

EXTENDED ABSTRACT

The goal of this project is to compare and to analyse the production of PET polymer by two different liquid state polymerization processes: one, with three transforming reactors and the second, with too single transforming reactors (eldest process).

Therefore, it were studied and observed every inherent components/parameters throughout every production of the polymer from both processes.

For the polyester polymer production are necessary the following raw material: monoethyleneglycol (MEG), terephthalic acid (TA) e isophthalic purified acid (IPA).

Selenis S.A. has a polymer production unit, which is a polymerization in liquid phase – target of this project.

In this unit there are seven production lines with a nominal capacity of 70 000 ton/year. In one of them (Line 5), the production process is different, considering that it is constituted by an intermediate stage between esterification and polymerization. This difference is the comparison goal of this project.

Here is produced the polymer to different destinies: it may be used for the production of textile fibres or for the production of resins PET (after passing by a last stage of crystallization – polymerization in solid phase).

The main process of PET production involves a total of five stages:

- Formation of the paste and load;
- Esterification;
- Polymerization;
- Extrusion and cut;
- Crystallization.

The first and last stages of the processes are independent from the discontinuous lines of polymer production (crystallization is not broached in this study, therefore, matters merely to analyse the two processes until the polymer production).

The paste is formed in an appropriated deposit, with the capacity of 16.5 m³, where the raw material constituents of the polymer are mixed (monoethyleneglycol-MEG, terephthalic acid -TA and isophthalic purified acid-IPA), obtaining a density of about 1.37 g/cm³. The paste's temperature is kept around 70 °C for intermediate of steam coils.

The main raw material is the TA (67.6% of the paste), that comes in 1 ton bags or in 23.5 ton trucks. It is unloaded into two silos, 350 ton each, through a process formed by compressed gas pumping systems (*blow eggs*) with a capacity of 1 ton. Hit makes the transportation by dragging with nitrogen gas, whether to the silos, as later to the hopper of TA, with a pressure of 100 psi and at ambient temperature. The hopper has a capacity of 7.5 ton which feeds the paste's deposit by a dosing system *Ktron* (endless screw that debits a volume of 7 000 kg/h).

The MEG (with 1.5% of water, after the mixture with recovered glycol) constitutes 30.8% of the paste. It is transported in trucks with, approximately, 24 ton. It is unloaded in the glycol storage tanks (A and C), whether by usage of one of the truck's pumps or by the glycol pump of the system. Then, it is pumped to the deposit of preparation of the paste (being heated at a temperature of 80 °C before entering the deposit of the paste. The volume of the entry in the deposit is 3190 kg/h) or to preparation of the additives. The recovered glycol is picked in a storage tank (B), and it is mixed with new glycol and again used as raw material to the paste.

Composed only by 1.6 to 2% at maximum of the paste, is the IPA. The isophthalic purified acid comes in bags of one ton and after being unloaded, it is transported to a feeding hopper to the dosage system and then, it goes to the deposit of the paste through a dosage system "Schneck" (endless screw which debits 165.2 Kg/h).

The additive solutions (*masterbatches*) used in the production of polymer are prepared in the room of additives preparation.

Starting at the paste deposit, each of the seven lines is fed by a ring system, where the circulation of the paste is constant (granted by two pumps) to not become solid and obstruct the feeding pipes of the esterification reactor at the same time, and the counting is made by a volume counter placed in the entrance of each reactor.

The esterification reactor is pressurized and heated before the paste is injected, in order to not let air enter during the loading and unchain the reaction of esterification with elimination of the water.

After the esterification, the monomer is transferred to the autoclave, with the purpose of proceeding to the polymerization in vacuum and at a higher temperature than the esterification. With the polymerization, the glycol in excess is eliminated and the viscosity of the polymer increases.

On the process with three reactors, there is a middle stage of the process, where the monomer is transferred into the pré-poly reactor in order to finish the esterification's second phase and to start the first phase of the polymerization transformation, in similar conditions to the ones applied separately in esterification and polymerization's reactors.

After achieving the intended viscosity, the polymer is in the proper conditions to be extruded and cut. The autoclave is then pressurized with nitrogen and extruded polymer through a row, cooled by water and cut in grain.

After that, it passes through a dryer where the water is separated, enters a sifter and follows to the storage hopper where it awaits its destiny according to the result of the laboratorial analyses made to a sample picked at the extrusion.

If the polymer is in conformity, it is transported to new storage silos and, after that, directed to a continuous or discontinuous polymerization unit in solid state (SSP) (composed by two pre-crystallizers and five rotating reactors of poly-condensation in solid state) or, directed to the textile fibres production. In case it is a nonconforming product, it is sent to deposits called "eurobines".

The PET resultant from the SSP process is stored and then unloaded in trucks or bags of one ton, to be delivery to clients.

One great advantage from the PET to packages is the fact that it may be recycled. In the factory there's a recycling unit where the packages, after suffering a transforming cycle, are cut in "pellets" and mixed with polymer, according to the international norms.

The PET

The polyethylene terephthalate (PET) is the most important member of the family of polyesters, group of polymers discovered in decade of 1930 by W.H. Carothers, from Du Pont, and for over 40 years, has been used in several activity sectors, from textile fibres to containers to aerated drinks, from films and photography, to packages and components to cars. In general, the polyethylene terephthalate is known as polyester, and in the segment of packages, as PET.

In the final of the 70th decade, the usage of polyethylene terephthalate presented a notable grow due mostly to its usage in the production of bottles to beverages. The first PET bottles were produced in the USA in 1977.

Nowadays, there's a great expectation for the growth of the usage of the resin PET due a major penetration degree in markets supplied today by substitute products. ^[1]

[1] Montenegro, Ricardo e Pan, Simon – PET resin for packing products.

The main difference between the types of polyethylene terephthalate consists in the molecular weight or degree of polymerization that origins different property from the resultant materials. The bigger the molecular weight, the bigger the mechanical, chemical and thermal resistance of the polyethylene terephthalate.

The molecular weight of the polyethylene terephthalate, in the other hand, is measured and expressed indirectly, through the values of the intrinsic viscosity (VI), in a relation of direct proportionality. The bigger the intrinsic viscosity (IV), the higher the molecular weight of the resin.

The several types of polyethylene terephthalate may be classified into two big main groups:

- Polyethylene terephthalate of low IV (inferior to 0,7 ml/g). used to the protection of the fibres and films;
- Polyethylene terephthalate of high IV (above to 0,7 ml/g), used to the production of plates, blown packages (bottles, jars) and engineering plastics.

The PET is a synthetic polymer from an acid and an alcohol according the following reactions:

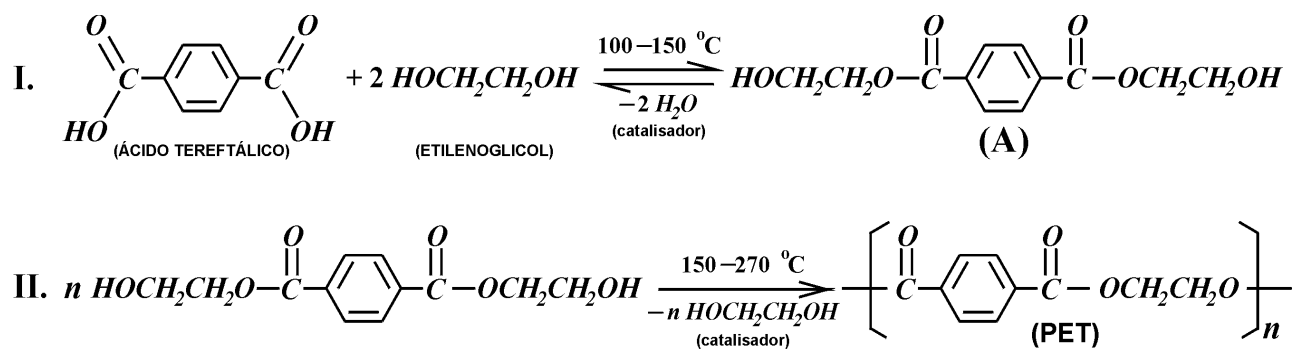


Figure 1 – Esterification (I) and polymerization (II) reactions. [2]

In reaction I, the terephthalic acid reacts with the ethylene glycol originating a monomer A (bis-hydroxyethyl terephthalate), composed by three functional groups: an ester, an alcohol and an aromatic hydro carbon – esterification reaction – and there is release of water molecules.

It is a balanced reaction. According to the principle of Le Chatelier, the balance may be displaced in the direction of the formation of the composition A, increasing the concentration of reagents. Therefore, the excess of ethylene glycol allows that every terephthalic acid is converted into **A** and it has the possibility of being reused.

In reaction II, the composition A suffers a polymerization reaction with the release of the glycol, originating amorphous polyester (transparent) with properties similar to the ones from the glass.

At last, the amorphous polyester (transparent) is crystallized, originating therefore, the polymer opaque PET, which represents an alignment of the two chains in relation to the others.

An important characteristic, concerning the structure of a polymer material is its crystallinity. The crystallinity of a polymer is determined by the form of its molecules, symmetry, ramification, stiffness, regularity and by its proceeding parameters. Usually, this one is superior to 50 %.^[3]

The PET has several forms of application, from the alimentary industry (undistensible bottles with or without gas, bottles to alimentary oils and packages to foods) to the automobile industry (seats, acoustic isolation and license plates), from the textile (pillows and blanket's filling, caps and scarfs, tissues and underwear) and even the sporting industry (wires for rods for fishing or fishing nets) due to a set of properties.^[4]

By comparing the three transformation reactors process with the two reactors, we obtain different results in the process. Therefore, the total time of one load process, is reduced in 20 minutes than the first one (300 e 320 minutes, respectively).

This result predicts that the daily production of polymer on three reactors process is superior because there can be obtained a higher number of daily loads (10 vs 7 loads).

The fact that in the three reactors process there are MAAG and Viking pumps, allows a constant recirculation of the load during transformation process, promoting a bigger reaccional homogenization of the material contained in the respective reactors. In the extrusion phase, the MAAG pump prevents a bigger thermal degradation of polymer (polymer doesn't stand still in polymerization reactor interior at high temperature). This way, it maintains its optical properties unchanged. The laboratorial results proves that the polymer quality obtained by the three reactors process is rather regular. These results are achieved by a better conditions control of the process with three reactors. However, the same doesn't happen in the two reactors process.

The production of "extruded scrap" and "coarse grains" is practically the same in both process (~18 Kg/load), but in the three reactors process, as the daily production is bigger (a

[3] Ogorkiewicz, R.M.; Thermoplastics Properties and Design.

[4] Selenis – Polymer Industry. www.selenis.com

higher number of loads in 24h) it is obvious that the daily quantity of “extruded scrap” and “coarse grains” will get higher (equivalent to the number of daily loads produced).

The quantity of unqualified loads in the three reactors process is bigger. It presents an unqualified product index of 4.53% to 1.09%, averagely, in the two reactors process because there is a higher probability to occur a problem during the production process (such as DEG formation, breakdowns of vacuum, MAAG and Viking pumps or the transfer production lines lockout).

Even though the efficiency is identical in both processes (81% until 83%), the quantity of unqualified product is quite higher in three reactors process. However, this value is rewarded by a higher annual production of qualified product, placed in 25% superior.