10H ₂ O	1.5	-
Potassium persulfate	0.3	0.3
SFS	0.1	-
Stabilizer	Varies	-

During polymerization, parameters such as temperature, flow rate and agitation are controlled to get the right conversion. Polymerization is normally allowed to proceed to about 60% conversion in cold polymerization and 70% in hot polymerization before it is stopped with a shortstop agent that reacts rapidly with the free radicals. One common short stopping agent is DEHA or diethyl hydroxylamine. Once the latex is properly shortstopped, the unreacted monomers are stripped off the latex. Butadiene is stripped by degassing the latex by means of flash distillation and reduction of system pressure. Styrene is removed by steam stripping the latex in a column. The latex is then stabilized with the appropriate antioxidant and transferred to blend tanks. In the case of oil-extended polymers or carbon black masterbatches, these materials are added as dispersions to the stripped latex. The latex is then transferred to finishing lines to be coagulated with sulfuric acid, sulfuric acid/sodium chloride, glue/sulfuric acid, aluminum sulfate, or amine coagulation aid. The type of coagulation system is selected depending on the end-use of the product. Sulfuric acid/sodium chloride is used for general purpose. Glue/sulfuric acid are used for electrical grade and low water sensitivity SBR. Sulfuric acid is used for coagulations where low-ash-polymer is

required. Amine coagulating aids are used to improve coagulation efficiency and reduce production plant pollution. The coagulated crumb is then washed, dewatered, dried, baled and packaged.

TYPES OF SBR

There is a large variety of E-SBR types based on the styrene content, polymerization temperature, staining or non-staining antioxidants, oil and carbon black content. Each of these basic classifications include a variety of SBR polymer variations with respect to Mooney viscosities, coagulation types, emulsifier type, oil levels, and carbon black types and levels. The basic groups of E-SBR are:

Table 3 Numbering System for E-SBR

Series	Types
1000	Hot polymerized polymers.
1500	Non-extended cold polymerized polymers.
1600	Non-oil-extended cold carbon black masterbatches
1700	Cold oil-extended polymers.
1800	Cold oil-extended carbon black masterbatches
1900	Miscellaneous high styrene resin masterbatches.

USES OF SBR

E-SBR is predominantly used for the production of car and light truck tires and truck tire retread compounds. A complete list of the uses of SBR includes house ware mats, drain board trays, shoe sole and heels, chewing gum, food container sealants, tires, conveyor belts, sponge articles, adhesives and caulks, automobile mats, brake and clutch pads, hose, V-belts, flooring, military tank pads, hard rubber battery box cases, extruded gaskets, rubber toys, molded rubber goods, shoe soling, cable insulation and jacketing, pharmaceutical, surgical, and sanitary products, food packaging, etc. The typical applications of E-SBR polymers are tabulated in Table 4 below.

Table 4 Typical Applications of E-SBR

	Hot Polymers	Cold E-SBR		High Styrene Masterbatch	Black Masterbatch
		Unextended	Oil Extended		
ADHESIVES					
Type & Label		x	x		
Caulking	x				
Laminating	x	x			
Mastic	x				
Panel	x				
Pressure Sensitive	x	x			
Sealant	x				
Sprayable (Crosslinked)	x				
Wall Tile	x				
AUTOMOTIVE					
Tire Treads		x			x

		Cold E-SBR			
	Hot Polymers	Unextended	Oil Extended	High Styrene Masterbatch	Black Masterbatch
Apex/Rim/Flange				x	
Bead	x	x			
Carcass		x	x		
Retread		x	x		x
Racing Tires		x	x		
Mats		x	x	x	x
MISCELLANEOUS					
Mechanical Goods	x	x	x	x	x
Rolls		x	x		x
Gaskets		x	x	x	x
Belts/Hoses		x	x		x
Hard Rubber Goods		x		x	
Cove Base	x			x	
Floor Tiles	x	x	x	x	
Footwear		x	x	x	x
Sponge		x	x	x	
Wire & Cable (Low Ash)		x			x