
POLYPROPYLENE PRODUCTION: THE SPHERIPOL PROCESS

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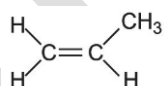
Abstract:

Polypropylene (PP) is a thermoplastic polymer produced by the combination of propylene monomer molecules in a polymerization process in the presence of a catalyst, usually Ziegler-Natta. There are different ways of producing polypropylene such as Spheripol, Novolen, Innovene, Unipool, Borstar, etc. as well as the latest achievements in the field of propylene polymerization. In this research work, it is restricted to the Spheripol production process because it is an efficient and cost effective production process and it is observed that at the pre polymerizer, the reaction is conducted in a small prepoly loop reactor at the following condition, Temperature: 20 °C Pressure: 36 kg/cm², it has a capacity of 0.46 m³. This article provides a comprehensive review of recent research in PP and its advanced functional applications.

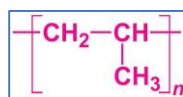
Key words: polypropylene, production, Spheripol, polymer, technology.

Introduction

In recent years, polypropylene has emerged as one of the most widely used thermoplastic polymers due to its exceptional properties, cost effectiveness, and ease of processing, (Watanabe R, et al, 2018). The versatility of PP originates from its unique molecular arrangement, which consists of propylene monomers joined together in an unbent chain. This linear configuration proposes several benefits, including increased crystallinity, superior chemical resistance, inferior density, and satisfactory mechanical strength, (Guezzout Z, et al 2023). Polymerization is the process in which small units (molecules) called monomers are combined chemically together to produce a very large chain-like network unit called the polymer by the influence of catalyst. Polypropylene (PP) is a thermoplastic polymer produced by the combination of propylene monomer molecules in a polymerization process in the presence of a catalyst, usually Ziegler-Natta. In a qualitative approach, PP is a colourless, translucent to transparent solid with a glossy surface. PP is a non-reactive product, stable at ambient temperature. It does not decompose in the air and does not release any harmful gases or other products, although PP may react with strong oxidizing agents and should not be stored near such materials



Propylene monomer



Polypropylene polymer

Background of Polypropylene

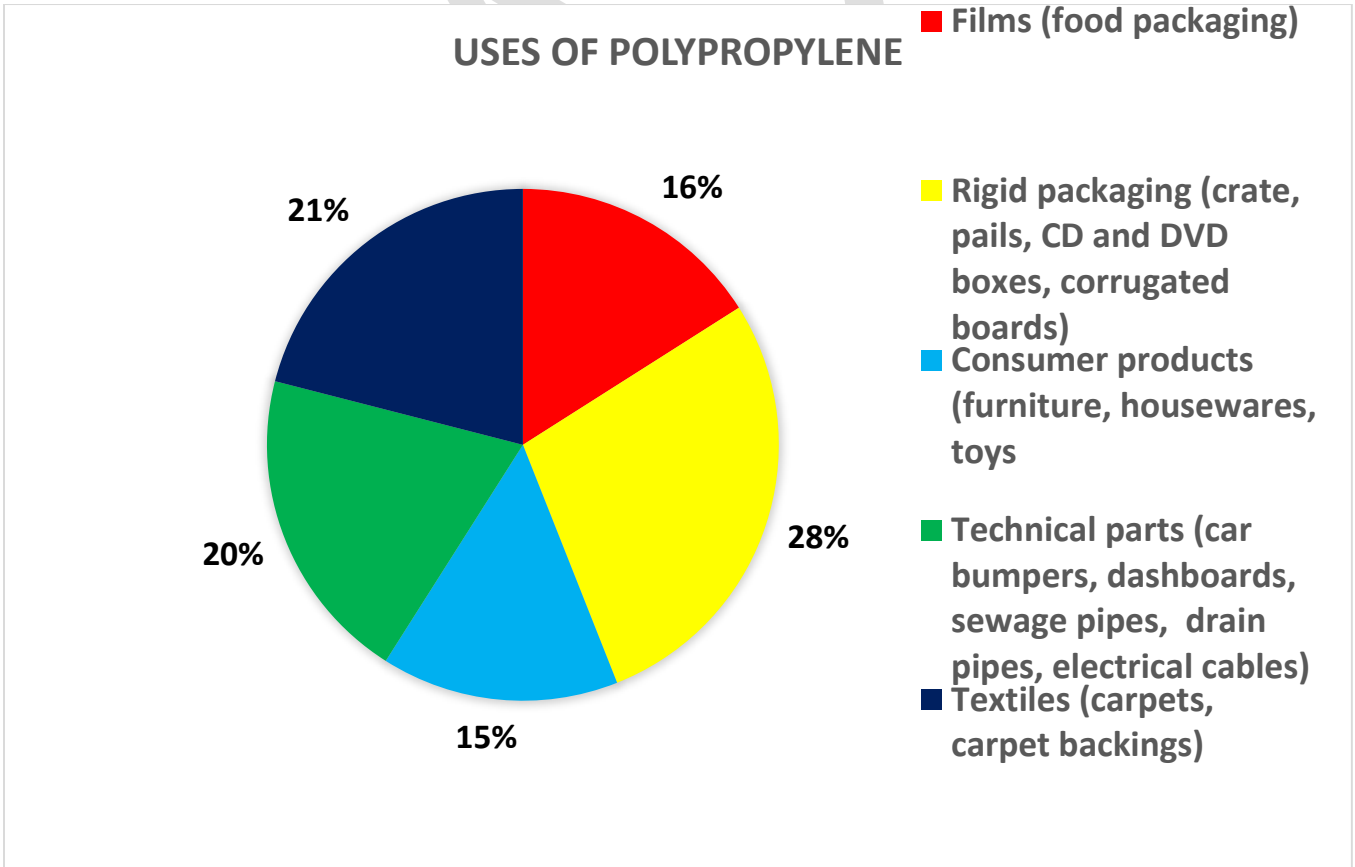
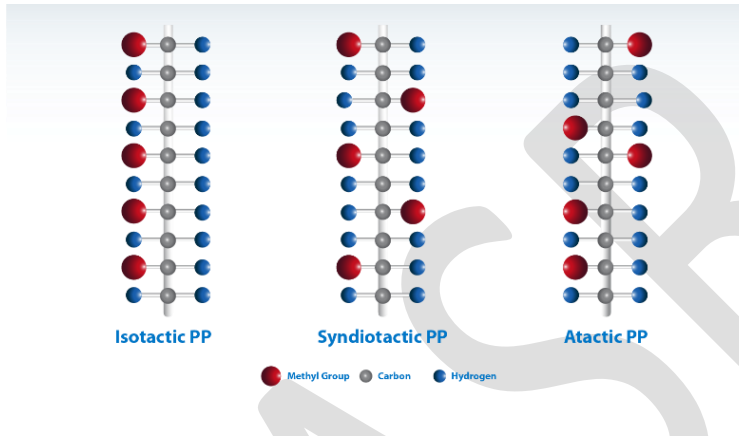
Stereospecific polypropylene was first discovered in 1954 by Italian chemist Giulio

Natta and his assistant Paolo Chini (Morris, Peter J. T. 2005). They employed catalyst of a

type invented by the German chemist Karl Ziegler for synthesizing polyethylene.

Commercial production of polypropylene began in 1957. In recognition of this achievement, Natta was awarded the Nobel Prize for Chemistry in 1963 along with Ziegler.

The process can form three basic chain structures dependent on the position of the methyl groups: two are stereoregular (isotactic and syndiotactic) and the third is termed atactic as shown.



Polypropylene Applications



- ▶ Commercial polypropylene is predominantly isotactic polymer containing 1-5 % by mass of atactic material.
- ▶ Annual production of polypropylene
 - World 52.2 million tonnes
 - Europe 13.1 million tonnes
 - Russia 0.64 million tonnes

Properties of Polypropylene

Polypropylene has remarkable properties, making it suitable to replace glass, metals, cartons and other polymers. These properties include:

- Lightest thermoplastics (density 0.905 g cm^{-3}), melting point of 440 K and a crystallinity of ca 50-60%.
- high stiffness * heat resistance * chemical inertness * steam barrier properties (food protection) * good transparency
- good impact/rigidity balance

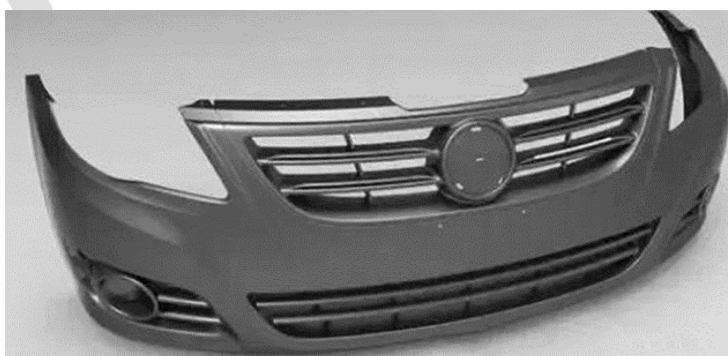


Fig.2: Car bumper, a product of polypropylene

Methodology

Production Process – Spheripol

Various production processes exist with some general similarities. They take place either in a gas-phase (fluidized bed or stirred reactor) or a liquid-phase process (slurry or solution). The

spheripol process employs the liquid-phase process in two tubular reactors for homopolymerization and random copolymers and a gas-phase reactor for copolymerization

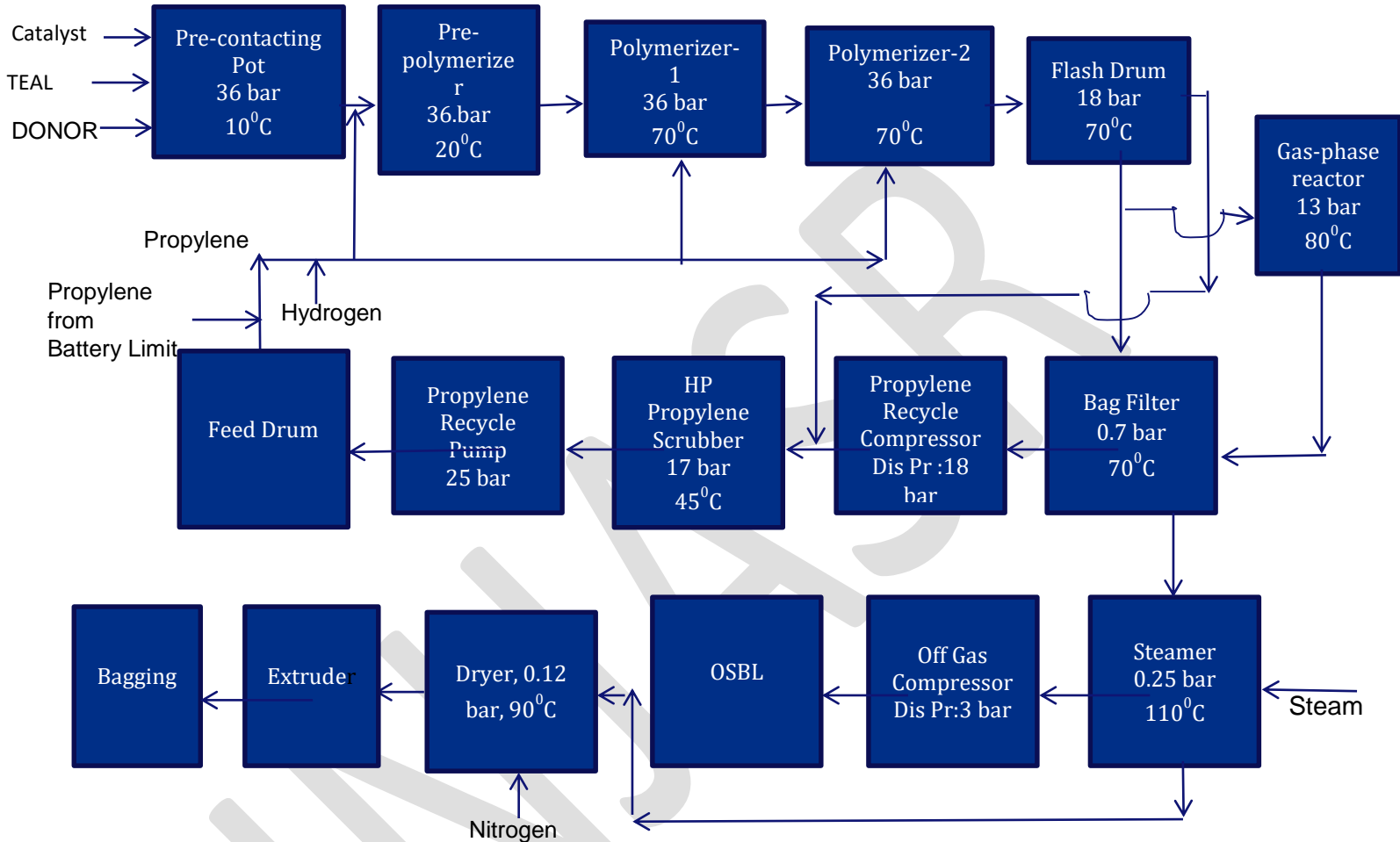
Raw Materials and Applications

- **Teal:** (Triethyl Aluminum): **Initiates reaction.**
- **Donor:** (Cyclohexylmethyldimethoxysilane, Dicyclopentylmethyldimethoxysilane: **Controls Isotacticity.**
- **Catalyst:** (Titanium tetrachloride supported on magnesium support: **Controls reaction.**
- **Propylene:** For polypropylene
- **Ethylene:** For copolymerization
- **Hydrogen:** For chain termination
- **Atmer (Alkyl amine) :** Kills residual catalyst.

ADDITIVES: For product stabilization

- **Irganox-1010** {tetrakis [methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate] methane} **antioxidant.**
- **Irganox-B215** {66.7% EVERFOS-168Tris (2,4-di-tert-butylphenyl) phosphite 33.3% EVERNOX-10 :
Pentaerythritol Tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate)} **antioxidant.**
- **Calcium Stearate:** acid scavengers.
- **Sodium Benzoate:** acid scavengers.
- **Glyceryl Monostearate:** antistatic agents

PROCESS BLOCK DIAGRAM

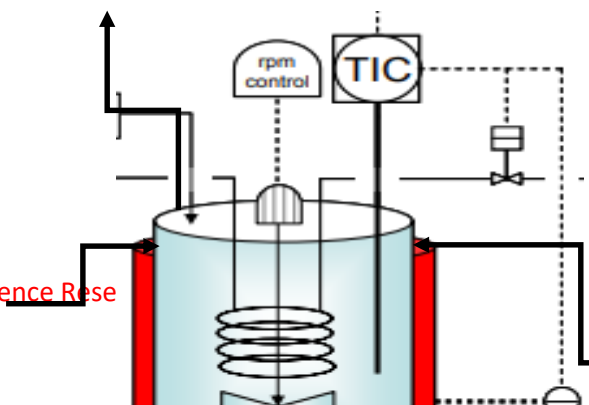


Process Description

► PRECONTACT POT:

- The catalyst suspension, the Donor and TEAL are pre-contacted in Pre-contact Pot (D-201 about 3 liters) at about 10⁰ C. by thermostated water recirculation in the jacket. A pressure of 36 bar is maintained.

Mixture



TEAL and DONOR

► PRE-POLYMERIZER (R-200) :

Catalyst paste

- The reaction is initiated in the pre-polymerizer R200 where encapsulation takes place to avoid increased violence in the loop reactors R201 and R202.
- The reaction is conducted in a small pre-poly loop reactor at the following conditions.
 - ✓ Temperature: 20 °C
 - ✓ Pressure: 36 kg/cm²
- It has a capacity of 0.46 m³.

► POLYMERIZATION CONDITIONS

- The polymerization reaction for homopolymer production takes place in two loop reactors in series and conditions are the same on both reactors, except the residence time which is higher in the first one.
- Reaction temperature: 70 °C
- Pressure: 36 kg/cm²
- Residence time 06-R-201: 1h (at max load)
- Residence time 06-R 202: 0.5 h (at max load)
- Slurry concentration: about 50 % wt
- An amount twice the plant throughput is usually fed into the loop reactors at any given time in anticipation of 50 – 60 % conversion

► **HYDROGEN FEED TO 06 R 201 AND 06-R 202**

- Hydrogen is used to control polymer intrinsic viscosity and MFI control. It is injected separately into the two total propylene streams being fed to the loop reactors.

► **SLURRY DISCHARGE FROM THE REACTORS**

- The reactor exit reaches the flash drum at 17 kg/cm², from where the overhead is sent to C301 for scrubbing and eventual condensation in E301, where recovered propylene is recycled back to the feed drum D301 via P302 for reuse.

► **FLASH DRUM (CY-301):**

- After leaving the flash piping, the solids are separated from the gas in Flash Drum (06-CY 301). The polymer collected from the bottom of the flash separator is discharged under level control to the Bag Filter (06-F 301).
- Flash drum is operated at 18 bar pressure and 70⁰ C.

► **Gas Phase reactor R401**

- The gas-phase reactor handles the production of copolymers. Copolymerization is the reaction of homopolymer and bi-polymer (a mixture of ethylene and propylene in a given ratio and reaction condition of 13 bar and 80 °C) to produce the impact copolymer

► **BAG FILTER (F-301) :**

- The solid polymer in flakes form leaves the bottom of the flash drum CY301 by pressure differential and gravity to the bag filter F301 where further separation from unreacted monomer occurs with the help of filter bags.

► **STEAMER (D-501):**

- From the low-pressure degasser 06-F 301, the polymer, which still contains 1% wt of dissolved monomer plus 1-1.5 % wt of gas flowing across the filter discharge valve, is fed by gravity to the steamer vessel. The steamer is operated at 0.25 bar pressure and 110 °C.

► **DRYING DRYER (DR-501):**

- Polymer leaving the steamer contains about 2.5% by wt of condensed water. This moisture is removed in a fluid bed dryer 06-DR 501 operated with hot nitrogen in closed loop. Dryer is operated at 0.1 bar pressure and 90 °C.
- Dried Polymer is transferred by pneumatic conveyor to storage silo called powder silo (D-801) from where the polymer is again transported to buffer silo (D-802) and subsequently to extruder for pelletization.

EXTRUSION OPERATION

► **Extrusion Process**

In the extrusion section, the polymer flakes are mixed with different additives for property modification, strength and compactness.

THE ENGINEER: PROCESS OPERABILITY

- The PP operation is performed in such a way to optimize the following
- Catalyst activity and Consumption of co-catalysts
 - Hydrogen Response
 - Operational stability
 - Yield
 - Quality Parameters: XS, bulk density, fines
 - PSD: particle size, tails

► Catalyst activity and Consumption of co-catalysts

- Activation of the $TiCl_4$
- Reduction of T^{4+} to T^{3+} resulting in about 85 % conversion. The active $TiCl_3$ give the alkyl groups the opportunity to position themselves on the carbon chain and at the same time creating a vacant site.
- The monomer is attracted towards the d-orbital which then forms a transition π complex with the Ti.

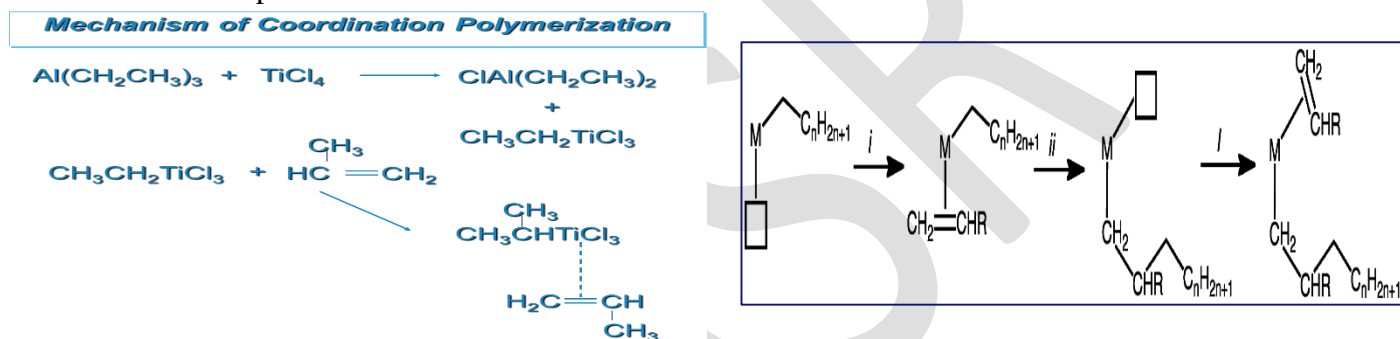


Fig.1: Mechanism of coordination polymerization

Table 1: History and catalytic composition of polypropylene.

Generation (Year)	Catalyst Composition	Productivity (Kg of PP/gm of cat)	Isotacticity (%)	Remarks
1st (1954)	$TiCl_3$, $AlCl_3$ + $AlEt_2Cl$	2-4	90-94	No morphological control, deashing & atactive removal required
2nd (1970)	$TiCl_3$ + $AlEt_2Cl$	10-15	94-97	Granular catalyst, deashing required
3rd (1971)	$MgCl_2/TiCl_4/Benzoate$ + $AlR_3/Benzoate$	15-30	95-97	First $MgCl_2$ based catalyst, low stereocontrol, low H_2 response, broad MWD
4th (1980)	$MgCl_2/TiCl_4/Phtalate$ + $AlR_3/Silane$	30 -60	95-99	Spherical with controlled porosity, Medium to high Stereocontrol, Medium H_2 response & Medium MWD
5th (1990 – 2000)	$MgCl_2/TiCl_4/Diether$ or $Succinate$ + $AlR_3/Silane$	60-70	95-99	Same as 4 th generation catalyst, but high activity & narrow/broad MWD

► Hydrogen response

- Chain terminator. *Molecular weight regulator. *MFI control *Production of various grade

► Operation Stability

The stability of the reaction depends on

- Pre-polymerization – catalyst encapsulation
- Steady rise and easy control of temperature (65 -70 °C)
- Steady rise in slurry density
- Reactor constant pressure
- Steady increase in power of circulation pump

► Yield

- Catalyst mileage * Particle size distribution

► Quality parameters

- Xylene soluble (TEAL/Donor ratio.) * Bulk density

► PSD

- Fines * Tails * marriages

Conclusion

There has been a continuous improvement of existing technologies in terms of used catalysts, as well as the conditions of polymerization. In terms of the representation of certain commercial practices in the course of the last ten years there has been a rising trend in the process of mass and in the gas phase, while the processes in suspension is underrepresented.

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