

EMULSION STYRENE-BUTADIENE RUBBER (E-SBR)

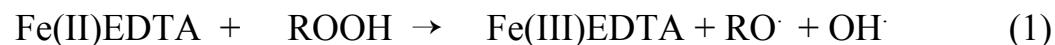
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1.0 INTRODUCTION: Emulsion polymerized styrene-butadiene rubber (E-SBR) is one of the most widely used polymers in the world today. The purpose of this article is to briefly review the history, production, chemistry, properties, and uses of E-SBR.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

2.0 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.

3.0 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, which include 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. 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 below). 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 $\text{RS}\cdot$ 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.

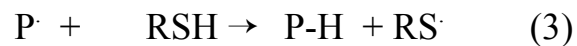


TABLE 1

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
Potassuim persulfate		0.3
SFS		0.1

Stabilizer	varies
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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. Some of the common shortstopping agents are sodium dimethyldithiocarbamate and 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 is 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.

4.0 Properties of E-SBR: E-SBR is commercially available in Mooney viscosities ranging from 30 to about 120 (ML1+4@125C). Lower Mooney viscosity E-SBR grades band more easily on the mill, incorporate fillers and oil more readily, show less heat generation during mixing, are calendered more easily, shrink less, give higher extrusion rates and have superior extrudate appearance than the higher Mooney viscosity grades. On the other hand, the high Mooney viscosity SBR's have better green strength, less porosity in the vulcanizate, and accept higher filler and oil loadings.

As the molecular weight of the SBR increases, the vulcanizate resilience and the mechanical properties, particularly tensile strength and compression set, improve. The processability of SBR improves as its molecular weight distribution broadens. Formation of high molecular weight fractions with the increase in the average molecular weight can however, prevent improvements in the processability. This is due to the fact that the tendency for gel formation also increases at higher molecular weights.

In addition to the polymer viscosity, polymerization temperature also plays an important role in shaping the processability. E-SBRs produced at low polymerization temperatures have less chain branching than those produced at higher temperature. At an equivalent viscosity, cold polymerized E-SBR is normally easier to process than hot polymerized E-SBR, and this applies particularly to a better banding on mills, less shrinkage after calendering, and a superior surface of green tire compounds. Hot rubbers give better green strength because they have more chain branching.

The styrene content of most emulsion SBR varies from 0% to 50%. The percent styrene of most commercially available grades of E-SBR is 23.5%. In vulcanizates of SBR, as styrene content increases, dynamic properties and abrasion resistance decrease while traction and hardness increase.

Polymerization temperature also affects the microstructure of E-SBR. In the cold polymerized E-SBRs, the butadiene component has, on average, about 9% cis-1.4, 54.5% trans-1.4, and 13% of vinyl-1.2 structure. At a 23.5% bound styrene level, the glass transition temperature, T_g , of SBR is about -50°C . As the styrene content in the SBR increases, the glass transition temperature also increases. Rubbers with very low T_g values are characterized by a high resilience and good abrasion resistance, but have poor wet traction. By contrast, those rubbers with high T_g , as, for instance, SBR 1721, exhibit a low resilience and poor abrasion resistance with an excellent wet traction.

The emulsifier remains in the rubber after coagulation can also have an influence on the processability. Rosin acid emulsifiers impart better knitting, tack and adhesion to the SBR polymer. Generally, polymers emulsified with rosin acid have better extrusion rates, slower cure rates, poorer heat resistance and can cause mold fouling and polymer discoloration. Fatty acid emulsified SBR polymers generally have less tack, faster curing, and high tensile properties. A compromise of the above properties is obtained by using a mixed rosin acid/fatty acid emulsifier system.

4.1 Mechanical Properties. Since SBR lacks the self-reinforcing qualities of natural rubber due to stress induced crystallization, gum vulcanizates of SBR have lower tensile properties. The tensile property of E-SBR vulcanizates depends in great measure on the type and amount of filler in the compound. Cured gum stocks have only 2.8 to 4.2 MPa tensile strength, while fine particle carbon black loadings can produce tensile strength of 27.6 Mpa. Though the compression set of some of the common E-SBR compounds is high, by proper compounding and blending, it is possible to obtain E-SBR vulcanizates with a low compression set.

4.2 Electrical Properties. SBR is a non-polar polymer and its vulcanizates are poor conductors of electricity. The electrical properties of E-SBR depend to a large extent on the amount and type of emulsifier and coagulating agent(s) used.

4.3 Resistance to Fluids. While E-SBR vulcanizates are resistant to many polar solvents such as dilute acids and bases, they will swell considerably when in contact with gasoline, oils, or fats. Due to this limitation, SBR cannot be used in applications that require resistance to swelling in contact with hydrocarbon solvents.

4.3 Cure Properties. SBR can be cured with a variety of cure systems including sulfur (accelerators and sulfur), peroxides and phenolic resins. Processing of SBR compounds can be performed in a mill, internal mixers or mixing extruders. SBR compounds are cured in a variety of ways by compression, injection molding, hot air or steam autoclaves, hot air ovens, microwave ovens and combinations of these techniques.

5.0 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. Table 1 shows the basic groups of E-SBR.

Table 1
Numbering System for E-SBR

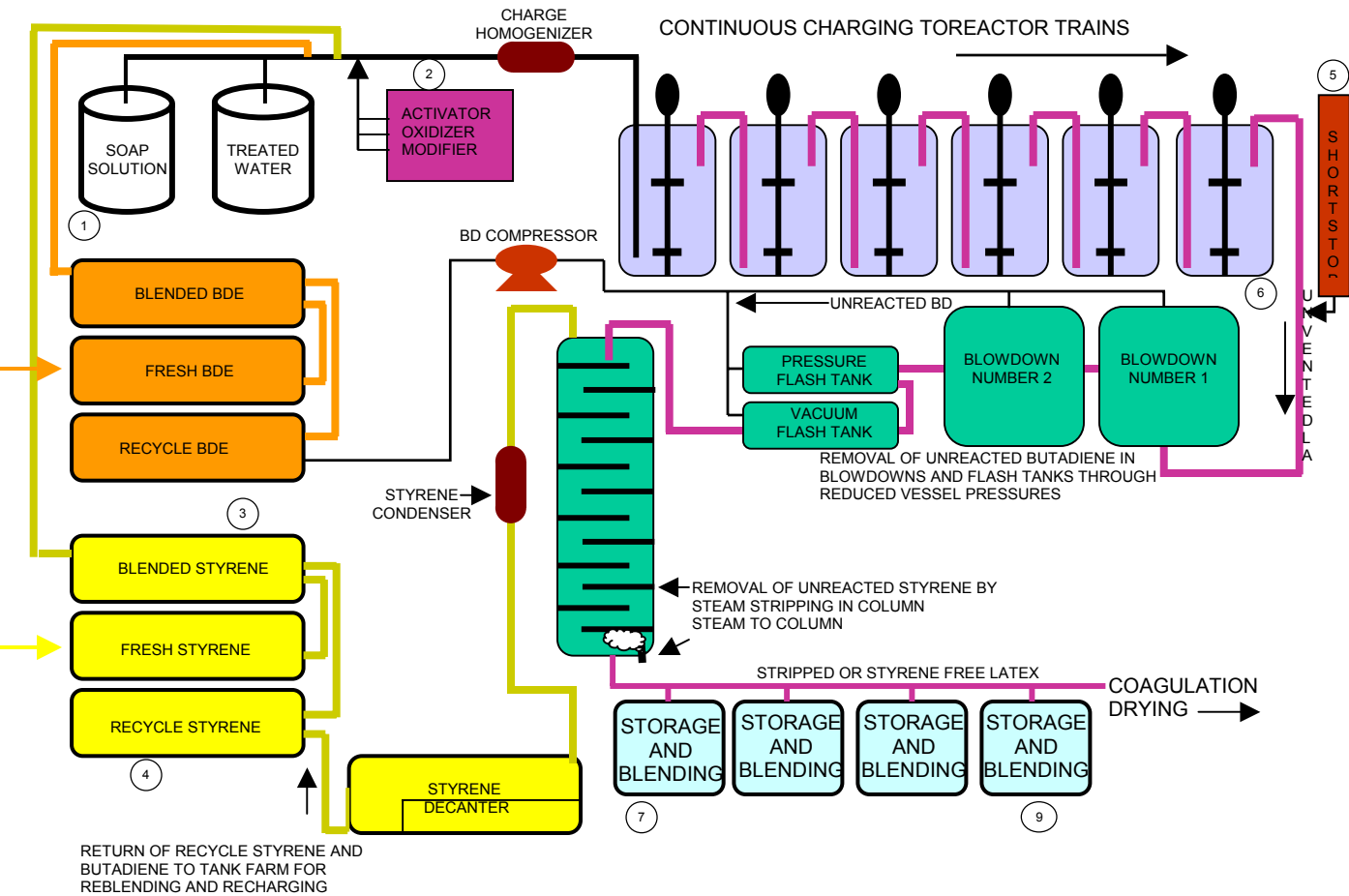
<u>Series</u>	<u>Comments</u>
1000	Hot polymerized polymers.
1500	Non-extended cold polymerized polymers.
1600	Non-oil-extended cold carbon black masterbatches
1700	Cold oil-extended polymers.
1800	Cold oil-extended carbon black masterbatches
1900	Miscellaneous high styrene resin masterbatches.

6.0 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 houseware 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, moulded 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 on Table 2 below.

TABLE 2
TYPICAL APPLICATIONS FOR E-SBR POLYMERS

	HOT POLYME RS	COLD E-SBR		HIGH STYRENE MASTER- BATCH	BLACK MASTER- BATCH
		UNEXTEND ED	OIL EXTENDE D		
<u>ADHESIVES</u>					
Type & Label	●	●	●		
Caulking	●				
Laminating	●	●			
Mastic	●				
Panel	●				
Pressure Sensitive	●	●			
Sealant	●				
Sprayable (Crosslinked)	●				
Wall Tile	●				
<u>AUTOMOTIVE</u>					
Tire Treads		●			●
Apex/Rim/Flange				●	
Bead	●	●			
Carcass		●	●		
Retread		●	●		●
Racing Tires			●		
Mats		●	●	●	●
<u>MISCELLANEOUS</u>					
Mechanical Goods	●	●	●	●	●
Rolls		●	●		●
Gaskets		●	●	●	●
Belts/Hoses		●	●		●
Hard Rubber Goods		●		●	
Cove Base	●			●	
Floor Tiles	●	●	●	●	
Footwear		●	●	●	●
Sponge		●	●	●	
Wire & Cable (Low Ash)		●			●

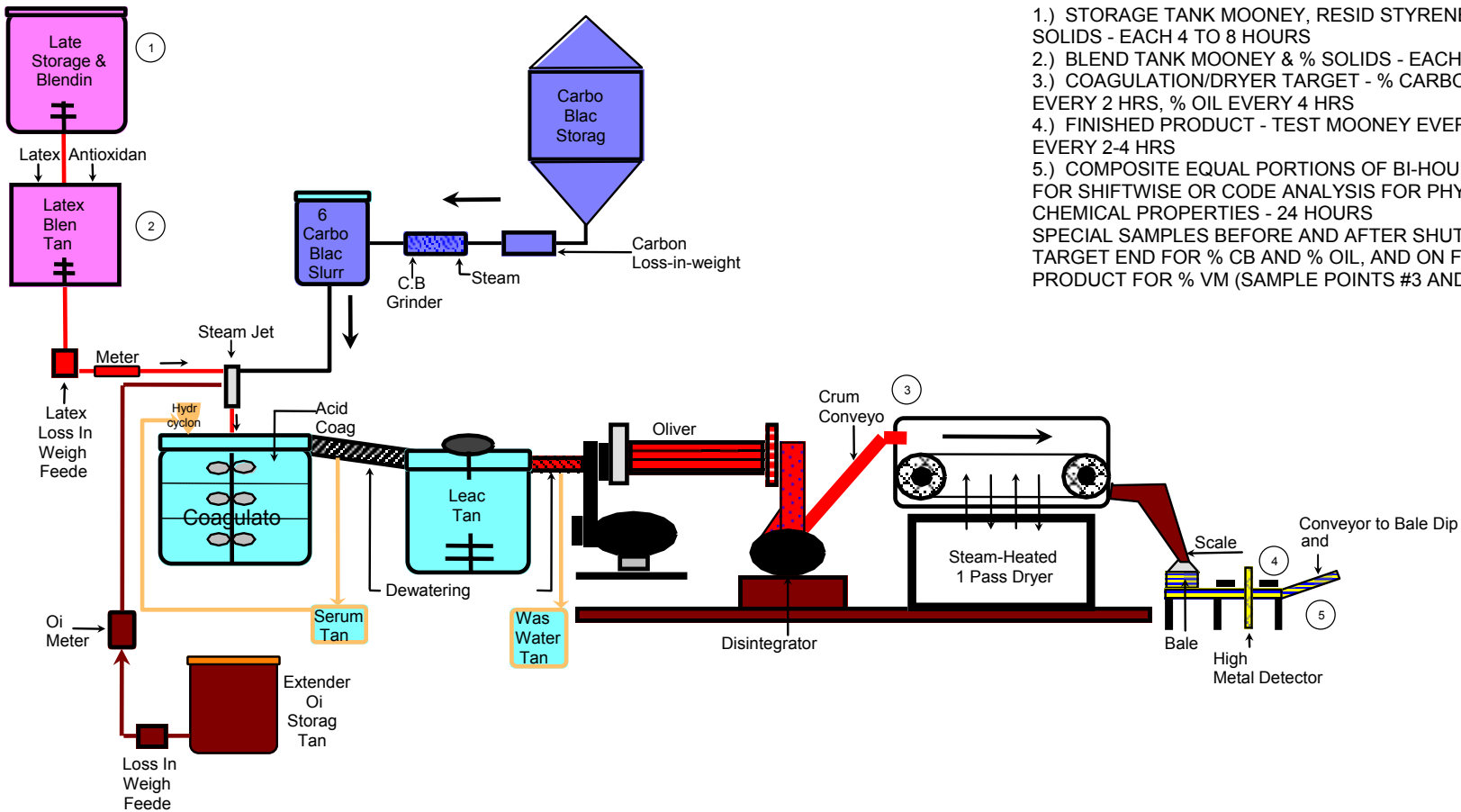
Continuous Polymerization of E-SBR



CARBON BLACK

PROCESS FLOW SHEET

MICROBLACK UNIT OPERATIONS



Sampling and Testing Schedule

- 1.) STORAGE TANK MOONEY, RESID STYRENE AND % SOLIDS - EACH 4 TO 8 HOURS
- 2.) BLEND TANK MOONEY & % SOLIDS - EACH BLEND
- 3.) COAGULATION/DRYER TARGET - % CARBON BLACK EVERY 2 HRS, % OIL EVERY 4 HRS
- 4.) FINISHED PRODUCT - TEST MOONEY EVERY 2 HRS, VM EVERY 2-4 HRS
- 5.) COMPOSITE EQUAL PORTIONS OF BI-HOURLY SAMPLES FOR SHIFTWISE OR CODE ANALYSIS FOR PHYSICAL AND CHEMICAL PROPERTIES - 24 HOURS
SPECIAL SAMPLES BEFORE AND AFTER SHUTDOWN, AT TARGET END FOR % CB AND % OIL, AND ON FINISHED PRODUCT FOR % VM (SAMPLE POINTS #3 AND #4)

