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ABS ONE-STEP® Technology- Major Improvements in Versalis' Proprietary ABS Continuous Mass Process

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Currently, ABS is produced by two different technologies: emulsion and continuous mass. Both technologies can produce materials with peculiar properties, but not always overlapping. The emulsion technology is more suited to produce high-performance materials for the injection molding sector. On the other hand, the continuous mass technology is more suited to produce high performance materials for the extrusion sector. In the ABS emulsion technology, polymerization is carried out starting from butadiene monomer while, in continuous mass, polymerization is carried out in presence of a preformed rubber.
The ONE-STEP® technology has been developed by Versalis to fill the above-mentioned gap and to further rationalize the process scheme, by eliminating redundant steps in the production and supply of the rubber. Moreover, this technology allows to widen the range of product morphologies obtainable; in fact, by avoiding the finishing and packaging section, the ONE-STEP ® technology, fully overcomes the constraints linked to rubber production, expanding the available rubber molecular weight range that can be used in the synthesis of continuous-mass ABS.
Versalis has designed and tested at pilot plant scale (kg/h of product) the above-mentioned new process scheme that integrates the two well proven and consolidated proprietary technologies for producing the rubber (anionic polymerization of butadiene) and mass ABS (radical polymerization of acrylonitrile-styrene). According to the new ONE-STEP® technology, the rubber solution from the anionic reaction is no longer steam stripped and finished in bales, but it is processed in a new non-conventional unitary operation, in which the solvent is exchanged with styrene, recovered and recycled.
Moreover, due to important process simplifications, the ONE-STEP ® technology significantly reduces investment and operating costs, as well as the CO2 footprint.

1. Introduction

The first commercial ABS polymer grades were simply obtained by mechanical blends of preformed rubber with styrene-acrylonitrile (SAN) polymer. Initially, a preformed nitrile rubber was used since it was found to be more compatible with the SAN resin than polybutadiene rubber. Although these early ABS polymers were superior to impact polystyrenes present in the market, it was recognized that their other properties were inferior to graft copolymers characterized by an actual chemical linkage between the continuous and elastomeric phase. Today, ABS is produced by the emulsion, suspension, mass (or bulk), or emulsion/mass hybrid polymerization of three monomers: acrylonitrile, butadiene, and styrene. The emulsion/mass hybrid is by the far the most widely used process commercially (Calvert, Bovey et. al.). The final properties of ABS may be varied by adjusting the concentrations of the monomers, the grafting degree of SAN onto the polybutadiene chains, or by adding an additional monomer (e.g., methyl-methacrylate or alpha-methylstyrene). The butadiene contributes toughness and low temperature impact strength, whereas acrylonitrile improves thermal stability and chemical resistance. The styrene portion of the polymer lends stiffness to the composition. Figure 1 shows the role of different monomers in ABS properties.

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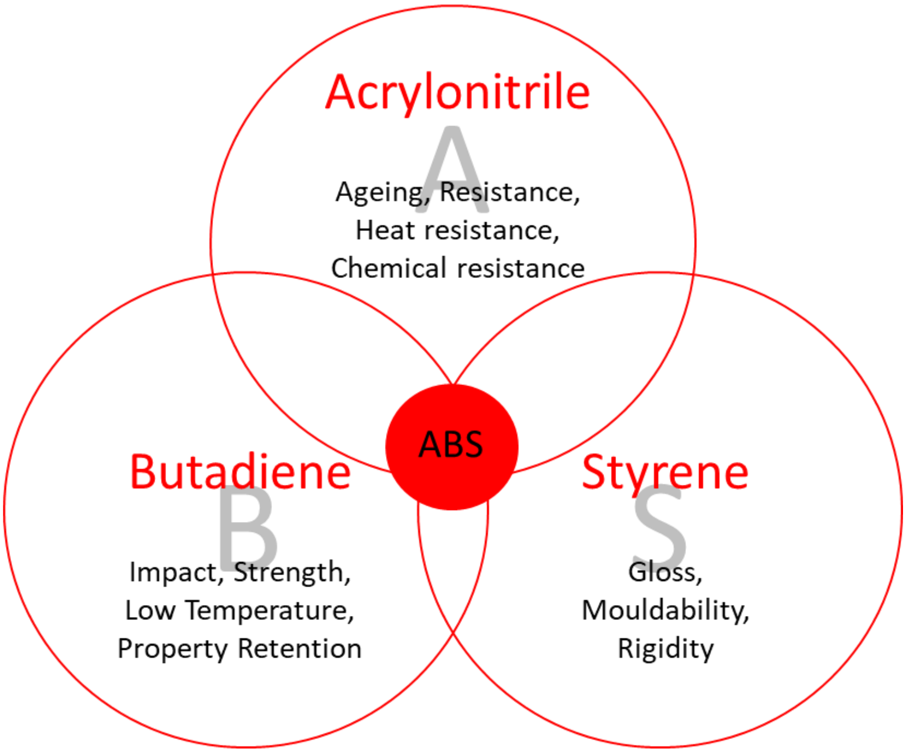

Figure 1: Role of different monomers in ABS properties

The mass or bulk process for ABS production is based on the co-polymerization of styrene-acrylonitrile mixtures in the presence of a rubber phase dissolved in this monomer phase. The emulsion process takes place in subsequent steps, carried out in an aqueous phase affording lower viscosity of the reaction medium and better heat transfer. In the mass process, rubber is usually introduced to the process via grounded preformed rubber, dissolved in styrene. Since no preformed rubber particles are present at the beginning of the grafting reaction as in the emulsion process, a different composition and distribution of elastomer phase in the SAN matrix results from the mass process as shown in Figure 2.

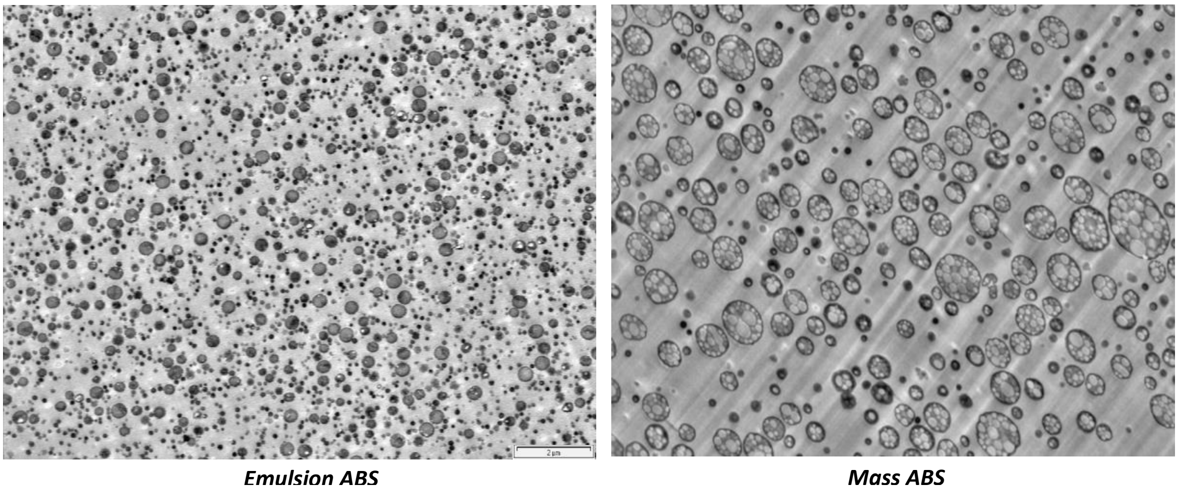

Figure 2: Comparison of rubber particles – Emulsion vs. Mass ABS

The mass ABS process tends to produce grades that have a matt, as opposed to glossy, finish. On the other hand, in mass ABS the different composition of the rubber phase (so the particle size distribution) is more efficient in term of rubber use for impact modification.
The mass process offers the benefits of no water or soap used and a product with a consistent light base color. The process is also simpler with fewer pieces of capital equipment. However, the material produced by

continuous mass is mostly matt or dull in its surface appearance, a characteristic which is valued in automotive interior parts, but not in most consumer appliance or electrical/electronic applications. In contrast, emulsion processes require the use of soap and water, and the resulting resin is variable in color, often with a light-yellow hue.
The ONE-STEP® technology has been developed by Versalis to fill the above-mentioned gap between emulsion and mass process in terms of material applications of finished product and with the intent to further rationalize the mass process scheme, by eliminating redundant steps in the production and supply of the rubber. Moreover, this technology allows to widen the range of rubber particles morphologies obtainable; in fact, by avoiding the finishing and packaging section, the ONE-STEP® technology, fully overcomes the constraints linked to rubber production, expanding the available rubber molecular weight range that can be used in the synthesis of continuous-mass ABS.

2. Technology development

The ONE-STEP® project is part of the research and development activities that Versalis is pursuing to expand its product portfolio and explore market sectors not yet investigated. Furthermore, this innovative technology allows Versalis to contribute to the sustainability goals and to reduce the carbon footprint of the processes.
The limitation of the continuous mass ABS process is precisely related to the minimum obtainable particle size of the dispersed phase: as also described in the literature (Echte, 1989) . In fact, given the in-situ formation mechanism, the flow characteristics (intensity, shear or elongational stresses) and interfacial tension, it would be necessary to have viscosity ratios between the SAN and polybutadiene phases significantly higher than those achievable in the continuous mass process to obtain small particles.
Since the SAN phase viscosity is constrained by the target final product MFI (Melt Flow Index), a polybutadiene phase with low viscosity is required to obtain very small particle size. Unfortunately, the viscosity range of the preformed rubbers obtained in the finishing section of an elastomer plant is limited by the technological constraints involved in this operation: very low viscosity rubbers can be easily synthetized, but they cannot be produced with a stable shape (bales) due to the so called “cold flow”. Theoretically, a possible solution could be that of using low viscosity polybutadiene/polystyrene di-block rubbers (the insertion of a polystyrene block in the chain gives more rigidity to rubber in the finishing phase). However, the use of this type of rubbers in the synthesis of bulk ABS brings two negative aspects. The first (of chemical nature), is due to the incompatibility of the polystyrene block of the rubber with the continuous phase of ABS (SAN phase). The second (of economic nature) impacts on the production costs, since di-block rubbers are more expensive than polybutadiene rubbers. It should be also considered that, for a given polybutadiene concentration in the final ABS product, higher elastomer quantities are required in the formulation if di-block rubbers are used.
The unavailability of rubbers with suitable viscosity limits the development of the ABS portfolio produced with mass-continuous technology, especially in the injection molding application sector, where emulsion technology ABS grades, that have no constraints regarding the formation of very small, dispersed rubber particles, find widespread use.
The ONE-STEP® process fully removes the above constraints for mass ABS, since it is possible to synthetize the most suitable rubber molecular weight which guarantees the required rubber phase solution viscosity needed in the continuous-mass ABS synthesis.
Therefore, the ONE-STEP® process represents a major technology improvement that integrates anionic batch polymerization of rubber with continuous bulk polymerization of styrene and acrylonitrile in presence of pre-formed rubber. The anionic polymerization process is carried out batchwise (batch reactors). At the end of the polymerization about 15-20% polybutadiene solution is obtained in a hydrocarbon solvent of aliphatic or cyclo-aliphatic type. The traditional rubber production process separates the solvent by means of stirred strippers, where the combined action of water and vapor ensure the solvent evaporation. The stream flowing out the strippers contains water and irregular shaped rubber agglomerates. After dripping on nets, the rubber/water stream is fed to a separation/drying section, where mechanical extruders first squeeze out most of the process water and then produce wet rubber granules. Final drying is accomplished by contacting the wet granules with hot air. The final rubber finishing section is very energy-intensive and prone to form insoluble substances (gels) that adversely affect the quality of the final plastic products (e.g., significant surface defects may be a problem). Therefore, great attention is required for defining and managing the finishing operating conditions of the rubber. Moreover, the frequency of analysis on the rubber to monitor its quality increases the production costs.
Versalis is committed in developing a new technology (Versalis ONE STEP® technology) that aims to produce ABS polymers by continuous mass process, but with emulsion-like characteristics.
To support and guide the technology development, Versalis has first carried out an in-depth program of experimental and analytical tests on a laboratory scale in its research center located in Mantova.

After that, a pilot plant in Mantova was started up in 2017, in which a dedicated development program, still being conducted today, has already confirmed the possibility of producing ABS grades through continuous-mass technology with emulsion-like properties.
The heart of ONE-STEP® technology is the solvent exchange operation, which consists of progressively replacing the aliphatic or cyclo-aliphatic solvent, used in the rubber synthesis with styrene, in order to obtain directly the styrene rubber solution to be fed to the ABS mass process. The solvent exchange operation is accomplished by means of a simple distillation, consisting of adding styrene to the polybutadiene solution. Due to the different volatility, the solvent is evaporated and replaced with styrene.
This unconventional and innovative unit operation makes it possible to eliminate some typical steps present in the anionic rubber process such as: stripping and finishing to obtain pre-formed bales. This process simplification (see Figure 3) completely avoids also the previously mentioned quality problems associated with the finishing sections. In addition, referring to ABS mass process, the ONE STEP® technology allows to eliminate also the rubber dissolution section, further simplifying the process scheme.

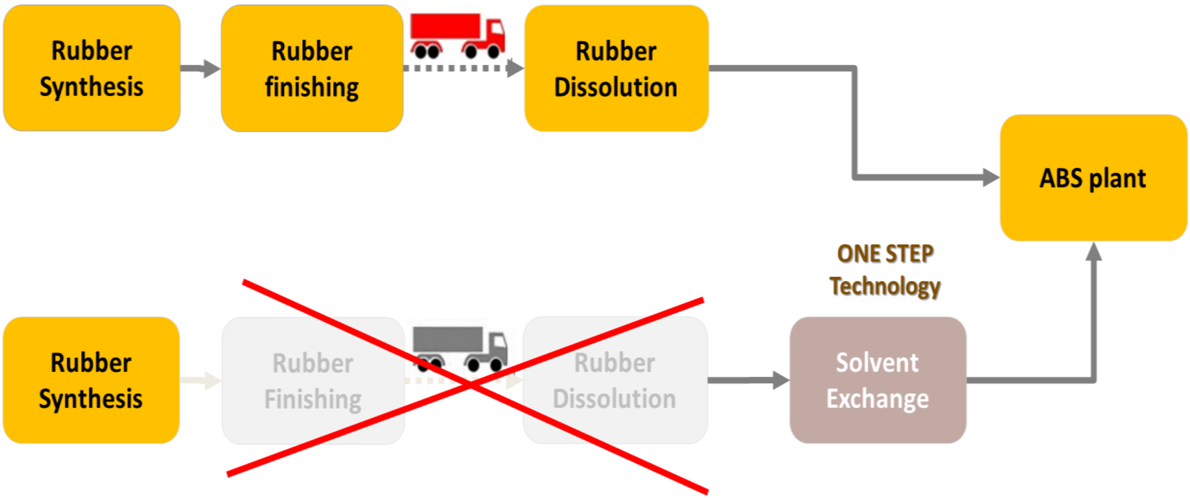

Figure 3: The advantages of ONE-STEP® technology.

3. ONE-STEP® Technology

As previously explained, this technology advancement overcomes the limitations imposed by the solution viscosity obtained with std preformed rubbers and allows to produce mass-ABS with rubber size particles comparable with those obtained via emulsion. Therefore, glossy, gel free mass-ABS grades (so called "emulsion like" grades) can be produced by means of this new methodology.
Thanks to an intensive R&D program, Versalis has acquired a strong know-how for the determination of the best rubber characteristics (molecular weight, functionalization), coupled with the operating conditions of the subsequent solvent switch and radical polymerization synthesis of mass-ABS.
A specific patent which covers the basic know-how of the ONE-STEP® technology has been also issued (Patent No. WO/2009/074244, 2009).
The ONE-STEP® technology core is represented by the solvent exchange operation: an unconventional unit operation that allows to simplify the overall process by eliminating entire sections of the two combined processes: rubber and mass-ABS.
Generally, a batch or semi-batch distillation is commonly applied to exchange solvents in a production process. The most common procedure usually imitates what was easiest for the chemist who developed the process in the lab. First, the batch is boiled down to remove much of the original solvent. Next, the replacement solvent is charged to the batch. Then, the batch is boiled down again to remove the remainder of the original solvent. The last two steps may be repeated to minimize the amount of original solvent left in the batch. With this method, the batch ends up mainly in the replacement solvent, with some trace left of the original solvent. Some of the replacement solvent also co-distills and is lost to the distillate.
The ONE-STEP® solvent exchange operation, carried out for the rubber solution stream obtained by anionic synthesis of the butadiene, consists of progressively replacing the solvent used in the rubber reaction with styrene. In such a way a rubber solution, ready to be fed to continuous-mass polymerization section, can be obtained.

In Figure 4 a simplified scheme of the solvent exchange operation is reported.

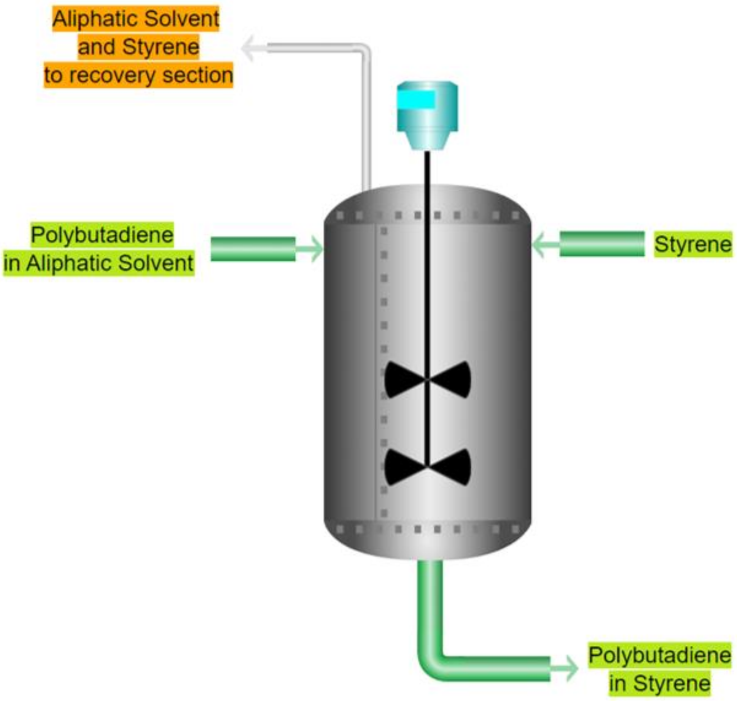

Figure 4: Simplified scheme of the solvent exchange operation.

Due to the peculiarities of styrene, which can spontaneously react at relatively low temperatures, care must be taken to avoid self-polymerization and possible run-away reaction. Therefore, use of vacuum to limit process temperatures is absolutely a must to ensure reliable and safe operations.
Other basic process features such as:

- Wider rubber molecular weight range (e.g. low molecular weight rubber, not manufacturable in bales) to produce the target rubber solution viscosity
- Possible rubber functionalization, in order to modify/improve final products performances
- Optimized and innovative process scheme for carrying out the solvent switch operation
- Most appropriate process temperatures to maintain rubber quality
- Use of specialized equipment for heat transfer with low temperature differentials

are all important aspects that have to be properly evaluated, designed and finally tested.
Therefore, based on the experience and know-how recently acquired, Versalis is now in the position to propose an industrial plant which incorporates all the design features needed to produce "emulsion-like" ABS products but with a continuous mass technology.

4. Industrial development

Versalis owns production facilities to make many kinds of rubbers in its plants located in Italy and Europe, according to traditional technologies; Versalis also owns plants to produce styrenics materials, based on the mass technology. The ONE-STEP® technology can be viewed as a bridge which links two consolidated production processes that have been developed separately. Moreover, new grass roots plants can also benefit, in terms of Capex and Opex, from the elimination of several sections that are needed by the two separate processes.
In order to allow the continuous development and to build up the know-how of this innovative technology, Versalis has started up in 2017 into the Mantua research center the ONE-STEP® technology pilot plant, which could then be replicated on an industrial scale. This technology has the characteristic of being flexible, allowing in fact the possibility to connecting the ONE-STEP section (traditional anionic polymerization of rubber and solvent exchange) both an existing continuous mass polymerization plant and a new installation.

5. Conclusions

Hybrid/emulsion technology accounts for about 97% of the ABS production globally. The mass process is actually lower in production cost than the hybrid/emulsion process due to lower utility and fixed costs. However, the hybrid/emulsion process produces a glossy ABS which is preferred in the marketplace in contrast to a matte finish provided by mass ABS.

The ONE-STEP® technology has been developed by Versalis to fill the gap between mass and hybrid/emulsion process. At the same time, it allows to rationalize the process scheme, by eliminating redundant steps in the production and supply of the rubber and by introducing only a new unconventional unit operation: the solvent exchange. Compared to the emulsion technology the mass process does not require any water or soap and, consequently, the liquid waste treatment is not required as well. Moreover, this technology allows to widen the range of product morphologies obtainable; in fact, by avoiding the finishing and packaging section, the ONE-STEP ® technology, fully overcomes the constraints linked to rubber production, expanding the available rubber molecular weight range that can be used in the synthesis of continuous-mass ABS.

In recent years, given the problems associated with pollution and the climate change, particular attention is being paid to the carbon footprint of the various production cycles. From this point of view the mass process offers the benefits of no water or soap and liquid waste treatment, generally present in the emulsion process. Moreover, due to reduced utilities consumption, carbon footprint of the process is significantly reduced.

In Versalis' strategy, the development of innovative technologies for production of new polymers is a fundamental step in terms of sustainability. The adoption of novel models allows to minimize the environmental impact and to maximize the sustainability of processes and products. In this respect, the ONE-STEP® technology can be regarded as a major contribution of the plastic industry towards forms of better sustainability, minimization of the environmental impact with a consequent reduction in GHG emissions.

Therefore, the ONE-STEP® technology allows to match some main targets, as high performances ABS production with carbon footprint reduction, with respect to the traditional processes, ABS emulsion and continuous mass.

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