Morphology control is an important issue in the field of polyolefins as well as catalyst development. New generations of supported catalysts often show complex fragmentation behaviour. Ideally, with stable skin formation, one polymer particle results from one catalyst particle. However, a combination of thermal and growth / mechanical stress can lead to so called particle disintegration ("external fragmentation") – the particle cracks into a number of smaller particles that polymerize and grow, leading to smaller than expected polymer grains which are referred to as "fines". Generation of fines has been a major problem in olefin (ethylene) polymerizations for a long time now. Production of fines in industrial processes leads to a multitude of problems like – wall sheeting, bad heat transfer characteristics, non-homogeneous polymerization, off-spec products, disturbances in downstream processes, and so on and so forth.

The main objective of this thesis was to develop a semi-quantitative method for characterization of fines generation in ethylene polymerization using MgCl2 - supported Ziegler-Natta catalysts based on a detailed analysis of the polymerization kinetics, molecular weight, crystallinity, particle growth and particle size distribution, pre-polymerization and catalyst pretreatment and their individual and combined impact on internal and external fragmentation.

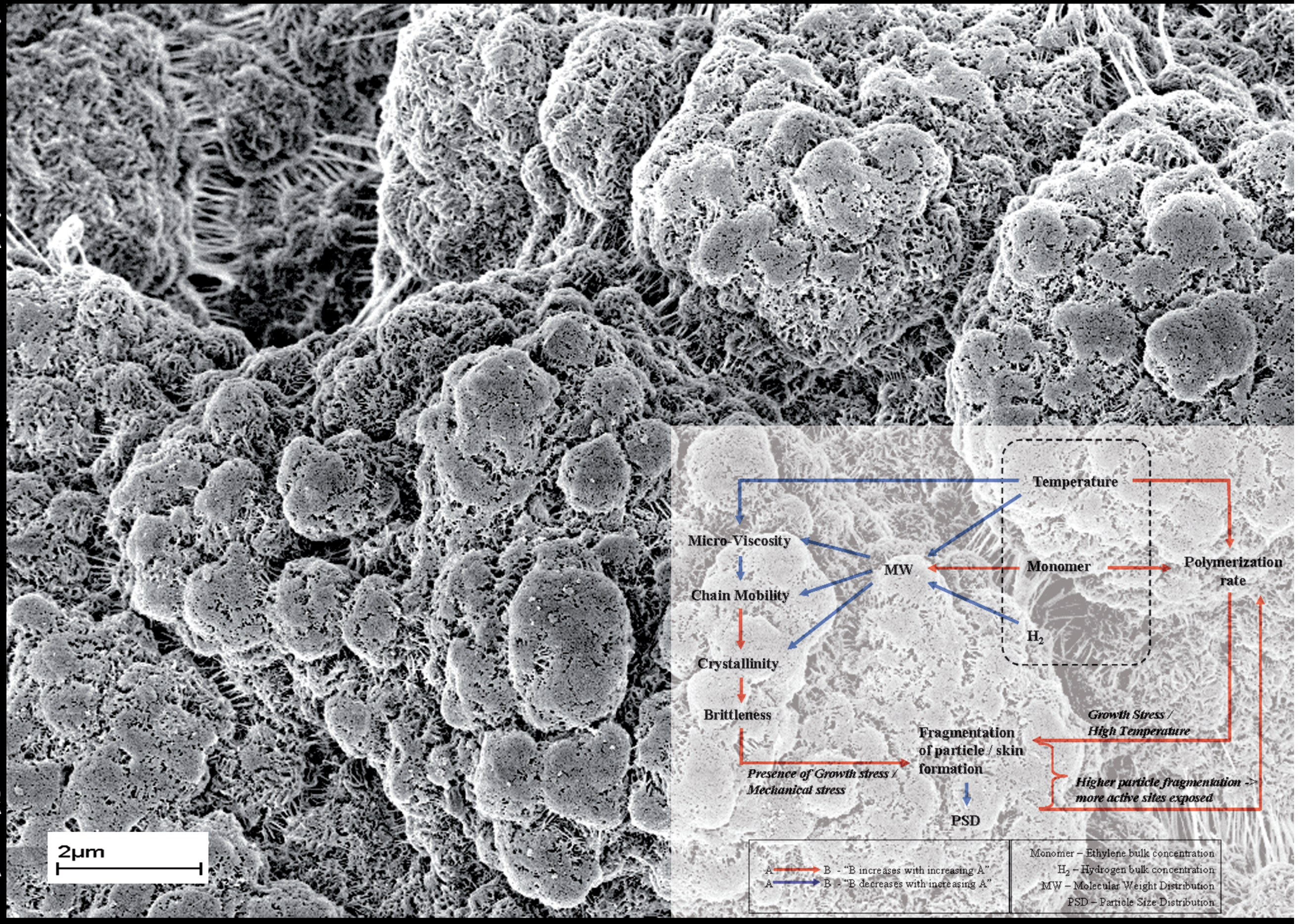
ISBN: 978-90-365-2907-5

Fragmentation in polymerizing PE particles

Shankara Keelapandal

Fragmentation in Polymerizing PE Particles

- Role of Stress, Brittleness and Skin



S.N. Keelapandal Ramamoorthy

Invitation

It is a great pleasure to invite you and your partner to the public defence of my doctoral dissertation:

"Fragmentation in Polymerizing PE Particles"

The defence will be held on
Friday, October 16, 2009
at 13:15 hrs
In "SP-2" of the "Speigel"
building at the University of
Twente, Enschede

To those less familiar with this particular research, I will give a brief introduction of my dissertation at 13:00 hrs

You are cordially invited for the reception immediately after the promotion

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FRAGMENTATION AND DISINTEGRATION OF POLYMERIZING PE PARTICLES

- *Role Of Stress, Brittleness And Skin*

S.N.Keelapandal Ramamoorthy

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The research described in this thesis has been performed at the University of Twente, the Netherlands. The work has been financially supported by Dutch Polymer Institute (DPI) – Project # 329: “Fines Generation in Ethylene Polymerizations”.

ISBN: 978-90-365-2907-5

FRAGMENTATION AND DISINTEGRATION OF POLYMERIZING PE PARTICLES

- *Role Of Stress, Brittleness And Skin*

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universitaet Twente,
op gezag van de rector magnificus,
prof. dr. H. Brinksma,
volgens besluit van het College van Promoties
in het openbaar te verdedigen
op vridag 16 oktober 2009 om 13:15 uur

Door

Shankara Narayanan Keelapandal Ramamoorthy

geboren op 28 Januari 1979
te Indien

Die proefschrift is goedgekeurd door de promoter,
Prof. dr. –Ing. Habil. Günter Weickert

To my parents and my wife…

Abstract

Morphology control is an important issue in the field of polyolefins as well as catalyst development. New generations of supported catalysts often show complex fragmentation behaviour. A single catalyst particle (catalyst on support) is composed of many micro-grains that are packed together. During the first seconds of polymerization, the monomer diffuses through the porous catalyst, leading to the production of polymer, which simultaneously fills up the catalyst pores. This occurs up to a critical degree after which the particle cracks into several sub-grains. Concurrently, a polymer skin also grows around the catalyst particle, and this skin holds the sub-grains together. Ideally, with stable skin formation, one polymer particle results from one catalyst particle. However, a combination of thermal and growth / mechanical stress can lead to so called particle disintegration ("external fragmentation") – the particle cracks into a number of smaller particles that polymerize and grow, leading to smaller than expected polymer grains (fines). "Fines" in general refer to an arbitrary fraction of particles that are far below the average expected particle size distribution.

Generation of fines has been a major problem in olefin (ethylene) polymerizations for a long time now. Production of fines in industrial processes leads to a multitude of problems like – wall sheeting of reactor walls leading to bad heat transfer characteristics; lumping and sometimes clogging of FBR's due to excessive accumulation of fines within the FBR thus disturbing particle fluidization, circulation and withdrawal; non-homogeneous polymerization leading to off-spec products; wall sheeting and clogging in downstream processes, like heat exchangers, compressors, etc. Hence, elimination / reduction of fines has been an important area of focus in industry.

The main objective of this thesis was to develop a semi-quantitative method for characterization of fines generation in ethylene polymerization using $MgCl_2$ - supported Ziegler-Natta catalysts based on a detailed analysis of the polymerization kinetics, molecular weight, crystallinity, particle growth and particle size distribution, pre-polymerization and catalyst pretreatment and their individual and combined impact on internal and external fragmentation. The polymerization rate profiles (*reflect the growth stress developing within a growing polymer particle*), crystallinity (*is an indirect measure of the brittleness of the produced polymer*), particle size distribution (*gives a direct measure of the particle disintegration*) and molecular weight (MW) of the produced polymer (*determines the intrinsic viscosity of the polymer matrix*) were used as a measure to quantify and understand the degree, extent and mechanism of particle disintegration during polymerization.

In this work we have developed a comprehensive semi-quantitative theory (**GRAF-S**: **_G_rowth Rate _A_ccelerated _F_ragmentation** – taking into account the role of the outer polymer **_S_kin**) for fines generation that clearly illustrates the underlying processes and their influences on the properties of the produced polymer and consequently on the final morphology of the particle during polymerization. The ***GRAF-S*** theory contributes deeply to a more complete understanding of different mechanisms in play, taking into account many factors (individual and combined) and the key influence of the role of the outer polymer skin, during polymerization.

Contents

Chapter 1: Introduction

1.1 History of Polyethylene

2008 was the 75th anniversary of the discovery of polyethylene (PE), the world's most produced polymer, by ICI chemists Reginald Gibson and Eric Fawcett. Gibson and Fawcett had begun their laboratory experiments to generate PE on Friday March 24, 1933 and returned to their laboratory on Monday March 27 to find a waxy polymerized substance lining their 18 millimeter high pressure reactor vessel. The chemists had difficulty in replicating the experiment which was subsequently shelved-partly on safety grounds-until 1935 (*Chemweek March 27, 2008*). It was then that a separate team of ICI chemists (Perrin) with access to safer high pressure equipment then managed replicate the initial experiment and polymerized ethylene at very high pressure into a semi-crystalline polyethylene. This discovery at the ICI laboratories led to the commercialization of low-density polyethylene in 1938. Low density polyethylene is produced in supercritical ethylene at high pressure (600 till 3500 bar) and high temperature (200 till 350°C). This radical polymerization leads to a highly branched polyethylene[1].

In 1950 Hogan and Banks, at the Phillips Petroleum Company, discovered that highly crystalline polyethylene could be produced at moderate temperature (70°C-100°C) and pressure (30-40 bars) using a chromium oxide catalyst supported on silica. This later came to be known as the Phillips catalyst[1].

It was in 1953, at the Max Planck Institute in Mülheim, that Karl Ziegler discovered that semi-crystalline polyethylene (with high crystallinity) could be synthesized under very mild conditions, atmospheric pressures and temperatures ranging between 50°C-100°C. Ziegler used a binary mixture of Titanium chloride in combination with alkyl derivative of aluminium as the catalyst. Polyethylene with varying densities (880 to 960 kg/m^3) can be produced with this Ziegler catalyst; from high-density polyethylene till linear low-density polyethylene.

The first low pressure catalytic process was developed and commercialized by Hoechst A.G. using a slurry process in a CSTR during the late 1950’s in Frankfurt, Germany. The activity of

Ziegler's catalyst was so low that the catalyst compounds had to be removed from the polyethylene. This additional step was an issue and was overcome in 1978 with the gas-phase Unipol process developed in 1978, using Ziegler-Natta catalysts[1] (supported on $MgCl_2$) with higher productivities. The productivity was so high that catalyst removal from the polymer was not required anymore[2].

Since then, phenomenal progress has occurred in the development of catalysts, improvements in product properties as well as the process, leading to many diverse commercial technologies being developed by different companies globally for the manufacture of polyethylene. These technologies can be broadly classified into three basic groups depending on the process conditions. They are: a) Solution process, b) Slurry processes, and c) gas-phase processes. In recent years, hybrids and combinations of the three processes have been used widely used in industry to produce a wide range of PE products and cater to the needs of the growing market.

1.2 Market and Outlook

The chemical industry currently produces about 70 million m.t./year of PE, a figure which is forecast to rise to about 100 million m.t./year in 2011 (*Chemweek March 27, 2008*). High density polyethylene (HDPE) accounts for nearly one half of the global polyethylene (PE) market (*ICIS Sep 26, 2008*). Its main outlet is in blow-molded products such as milk bottles, packaging containers, drums, car fuel tanks, toys and house wares. Film and sheet are widely used in wrapping, refuse sacks, carrier bags and industrial liners. Injection molded products include crates, pallets, packaging containers, house wares and toys. Extrusion grades are used in pipes, conduit, wire coating and cable insulation. Low density polyethylene (LDPE) is used mainly as a packaging film, either on its own or blended with linear low density polyethylene (LLDPE) to improve mechanical properties. Blown LDPE film has good processability and can be used in food and medical/pharmaceutical packaging in high purity grades, as well as in agricultural film and disposal nappies. LDPE is also used in sheathing for cables, the extrusion coating of paper and boards for liquids packaging, and in moisture barrier applications (*ICIS Feb 12, 2007*).

The key players globally in the PE industry are LyondellBasell, Borealis, Ineos Polyolefins, SABIC Europe, CPChem, and Dow Chemical company to name a few. Global demand for HDPE has been down off-late largely due to the sluggish housing and infrastructure market

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[1] An in-depth overview of the development of Ziegler-Natta catalysts is best described by Bohm et al[2] and Kashiwa et al[3].

and the financial crisis. However, producers estimate future demand growth at 3% per year in Europe and new HDPE capacities, particularly bi-modal PE plants, are coming online in the Mideast in the next five years. The growth of the LDPE market in Western Europe as forecast by Nexant ChemSystems is found to be essentially flat, at 0.4% per year, over the next five years. However, new capacity additions in Middle east and Asia are expected to rise in the next 5 years.

The latest trends in the industry are tailor made polymers. Superior polymer properties can be obtained by manipulating kinetics with process conditions in single reactors with different reaction zones[4] or using two different catalysts on one support, Univation. Improving polymer properties by manipulating kinetics can only be successful if the dependencies of polymer properties on required process conditions are known. Despite all research, only few academic research groups were able to provide information about reproducible and reliable polymerization kinetics at industrial conditions or properties of polymers produced under industrial conditions. Fines generation and morphology control have been a major issue in olefin (ethylene) polymerizations for a long time now with newer generations of supported catalysts often showing higher activities and complex fragmentation behaviour. During the last 4 years we have obtained a deeper insight and understanding of the mechanism of fines generation and the underlying factors that influence it with the GRAF[5] and the GRAF-S (this work, ***G****rowth* ***R****ate* ***A****ccelerated* ***F****ragmentation*, taking into account the important role of the outer polymer ***S****kin*) theories that have been simultaneously developed in our group. The following section proceeds on to discuss the objectives and the outline of this work.

1.3 Outline of this Thesis

The main objective of this thesis is to develop a quantitative method for characterization of fines generation in ethylene polymerization[2] using supported Ziegler-Natta catalysts based on a detailed analysis of:

- Polymerization rate profiles
- Molecular weight
- Crystallinity
- Particle growth and particle size distribution
- Pre-polymerization and Catalyst pretreatment

and their impact on

- Internal and external fragmentation[3]

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[2] main focus on slurry polymerization, but gas phase polymerization effects are taken into account

A systematic study has been carried out in this thesis to segregate the individual influences, by judiciously varying the following reaction parameters;
- *temperature, monomer (ethylene in this case) pressure, hydrogen pressure, co-catalyst concentration, pre-polymerization conditions,*

and monitoring their influence on the particle size distribution of the polymer produced. The kinetics of polymerization has been used as a measure to reflect the **growth stress** developed during polymerization. Crystallinity of the produced polymer has been used to relate to the **brittleness** of the system (the more crystalline the polymer, the more brittle it is). The lower the molecular weight (which is essentially controlled by hydrogen and temperature) the faster is the in-situ polymer crystallization. Furthermore, the impact of swelling of the amorphous polymer by slurryfying agents, i.e. n-hexane in this case, and . ethylene , as well as sorption of these components within the porous, growing particle has been considered. Another important factor is the “skin formation”. Without a skin around the particle that keeps the fragmented particle together, the particle would disintegrate under the influence of the growth stress – this can be quantified with PSD measurements.

The normalized particle size distribution has been used as a good measure to evaluate the extent of particle fragmentation during slurry ethylene polymerizations. Pre-polymerization and catalyst pre-treatment has been used in certain cases, to demonstrate the importance of early stage fragmentation of the morphology and particle size of the final polymer. It is obvious that the interaction between stress by particle growth and particle brittleness must be time dependent, because both major variables change dramatically during the course of polymerization.

This project has been funded entirely by the Dutch Polymer Institute (DPI) and all experimental work has been carried out at the high-pressure lab, University of Twente. The presented work has been completed in co-operation with Borealis Polymers Oy, Finland. A semi-quantitative theory has been developed to establish various factors that influence fines generation in ethylene polymerizations. The support of PRT GmbH for this work is also deeply appreciated.

Chapter 2 gives a basic introduction to fines generation and its drawback to the industry. It describes the various plausible explanations’ for this process and also states the methods employed by industry to counter the same. Currently, fines generation and agglomeration of particles (sheeting, lump formation) are major problems in almost all PO processes – and the

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[3] „internal“ stands for fragmentation without fines formation, the number of particles does not change

fundamentals of these phenomena are not well understood. It further proceeds on to discuss the “Our Theory” and the basis for this study.

Chapter 3 discusses the experimental setup with its features. The reproducibility of the kinetics, and subsequent methods for characterization and analyzing of the polymer produced have been dealt with in greater detail.

Chapter 4 discusses the influence of monomer pressure and the resulting growth stress on the polymerization kinetics and particle disintegration respectively.

Chapter 5 discusses the influence of pre-contacting the catalyst with TEA as co-catalyst as well as the influence of its concentration on the polymerization kinetics as well as on the particle size distribution.

Chapter 6 discusses the influence of hydrogen on the kinetics as well as the particle size distribution in ethylene polymerizations. Hydrogen decreases the chain length of the polymer produced – this leads to faster crystallization and higher brittleness. It also explains some of the observed peculiarities in ethylene polymerizations.

Chapter 7 deals with the importance of the pre-polymerization step and its influence on fines generation / production. In the absence of the outer skin, the micro-grains within a single catalyst particle would continue to polymerize independently leading to the production of only fines. This effect has been illustrated using the so-called 1-hexene effect. It further discusses the interesting issue of agglomerate formation from fines in this system.

Chapter 8 discusses the influence of temperature on all relevant parameters including the visco-elastic behaviour of the polymer matrix and its subsequent influence on particle disintegration.

Chapter 9 lists the learning from this study and gives future recommendations for further research in this field.

Appendix-1 – It includes a brief description of a method to measure the critical mechanical stress / energy required to fracture a particle, when a polymer particle of mass ‘m’ is accelerated with a velocity ‘v’ on to a hard flat surface (Stainless steel).

Appendix -2 – It gives a very brief overview of the major work that has been done in literature, regarding local particle overheating, heat and mass transfer effects in olefin polymerizations.

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Chapter 2: Mechanistic Understanding of Fines Generation

Abstract – Fines generation is a very complex issue that has always been a major industrial problem. Although a lot of research has been done to understand the mechanism of fines generation, a comprehensive theory has not yet been postulated. An effort has been made in this thesis, based on a state-of-the-art evaluation presented in this chapter, to study and understand the mechanism and underlying influences that lead to fines generation in ethylene polymerizations.

2.1 Introduction

Morphology control is an important issue in the field of polyolefins as well as catalyst development. New generations of supported catalysts often show complex fragmentation behaviour. A single catalyst particle (catalyst on support) is composed of many micro-grains that are packed together. During the first seconds of polymerization, the monomer diffuses through the porous catalyst, leading to the production of polymer, which simultaneously fills up the catalyst pores. This occurs up to a critical degree after which the particle cracks into several sub-grains. Concurrently, a polymer skin also grows around the catalyst particle, and this skin holds the sub-grains together[1]. Ideally, with stable skin formation, one polymer particle results from one catalyst particle. However, a combination of thermal and growth / mechanical stress can lead to so called particle disintegration ("external fragmentation") – the particle cracks into a number of smaller particles that polymerize and grow, leading to smaller than expected polymer grains (fines). "Fines" in general refer to an arbitrary fraction of particles that are far below the average expected particle size distribution. Under special conditions, without skin formation, one can fragment the catalyst support easily by the growth stress down to primary crystal size of the carrier ($MgCl_2$).

2.2 Fines – A problem to industry

Fines generation has been a major problem in olefin (ethylene) polymerizations for a long time now. Fines production / elimination / reduction are important issues for most industrial processes. Although fines production is perceived to be predominantly a problem for gas phase processes, it is also a concern for slurry and liquid pool[1] processes. There are huge differences between slurry and gas phase processes per se (heat balance of the polymerising particles are extremely different, sorption within the polymer and bulk monomer concentrations in the slurry are higher than in gas phase, crystallisation kinetics could be very different in each case, and so on and so forth.)[2]. However, the mechanism of external fragmentation must be the same in both cases, only the conditions for the fragmentation are extremely different.

In addition, many processes involve a first stage polymerization in slurry / loop, followed by a final stage polymerization in fluidised bed reactors. Production of fines during the slurry / loop would cause severe problems during the subsequent gas phase fluidisation and in almost all downstream operations including polymer processing (wall sheeting, electrostatics, entrainment, low product bulk density, etc.)

Conventional fluidised bed reactors used in industry consist of a cylindrical shaped fluidised bed section, which sometimes extends into an enlarged conical disengaging section at the top (*Figure 1*). The catalyst or pre-polymer is fed above the gas distribution plate and monomer is fed from the bottom at a certain gas velocity to enable fluidisation of the bed. Polymerization starts instantaneously leading to final polymer particles the diameter of which depends on the individual residence time of the particle. During the course of polymerization, polymer particles are projected upwards into the disengaging section through the flowing gas. Most of these particles fall back into the fluidised bed, by gravity (gas velocities above the bed are always lower). However, some of the particles, which are extremely fine and light are elutriated out and do not return to the fluidised bed[3]. These particles, “fines”, either accumulate in the disengaging section or leave the reactor along with the flowing gas through the reactor outlet. This holds true especially for highly active small particles (catalyst particles with low individual residence time) and can cause operational problems within the reactor (fluidised bed) or in other downstream processes like the piping, heat exchangers, compressors and the gas distribution grid. In addition, the more the fines, the bigger the size of the disengaging section required, and hence higher the investment costs.

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[1] polymerization of liquid propylene; often carried out in loop reactors

[2] see thesis of Majid Daftaribesheli, University of Twente[2]

[3] in some processes, fines from the cyclone are recycled into the FBR, see below - in case of non-active fines this can lead to another problem: fines enrichment in the FBR

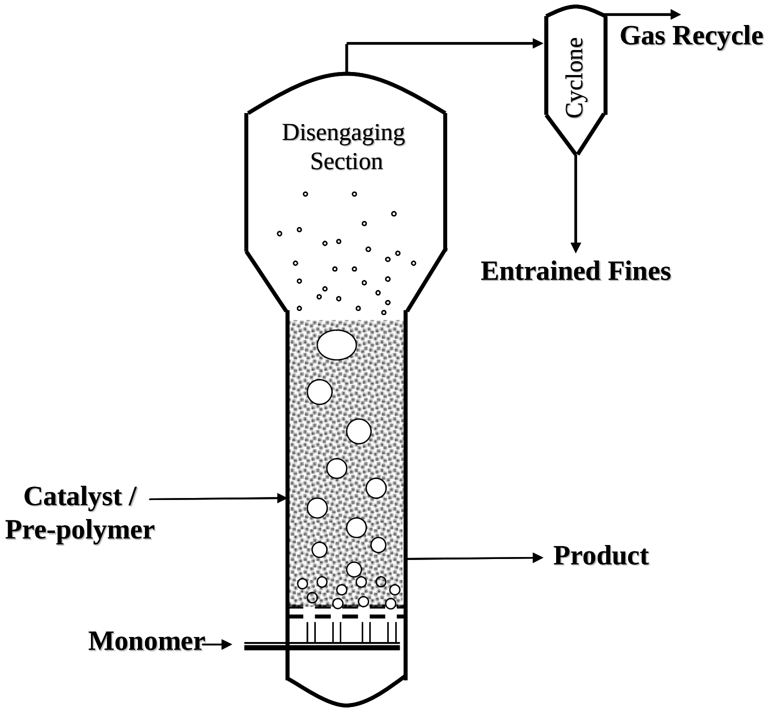

Figure 1: A conventional fluidised bed used in olefin polymerizations.

Within the fluidised bed section, fines accumulate and are considered the major reason for wall sheeting in reactors. Fines tend to accumulate along the reactor wall in the fluidisation zone, due to electrostatic forces caused by their high surface area to mass ratio. Along the reactor wall, the accumulated fine particles continue to polymerise independently and exothermally leading to melting and fusing of polymer particles into sheets along the reactor wall. These initial sheets continue to grow, forming layers on the reactor wall. Sometimes, over time, such layers accumulate and become thick and heavy enough (“lump formation”) to drop off the walls and into the fluidised bed due to their own weight, leading to problems with particle fluidisation, circulation and withdrawal. In some cases, if the sheets are large enough, they may significantly disturb the normal fluidisation (clogging the gas distribution plate) and the circulation of gas and solids of the entire fluid bed leading to extensive fusing of the main bed and subsequent reactor shutdown and stoppage in production. This is an extremely costly and time-consuming operation and preventing this would result in significant savings for the industry.

Fines have a tendency to accumulate in regions of lower gas velocities. The sloping reactor wall in the disengaging section above the fluidising bed section provides such a region of lower gas velocity. Big particles are not present and cannot remove adhesive fines from the wall. If the fines accumulate along these sloping walls in the disengaging section, the polymerization heat load along the sloped wall would increase substantially with time leading to melting and fusing of the particles into sheets along the wall. This wall sheeting leads to the same operational problems as explained above.

In addition to the problems caused within the fluidised bed reactors, fines exiting the disengaging section with the recycle gas pose other problems to downstream processes. They could attach to surfaces of piping, heat exchangers, compressors, bottom of the reactor, and gas distribution grid creating sheets and lumps of polymer. Such sheets reduce the heat transfer efficiency of the heat exchangers, and reduce the flow of recycle gas and over time if left unnoticed may lead to clogging of pipes and subsequent shut down of the reactor.

Fines production has serious ramifications in slurry / loop ethylene polymerization processes too. Wall sheeting is one major concern, leading to higher required heating capacities or blockades and subsequent higher operational costs. Therefore, prevention of fines formation is a major issue in olefin polymerization technology. This prevention needs understanding of the fines formation mechanisms.

2.3 Industrial Strategies for prevention / control of fines

Industry has long been dealing with the issue of fines and over the years has developed many strategies to counter it. Industrial strategies for countering fines are based on three major principles:

1. *Engineering the catalyst*

The particle size distribution (PSD) of the final polymer depends on the PSD of the catalyst, the RTD (i.e. residence time distribution) of the reactor system, and the fragmentation behaviour (of the catalyst / support) it exhibits during polymerization. Engineering the catalyst includes optimising activity / performance of the catalyst, identifying the best support (morphology, mechanical strength, porosity) for the catalyst system, supporting techniques, PSD of the final catalyst and the corresponding activities it displays during polymerization[3,4]. Changing or modifying the catalyst system affects the properties of the produced polymer (as molecular weight, molecular weight distribution, co-monomer composition, incorporation and distribution) and the polymerization process parameters since the catalyst’s response to hydrogen, co-monomer, temperature and pressure is highly influenced by the type of catalyst used. Furthermore, the individual residence time of the particle, characterized by the “RTD” of the reactor, must have a dominating impact on its fragmentation behaviour. In this work, all experiments are carried out in batch mode, therefore, all particles show the same “residence time” – this way we exclude the influence of the RTD. However, the RTD influence could be important if one wants to upscale the results of this work. In this case continuous (mini) plants are required to generate reliable data for fines generation studies.

2. *Engineering solutions*

Engineering solutions mainly refer to reduction in fines generation by implementing modifications in process equipment. Painter et al[5] (1995) disclosed a strategy for fines reduction by modifying the circulation pattern in the disengaging section. Generating a tangential gas or gas-solids flow in the expanded disengaging section of a gas phase fluidised bed reactor, would reduce fines entrainment in the gas-recycle system and minimises solids build-up on the inner surface of the disengaging section.

The usage of cyclones is another strategy that as been successfully implemented in industrial FBRs. Cyclones are used to separate active fines from the outlet gas stream. The active fines are returned back into the FBR by ejectors[6]. Other improvements include, coating of the inner surfaces of heat exchanger tubes to reduce adhesion of fines on to their surface, preventing sheeting and the eventual clogging of the heat exchanger tubes[7]. Additionally several improvements have been proposed to minimise the accumulation of fines below the gas distribution grid[8,9]. In some cases, sound waves have been used in a direction tangential to the reactor surface to reduce surface adhesion of fines due to electrostatics[10]. Chemicals have also been added to the fluidising section to reduce surface adhesion of fines to the reactor wall[11].

3. *Process solutions*

These refer to modifications in process steps, for example, performing a pre-polymerization before main polymerization. Several examples could be found in literature, see for instance[12,13]. It is well known in industry that pre-polymerization helps in greatly reducing fines production in main polymerization. However, the conditions for pre-polymerization are important. Most industrial processes include a first stage pre-polymerization step followed by subsequent main polymerization.

Other process solutions include the controlled addition of hydrocarbons[14] (that are inert to the polymerization reaction) to the fluidising bed and maintaining the ratio of the dew point pressure to the total reactor gas pressure between 0.4 and 0.99. Addition of hydrocarbons would reduce local overheating, which is one of the major reasons for fines generation. This happens for example in *condensed mode operation*. The major target of condensed mode is a higher production rate.

The catalyst system could also be pre-treated or pre-contacted with hydrocarbons (low boiling) before they are charged into the FBR ("wetting the catalyst"). Wetting the catalyst reduces local particle overheating significantly, with the low boiling hydrocarbon absorbing the heat of vaporisation and boiling off during the most critical stage in the life of growing particles. Other studies include continuously, monitoring and controlling the instantaneous properties (mechanical, physical and dielectric) of the reacting particles[15].

2.4 Current understanding of fines formation

Different hypotheses have been put forth to explain the mechanism and formation of fines in ethylene polymerizations, such as:

- Undesirable external fragmentation of the catalyst / support / pre-polymer, occurring due to the high stresses (hydraulic and thermal) generated within the matrix (pre-polymer / polymer / catalyst matrix) in the first seconds of polymerization. This varies between different catalysts depending on the type of support, mechanical strength of the support, catalyst loading (distribution and concentration), particle size distribution (broad / narrow), porosity, functional species, kinetic behaviour (activation / deactivation profile, activation time, peak activity), etc.
- the non-uniformly distributed intra-particle polymerization rate[16] (caused by diffusion resistance and site heterogeneity).
- Temperature and concentration gradients within a particle leading to resistances in inter/intra particle heat and mass transfer, and subsequent overheating / deactivation of the active sites.
- Residence time distribution of the particle within the reactor, with non-uniform residence time distributions (segregation in FBR) leading to non-uniform particle size distributions
- Faulty / insufficient reactor design leading to local hot spots or dead zones where monomer concentration is substantially higher than the common bulk

- Impurities in the feedstock could lead to deactivation / poisoning of some of the active sites leading to slower / no polymerization and non-uniform particle size distribution
- Fluctuations or gradients in local conditions would influence the physical / instantaneous mechanical properties of the polymer (crystallinity, sorption, etc.) leading to fines production. Banat et al[17] observed that performing polymerizations at lower temperatures led to a substantial increase in fines production.

Progressive sections and chapters of this thesis would help in establishing the fact that "*the mechanism of Fines Generation depends on the stresses generated within the matrix (supported catalyst / pre-polymer / polymer) and the brittleness of the system (both the parameters are non-uniformly distributed within a given particle and are changing with time).*

2.5 Fines Generation: Working Hypothesis – (GRAF-S)

The following hypothesis for our theory **GRAF-S** (***G**rowth **R**ate **A**ccelerated **F**ragmentation*, taking into account the important role of the outer polymer ***S**kin*), contains both the state of the art[2] and conclusions from the experiments done in this work.

The major influences on fines generation are:

1. intra-particle stress, with the components
    a. particle growth stress by polymer production within a solid particle taking into account radial concentration and temperature profiles; due to the exothermic reaction, this internal stress is always joined by thermal stress – the latter depends on the particle heat balance,
    b. mechanical/external stress
        i. during catalyst preparation
        ii. during catalyst injection
        iii. by stirring and particle flow
        iv. during gas-solid separation between reactors etc.
2. particle brittleness / fragility, with the components
    a. brittleness of the support
    b. brittleness of the polymer formed[4]
3. the outer “skin” formation during the early stage (low yield) polymerization
4. solubility of a certain part of the polymer in slurry polymerizations
5. “homogeneous” polymerization (in slurry processes) of non-supported parts of the catalyst

For a given supported catalyst, brittleness and stress are distributed parameters, which depend on many variables during the polymerization process. Fragmentation occurs where high stress and high brittleness come together at given local positions within a particle. Clearly, these properties

- depend on particle size,
- depend on the radial position[5] within the particle,
- can vary from particle to particle within a given size fraction,

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[4] a highly crystalline polyethylene is more fragile than an amorphous one

[5] especially the formation of a solid skin on the outer surface of a growing particle is of importance

Homogeneous polymerization in slurry processes - caused by “leaching”, for example -leads to extremely fine polymer particles with subsequent fusion on surfaces (reactor wall => “sheeting”); or with other particles in the neighbourhood. The investigation of homogeneous polymerization is out of the scope of the project presented here. Our focus is on all factors that are changing stress and brittleness. In the following section, we shall briefly discuss the major influences (stress and brittleness) in detail.

2.5.1 Stress

The stress consists of two components as stated above. The polymer growth stress within a growing polymer particle (along with the thermal stress, due to local particle overheating) and mechanical or external stresses caused by a number of factors. We shall deal with each of these components individually in the following sub-sections.

1. Growth Stress

The first few seconds of polymerization are extremely critical for morphology control in heterogeneous olefin polymerization. It is in these first seconds, that the first polymer skin is formed around the catalyst particle. The monomer also diffuses into the catalyst particle and into its pores, where it encounters more active sites leading to polymerization in the pores. As the reaction proceeds, the polymer begins to fill the pores of the catalyst support, while simultaneously, the skin continues to grow on the outer side of the catalyst particle. The filling of the pores with polymer, occurs to a certain critical degree, and during this process, it exerts a pressure on the outer skin of the particle. Once the filling crosses the critical degree, it leads to fragmentation of the particle into several sub-grains that continue to polymerise. If the skin is thick enough, it will hold these sub-grains together preventing particle fragmentation and hence, fines generation. The local stress depends on the local reaction rate and the local matrix resistance. The higher the reaction rate, the higher would be the growth stress leading to a higher degree of fragmentation and smaller particles, thus leading to fines generation (*if the particle is brittle enough, see below*).

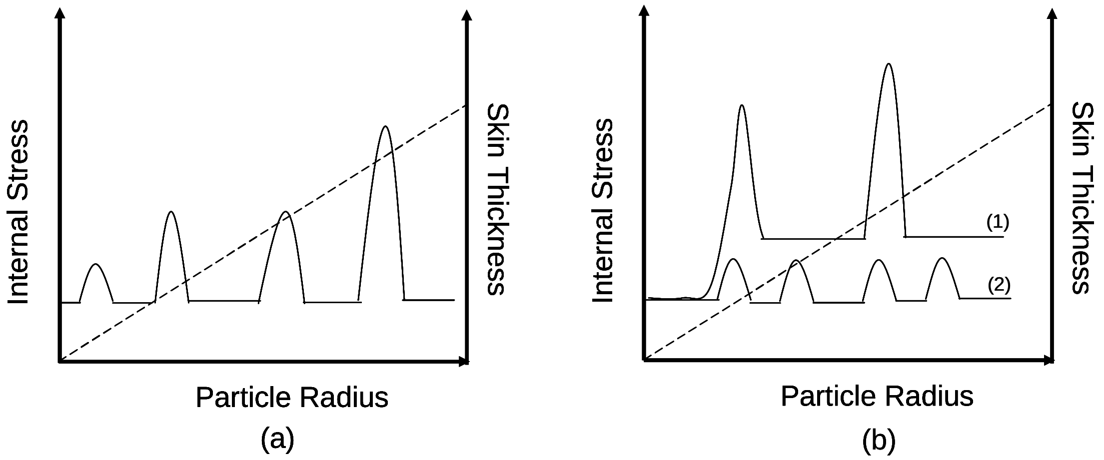

Figure 2: Schematic of stress generation and skin growth within a growing polymer particle over time: (a) Skin growth/thickness is faster than stress generation; (b) with the internal stress being much higher leading to disintegration of particle (case1) and during pre-pol conditions (case2).

Figure 2 represents the importance of both the internal stress and skin growth as a function of the particle diameter during polymerization. The following can be inferred from *Figure 2*:

> Case (a): if the rate of skin growth is faster and strong enough to resist the internal stress generated due to polymerization, one can expect the skin to hold the growing macro-particles together thus preventing particle disintegration.
>
> Case (b): when the internal stress generated is very high during the first seconds of polymerisation much higher than the initial rate of skin growth, it would lead to disintegration of the particle thus leading to production of fines as represented by (1). However, by controlling this initial high stress by polymerizing under mild conditions (pre-polymerization) one can expect to avoid fines generation (2).

It must also be noted that local overheating – in gas phase - often leads to softening of the polymer matrix that is swollen with gases and liquids under pressure. This can contribute to lesser fines formation[3] and even agglomeration is possible. Clearly, the effect of thermal stress also depends on the thermal response of the material - catalyst / support / polymer (>90% $MgCl_2$ at the beginning of polymerization, but nearly 100% partially crystallized polymer at the end of the polymerization process).

Growth stress and its distribution across the particle, cannot be measured quantitatively – we need to rely on indirect observations, like for instance, polymerization rate, to judge growth stress. The rate of increase of the polymerization rate over unit time directly correlates to the particle growth rate and hence the average stress generated within it. This is always combined with thermal stress during the exothermic reaction and cannot be separated from the same. Performing experiments in slurry, however, minimises the local over heating due to higher heat transfer coefficients in slurry as compared to gas phase polymerization. Therefore, it is a wise strategy (for studying fines generation) to start with slurry polymerizations.

The growth stress also depends on the *activation state* of the catalyst (active sites), *especially in slurry polymerizations with highly active catalyst systems*. If the catalyst is pre-activated with co-catalyst, it would tend to display a faster activation profile than one, which is pre-activated in-situ during polymerization. This initial faster activation, would lead to a higher growth stress in the first seconds of polymerization, and hence undesired particle fragmentation and eventual fines production. However, this depends on pre-contacting time, monomer/ co-monomer concentrations and temperature.

2. External or Mechanical Stress

External or mechanical stresses include all physical or external forces influencing fragmentation or disintegration of a particle (polymer / catalyst / support), during any of following stages of a polymerization process.

— Catalyst preparation

  Handling of catalysts in a process is extremely important. The significance of catalyst preparation is paramount, especially in the polyolefin industry, as even small traces of impurities could lead to deactivation of catalysts. This step is also the first source of problems with respect to fines production. Ideally, the catalyst / support should be such that, during polymerization, it is fragile enough to break into individual sub-grains that continue to polymerise into bigger particles, but strong enough not to disintegrate completely into very small sub-grains, leading to the production of fines. However, shearing of the catalyst / support, by stirring for instance (as is done in some industrial slurry processes), could lead to undesired fragmentation of the catalyst / support. The undesired fragmented catalyst particles would polymerise independently during subsequent polymerization leading to the production of polymer particles with smaller than expected particle size distributions (fines). In addition, fragmentation of the catalyst / support, could also influence the kinetics of the catalyst and its performance (activity) during polymerization (higher surface area / unit volume), leading to higher than expected growth stresses. This could lead to an increase in fines production.

- Catalyst injection

  In most processes, the catalyst is prepared elsewhere and transported to the reactor through pipes, before it is injected into the reactor. During transportation in the pipes, flow stress induced, especially in pipe bends and near the pipe walls, would lead to undesirable catalyst fragmentation. In addition, catalyst impinging on the reactor walls at high velocities during injection (especially, if the catalyst support is fragile) would lead to undesirable fragmentation of the catalyst / support and eventual fines generation during subsequent polymerization as explained above. This could be an extremely critical criterion for fines production, especially in gas phase processes, and in processes where the catalyst in injected into the reactor at higher pressures using nitrogen or monomer.

- Stirring and particle flow

  During polymerization, particle fragmentation / breakage due to mechanical stresses can occur due to stirring (due to high shear stresses) and during particle flow through pipes, cyclones, etc. (due to the particles impinging on the walls of the pipes or cyclones at high velocities). Fragmentation could also occur due to wall friction and inter-particular friction, especially in gas phase polymerizations.

- Gas-solid separation between reactors etc.

  In some processes, the polymer particles are flashed from high pressures to low pressures before subsequent polymerization in fluidised bed reactors. During such operations, particle velocities could be greater than 50m/s, and particles impinging on the hard surfaces of the walls at such high velocities would tend to fragment and thus lead to fines production in the process, especially if the particle crystallinity is high.

As explained above, the stress is mainly due to high physical forces on the particle (supported catalyst / polymer), due to any of the above reasons, causing fracture in the particle and thus fragmenting it. We have developed a method to measure the critical mechanical stress / kinetic energy required to break a polymer particle. It is dealt with briefly in Appendix 1.

2.5.2 Brittleness

The distribution of brittleness across the particle cannot be measured, especially under polymerization conditions. We simplify the modelling problem by taking the crystallinity of a polymer sample as measure for the averaged brittleness – averaged over all existing particle size fractions and averaged over the radius of a single particle. The more crystalline the polymer, the more brittle one would expect it to be and the greater would be its tendency to break into smaller particles / fines. We come back to this working hypothesis under "quantitative results" below. Lower fines formation at increasing temperature, see Banat et al[3,17], can be explained with decreasing brittleness of the polymer. The averaged brittleness can be characterized by measuring the critical mechanical stress that leads to disintegration of a given particle (mass m, velocity v) when it crashes at a vertical wall, see Appendix 1.

2.5.3 Low Yield Polymerizations and the importance of the outer "Skin"

At the beginning, the brittleness of a given ZN catalyst is determined by the brittleness of $MgCl_2$, because it forms the continuous phase with the $TiCl_4$ distributed within. At yields larger than 1g polymer/g-catalyst, the polymer becomes the continuous phase and consequently the brittleness of the particle is increasingly determined by the polymer properties.

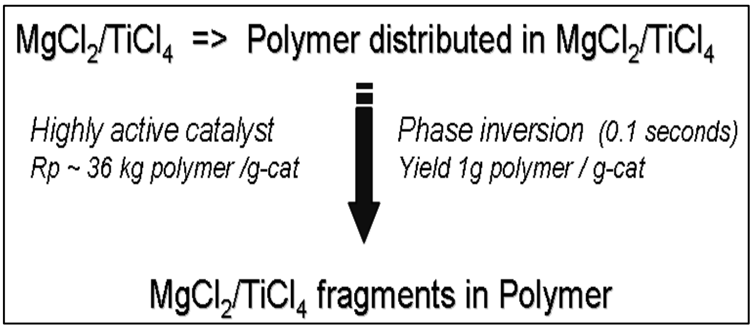

Figure 3: Schematic showing the phase inversion in a highly active Ziegler-Natta catalyst on a $MgCl_2$ support

A catalyst under industrial conditions, showing a polymerization rate of 36 kg polymer / g-cat hr would reach the critical phase inversion yield of 1g polymer / g-cat within 0.1 second, see *Figure 3*. During this 0.1 second, a dramatic change of both stress and brittleness (and their distributions) occurs accompanied by quickly changing particle composition in the sequence

This is overlapped by a simultaneous polymer skin formation at the outer surface of the particle – along with a temperature rise caused by the exothermic polymerization and the in-situ swelling and crystallization behaviour of the polymer formed.

All these fast and hard-to-control processes can be delayed to a large extent, by slowing down the polymerization rate by some orders of magnitude. This can be achieved by operating at low temperatures and/or low monomer concentrations within a so-called pre-polymerization. However, it should be clear that all these processes remain complex. For instance, even at drastically decreased polymerization rates, the optimum conditions for a pre-polymerization must be found. In such a scenario, fragmentation depends more on the stress tolerance of the catalyst / support. If enough polymer is produced, so as to form a thick skin around the particle, then this particle would continue to grow bigger in the main polymerization without fines formation. If the catalyst support is brittle enough, then the particle tends to crack up even at such low yields during pre-polymerization, leading to production of smaller particles (fines generation) in main polymerization. These fines could also fuse with bigger particles leading to agglomeration.

The importance of the polymer skin can also be investigated under low yield conditions (low growth stress) if the polymer formed is soluble in the solvent used. This is the case, for example, for 1-hexene polymerization in hexane slurry[1]. In absence of the fragment-covering polymer skin, the growth stress can lead to complete disintegration of the catalyst and nearly 100% fines can be formed by means of this kind of pre-polymerization. Similarly, the role of mass transfer limitations is to be taken into account. At low-rate conditions, the influence of mass transfer is also low and the critical brittleness can be reached before a fragment-covering skin is strong enough too keep all parts together, and disintegration would take place. Mass transfer limitation of the monomer will lead to a maldistribution of the growth stress[18].

A pre-polymerization step implies higher investment and operational costs in industry. Driven by economic needs, pre-polymerization yields in industry are seldom higher than 500g polymer/g-cat and most of the polymer is formed during the main polymerization under high-rate conditions.

2.6 Basis for Experimental Design

Taking into account all the above influences, an experimental program was designed, to segregate key variables (while keeping all others constant) and studying their influence / impact on fines generation in slurry ethylene polymerizations. The following rationale was used in designing the experiments

Monomer pressure

The monomer pressure directly relates to the rate of polymerization. Higher polymerization rate causes higher growth stress. Depending on mass transfer limitations and uneven active site distribution, the growth stress is different at different positions.

Hydrogen influence

The higher the hydrogen-to-monomer ratio, the lower is the molecular weight of the PE formed. Low molecular weight (shorter chains) PE crystallizes faster and hence would tend to be more brittle. In addition, the shorter chains also lead to the reduction in the micro-viscosity of the polymer matrix, thus enabling a higher sorption and diffusion (of both monomer and hydrogen) locally within a polymer particle.

Effect of co-catalyst

High co-catalyst concentrations lead to increased external fragmentation with certain highly active catalysts. Higher co-catalyst concentrations can lead to higher polymerization rates, and consequently an increased growth stress. The higher growth stress consequently leads to an increase in crack generation (micro-cracks) within the growing polymer particle and thus promoting a faster back diffusion of monomer and co-catalyst despite the convective polymer flow leading to dilution of the same.

Effect of pre-polymerizations

Pre-polymerization refers to polymerization under “mild conditions” (lower temperature / monomer pressure) thus leading to a lower build-up of growth stresses during the early stages of polymerization. However, the kind of pre-polymerization determines the final particle morphology – for instance, removal of the outer polymer skin, by performing a pre-polymerization step would lead to the generation of mostly fines during main slurry homopolymerization.

Effect of reaction temperature

With changing temperature the following parameters are changing:

- polymerization rate
- molecular weight of the polymer produced
- monomer / hexane sorption in the polymer
- all material and transport properties

  (For instance, with increasing temperature the local micro-viscosity within a particle decreases, thus enabling a higher mobility of freshly formed polymer chains).

On a macro-scale, the global (experimental) parameters that influence fines generation are as presented in *Figure 4*. On a micro-scale (within a polymer particle) the various factors that influence and lead to external fragmentation are as shown in

Figure 5 (***GRAF-S*** theory). All the above influences (macro and micro) are discussed in detail in the latter chapters of this thesis. The following chapter describes the experimental set-up, protocols and the analytical procedures that have been used and followed throughout this study.

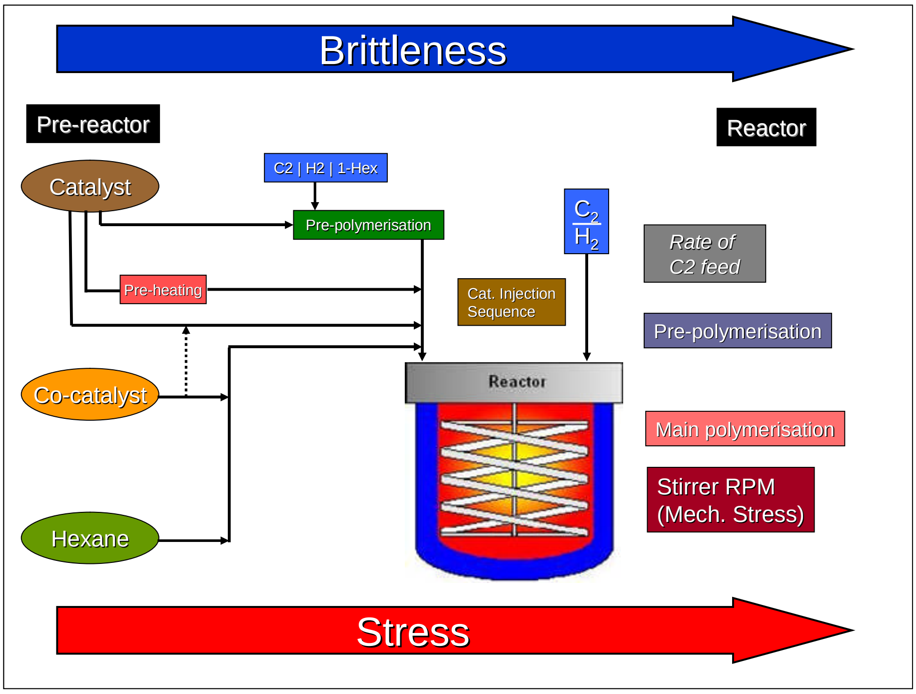

Figure 4: Schematic representation of experimental parameters influencing fines generation.

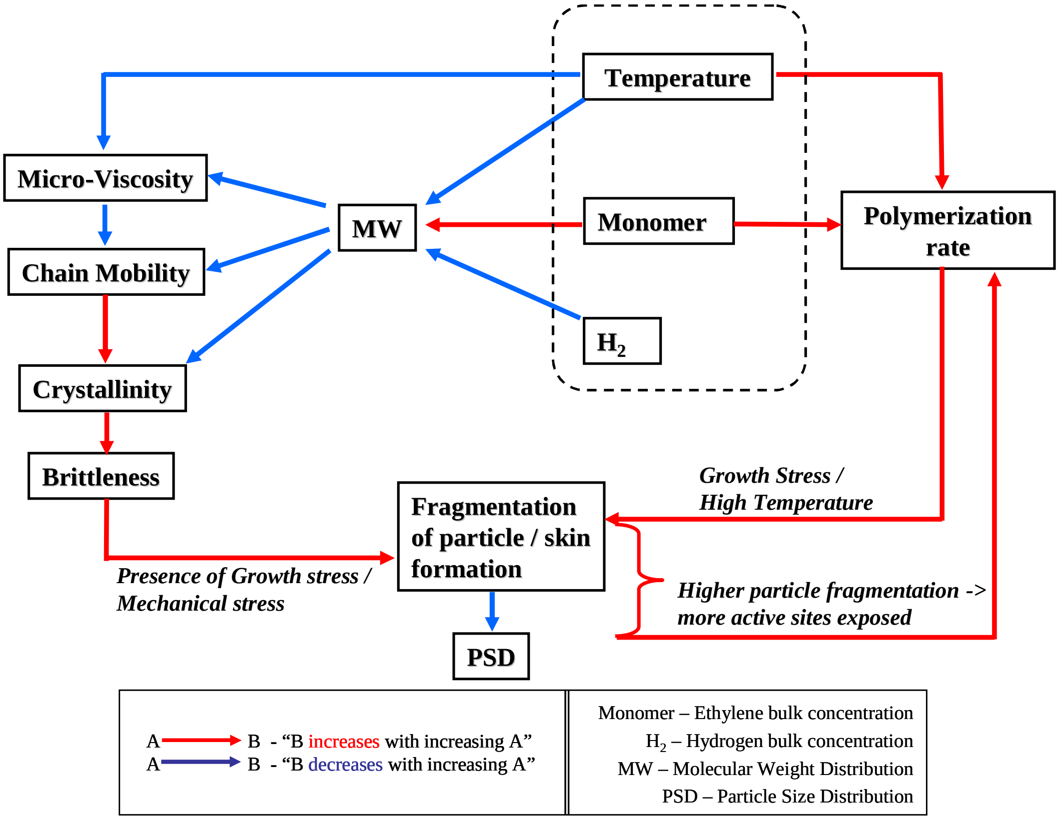

*Figure 5: **GRAF-S**, a semi-quantitative theory of fines generations and the various factors influencing particle fragmentation and fines generation.*

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Chapter 3: Experimental methods

3.1 Set-up

The experiments were performed in a 1.6*l* jacketed Buchi reactor, for slurry and gas phase polymerizations.

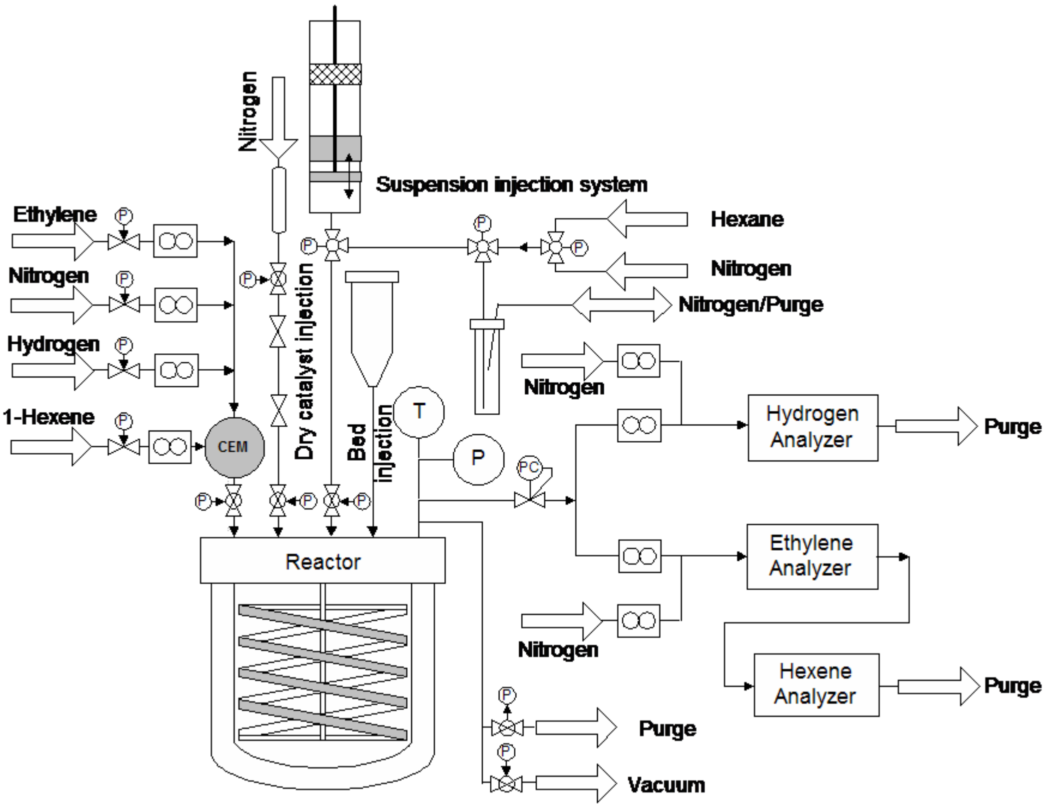

Figure 1: Schematic of the 1.6l semi-batch Buchi reactor used in this study[1].

Figure 1 gives the schematic representation of the experimental setup. The reactor is a 1600 ml jacketed, stainless steel, semi-batch, Buchi reactor, designed for operating at pressures up to 40 bars and temperatures up to 125°C. The setup is equipped with automated catalyst injection systems suitable for both dry powder and slurry catalysts. The slurry catalyst injection unit can also be used for the addition of liquids (hexane, for instance). The reactor is equipped with a helical stirrer combined with a propeller at the tip ensuring good powder circulation. This forced circulation improves heat transfer from the polymerising particles to the cooled reactor wall. The stirrer speed can be varied in the range from 50rpm up to 2000rpm.

The jacket and the cover plate of the reactor are heated with circulated hot water from individual water baths. The reaction temperature is measured above the helical stirrer. The reactor temperature for isothermal experiments is maintained within 0.2°C by controlling the jacket temperature by cold water addition using a PID cascade controller.

A HP3852A Data Acquisition/Control Unit (DACU) measures all the temperatures, pressures and mass flows. The entire set-up is controlled and monitored from a PC using HPVEE software.

3.2 Materials

The catalyst used in this study is a highly active industrial Ziegler-Natta catalyst (with a $TiCl_4$ loading of > 6% on a $MgCl_2$ support) kindly provided by Borealis. The catalyst is a suspension (22.6 wt %) in mineral oil slurry and needs to be activated with a co-catalyst such as Tri-ethyl aluminium (TEA). TEA (>99.9% purity) used in this study was obtained from Akzo-Nobel and was used as both scavenger and co-catalyst.

Ethylene (purity > 99.9%, C2H2 < 7 ppm, feed quality, Hoekloos) is further purified over a 1*l* column with oxidized BASF R3-16 catalyst, two 3.3*l* packed columns one filled with reduced BASF R3-16 catalyst and one with molecular sieves (13X, 4A and 3A, Sigma-Aldrich) and a 1*l* column with Selexsorb® COS[2].. This extended purification unit removes CO, oxygen, water, CO_2, H_2S and COS from the ethylene monomer. Nitrogen (purity >99.999%, O2 < 1-10 ppm, H2O < 1-10 ppm, Praxair) and hydrogen (purity >99.999%, Praxair) are purified over BASF R3-11 catalyst and molecular sieves (13X, 4A, 3A).

Hydrogen (purity>99.999%, Hoekloos), Nitrogen (purity >99.999%, O_2 < 1-10 ppm, H_2O < 1-10 ppm, Praxair) and hexane (purity >99%, pro synthesis, Prolab) were also purified in the separate proper purified equipments including two columns, reduced BASF 3R-11 catalysts in order to chemically absorb oxygen and molecular sieves (3A, 4A, 13X, Sigma-Aldrich) to physically absorb CO_2, H_2O and other impurities, respectively. For nitrogen two 19*l* packed columns are used and for hydrogen four 0.5*l* packed bed reactors are used.

3.3 *Experimental Protocol*

3.3.1 Catalyst Preparation

Approximately 7 mg of catalyst has been used for all experiments, unless otherwise mentioned.60mg of TEA is used as the co-catalyst for all experiments, unless otherwise mentioned. Additionally, for all experiments, 90 mg of co-catalyst (TEA) is used for scavenging the reactor.

3.3.2 Standard Experiment

A typical standard experiment involves the following steps:-

- A leakage test is performed with nitrogen, to ascertain if there is any leakage in the system.
- An automated flushing procedure is performed at high temperature (80-90C) using nitrogen. This procedure takes about 45 minutes and the reactor and all lines connected to it are flushed about 12 times during the same period.
- Once the flushing is over, the reactor is evacuated.
- The Eurotherm is set to the required temperature set point. The reactor is filled with the required amount of hydrogen (if the experiment contains hydrogen). *Note: Hydrogen has always been filled on empty reactor basis, in all the experiments performed*.
- After this, hexane is fed into the reactor using a liquid injection system, (typically about 800 ml)
- The co-catalyst (normally 150~160 mg) is injected into the reactor using the liquid injection system. The total TEA is divided into two parts: 90mg of TEA as scavenger and the remaining 60mg performs the role of the co-catalyst.
- Once the co-catalyst has been injected into the reactor, an allowance of 5-10 minutes is given, for scavenging and equilibration, before feeding in monomer (ethylene in this case) to the required pressure.
- Meanwhile, the catalyst is prepared. The catalyst amount has more or less been kept constant (~6-7 mg) for all experiments, except in experiments where we study the influence of catalyst amount on reaction kinetics and particle breakage. The stirrer speed has always been kept constant at 400 RPM for all experiments, .unless mentioned otherwise. The catalyst used for all the experiments is the same as mentioned above, unless mentioned otherwise.
- The prepared catalyst is injected into the reactor, using the liquid injection unit (using n-hexane). The injection unit is flushed typically 4-5 times, to make sure there is no residual catalyst left in the injection lines. This typically signals the beginning of the reaction.

- The mass-flow controllers typically take a minute or two to show a response. Most experiments are performed for a one-hour duration. During this period, the HPVEE software controls and stores all the online parameters as a text file in the computer.
- At the end of the experiment, the data is saved and the program is stopped.
- The reactor is then purged slowly and the jacket of the reactor is cooled to room temperature.
- Once, the reactor has cooled down, it is opened and the polymer along with hexane is removed. The polymer is then separated and dried in a vacuum oven at 60°C for four hours. Care is taken to ensure minimal product losses during the filtration vacuum drying.

The data obtained from the HPVEE software is processed to obtain the temperature, pressure and rate profiles for individual experiments.

3.4 Reaction rate measurement and reproducibility

Under isobaric-isothermal conditions, neglecting the influence of

- the freshly produced polymer (in terms of sorption of components),
- a possible deviation from the equilibrium monomer concentration,
- changes in volume and temperature during the catalyst injection,

the polymerization rate corresponds directly to the mass flow of ethylene that is required for keeping the pressure constant. At the beginning of a given experiment, the system needs some seconds to start the mass flow controller operation.

Figure 2 shows a typical rate profile for a standard experiment (4 independent experiments for comparison). Cat1 shows a typical activation period (the time of which depends on reaction conditions), reaches a maximum before deactivating. The fluctuations observed are due to fluctuations in the thermocouple couple. The kinetics is reproducible with deviations of ± 5% of the polymerization rate.

It should be noted that all experiments were performed in the absence of gas-liquid mass transfer limitations. Preliminary experiments were performed to optimise the stirrer speed to ensure that we were outside the regime of gas-liquid mass transfer limitations. Diffusion limitations on a micro-particle scale can be neglected [3-5]. In this case, it takes about 35 min to reach the rate maximum, where the activation and deactivation counter-balance each other. The polymer yield is measured directly by weighing the dried polymer after filtration and drying. This amount is rechecked with yield obtained from the integrated rate curve.

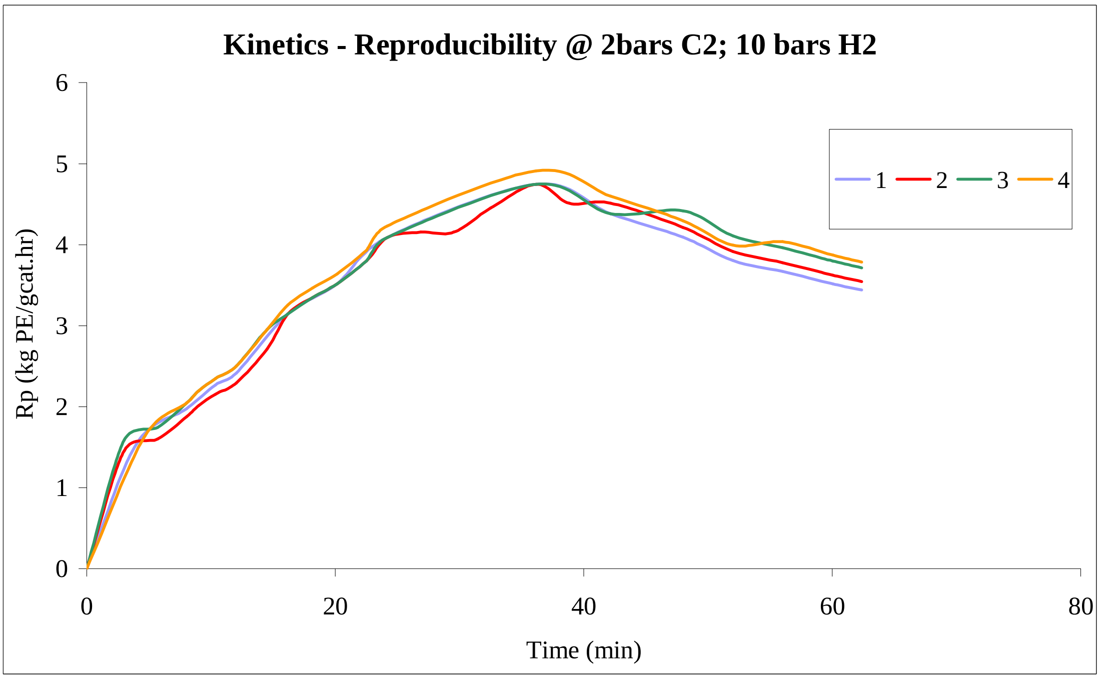

Figure 2: Kinetics reproducibility over 4 experiments at 2 bars C2 and 10 bars H2, 70℃

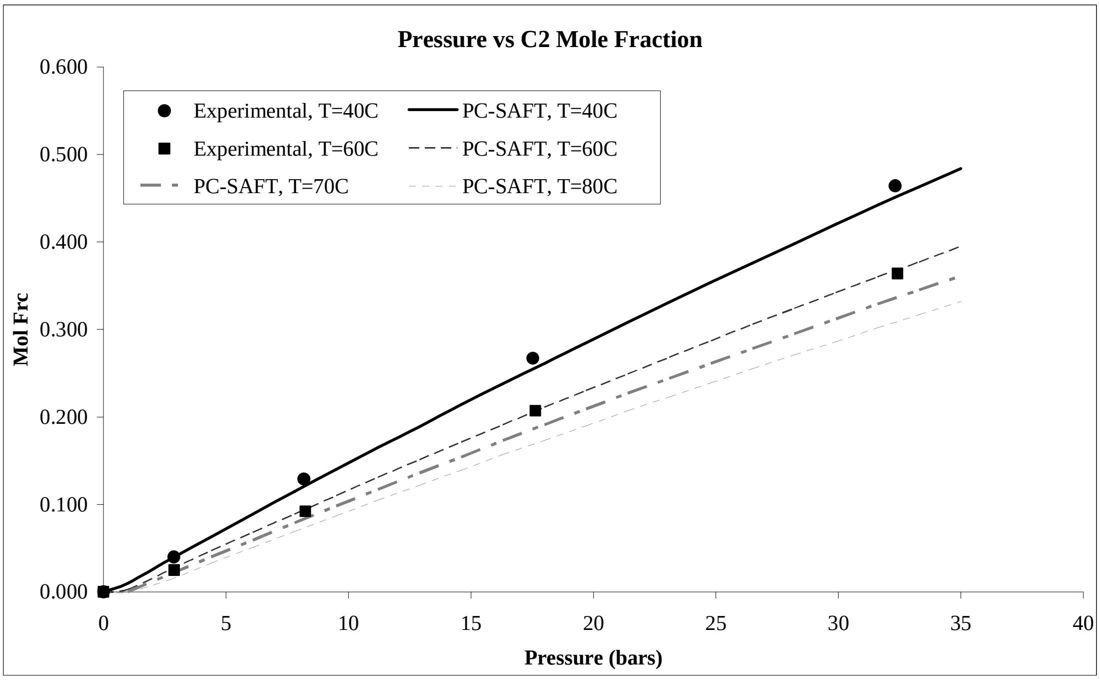

Figure 3: Experimental solubility of ethylene in n-hexane at 40°C (●) and 60°C (■) and modelled with PC-SAFT EOS with an interaction coefficient of 0.028.

The monomer bulk concentration in the slurry is given by its solubility in the solvent, i.e. the solubility of ethylene in n-hexane in this case. Experimental solubility of ethylene in n-hexane at 20°C, 40°C and 60°C [6] was modelled with PC-SAFT-EOS and extrapolated to 70°C and 80°C with an interaction parameter of 0.028[7] in all cases, as shown in *Figure 3*.

3.5 Product Characterisation methods

3.5.1 Particle size analysis

In this study, the Malvern Mastersizer 2000 was used to measure the particle size distribution (PSD) of the produced polymer samples. The system uses equivalent sphere approximation to accurately measure the PSD (with an accuracy of up to 10-15 µm from our observations).

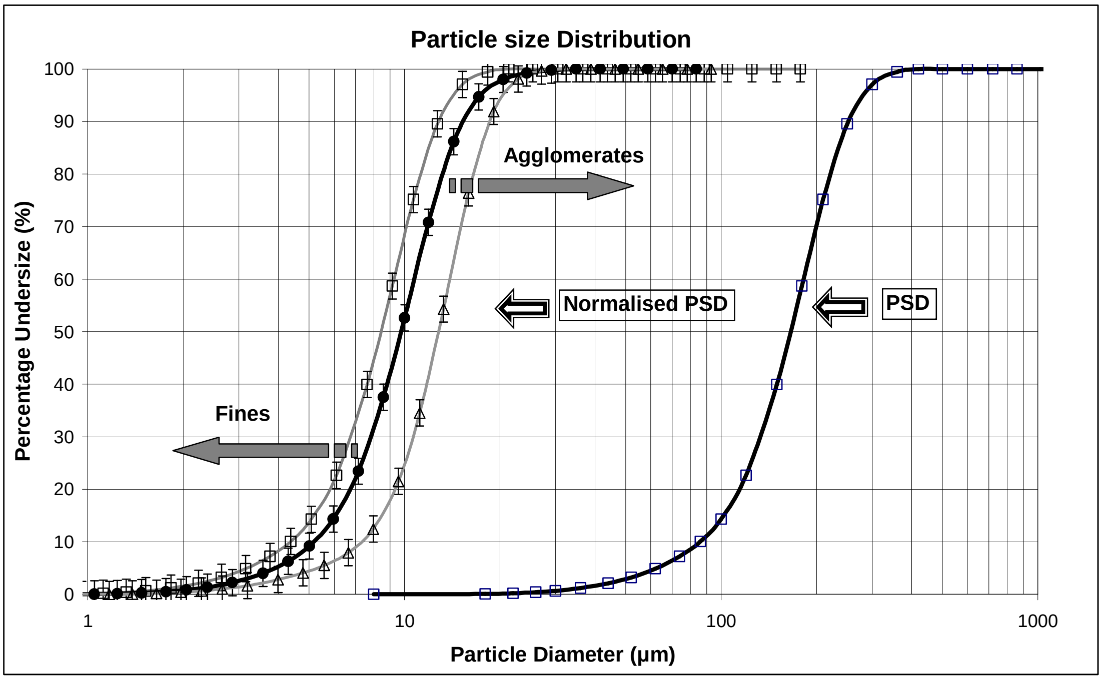

Figure 4: Normalising the particle size distribution with the yield

The particle size distribution depends a lot on the yield of polymerization (higher yield typically should produce bigger particle sizes, assuming there is no fines production). Hence, it is incorrect to compare PSDs across experiments with different polymer yields. The particle size (d_{pol}) across these experiments with varying yields can be compared by normalization using the following equation:

$$\frac{d_{pol}}{d_{cat}} = \sqrt[3]{\frac{\rho_{cat}(1-\varepsilon_{cat})}{\rho_{pol}(1-\varepsilon_{pol})}\left[\int_0^t R_p dt + 1\right]}$$

$$d_{cat} = \frac{d_{pol}}{b \cdot \sqrt[3]{[Y+1]}}$$

b = constant, assuming porosity and density of polymer is constant throughout polymerization

Figure 4, shows the percentage undersize against the normalised diameter. Trends tending to the left indicate fines production (lower particle sizes) and those tending to the right indicate bigger particles or agglomerates.

3.5.2 Differential Scanning Calorimetry (DSC)

The apparatus used here is a Pyris 1 from Perkin Elmer. About 5-6 mg of the polymer sample is weighed in the aluminium pan. The analysis is then carried out by running two ramped heating cycles with a cooling cycle sandwiched in between. The cycles are as illustrated below:

1. Heat from 30 to 160°C at 10°C/min and cool from 160 to 30°C at 10°C/min
2. Heat from 30 to 160°C at 10°C/min and cool from 160 to 30°C at 10°C/min

The first cycle simply serves to eliminate the crystallisation occurring during the polymerization and it is the second heating cycle that is typically considered. A third heating cycle may be repeated after the second cooling cycle, if necessary, to ratify the preciseness of the result. Typically, the 2nd and 3rd heating peaks are identical. The enthalpy (crystallinity is calculated from it) and polymer melt temperatures are thus taken from the values obtained in the second cycle. The polymer melt temperature is the temperature at which the heat flow is maximum, i.e. at a value where all the polymer chains have melted. As for the crystallinity, the DSC measures the change in enthalpy as the polymer melts. The crystallinity is then calculated as the enthalpy change of the sample divided by the enthalpy of pure polyethylene, as shown in equation (12).

$$Crytallinity(\%) = \frac{\Delta H_{sample}}{\Delta H_{PE(100\%)}} \cdot 100$$

The heat of crystallization of 100% crystalline polyethylene ($\Delta H_{PE\ (100\%)}$) is equal to 290 J/g (Borealis standard).

3.5.3 Gel Permeation Chromatography (GPC)

The sample (depending on the molecular mass but generally about 1 mg polymer / ml solvent) is dissolved in Tri-ChloroBenzene (TCB) and heated at 160°C for about 2h (or until complete dissolution). A small part of the sample is then passed through the GPC. The measurements in this study were carried out using a Waters 2000 GPC, and the treatment of data was done using the Millenium software package. Molecular weight distribution and averages were determined using the universal calibration curves obtained from narrow polystyrene standards. The sampling and measurements of molecular weight distributions are carried out using a carousel holding 24 samples. During the measurements, this carousel is kept at 160°C,. As each sample takes 90 minutes to analyse, the samples might stay up to 36 h in high temperature, thus provoking a certain risk of degradation of the polymer chains. A standard is in place in the first and last measuring position of the carousel and if no drift between these two points is observed the samples are considered correct. The used standard has a significantly higher sensitivity towards polymer chain decomposition than the polyethylene samples.

Notation

d_{pol} = diameter of polymer particle (μm)
ρ_{pol} = density of polymer (kg/m^3)
ε_{pol} = porosity of polymer
d_{cat} = normalised catalyst diameter (μm)
ρ_{cat} = density of catalyst (support) (kg/m^3)
ε_{cat} = porosity of catalyst
l = Litre
R_p = polymerization rate ($g_{polymer}$ /g-cat hr)
Y = yield of polymer ($g_{polymer}$/g-cat)

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Chapter 4: Fragmentation: Influence of Monomer Pressure

4.1 Introduction

As already pointed out in Chapter 2, fragmentation and polymerization rate influence each other. We describe this issue with some more results from public sources. The polymerization rate can be varied by monomer pressure, by temperature and by catalyst loading, for example. We selected the monomer pressure to study the influence of the polymerization rate on particle fragmentation and vice-versa in slurry ethylene polymerizations. The influence of monomer pressure on the kinetics of ethylene polymerizations (slurry and gas phase) has been widely researched and documented[1-7]. It is well known that with increasing monomer pressure the polymerization rate increases, showing a first order or broken order dependency regarding the bulk monomer concentration. It is a well accepted fact that the particle fragmentation can have a strong influence on the observed kinetics during the polymerization reaction[8-13].

Buls and Higgins[14-16] showed that fragmentation occurred during the early stages of propylene polymerization in slurry for their $TiCl_3$/ $AlEt_2Cl$ catalyst system. They observed that as the polymerization progressed, the catalyst fragments were gradually dispersed within the expanding polymeric matrix within the particle. The catalyst fragments coated with polymer were dragged outward from the centre of the particle, presumably with a velocity determined by the polymerization rate. This analysis was the earliest concept that linked the polymerization rate to particle fragmentation[1]. Prior to Buls and Higgins, Chanzy et al.[15,17,18] had studied the influence of monomer pressure on particle morphology in ethylene polymerization with a catalyst system based on VCl_3 / $AlEt_3$ on various substrates. They found that after a long polymerization time, worm like fibres of PE were obtained which when examined closely resembled a network of aligned fibres, more commonly termed as the “cobweb” morphology.

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[1] we introduced this concept as “convective polymer flow”, see chapter 2

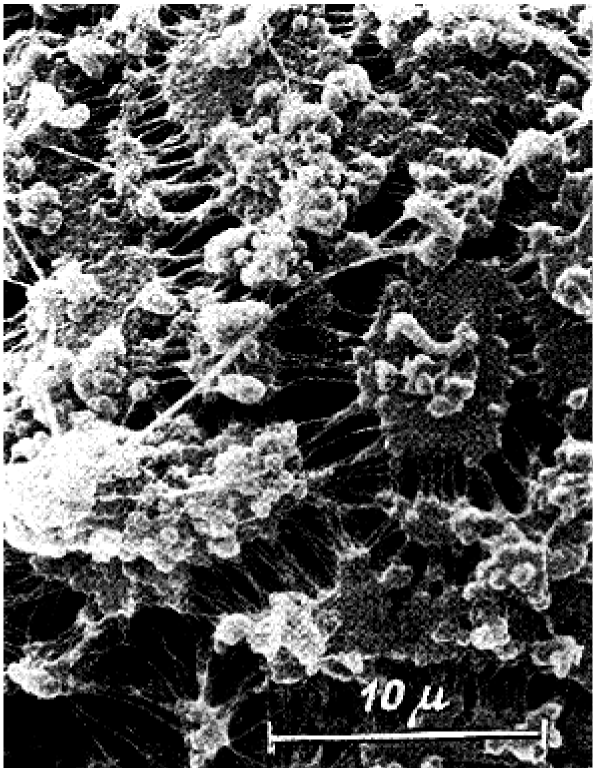

Figure 1: Cobweb structure of a nascent PE film as observed by Chanzy et al[18] (reproduced).

According to the authors, this structure was due to the polymerization process that induced a tangential stress that is distributed over the particle radius (the authors call the polymer layer at a certain radial position "membrane"), see *Figure 1*, due to expansion of the inner layers. To counterbalance this effect, the outer "membrane" developed biaxial stresses (radial and tangential) as polymerization progressed. As a result, the applied deformation generated some deep cracks in the "membranes" bridged by fibres that stemmed from the polymer matrix stretching (when the polymer was led beyond its elastic limit). This study is one of the first to mention the development of an internal stress during the polymerization process[2].

By varying the monomer pressure, we can control the internal stress and it becomes interesting how the growing particle responds in both polymerization rate and morphology. Modelling can strengthen our understanding of such processes, even if we take into account that modelling of such a complex process is always a simplification of the reality. Laurence and Chiovetta[13] were the first to treat the subject of fragmentation in detail with their multi-grain model based on the morphology of the particle. It was assumed that the particle fragmented when a certain arbitrary amount of polymer was deposited on the active sites at a given position, and that the rates of diffusion were different in the fragmented and unfragmented parts of the particle. While

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[2] we introduced this concept as "internal fragmentation", see chapter 2

interesting, this and later extensions of this and other concepts[19-24] remained very simple, and did not allow polymer properties or the rate of reaction to be directly related to particle morphology in a wide field of operation variables (temperature, pressure, concentrations, catalyst preparation). Simonazzi et al[25] proposed the use of stress balance models to describe particle fragmentation and growth. Such a model based on the build-up of stress within a growing polymer particle was actually developed by Kittilsen et al[10,26]. A simplified mathematical model related to the rate of reaction to the build-up of tension inside the particles linking chemistry, mass transfer, polymer properties and particle morphology. It was shown in this study that extremely rapid reactions could lead to a rapid increase in the stress inside the particle, sometimes to a point where the macro-particle will rupture than continue to grow homogeneously. Later, Grof et al[27,28] and Merquior et al[29,30] have also made an effort to study the same in their morphogenesis model and heterogeneous model for polyolefins, respectively.

In this work an effort has been made to study the influence of monomer pressure (and hence polymerization rate and the resulting growth stresses within the particle), on growth and fragmentation of the particle for slurry ethylene polymerizations using a highly active conventional Ziegler-Natta catalyst. It is well accepted that growth stress (varied by monomer pressure via the polymerization rate) and brittleness (varied by crystallinity via the molecular weight and matrix properties) determine the fines generation (measured by PSD) as part of the morphology, but nobody[3] studied experimentally and interpreted the interaction between

- Polymerization rate (Rp)
- Particle size distribution (PSD)
- Crystallinity
- Molecular weight (Mw)

4.2 Experimental

The experiments were performed in a 1.6*l* jacketed Buchi reactor[1]. The details of the experimental setup and the experimental protocol are as explained in Chapter 3. All experiments were performed at a constant temperature of 70°C. The catalyst (7mg) and co-catalyst amounts were also kept constant for all the experiments.

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[3] the same concept is used in the thesis of M. Daftaribesheli[31] in the same research group who focused on the comparison of slurry and gas phase PO processes in 2009 too

4.3 Results and Discussion

The molecular weight, crystallinity, yield of produced polymer and the maximum polymerization rate at different monomer pressures are as listed in Table 1. It can be clearly seen from Table 1 that with increasing monomer pressure, the molecular weight increases with nearly no influence on the crystallinity of the polymer. The poly-dispersity index (M_w / M_n) is also constant for all the experiments.

Figure 2 and *Figure 3* represent the kinetics of polymerisation at different monomer pressures and the normalised particle size distribution (as described in Chapter 3) of the final polymer respectively. In the absence of any influence of crystallinity, there are only two influences that play an important role – the skin formation and the internal stress (which is directly related to the polymerization rate) within the growing particle. It can be seen from *Figure 2* and *Table 1* that with increasing monomer pressure the maximum polymerization rate also increases. From the particle size distribution (*Figure 3*) we observe the following:

- At 2 and 5 bars monomer pressure we can observe disintegration of the particle leading to a shift in the PSD towards smaller particles. *Plausible reason: the outer skin does not keep the fragments together*.
- At 8 bars monomer pressure, we see the optimum conditions with no disintegration. *Plausible reason: We can clearly see that we have internal fragmentation in this case with the higher slope in the polymerization rate. However, the formation of a thick skin could hold these fragmented micro-grains together*.
- At 10 bars monomer pressure, we see clearly see particle disintegration with a shift to the left in the PSD. *Plausible reason: Internal stress is too high for the skin to withstand leading to particle disintegration*.
- At 20 bars monomer pressure, a complete disintegration of the particle is observed. *Plausible reason: Very strong internal stress leading to early disintegration of the particle, and as a result leading to more active sites available for polymerization. This can also be clearly observed from the steep slope of the polymerisation rate curve*.

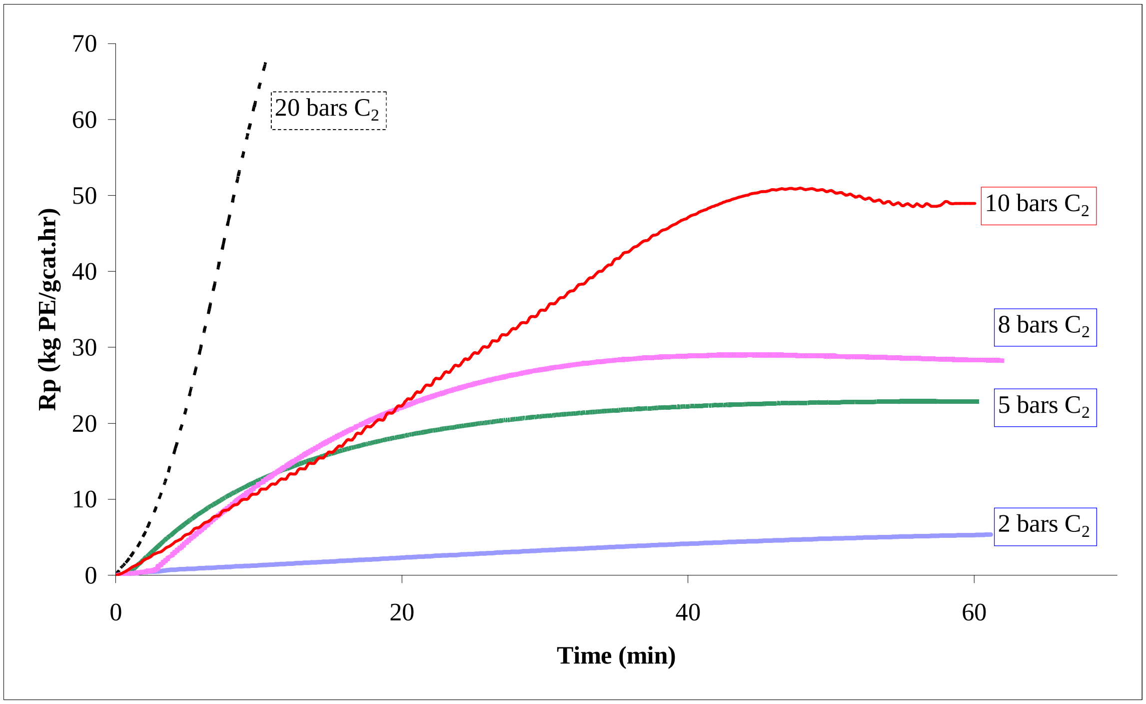

Figure 2: Influence of monomer partial pressure on the polymerization kinetics of ethylene slurry polymerization, at a temperature of 70°C.

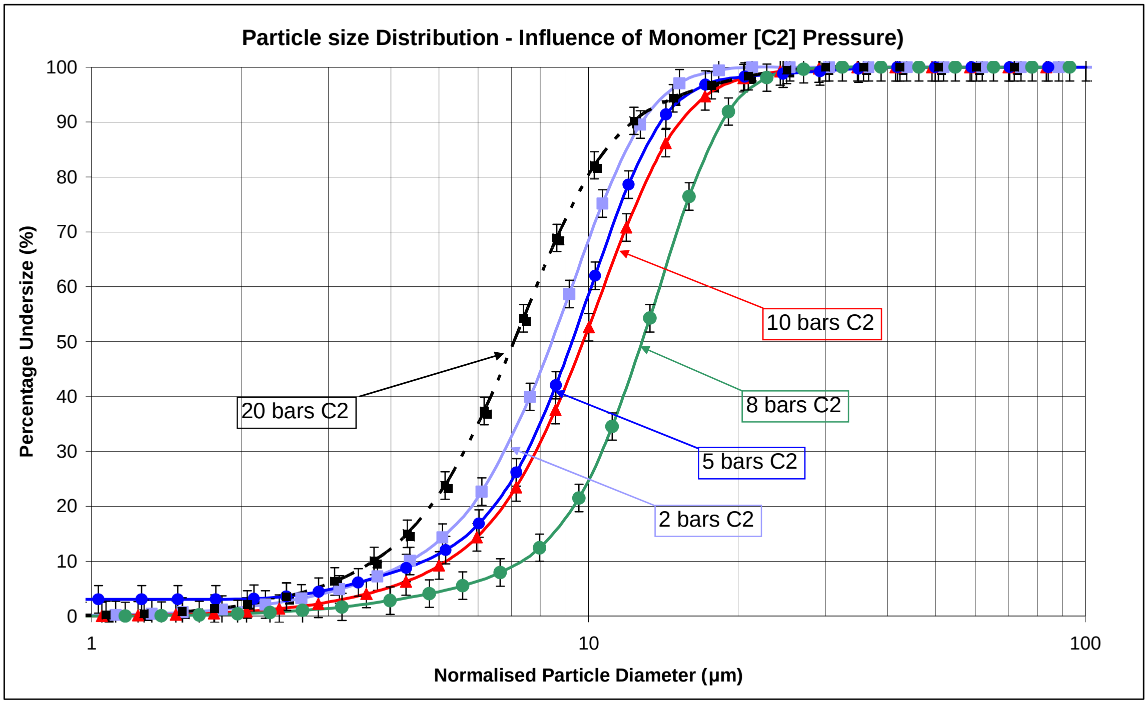

Figure 3:Influence of monomer partial pressure on the particle size distribution of ethylene slurry polymerization, at a temperature of 70°C.

P_{C2} (bars)	Rpmax (kg PE /gcat hr)	Yield (g PE / gcat)	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w / \overline{M}_n$	% Crystallinity
2	5	3309	601100	131000	4.5	47.6
5	23	18459	826200	202000	4.1	46.7
8	29	23154	973800	238700	4.1	46.3
10	51	32080	1223000	263900	4.6	45.9
20	*100*[*]	50000	1095000	227800	4.8	45.9

Table 1: Influence ethylene pressure on maximum polymerization rate, yield, MWD and crystallinity at 70°C.

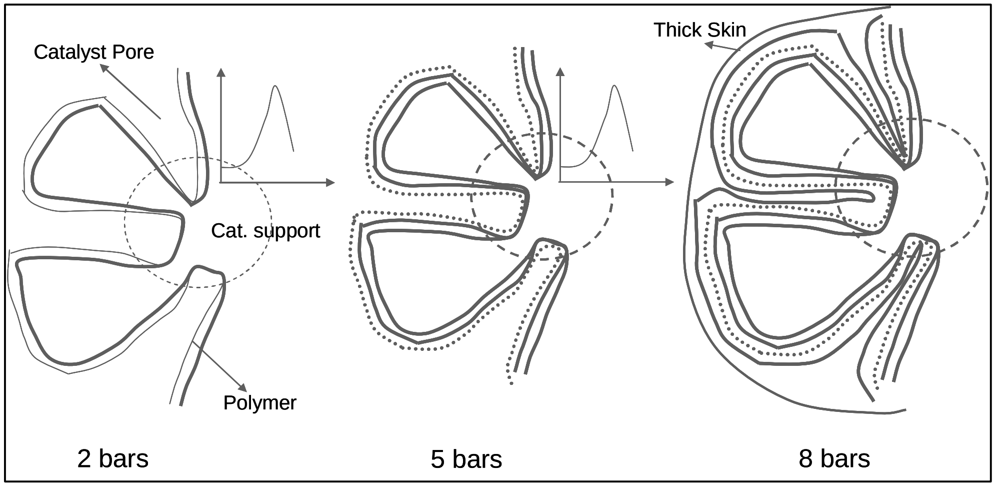

Figure A: Schematic showing the filling of polymer within the catalyst pores at different monomer pressures.

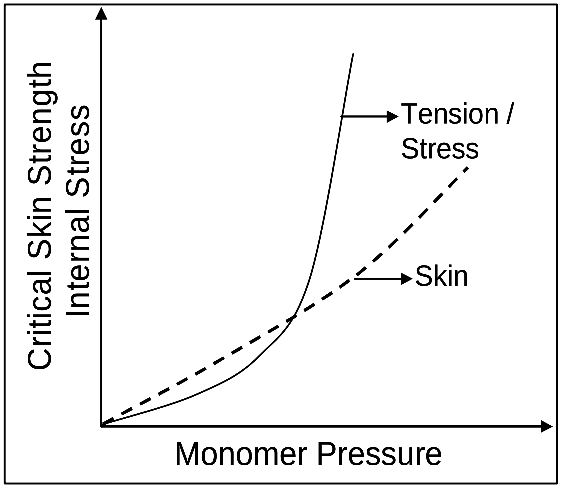

Figure B: Plot of critical skin strength and internal stress versus monomer pressure

How can all this happen ?

The most plausible explanation for the above observations could be related to the catalyst: the pore structure (which could be different on the outside and the inside of the catalyst particle, for instance consider a conical pore structure, see *Figure A*) and the activity of the catalyst (could also be different on the inside and the outside, depending on the catalyst preparation). Clearly, at low crystallinities (as is the case here), disintegration must occur mostly during the early stages on the polymerisation.

Consider the active sites on the surface of the catalyst particle and in the pores during the early stages of polymerization (*Figure A*). The active sites at the surface of the catalyst particle encounters the monomer first and polymerization starts leading to the formation of the outer skin. During this process, the monomer also diffuses into the pores of the catalyst where it encounters more active sites, and polymerizes leading to filling of the internal pores with the polymer. Since the inner pores are smaller than those on the exterior, the filling occurs faster leading to a higher internal stress. After a critical filling degree, this high internal stress would lead to internal fragmentation within the growing particle, and if the skin formed is not thick enough (which is the case at low monomer pressures, 2 bars and 5 bars), would lead to disintegration of the particle. If the skin is thick enough, it holds these internal fragments together and hence does not allow the particle to disintegrate (this is the case at 8 bars monomer pressure). It must be noted that in this case the internal fragmentation continues to occur as can be seen from the slope of polymerization rate profile.

At higher pressures, the internal stress generated within the growing particle is more than the elastic limit of the skin leading to its rupture and thus leading to disintegration of the particle. This is the case at 10 bars. At very high pressures (20 bars) the internal stress is extremely high, thus leading to complete disintegration of the particle during the early stages of polymerization. This complete disintegration of the particle leads to more active sites being exposed to monomer (higher surface area / volume) and thus contributing to the very high polymerization rates. The entire phenomenon is illustrated in a more simplified manner in *Figure B*, where the critical skin strength and the internal stress is plotted as a function of the monomer pressure. Skin stabilisation depends on the rate of skin growth and the internal stress generated. If the stress generated due to polymerization is higher than the rate of skin growth, it would destabilize the skin leading to its rupture and eventual disintegration of the particle. It must be noted that at a local position the skin properties are also distributed.

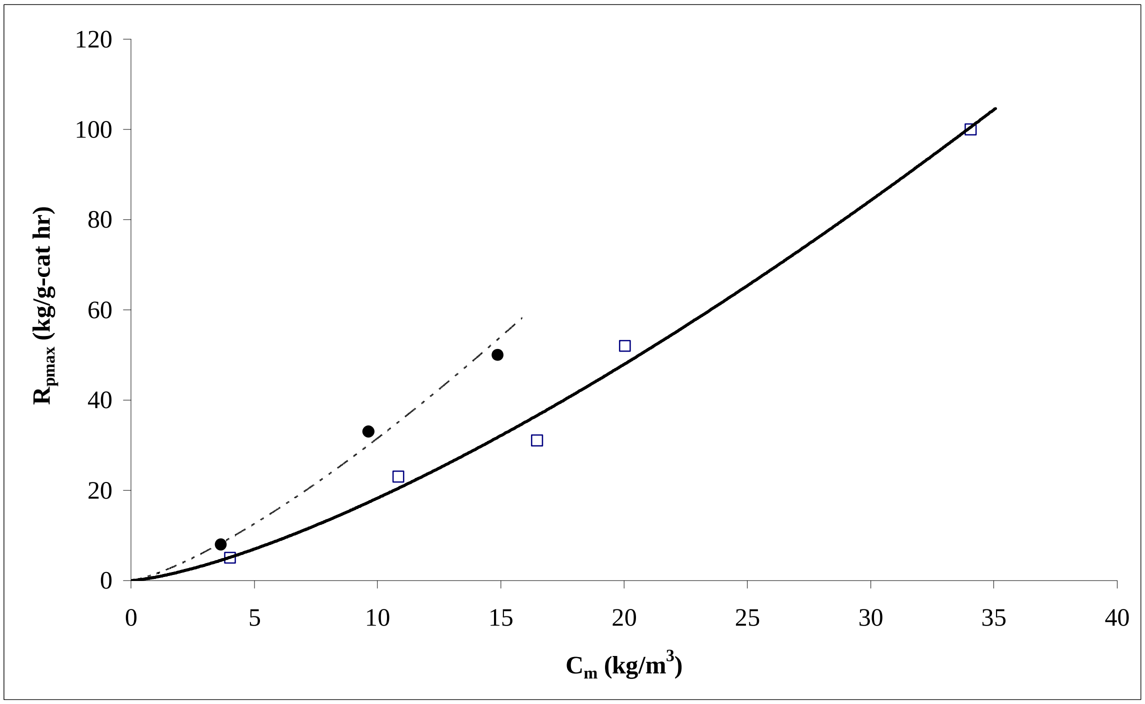

Figure 4: Maximum polymerization rate vs. ethylene partial pressure in slurry at (□) 70℃ and (●) 85°C.

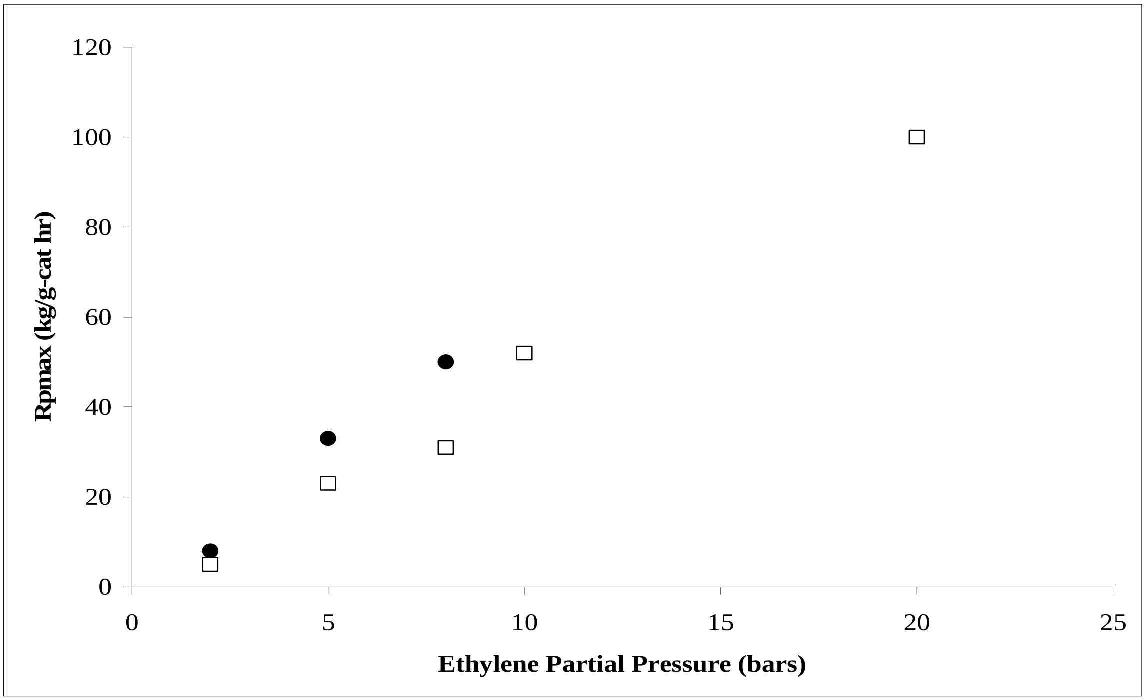

Figure 5: Order of polymerization reaction at (□) 70℃ and (●) 85°C was found to be ~1.3-1.4

Figure 4 and *Figure 5* show the influence of monomer pressure and the influence of the monomer bulk concentration, respectively, on the maximum polymerization rate. It can be clearly observed that after full fragmentation of the particles, the polymerization rate bears a linear dependence on the monomer pressure at both 70C and 85C, except at lower monomer pressure (2 bars). From the polymerization rate profile (*Figure 2*) it can be seen that the polymerization continues to increase at 2 bars ethylene pressure. This means that if this experiment was continued some more time, the polymerization rate would have reached a maximum. At this maximum, the fragmentation of the particle would also be complete. This higher Rpmax would then bear a linear dependency on the monomer pressure exhibiting a first order behaviour throughout. This could possibly explain the broken order dependency of polymerization rate on the monomer concentration that has been reported in literature[2-7,32-34].

4.4 Conclusion

The different factors that influence and contribute to particle disintegration with increasing monomer pressure are best illustrated in *Figure 6*.

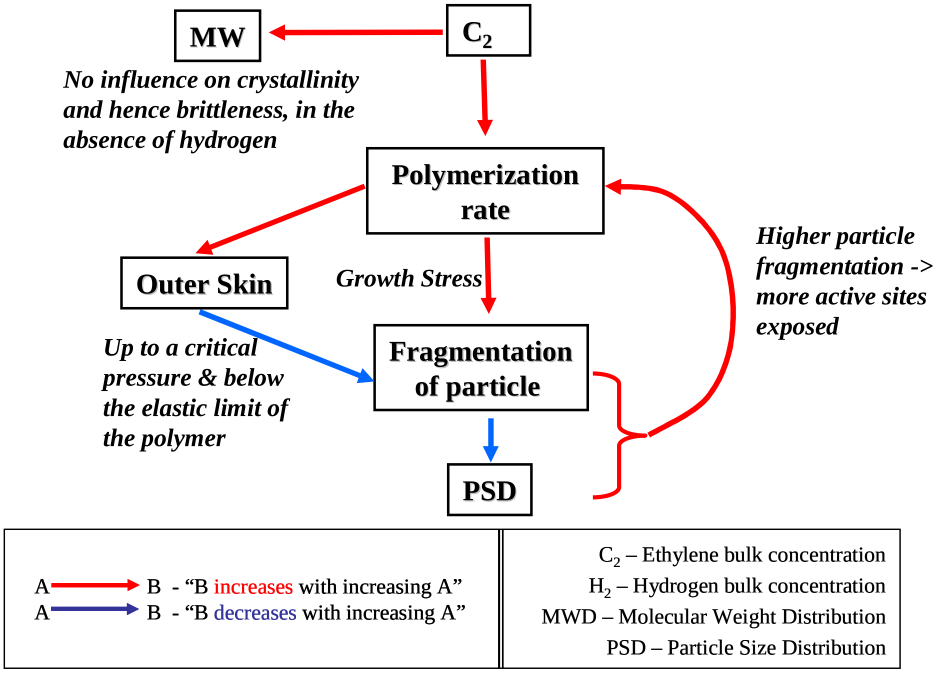

Figure 6: Schematic of factors influencing particle disintegration with changing monomer pressure.

The local pressure or growth stress, developing within a particle during the early stages of polymerization determines the extent of external fragmentation or particle disintegration. The growth stress and its distribution directly correlates with the polymerization rate – the higher the polymerization rate, the higher is the growth stress within the growing polymer particle. However, particle fragmentation is an extremely complex process and depends not only on the growth stress developed within the particle but also on other factors like the physical response (stress relaxation, porosity, elastic/rigidity modulus, etc.) of the catalyst support, the polymer and the thickness of the outer polymer skin.

8 bars ethylene partial pressure seems to be the critical limit for this catalyst system (under these conditions), where the polymer and the catalyst support along with the outer skin, are able to counter balance the internal growth stresses due to polymerization for this catalyst system. At higher monomer pressures (10 bars and 20 bars), the internal growth stresses exceeds the elastic limit of the polymer as well as the critical stress that the support can hold, leading to external fragmentation of the growing particle, thus resulting in smaller particles and fines generation . In addition, this external fragmentation further leads to more active sites being exposed to monomer (higher surface area / volume), reduced mass transfer resistance, leading to a higher reaction rate. This is more prominently exhibited at 20 bars monomer pressure.

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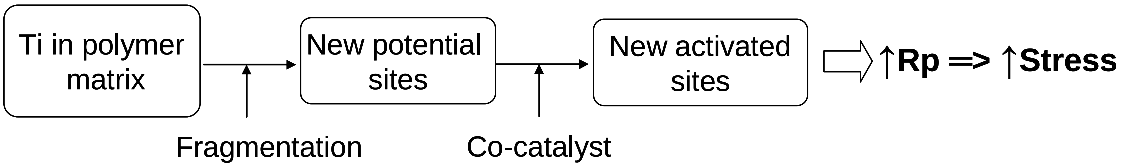
Chapter 5: Fragmentation: Influence of Co-catalyst

4.1 Introduction

The growth stress (which depends on the polymerisation rate) also depends on the *activation state* of the catalyst (active sites), *especially with highly active catalyst systems*. If the catalyst is pre-activated with co-catalyst, it would tend to display a faster activation profile than one, which is activated in-situ during polymerization. This initial faster activation, would lead to a higher growth stress in the first seconds of polymerization, and hence undesired particle fragmentation and eventual fines production. Active sites, which are generated by fragmentation (*Schematic A*), can contribute to the polymerization rate only after activation – this means: there must be cocatalyst present at the local position where new potential sites are generated by fragmentation. This activation process of new active sites is – of course – faster in case of external fragmentation, because – in case of internal fragmentation – the cocatalyst has to diffuse to the micro-crack inside the particle where the new sites are generated.



Schematic A: Generation of new active sites due to fragmentation

As with the monomer influence, the combined influence of the catalyst pre-contacting[1] and co-catalyst concentration on the polymerization rate, particle size distribution, crystallinity and molecular weight and their interaction has not been dealt with in detail previously.

We construct the following working hypothesis:

1. we assume the dependency of the polymerization rate as function of the co-catalyst concentration shown in *Figure 1*. This is an equilibrium curve – the influence of cocat

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[1] Nooijen et al.[1] studied the influence of co-catalyst diffusion and pre-contacting on the polymerization rate profiles for heterogeneous Zeigler-Natta catalysts. However, they did not report its influence on the particle size distribution of the final polymer.

mass transfer limitation (internal fragmentation!) and the kinetics of activation at relative low co-cat concentrations in the reactor are not taken into account.

2. we assume an equilibrium between potential active sites (i.e. “new sites”) and activated sites that can be described by

$$C + TEA \leftrightarrow C^{*} \qquad (1)$$

This explains the fact that much more TEA than 1 molecule per molecule Ti is required to reach the maximum polymerization rate (shown in *Figure 1*).

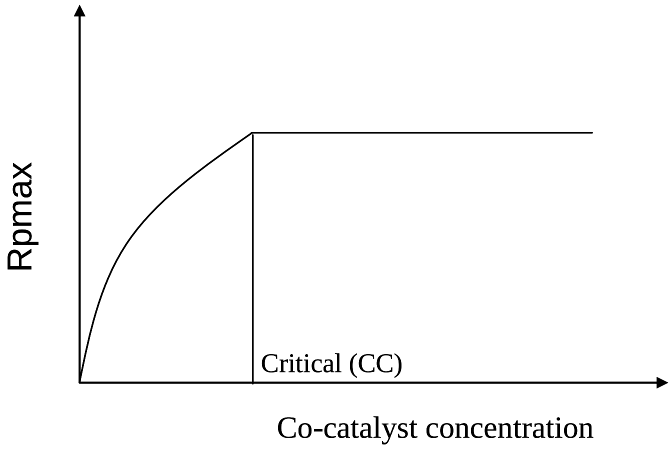

Figure 1: Influence of co-catalyst concentration on the polymerization rate

3. we assume that a pre-activated ZN catalyst “sees” a relatively high TEA concentration ([CC]) near the active sites at the beginning of the polymerization process. All potential active sites (that can be reached by the cocat) contribute to the Rp. Under pre-contacting conditions, the equilibrium is reached quickly.

4. as soon as the polymerization starts, pure polymer flows away from the active sites. This convective flow[2] depends linearly on the specific polymerization rate and moves all components – especially the excess co-catalyst - away from the active site. All components show a back-diffusion as demonstrated in *Figure 2*.

5. The co-catalyst is a relatively heavy molecule exhibiting a low diffusion coefficient through the polymer layer. This can lead to starved co-catalyst conditions near the active sites even if enough TEA is available at some distance from the active site – we will call it **“TEA transport effect”**.

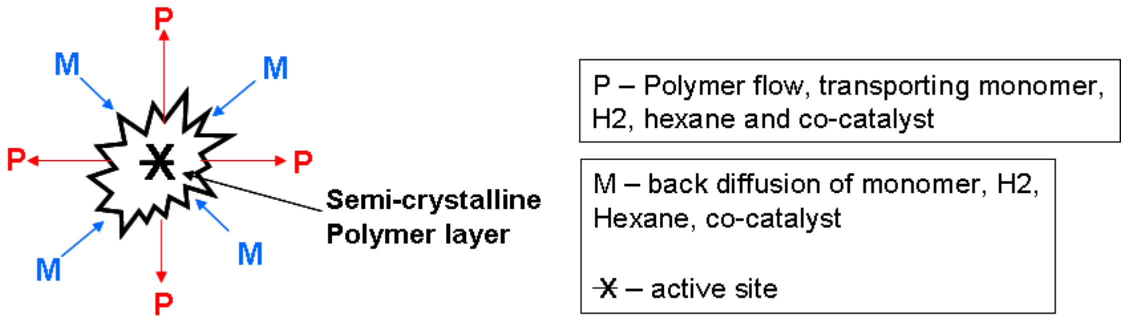

Figure 2: Convective polymer flow during polymerization leading to back diffusion of monomer, n-hexane and co-catalyst

6. Even if the back-diffusion rate of the cocatalyst is high enough, the freshly produced polymer leads to a **“TEA dilution effect”** if the cocatalyst is “solved” in the polymer phase.

7. The last two statements explain that [CC] can decrease below the critical concentration near the active site and the equilibrium activation reaction (*Equation 1*) can shift to the left resulting in lower polymerization rates

8. The back-diffusion is faster at low polymer phase viscosity, for example in hexane slurry – with hexane swollen polymer phase - much faster than in gas phase.

9. The back-diffusion of CC should depend strongly on the polymer layer formed around the active site.

4.2 Experimental

The experiments were performed in a 1.6*l* jacketed Buchi reactor[3]. The details of the experimental setup and the experimental protocol are as explained in Chapter 3.

For the experiments to study the influence of pre-activation of catalyst on the kinetics and particle fragmentation, the following conditions were used: 10 bars ethylene partial pressure, 4 bars hydrogen, 90 mg TEA as scavenger. The temperature was kept constant at 70°C. For the experiment with catalyst pre-activation, the catalyst (7mg) is activated by adding 60mg TEA into the same vial along with 2-3 ml of n-hexane. The pre-activation is done for a very short period of 3 minutes before injection of the mixture into the filled reactor using the liquid injection unit. In experiments without pre-activation, 150 (90+60) mg TEA or 270 (90+180) mg of TEA were added as scavenger & cocatalyst; the catalyst was injected without TEA in this case.

Following the working hypothesis presented above, one can expect the following:

- without pre-activation: the monomer diffuses faster to the active sites, faster than the TEA, but the polymerization can start only after arrival of both TEA and monomer[4]. The slow diffusion rate of TEA should lead to a skin growth by activation of the sites at the outer particle surface relatively long time before the potentially active sites in the centre of the particle can be activated.
- Therefore, there is – at the beginning – a skin growth without internal stress and fragmentation. This will lead to a reduced fines generation probability accompanied by much lower activation of the potential active sites inside the particle, because the polymer production front goes from outside to inside, and the TEA is forced to diffuse against the convective solid flow.
- In case of a limited deactivation, both experiments, with and without preactivation, should lead to similar maximum polymerization rates – if all potential active sites are activated. This maximum polymerization rate is expected at longer reaction times in case of experiments without preactivation.
- At very high TEA concentrations eventually combined with higher monomer pressure, one can expect that the outer layers of the polymer particle are destroyed by the tension generated within the reaction front while the core of the particle remain inactive.

4.3 Results and Discussion

Figure 3 and *Figure 4* represent the kinetics and the particle size distribution respectively for experiments with and without catalyst pre-contacting. The polymerization rate, experimental conditions, molecular weight & crystallinity of the obtained polymer are as listed in *Table 1*. From *Figure 3* it can be clearly observed that pre-contacting the catalyst with co-catalyst even for a very short time (~3 minutes) has a big influence on the kinetics of polymerization. The initial slow activation period of ~20 minutes seen in the standard reaction (without catalyst pre-contacting / pre-activation) is drastically reduced to ~ 5 minutes. This is clear and expected, as pre-activating the catalyst allows more active sites to participate in polymerization instantaneously thus leading to the observed high initial polymerization rates and subsequent reduction in the activation profile exhibited by the catalyst under normal experimental conditions (i.e. without catalyst pre-activation). The slower activation profile in the case of non-preactivation is definitely due to slower diffusion of the TEA to the centre of the macroparticle and in the presence of the convective polymer flow.

As expected the maximum polymerization rate (Rpmax) is the same in both experiments (with and without pre-contacting). From *Table 1* it can be also seen that the crystallinities of the two samples are the same – obviously the production rate does not influence the crystallinity of the in-situ formed polymer. This also supports the assumption of a low contribution to the dead polymer formation by cocatalyst transfer (the average cocatalyst concentration near the active sites is lower in case of the non-preactivated catalyst).

The high initial polymerization rate with catalyst pre-activation implies high initial growth stresses within the growing polymer particle during the early stages of polymerization. This high stress (at this crystallinity) during the early stages of polymerization leads to higher internal fragmentation within the particle. In addition, higher internal fragmentation would facilitate faster back diffusion of monomer / co-catalyst / n-hexane, leading to higher accessibility to the active sites. In the absence of a thick outer skin, which is especially the case during the early stages of polymerization, this combined influence leads to particle disintegration and hence fines generation. This can be clearly observed in *Figure 4*.

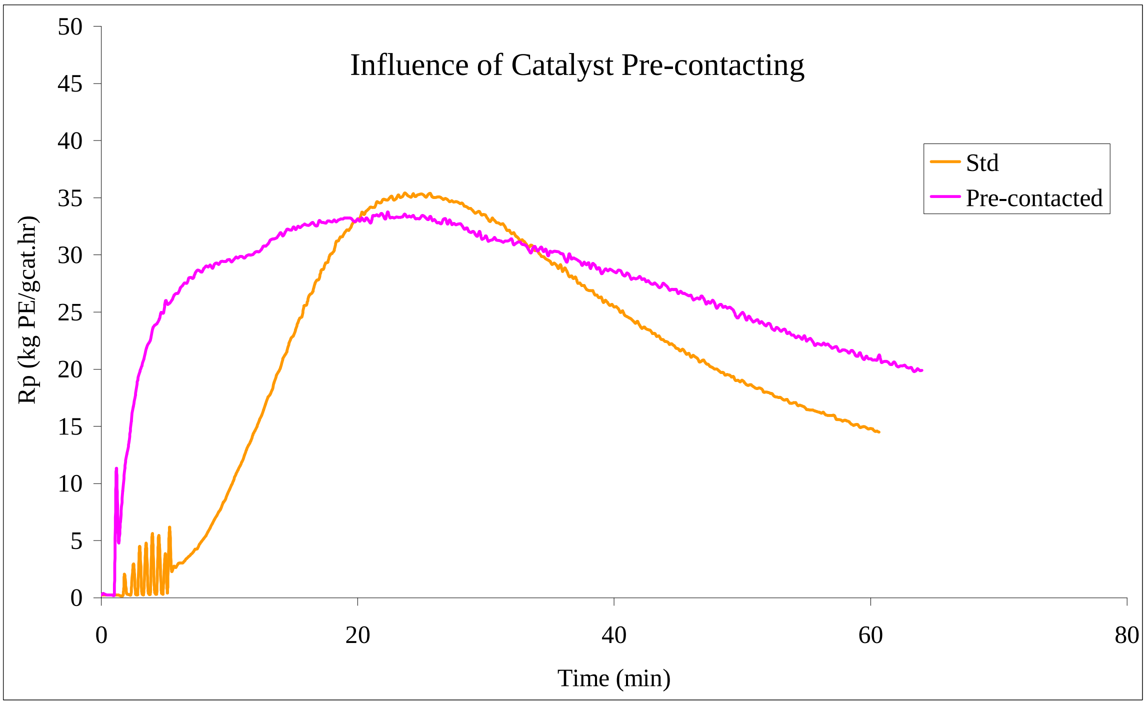

Figure 3: Influence of pre-contacting the catalyst (~ 3 minutes before injection) on the polymerization kinetics at 2 bars ethylene partial pressure.

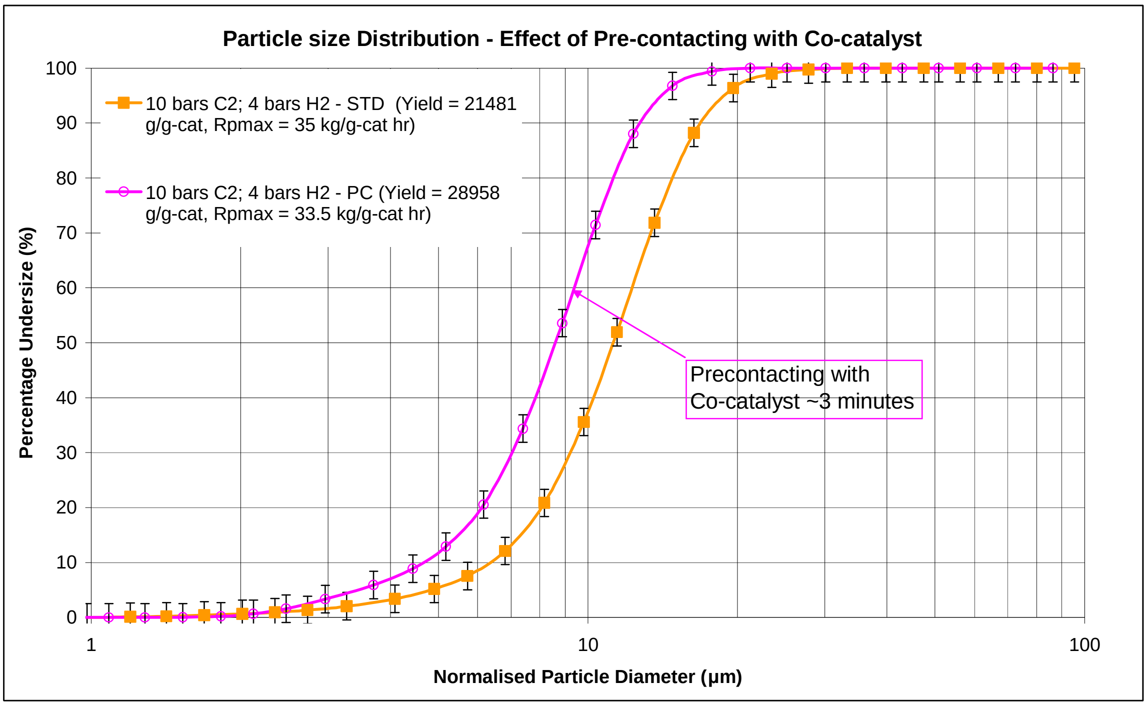

Figure 4: Influence of pre-contacting the catalyst (~ 3 minutes before injection) on the particle size distribution at 2 bars ethylene partial pressure.

P_{C2} (bar)	P_{H2} (bar)	Co-cat (mg)	Cat_{PA}[2]	Rpmax (kg PE /gcat hr)	Yield (g PE / gcat	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w / \overline{M}_n$	% Crystallinity	Tm °C
10	4	60	NO	35	21481	158600	16800	9.4	63.4	134.6
10	4	60	YES	34	28958	113,300	11600	9.7	64.1	134.3

Table 1: Influence of catalyst pre-activation on MWD and Crystallinity (using Cat1) at 10 bars ethylene and 4 bars hydrogen and temperature of 70°C.

P_{C2} (bar)	P_{H2} (bar)	Co-cat (mg)	Rpmax (kg PE /gcat hr)	Yield (g PE / gcat)	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w / \overline{M}_n$	% Crystallinity	Tm °C
10	4	60	35	21481	158600	16800	9.4	63.4	134.6
10	4	180	50	31938	134,100	13200	10.1	63.5	134.5

Table 2: Influence of co-catalyst concentration on MWD and Crystallinity (using Cat1) at 10 bars ethylene and 4 bars hydrogen and temperature of 70°C.

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[2] Cat_{PA} refers to pre-contacting the catalyst with the co-catalyst (TEA) for a short period of ~3 minutes prior to catalyst injection i.e. start of the experiment

The experiments with pre-contacting have shown a big shift towards the left i.e. towards fines / lesser particle size distributions as compared to that without catalyst pre-contacting / pre-activation. The high initial growth stresses during the early stages of polymerization have led to particle disintegration / external fragmentation leading to the production of fines.

In another experiment, it was intended to study the influence of the co-catalyst concentration (*without catalyst pre-contacting*) on the kinetics of polymerization (growth stress) and the particle size distribution of the polymer. The co-catalyst concentration was tripled keeping all other parameters constant. The kinetics and particle size distribution of the obtained powder are as listed in *Figure 5* and *Figure 6* respectively. The MWD and crystallinity of the polymer are as listed in *Table 2*. It must be noted that by changing the co-catalyst amount the Al/Ti ratio is altered. From *Figure 5*, a faster activation profile[3] and a higher polymerization rate (Rpmax) is observed with higher co-catalyst concentration.

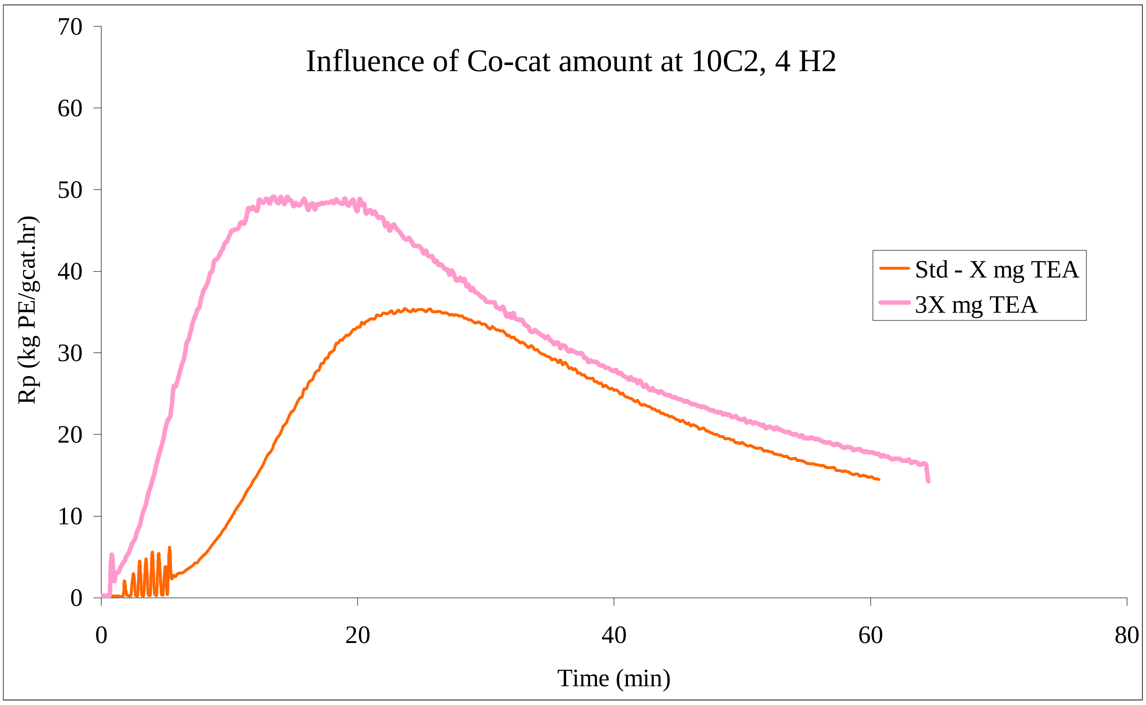

Figure 5: Influence of co-cat (TEA) amount (3X) on polymerization rate at 10 bars ethylene and 4 bars hydrogen.

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[3] Higher concentrations of TEA lead to faster activation of the catalyst / active sites but also lead to a faster deactivation.

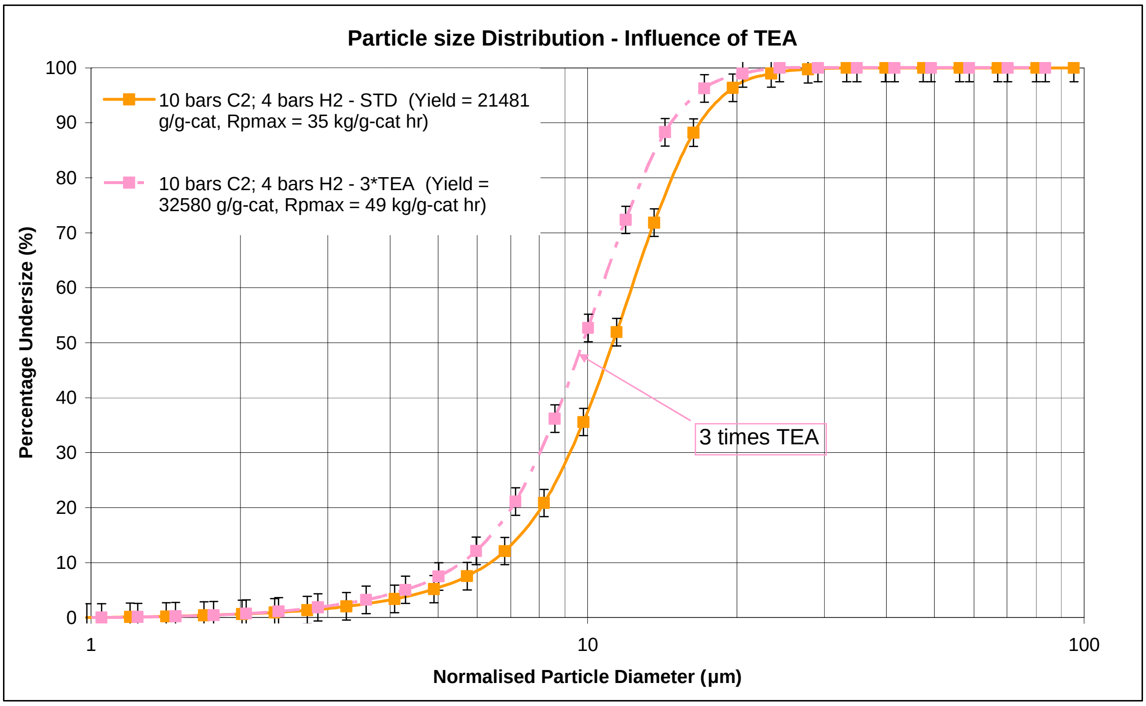

Figure 6: Influence of co-cat (TEA) amount (3X) on the particle size distribution at 10 bars ethylene and 4 bars hydrogen.

This is anticipated as a higher co-catalyst concentration would lead to activation of more potential sites thus leading to the observed faster activation profile as well as higher polymerization rate (*Figure 1*). Higher co-catalyst concentrations in the bulk (slurry) would imply higher co-catalyst concentration in the polymer matrix (due to sorption) and hence increase its availability to more active sites and consequently their activation, within the growing particle. This in turn contributes to the observed higher polymerization rate. The higher polymerization rates lead to the development of higher growth stresses within the growing polymer particle (at the same crystallinity –*Table 2*) during the early stages of polymerization, thus leading to external fragmentation / particle disintegration and production of fines. This can be clearly observed in *Figure 6* where the normalized particle size distribution shifts to fines (to the left) in the experiments with higher catalyst concentrations.

One must also keep in mind, that TEA is a bulky molecule and diffuses slower than the monomer. The slow TEA/ activation front (moving inwards to the core of the macroparticle) is counter balanced by the faster reaction (polymerization) front leading to production of greater amounts of polymer on the outermost shell of the catalyst / polymer particle. This would consequently lead to a stress buildup on the outer shell of the polymer. This high convective polymer flow could lead to lower concentrations of TEA in the core of the macroparticle thus starving the active sites there and consequently leading to a drop in the polymerization rate. This would mean that if an experiment is performed under very high

TEA concentrations, and high monomer pressures (20 bars partial pressure, for instance), one can expect that the outer layers of the polymer particle are destroyed by the high tension generated within the reaction front while the core of the particle remain inactive due to transport and slower back diffusion of the relatively bulky TEA molecule.

4.4 Conclusion

The local pressure or growth stress, developing within a particle during the early stages of polymerization determines the extent of external fragmentation or particle disintegration. The higher the increase in the polymerization rate, the higher is the local growth stress generated within the particle. If this internal stress exceeds the critical elastic limit that the particle can withstand, it leads to external fragmentation or particle disintegration

Pre-activation of the catalyst led to a higher initial polymerization rate and reduced the activation period drastically. This high polymerization rate, directly translates to very high growth stresses, and in the absence of a thick polymer skin during the early stages of polymerization, led to complete disintegration of the particle and consequently to the production of fines. It must be noted that the maximum polymerization rate in both preactivated and non-preactivated case was the same. The crystallinity of the two samples were also similar.

In the absence of catalyst pre-activation the build up of the stresses is slower due to slower reaction kinetics primarily due to slower diffusion of the TEA into the growing polymer particle. However, at high TEA concentration, there is a greater stress on the outer skin due to the counterbalance of the TEA/activation front and the expanding polymer / reaction front leading to a greater production of polymer in the outer shell of the macroparticle vis-à-vis the inner core, thus leading to rupture of the outer shell and hence fines generation.

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Chapter 6: Fragmentation: Influence of hydrogen

6.1. Introduction

Almost all the existing theories are focussed on the chemical influences of hydrogen on the kinetics of ethylene polymerization; i.e. slower re-initiation of active centers, following chain transfer to hydrogen [1-4], or as a consequence of reversible coordination reaction [5-7] or deactivation of active sites in the presence of hydrogen [8-11]. All these studies have reported decreasing polymerization rate in presence of hydrogen, however, a few studies have reported otherwise[12]. In all these studies, only a little information on the physical impact of parameters is discussed; e.g. influence of crystallinity on monomer diffusion [3]. The influence of hydrogen on the brittleness and the fragmentation combined with new active site generation has not been discussed – but this seems to be obvious from our theory presented in chapter 2. In this chapter and in the work of Daftari et al[13], it has been shown that one can observe both rate depression (due to the chemical effects), as well as acceleration of the polymerization rate[14] (due to physical effects like disintegration or external fragmentation of catalyst / polymer particle) with the introduction of hydrogen in ethylene polymerizations.

The main processes that determine the influence of hydrogen on the polymerization rate have been identified. They are,

1. **Chemical Effects**

   1.1 Slow first monomer incorporation

   The retarding effect of hydrogen has been well observed and reported in literature. The depressing effect of hydrogen has been found to be reversible[4,5,8].

   $$P^* + H_2 \xrightarrow{k1} C^*\text{–}H + P_n \qquad (1)$$

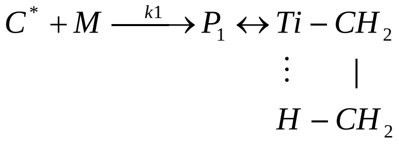
   $$C^* - H + M \xrightarrow{k2} P_1 \qquad (2)$$

   Equation 1 represents a chain transfer to hydrogen where P^* represents an active polymer chain, C^*-H represents the active site-hydrogen complex and P_n the dead chain. k_1 is the rate constants of the reaction. *Equation 2* describes the incorporation of the first monomer unit by the Ti-H, with a rate constant k_2. If the rate of (2) is smaller than the rate of (1) than we would observe an increase of the C^*-H concentration and consequently a decrease in the observed polymerization rate i.e. a retarding effect.

1.2 β-agostic deactivation

The Ti-C_2H_5 specie (P_1) that results

- after 1st insertion of one monomer unit into the Ti-H bond or
- after chain transfer to ethylene,



$$C^* + M \xrightarrow{k1} P_1 \leftrightarrow \begin{array}{l} Ti - CH_2 \\ \vdots \quad | \\ H - CH_2 \end{array} \qquad (3)$$

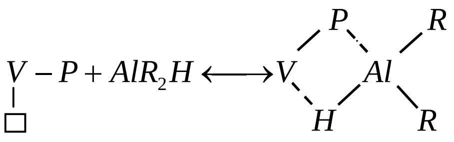
exists in equilibrium with a β-agostic structure shown above (*Equation 3*). This structure is assumed by Kissin to be dormant.

1.3 Retarding effect of the co-catalyst[9]

Reversible retardation of the polymerization rate has been observed with the introduction of hydrogen for Vanadium Magnesium chloride (VMC) catalyst.

$$V - P + H_2 \rightarrow V - H + polymer \qquad (P - polymer\ chain) \qquad (4)$$

$$V - H + AlR_3 \rightarrow V - R + AlR_2H \qquad (5)$$



(Cp) (Cp^d) (6)

According to this theory[9], catalyst deactivation is caused by dialkyl aluminumhydride that is formed due to a side reaction between the co-catalyst (tri-alkyl aluminium) with the V-H bonds and then being adsorbed onto the catalyst active sites. These species adsorb on active sites transforming them into the inactive “dormant” state, thus leading to a reversible reduction in the polymerization rate.

2. Physical Effects

2.1. Mass transfer limitation

At high crystallinities, some of the active sites especially in the region of crystallites, can be blocked by the crystalline phase, where monomer diffusion is very limited, leading to a mass transfer limitation and consequently to a reduction in the polymerization rate.

2.2. Our theory

The principles of our theory are given in chapter 2. With the focus on the hydrogen influence we can summarize as follows:

- The influence of hydrogen on the MWD and crystallinity is well known and stated in literature[1,15-18]. Higher concentrations of hydrogen in the system lead to shorter polymer chains
- shorter polymer chains crystallize faster due to their higher mobility (and form larger crystals?[13])
- low molecular weight polymers form a matrix with lower viscosity; the chains moving within such a matrix show a higher mobility. In slurry polymerizations, this matrix is partially swollen with the slurryfying agent, which increases the mobility of all molecules further leading to higher crystallization rates.
- High crystallinity implies higher brittleness, and in the presence of critical growth stresses, this leads to faster fragmentation
- Especially during the initial period, this fragmentation of particles leads to more active sites – with or without disintegration of particles – and consequently (after contact with cocat) to higher polymerization rates.

Disintegration depends on the ratio of skin formation rate and internal stress generation rate.

Note: We do not exclude the chemical effects described above, but we claim that these effects can be overlapped and sometimes over-compensated by physical effects as described by our ***GRAF-S*** *theory, some of which has been shown by Daftari's work*[13] *and will be also be shown in this work.*

6.2. Experimental

The experiments were performed in a 1.6*l* jacketed Buchi reactor [19]. The details of the experimental setup and the experimental protocol are as explained in Chapter 3.

All experiments were performed at a constant temperature of 70°C. The catalyst (7mg) and co-catalyst amounts were also kept constant for all the experiments.

6.3. *Results and Discussion*

Case 1: External particle disintegration

This case has been extensively discussed in PhD thesis of Majid Daftaribesheli[13]. A conventional Ziegler-Natta catalyst with a high sensitivity of hydrogen pressure was used in this study. It was observed that increasing hydrogen pressure (at constant monomer pressure, 2bars) leads to intensive particle fragmentation. The basis for this observation is the same as has been explained in Chapter 2 and earlier in this chapter in “Our Theory”. Increasing hydrogen concentration, leads to lower molecular weights due to chain transfer, thus resulting in the production of shorter chains, which crystallise faster. This high crystallinity, in the presence of a critical growth stress leads to disintegration of the particle, in the absence of a thick skin.

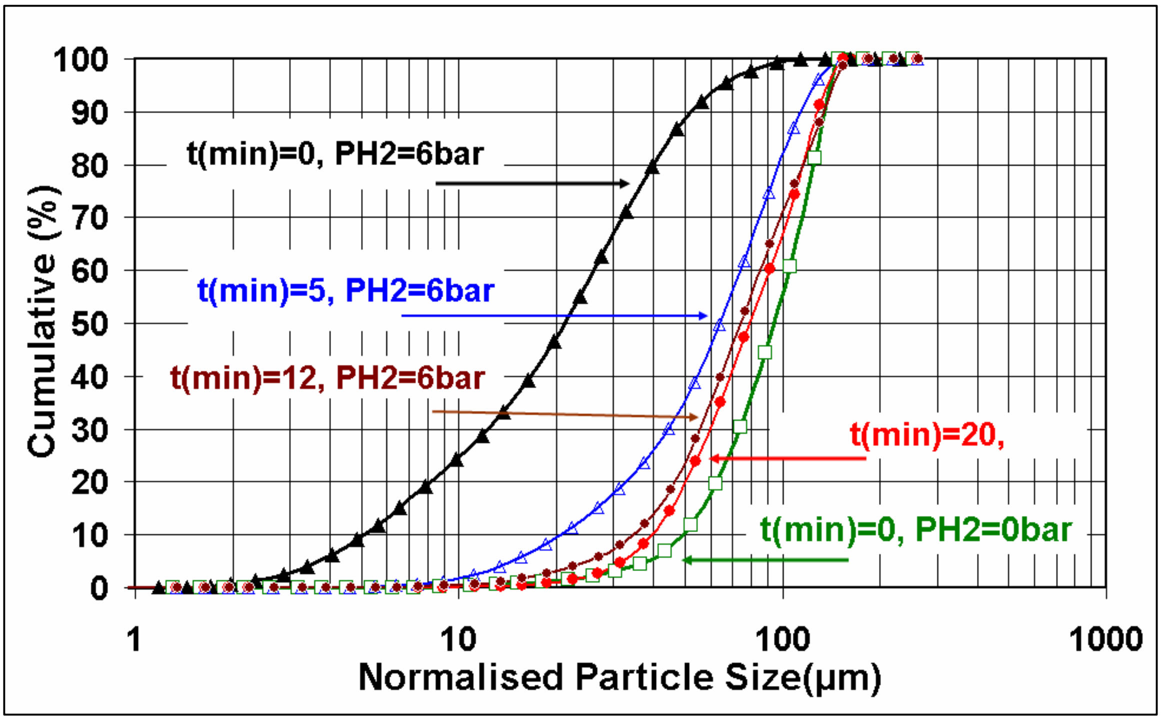


Figure 1: Time series experiments with Hydrogen (6bars): Influence on particle size distribution (using a ZN catalyst) at 2 bars ethylene pressure and temperature of 80°C[1]*.*

An interesting aspect of this study, were Daftari’s two stage experiments that were performed to investigate the influence of hydrogen during early stage polymerization (see *Figure 1*). It can be seen that particle fragmentation is the maximum when hydrogen is introduced right from the beginning of the experiment – producing lower molecular weight polymers (shorter chains which crystallise faster) with higher crystallinity, leading to disintegration of the particle in the presence of a critical growth stress. When the introduction of hydrogen is

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[1] PhD thesis of Majid Daftaribesheli, TNW, University of Twente

delayed even by a short time (5-20 minutes) a huge shift away from fines is observed in the particle size distribution. This is clearly due to the formation of amorphous, ductile PE during the early stages of polymerization, and the formation of a thick outer skin (with a lower crystallinity and hence brittleness) which prevents particle disintegration.

Case 2: Internal particle disintegration within the polymer skin

The outer polymer skin has a very important role to play during polymerization[20]. It must be noted that particle disintegration could occur internally within a particle, with the outer skin holding the fragmented grains up to a certain crystallinity

The polymerization kinetics and the corresponding particle size distributions at 2 bars ethylene partial pressure (70°C) and different hydrogen concentrations (0,2,10,18 bars) is as shown in *Figure 2* and *Figure 3*, respectively. The corresponding molecular weights and crystallinities of the obtained polymer are as listed in *Table 1*.

P_{H2} (bar)	$\overline{M_w}$	$\overline{M_n}$	$\overline{M_w}/\overline{M_n}$	% Crystallinity	Tm °C
0	601100	131100	4.6	47.1	134.7
2	83100	9470	8.8	70.7	131.0
10	41900	5030	8.3	76.7	129.0
18	22900	2310	9.9	86.3	128.2

Table 1: Influence of hydrogen on MWD and Crystallinity (using Cat1) at 2 bars ethylene pressure and temperature of 70°C.

From *Figure 2*, an increasing polymerization rate profile is clearly observed with the introduction of hydrogen. With increasing hydrogen partial pressure, along with a steeper activation in the rate profile, a deactivation profile is also observed. This increase in the activation slope is expected as increasing hydrogen concentration would lead to the production of lower molecular weights and hence more crystalline polymer (see *Table 1*). The crystalline polymer, by virtue of being more brittle would tend to fragment in the presence of a critical internal stress. This internal fragmentation and / or disintegration, would lead to the production of more active sites. In addition, it also leads to an increase in the micro-porosity of the particle, thus enabling a higher transport of monomer / hydrogen / solvent/ co-catalyst. Both these factors together contribute to the higher polymerization rate.

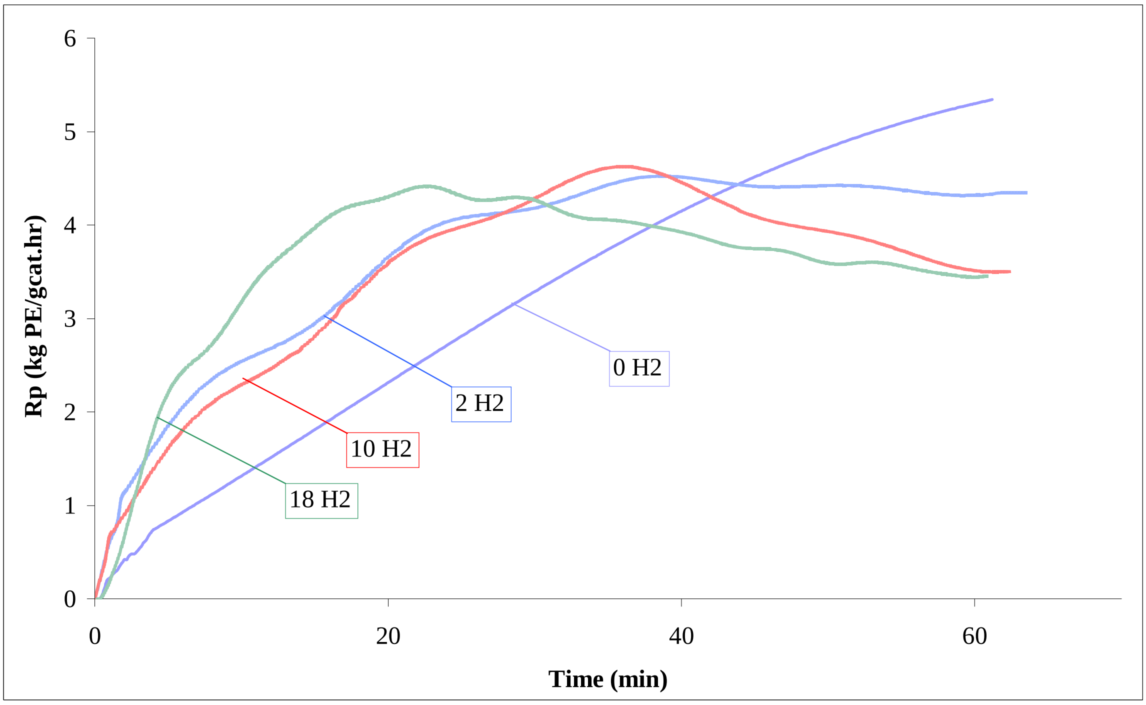

Figure 2: Influence of hydrogen on kinetics of ethylene polymerization at 2 bars ethylene pressure and temperature of 70°C.

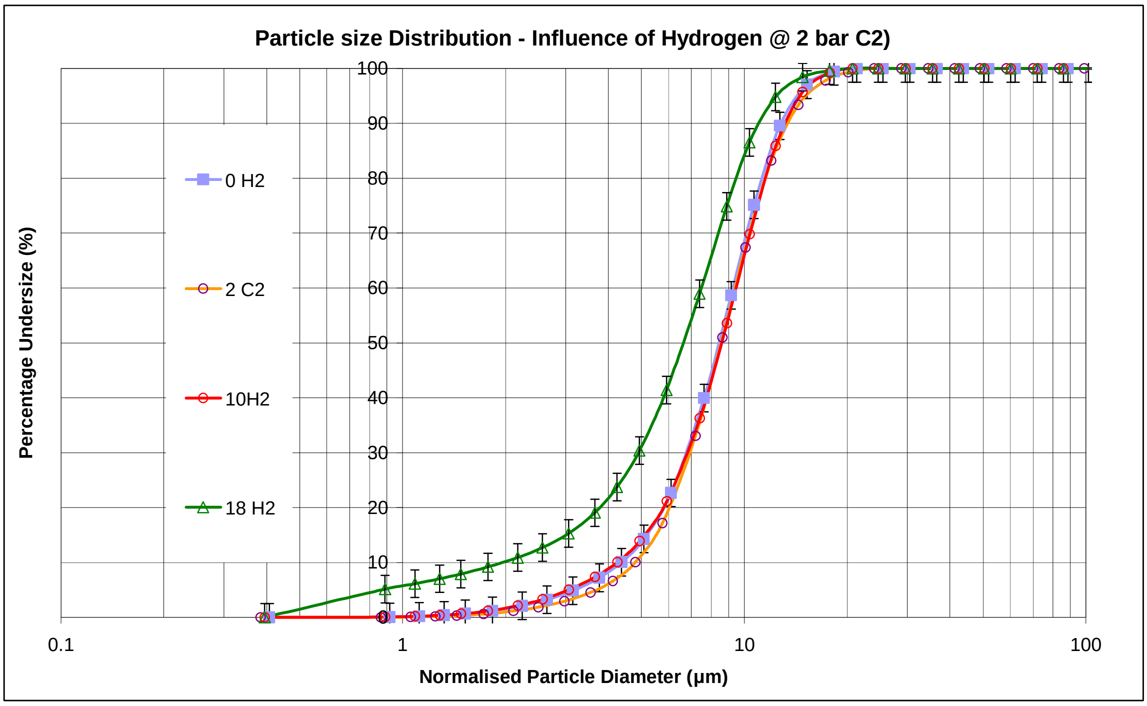

Figure 3: Influence of hydrogen on particle size distribution at 2 bars ethylene pressure and temperature of 70°C.

From *Figure 3* it can be seen that hydrogen shows no influence on the particle size distribution up to 10 bars. Particle disintegration is clearly observed only at high hydrogen pressure (18bars). This result at up to 10 bars hydrogen seems quite contrary to expectations. This slightly different behaviour at lower hydrogen pressures (≤10 bars) can be better explained if the we take into perspective, the influence of internal fragmentation (on the polymerization rate), the role of the outer particle skin holding the fragments together and the crystallinity of the produced polymer. The role of the outer polymer skin is extremely important in this case, as up to a certain critical crystallinity (up to 76%), the outer skin is thick and elastic (not brittle) enough to hold the internal fragments together thus preventing particle disintegration. Above this critical crystallinity (76%) the skin formed is too brittle to withstand the local growth stress even at low polymerization rates thus leading to disintegration of the particle and hence fines generation. This critical crystallinity was also observed in the investigations by Daftaribesheli[13]. Particle disintegration was extremely pronounced at crystallinities > 76%.

An interesting experiment was performed to verify internal fragmentation and the importance of the outer polymer skin. This has been dealt with in detail in the subsequent chapter (Chapter 7) that deals on the importance of pre-polymerization during ethylene polymerizations. It was observed that under the same conditions (2 bars ethylene, and 10 bars hydrogen), the removal of the outer polymer skin lead to complete disintegration of the particles, producing mostly fines. Clearly, a faster activation profile and a higher R_{pmax} was observed in this case. This clearly illustrates the importance of the outer polymer skin and also the presence of internal fragmentation during polymerization in the presence of hydrogen.

6.4. *Conclusion*

Hydrogen is a good chain transfer agent, and its introduction alters not only the chemistry but also the physics during polymerization. Production of shorter chains leads to the lowering of the local micro-viscosity, consequently facilitating higher chain mobility and faster crystallisation kinetics. High crystallinity implies higher brittleness, and in the presence of critical growth stresses, leads to increased particle disintegration. The overall increase in the number of active sites exposed per unit volume due to particle disintegration, results in higher monomer diffusion and availability around the active sites, consequently resulting in a higher polymerization rate.

An overview of all the related influences is best illustrated in *Figure 4*. It clearly shows how hydrogen (and of course hydrogen / monomer ratio) influences the properties of polymer matrix and consequently that of the final polymer particle. Increasing hydrogen concentration leads to production of a polymer with lower MW and microviscosity, thus facilitating higher chain mobility. The low MW implies higher crystallinity of the produced polymer, and hence a more brittle polymer, which in the presence of a critical stress and in the absence of a thick skin, would lead to particle disintegration.

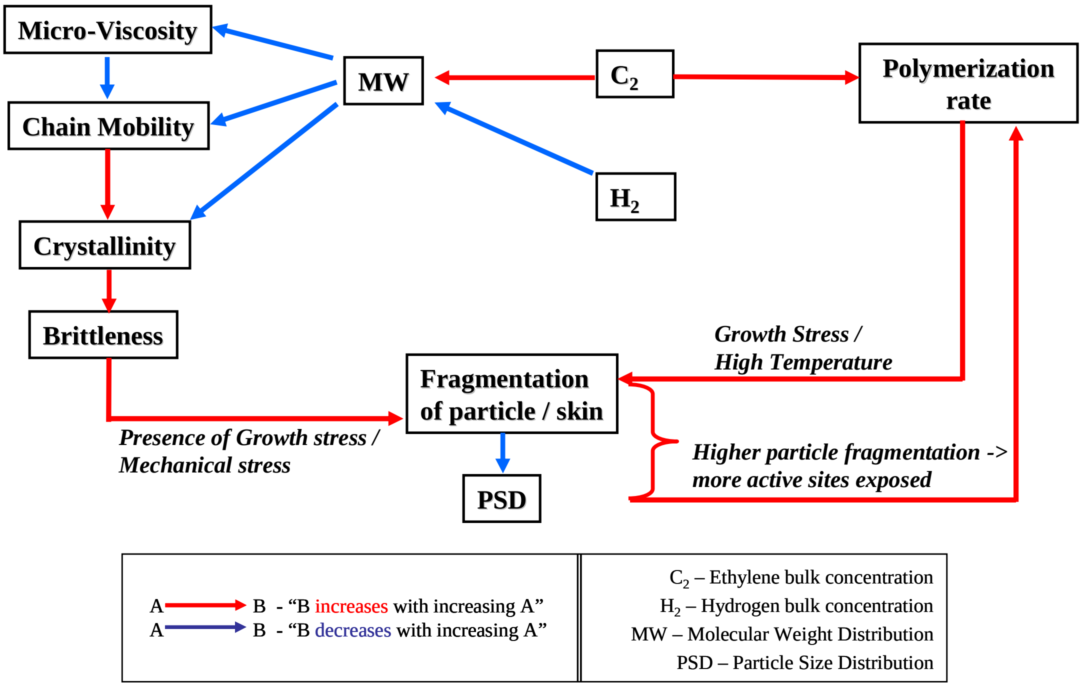

Figure 4: Overview of the factors that control and influence particle fragmentation in ethylene polymerizations

This study clearly illustrates that polymerization kinetics cannot be interpreted correctly without taking into account the influence of the physics of the system, **i.e. particle disintegration.** A higher polymerization rate is not always related to chemical complexation.

The importance of the particle skin and internal particle disintegration is clearly illustrated for this catalyst. It must be noted that particle disintegration could occur internally within a particle, with the outer skin holding the fragmented grains up to a certain crystallinity (< 76%). This internal disintegration (in the presence of an outer skin), would again lead to an increase in the number of active sites and an increase in the internal porosity of the growing polymer particle, higher monomer / hydrogen diffusion and consequently leading to an increase in the polymerization rate. The importance of the outer polymer skin and its influence on the kinetics of polymerization and particle size distribution is further discussed in the next chapter.

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Chapter 7: Influence of pre-polymerization: the counterbalance of fragmentation and agglomeration

7.1 Introduction

The influence of pre-polymerization (i.e. polymerization under “mild” conditions) using ethylene has been studied extensively by Daftaribesheli[1]. In this chapter we focus on the impact of a pre-polymerization with different co-monomers followed by main ethylene homopolymerization. The background is:

- alfa-olefins are more bulky and should show a different fragmentation behaviour
- we can expect a different crack formation after reaching a different critical stress
- correspondingly, we can expect a different skin formation process
- the solubility of poly-hexene (PH) in alkanes (hexane) is high. This will avoid the skin formation,

Chien et al[2] studied the influence of 1-hexene on the kinetics of ethylene polymerization using a Ziegler-Natta catalyst. They reported an increase of up to 70% in the polymerization rate with the addition of 15mol% 1-hexene. Chen et al[3] in their study found that propylene causes a rate enhancement (25%-30%) for a subsequent ethylene polymerization but that ethylene causes a rate reduction for a subsequent propylene polymerization. They further observed that the rate enhancement/reduction effect increased with the duration of the preceding polymerization. Chemical/kinetic effects (active sites and their modification; the activation of new or dormant sites by reactions involving comonomer; the displacement by comonomer of adsorbed or complexed molecules on the sites; and the inability of some types of sites to initiate or homo-polymerize a certain monomer) as well as physical effects (exposure of more active sites by improved catalyst breakup during copolymerization; the reduction of mass transfer resistance caused by the formation of more amorphous copolymer; and the enhanced solubility of monomers caused by amorphous copolymer formed or increased polymer swelling by the heavier comonomer) were attributed as the likely causes of both the rate enhancements and the rate reductions observed during sequential polymerization.

Karol et al[4] in their investigation using highly active titanium and vanadium based catalysts observed an increase in the polymerization rate in the presence of an α-olefin. The magnitude of the rate increase was found to depend on the specific alpha-olefin; propylene > 1-butene > 1-hexene. Soares et al[5] in their study observed that pre-polymerizing the catalyst with propylene increased the polymerization rate of ethylene as compared with the rate of ethylene polymerization without pre-polymerization. Kissin et al[6] later developed a kinetic model to explain the increase in polymerization rate observed in ethylene polymerizations. Kissin[7] also reported an increase in the reaction rates with α-olefin addition in ethylene polymerizations. They also reported a rate increase when ethylene polymerization was preceded by propylene polymerization. Contrary to most other results, Bialek et al[8] in their investigation using titanium and vanadium supported catalysts, reported a decrease in the polymerization rate with the introduction of α-olefins in ethylene polymerizations. Bergstra et al studied the influence of co-monomer (1-hexene) incorporation on the kinetics and product properties in gas phase ethylene polymerizations using a metallocene catalyst. They reported an increase in the reaction rate with increasing 1-hexene concentration and also developed a complexation model to explain the same. Pimplapure et al[9] studied and reported an increase in the polymerization rate in propylene polymerization and complete disintegration of the particle when pre-polymerization was performed using 1-hexene. Smit et al[10] investigated particle growth characteristics in ethylene/1-hexene co-polymerizations using a zirconocene catalyst on a silica support. They observed that the presence of 1-hexene led to higher productivity and easier fragmentation of the support during particle growth.

In this work an effort has been made to investigate the influence of low (≤10g polymer/g-cat) / very low yield (≤1g polymer/g-cat) 1-hexene and propylene pre-polymerizations, on the kinetics, particle size distribution and morphology during subsequent main ethylene homo-polymerization using a highly active conventional Ziegler-Natta catalyst supported on $MgCl_2$.

7.2 Experimental

The experiments were performed in a 1.6*l* jacketed Buchi reactor[11]. The details of the experimental setup and the experimental protocol are as explained in Chapter 3. The co-catalyst concentration in the n-hexane slurry was kept constant in both the pre-polymerization and the main polymerization steps. Two different pre-polymerizations were attempted: one with 1-hexene and the other with propylene.

Pre-polymerization with 1-Hexene

About 7mg of catalyst was taken in a glass vial with 3 ml of n-hexane (with TEA, same concentration as in the slurry for main polymerization). To this the required amount of 1-hexene is added (using a weighed syringe) based on the targeted yield. In this study we tried 1g PH[1]/g-cat and 10g PH/g-cat with a pre-polymerization time of 5 minutes (1-hexene is extremely reactive and forms PH almost instantaneously at room temperatures[9]) before injection of the pre-polymer into the reactor. The entire pre-polymerization was carried out at room temperature. The pre-pol time is always 5 minutes unless otherwise mentioned (see also *Table 1*).

Pre-polymerization with Propylene

A similar procedure as explained above for 1-Hexene was followed for propylene pre-polymerization. The pre-polymerization was done for varying prepol yields from 0.15g PP[2]/g-cat to 10g PP/g-cat before injecting it into the reactor. The pre-polymerization was carried out at room temperature in a glass vial.

Main polymerization

One set of standard experiments were performed at a constant ethylene partial pressure of 5 bars and a temperature of 70°C. The co-catalyst (Triethyl Aluminium) concentration is the same in all experiments (60 mg). As in all our experiments, 90 mg TEA was used for scavenging the reactor.

Another set of 1-hexene pre-polymerizations was performed prior to main polymerizations at 2 bars ethylene partial pressure. Hydrogen (10 bars partial pressure) was also used in a couple of experiments during main polymerization. All other parameters were the same as in the previous set of experiments.

All properties (particle size distribution, crystallinity and molecular weight) of the final polymer were measured as explained in Chapter 3.

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[1] PH refers to Polyhexene
[2] PP refers to Polypropylene

Following the experimental plan presented above, one expects to observe the following:

- With 1-hexene prepolymerization should lead to complete disintegration of the particle, thus leading to the production of mostly fines.
- At higher polyhexene yields, not all the polyhexene is dissolved by n-hexane. The left over polyhexene, due to its sticky nature, could lead to agglomerate formation.
- Presence of hydrogen in the main polymerization, should lead to increased disintegration of the particle and higher crystallinity.
- Limited disintegration of particles with propylene pre-polymerizations due to the presence of a thick outer skin.

7.3 Results and Discussion

The influence of low yield pre-polymerization using different co-monomers (1-hexene and propylene) on the subsequent main (ethylene) polymerization has been discussed in this section. The importance of the outer polymer skin has been illustrated using 1-hexene. This discussion has been structured into 4 parts:

- *Case 1:1-Hexene pre-polymerization with different yields*: Low (10g PH / g-cat) and Very Low (1g PH / g-cat) yield pre-polymerizations.
- *Case 2: Low yield 1-hexene pre-polymerization with different prepol times*
- *Case 3: Very low yield 1-Hexene pre-polymerization followed by main polymerization in the presence and absence of hydrogen*
- *Case 4: Propylene pre-polymerization*

7.3.1 Case 1: 1-Hexene pre-polymerization with different yields – Importance of the polymer skin.

Hexene pre-polymerization was performed as discussed in the experimental section with varying pre-polymer yields: 1g PH / g-cat and 10 g PH / g-cat. The two are referred to in this section as Very low Yield pre-polymerization and Low Yield Pre-polymerization. The pre-polymerization time was kept constant at 5 minutes for all experiments in this case study. The pre-polymerization was followed by main polymerization at 5 bars ethylene partial pressure and a temperature of 70°C.

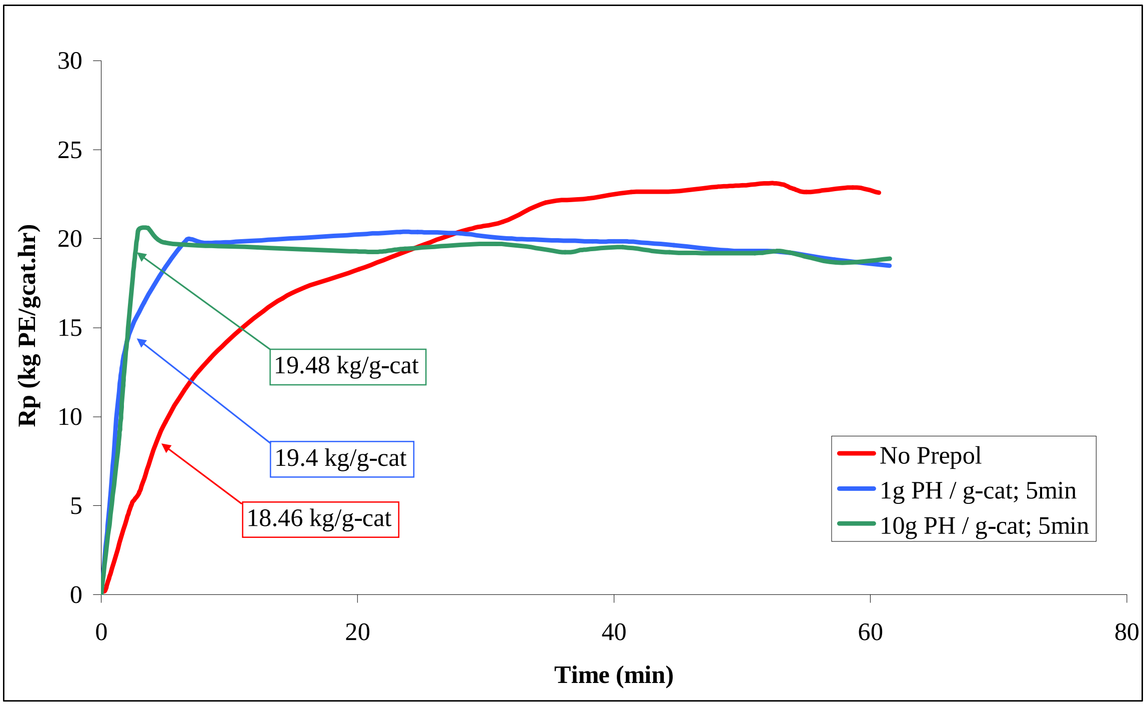

Figure 1: Comparison of Kinetics for Low (10gPH/g-cat) and Very Low Yield (1gPH/g-cat) 1-Hexene pre-polymerization followed by 5 bars C2 main Polymerization at 70°C; the numbers stand for the final yield

The influence of pre-polymerization on the kinetics and the particle size distribution (PSD) are as shown in *Figure 1* and *Figure 2* respectively. The influence on the polymer end properties i.e. molecular weight distribution (MWD) and crystallinity are as listed in *Table 1*.

Ppol (g PH/g-cat)	Ppol Time (min)	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w / \overline{M}_n$	% Crystallinity	Tm °C
0	0	826200	202000	4.1	46.7	135.0
1	5	939000	189000	5.0	57.7	134.8
10	5	902000	184000	4.9	56.7	134.5
10	90	909000	133000	6.8	56.7	134.9

Table 1: Influence of 1-hexene pre-polymerization on MWD and Crystallinity at 5 bars ethylene pressure and temperature of 70°C.

It can be observed from *Figure 1* that there is a slow induction / activation period in single step (without pre-pol step) polymerization at 5 bars ethylene pressure. In the experiments with the pre-polymerization step, this activation period is completely absent and the reaction starts with a high polymerization rate (R_p). This implies, during the early stages of polymerization we have an extremely high growth stress. From *Figure 2* it can be observed that the PSD shifts to the left with the pre-polymerization yield and we produce predominantly fines. A similar observation was reported by Pimplapure et al[12] for propylene polymerizations. They observed a rate increase and reported complete fragmentation of the catalyst with extremely small average particle sizes of the final polymer, when the pre-polymerization was performed with 1-hexene.

The increase in the polymerization rate as well as the reduction in the PSD can be explained if we understand the pre-polymerization step and the properties of the pre-polymer (Poly-Hexene). The polymerization of 1-hexene to polyhexene is an extremely fast and instantaneous reaction even at room temperatures. Polyhexene is a sticky polymer; however, it is also highly soluble in n-hexane. As a result of the same, there is no outer polymer skin holding the catalyst sub-grains (micro-grains) together leading to complete disintegration of the catalyst. When the pre-polymerization is followed by subsequent main polymerization (at 5 bars ethylene pressure), the higher fragmentation (higher surface area / unit volume, implying more active sites are exposed to the monomer) and pre-activation of the catalyst leads to the observed high initial reaction rate. In addition the solubility of ethylene in polyhexene is also higher. It must also be noted that viscous nature of polyhexene implies slower or limited diffusion of polyhexene (formed during the pre-polymerization step) from the core of the macroparticle to the outside (see *Figure 4*). This is especially the case with the bigger particles leading to very different stress profiles within the particle; in the shell (low stress) and the core (high stress).

All these factors along with the high polymerization rate together contribute to higher buildup of growth stresses within the particle, and in the absence of an outer skin (since PH dissolves in n-hexane), leads to complete disintegration of the particle and hence to the production of pre-dominantly fines. This can be clearly seen in the PSD (*Figure 2*) even at very low yield polymerizations (1g PH/g-cat). At higher pre-polymerization yields (10g PH/g-cat), these fines, could stick together in the presence of a sticky interface of polyhexene leading to the formation of agglomerates (see *Figure 4*). This clearly explains the different slope and shift to agglomerates in the upper half of the PSD curve at higher prepolymerization yields (see *Figure 2*).

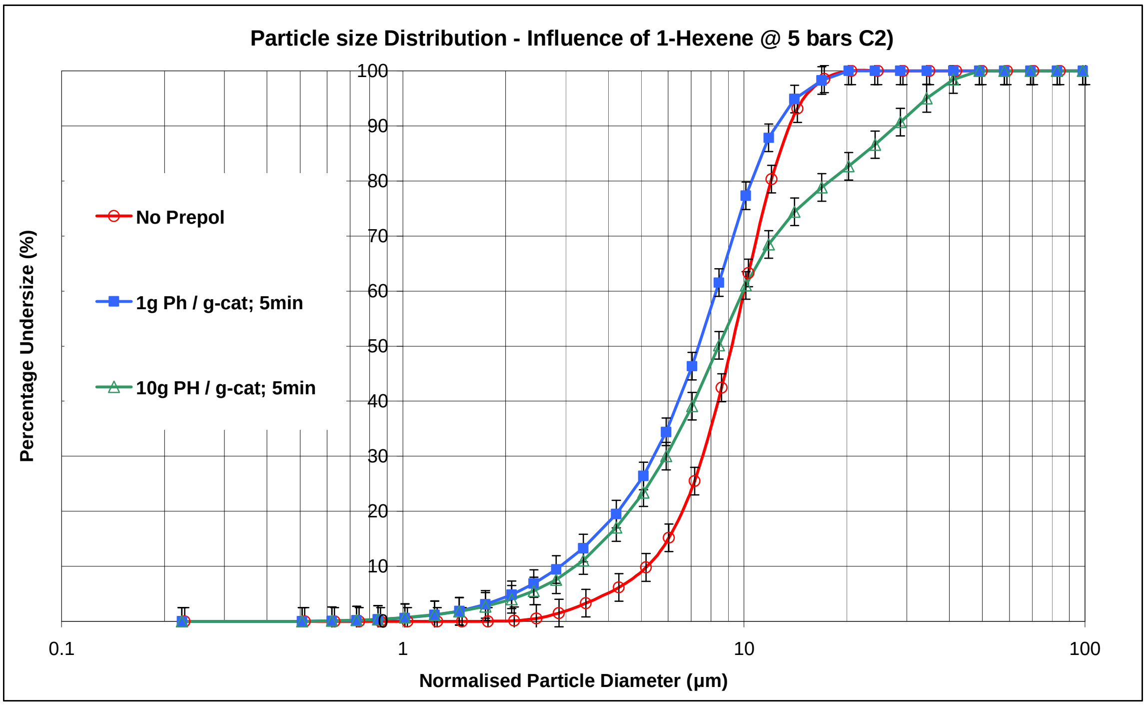

Figure 2: Comparison of PSD for Low and Very Low Yield 1-Hexene pre-polymerization followed by 5 bars C2 main Polymerization at 70°C

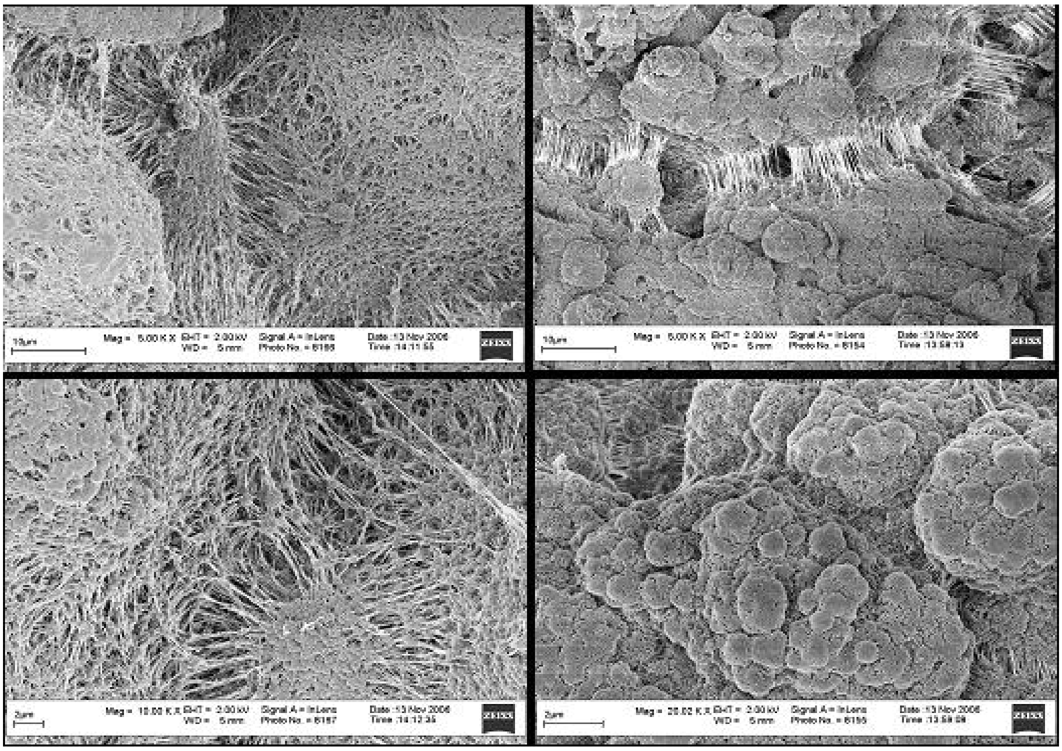

Figure 3: SEM images (10µm, 2µm) of polymer with (right) and without (left) pre-polymerization (with 1-hexene, 10gPH/g-cat)

Figure 3 shows the scanning electron microscope (SEM) images of the final polymer morphology (after main polymerization at 5 bars ethylene pressure) with and without 1-hexene pre-polymerization. The fragmentation of the catalyst with 1-hexene pre-polymerization is clearly visible at both 10µm and 2µm. *Table 1* presents the MWD and the crystallinity of the final polymer with and without pre-polymerization (Low yield and Ultra Low yield). It can be seen that the M_w and crystallinity of the polymer with 1-hexene pre-polymerization are both higher than in the experiments without the pre-polymerization step. The higher M_w could be attributed to the higher bulk concentrations of the monomer (ethylene in this case) in polyhexene. In addition, the accessibility of the monomer to the individual active sites is also higher, and the mass transfer limitations are also far more reduced with 1-hexene pre-polymerization. The observed higher crystallinity with 1-hexene pre-polymerization is plausibly due to faster crystallization facilitated by the fragmented morphology of the particle (*Figure 3*). The morphology of the particle without the pre-polymerization step is extremely fibrous and interconnected. This kind of structure does not facilitate faster crystallization as the energy required to break this network is high. The fragmented morphology (obtained with 1-hexene pre-polymerization) does not have too many inter-connections, thus facilitating a faster crystallization and hence displays higher crystallinity.

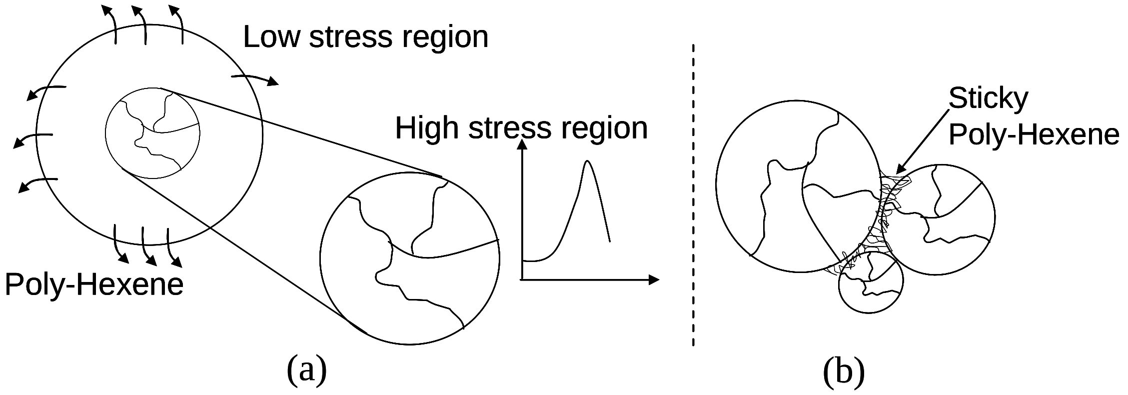

Figure 4: Schematic representation: (a) stress buildup in a large particle due to slower diffusion of polyhexene from the core of the macroparticle, (b) Agglomerate formation due to sticky polyhexene.

7.3.2 Case 2: Low yield (10g PH /g-cat) 1-Hexene pre-polymerization with different prepol times – Fines and agglomerates

In this set of experiments low yield pre-polymerization (10g PH/g-cat) with 1-hexene was performed for different times (5 minutes and 90 minutes). The prepol time refers to the time 1-hexene was added to the catalyst and kept before injecting into the reactor for main polymerization (at 5 bars ethylene partial pressure, 70°C). *Figure 5* and *Figure 6* represent the kinetics and the particle size distribution respectively of the experiments with 5 minutes and 90 minutes pre-pol time and also without pre-polymerization. The MWD and the crystallinity of the produced polymer are presented in *Table 1*.

It can be seen that there is a big drop in the reaction rate and there is also a shift in the PSD towards agglomerates / bigger particles with 90 minutes pre-polymerization. The reduction in the polymerization rate can be attributed to long pre-contacting time of 90 minutes. It is well known that long pre-contacting times in the presence of TEA can lead to deactivation or reduction in the catalyst activity. It must be noted that at short prepol times (5minutes) there is production of both fines and agglomerates. Agglomeration happens at a critical surface concentration of sticky polymer (polyhexene, in this case) in the interface of two or more particles as illustrated in *Figure 4*. The growth stress is higher in the case with low prepol times due to the high reaction rate. With longer prepol times (90 minutes), the polyhexene (which is extremely viscous and sticky) holds the fragmented catalyst micro-grains together (the long prepol time allows the polyhexene to bond the fragmented micro-grains like an adhesive) leading to the production of agglomerates. In addition, due to the low polymerization rate, the growth stress is also substantially lower in this case. It can also be observed that the top end of the PSD for both the low yield pre-polymerizations is the same.

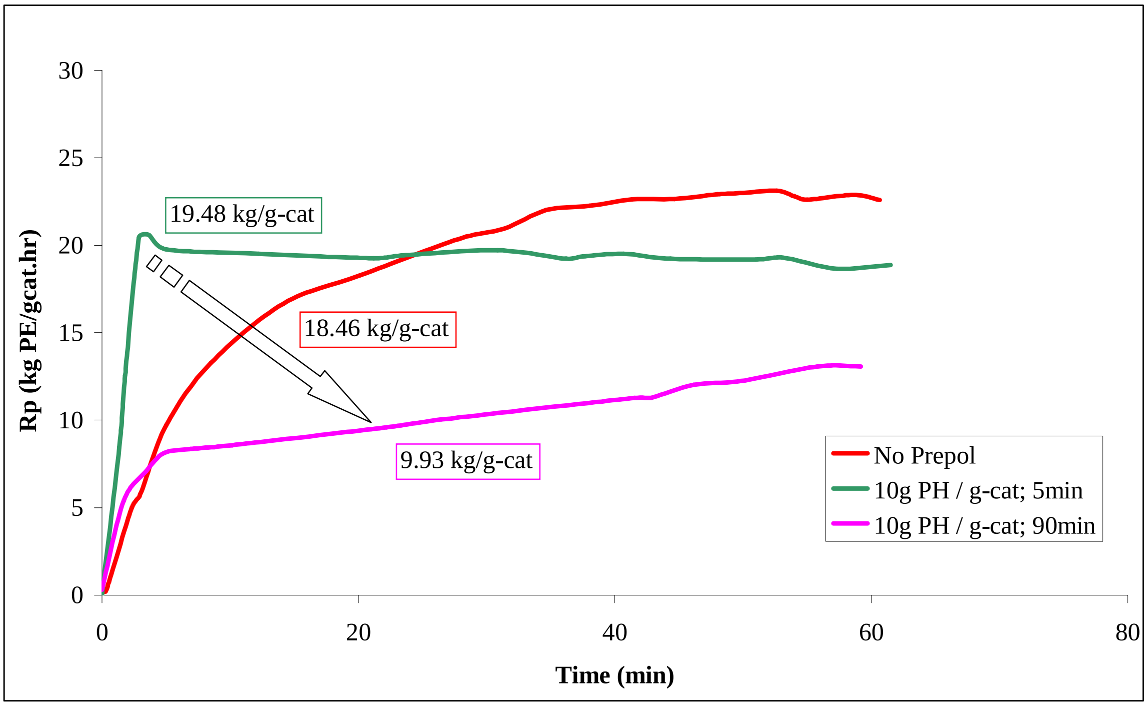

Figure 5: Influence of pre-polymerization time on the kinetics for Low Yield 1-Hexene pre-polymerization followed by 5 bars C2 main Polymerization at 70°C

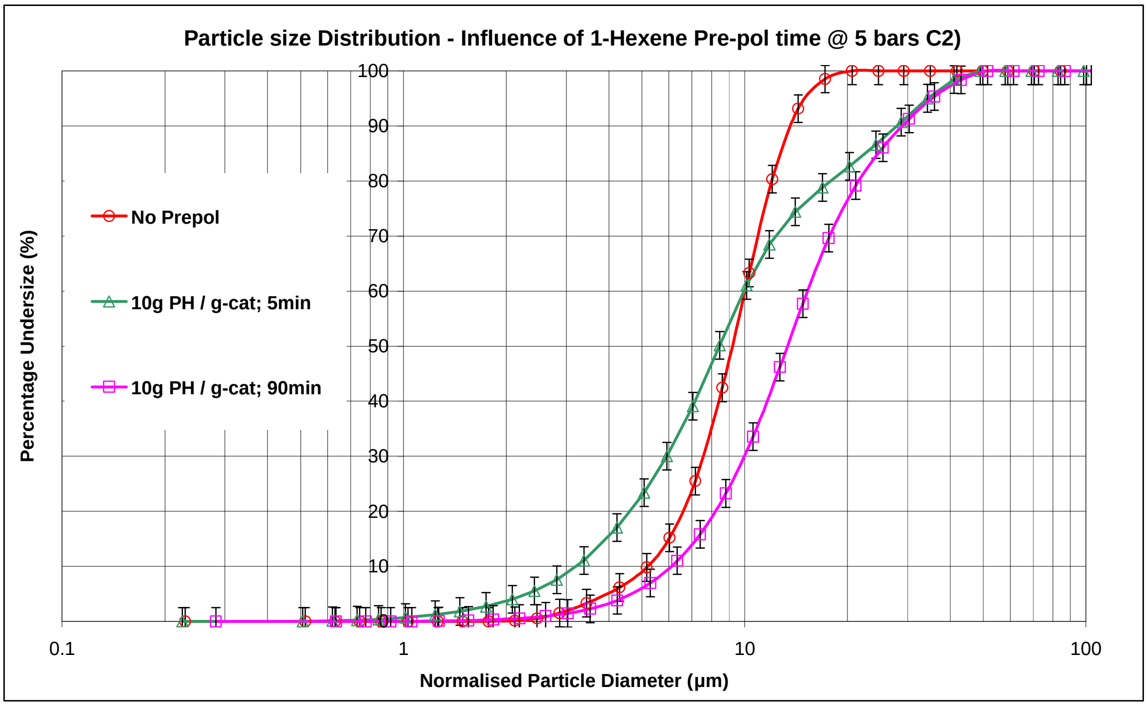

Figure 6: Comparison of PSD at different pre-pol times for Low Yield 1-Hexene pre-polymerization followed by 5 bars C2 main Polymerization at 70°C

7.3.3 Case 3: Very low yield 1-Hexene pre-polymerization followed by main polymerization in the presence and absence of hydrogen

Very low yield (1g PH /g-cat) 1-hexene pre-polymerizations were carried out with prepol times of 5 minutes, followed by subsequent main polymerization at 2 bars ethylene pressure in the absence and presence of hydrogen (10 bars partial pressure) at a temperature of 70°C. The kinetics and the particle size distribution are as observed in *Figure 7* and *Figure 8* respectively. There are a number of influences that can be observed from *Figure 7*. To facilitate better understanding, we shall discuss the influence of 1-hexene pre-polymerization on the subsequent main polymerization, in the absence and presence of hydrogen separately.

No hydrogen in main polymerization: 1-Hexene pre-polymerization (5 minutes prepol time) showed an increase in the reaction rate and a reduction in the PSD leading to the production of predominantly fines similar to that observed in *Case1* with 5 bars ethylene during main polymerization. The M_w and the crystallinity (refer *Table 2*) also showed an increase as was observed in *Case1*.

In the presence of 10 bars hydrogen: In the presence of hydrogen (without the pre-polymerization step), this catalyst showed a faster activation and also a deactivation profile. The results of the same have been discussed in detail in Chapter 6. In this case, the increase in the reaction rate was attributed to internal fragmentation within the particle (with the outer skin holding the fragmented micro-grains together), as a result of which there was no apparent difference in the PSD on the produced polymer.

When the main polymerization (with 2 bars ethylene and 10 bars hydrogen partial pressure) was carried out after short pre-polymerization (5 minutes) with 1-Hexene, it can be observed (from *Figure 7*) that the reaction rate was enhanced further more, which implies higher growth stress during the early stages of polymerization. We can clearly observe particle disintegration and production of fines (see *Figure 8*). The importance of the outer polymer skin is clearly established in this experiment. The absence of the outer polymer skin (holding the micro-grains together) in this case, contributes to the disintegration of the particles and hence the observed shift in the PSD towards fines.

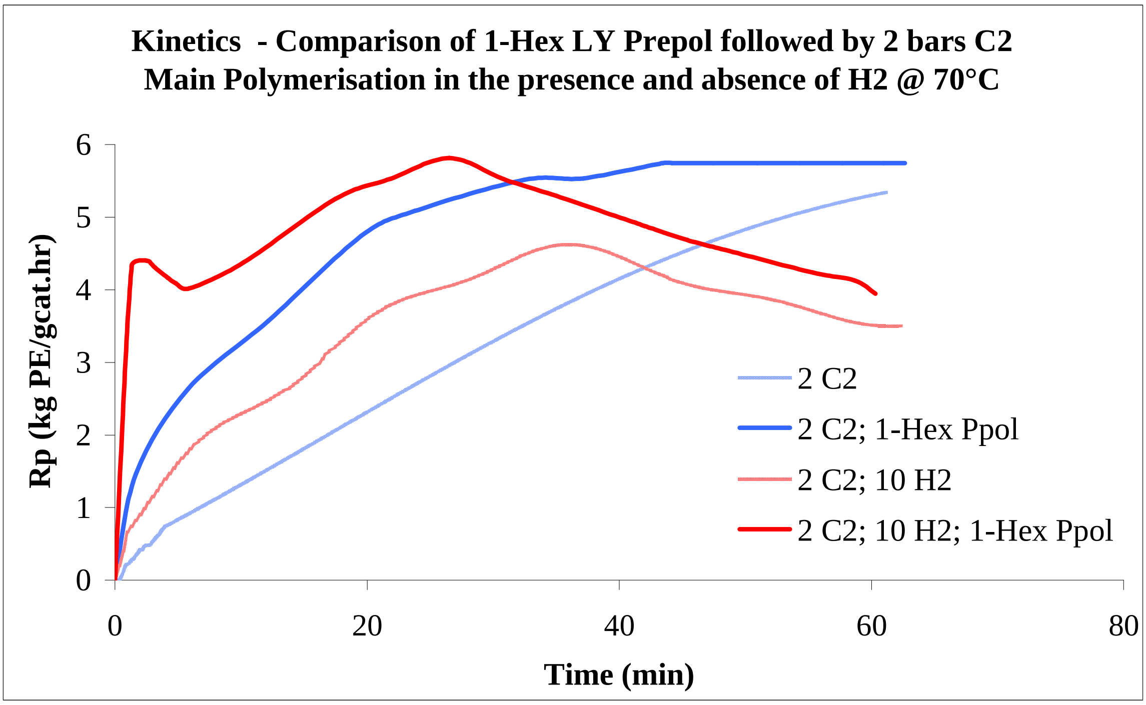

Figure 7: Comparison of Kinetics for Low Yield 1-Hexene pre-polymerization (1g PH/ g-cat, Prepol time = 5 minutes) followed by 2 bars C2 main Polymerization at 70°C

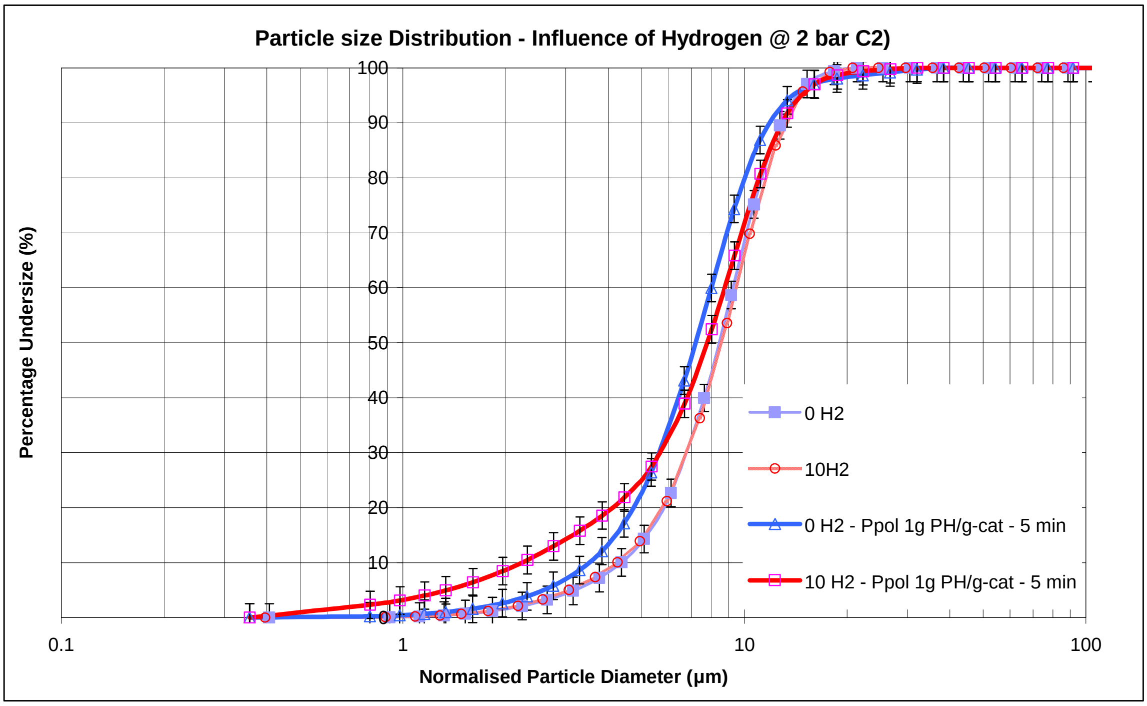

Figure 8: Comparison of PSD for Low Yield 1-Hex pre-polymerization (1g PH/ g-cat, Prepol time = 5 minutes) followed by 2 bars C2 main Polymerization at 70°C

P_{H2} (bars)	Ppol (g PH/g-cat)	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w / \overline{M}_n$	% Crystallinity	Tm °C
0	0	601100	131100	4.6	47.6	134.7
0	1	686000	113000	6.1	60.3	134.5
10	0	41900	5030	8.3	76.7	129.0
10	1	23000	2770	8.3	82.2	129.1

Table 2: Influence of 1-hexene pre-polymerization (in the presence and absence of hydrogen) on MWD and Crystallinity (using Cat1) at 2 bars ethylene pressure and temperature of 70°C.

From *Table 2* it can also be observed that the MW of the polymer decreases and the crystallinity of the polymer sample increases in the case with the 1-Hexene pre-polymerization step. This is due to the higher bulk concentration of hydrogen in the matrix (assuming that PH is still present all the time) and in addition its increased accessibility to the active sites due to the initial fragmentation of the catalyst. This would favour more transfer reactions, thus leading to the production of shorter chains and hence a lower MWD and consequently higher crystallinity of the sample.

7.3.4 Case 4: Propylene pre-polymerization

Propylene homo-pre-polymerization was performed as discussed in the experimental section with varying pre-polymer yields: 0.14 g PP/g-cat, 1g PP / g-cat and 10 g PH / g-cat. These are referred to in this section as Ultra low Yield, Very low Yield pre-polymerization and Low Yield Pre-polymerizations. The pre-polymerization was carried out at room temperature with very low propylene concentrations in a glass vial. The pre-polymerization was followed by a main homopolymerization at 5 bars ethylene partial pressure at a temperature of 70°C.

The influence of propylene pre-polymerization with varying yields on the kinetics and the particle size distribution is as shown in *Figure 9* and *Figure 10* respectively. As can be observed, a substantial increase in the polymerization rate was observed in the main polymerization (with 5 bars ethylene) when the pre-polymerization was performed even for extremely small yields of 0.14 g PP/g-cat.

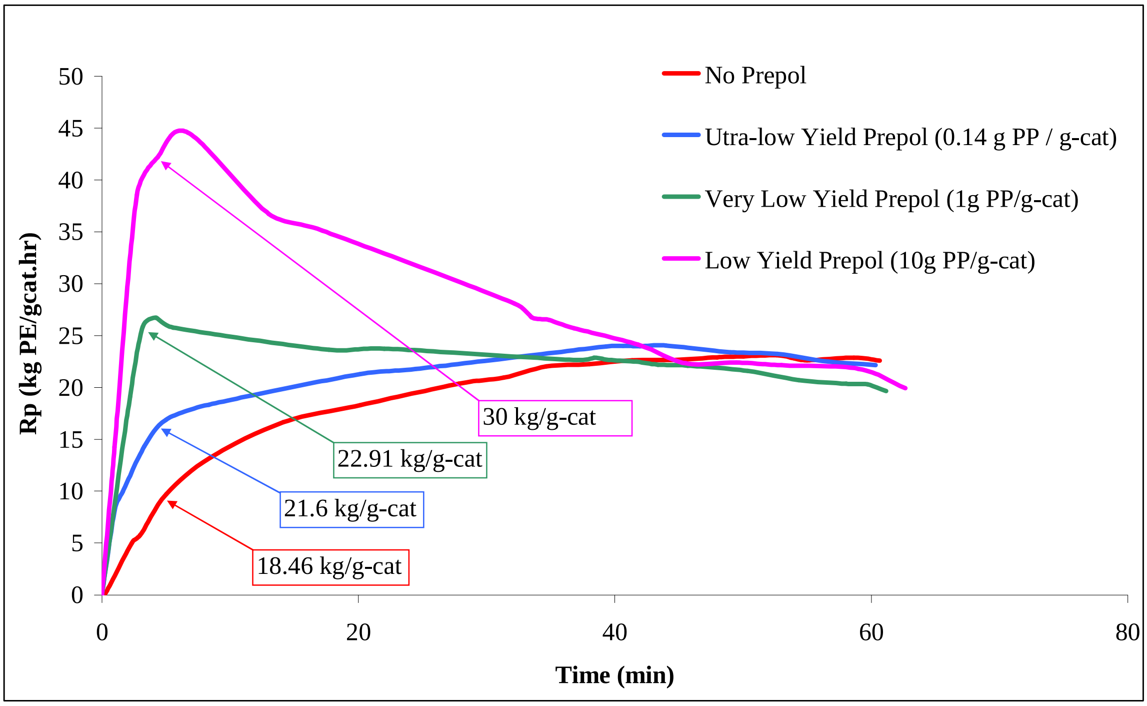

Figure 9: Influence of pre-polymerization (with propylene) on the polymerization kinetics at 5 bars ethylene partial pressure.

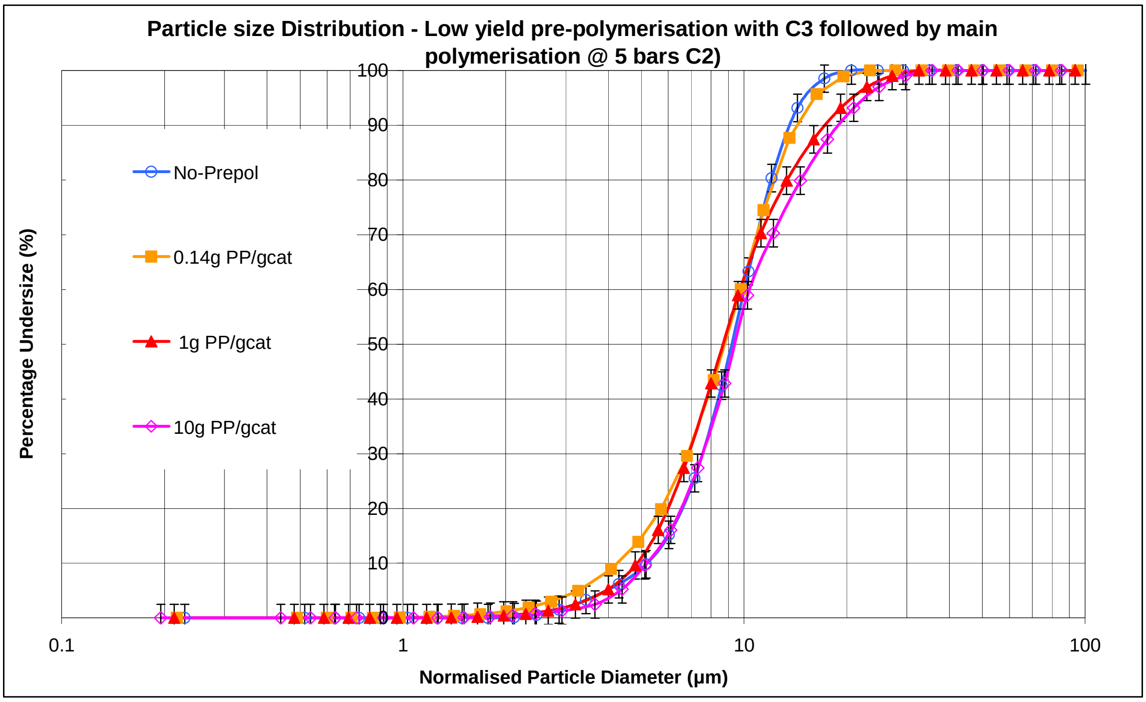

Figure 10: Influence of pre-polymerization (with propylene) on the particle size distribution at 5 bars ethylene partial pressure.

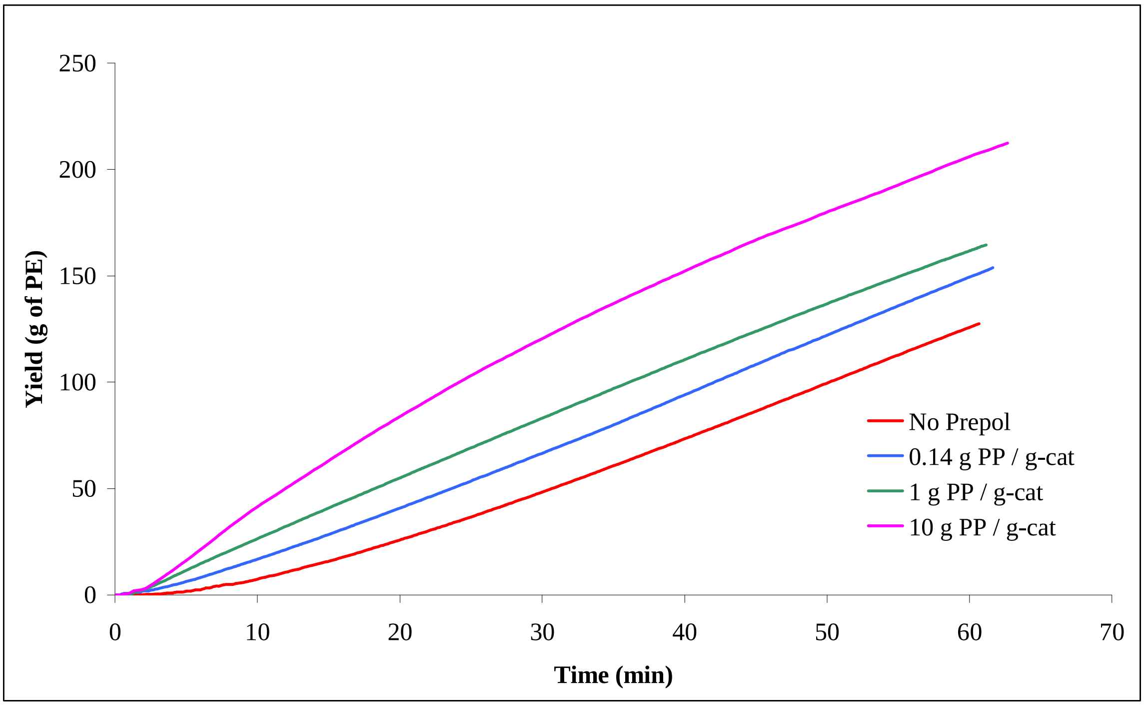

Figure 11: Influence of low yield propylene polymerization on the total yield during main polymerization with 5 bars ethylene

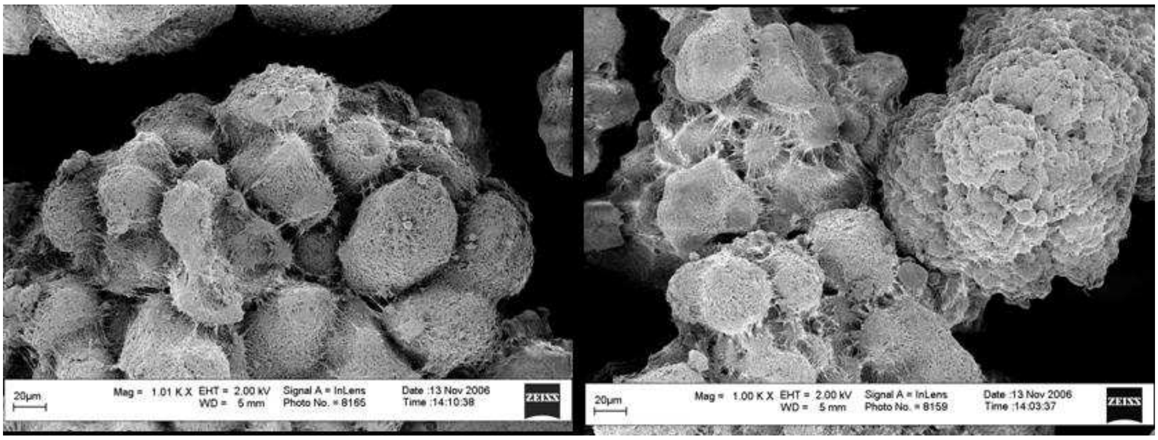

Figure 12: SEM images (20µm) of polymer with (right) and without (left) pre-polymerization (with propylene, 10g PP/gcat)

With increasing prepol yields the reaction rate continued to increase substantially. This can also be seen in *Figure 11* which represents the polymer yields for the different experiments. The highest yield is obtained with a prepol yield of 10g PP/g-cat. In order to check if this increase is due to any pre-polymerization step or if it is due to a chemical effect due to propylene as reported in literature[3-5,7] two experiments were performed: one with an ethylene pre-polymerization step and the other when small amounts of propylene were fed into the reactor as a co-monomer after filling the reactor with ethylene and before catalyst injection. In both cases no increase in the reaction rate was observed confirming the chemical influence of propylene pre-polymerization on the kinetics of ethylene main polymerization.

From the particle size distribution (refer Figure 10) it can be observed that there is not much influence of propylene pre-polymerization on the PSD and hence there is no production of fines during main ethylene polymerization. There is also no observable difference in the polymer morphology as can be observed in the SEM images shown in Figure 12. This clearly should be due to the presence of a thick outer skin that holds the micro-grains together, thus preventing particle disintegration. This has also been observed and reported in literature[9,12,13]. It can be also observed from Figure 10 that there is a shift towards agglomerates at the higher end of the PSD at higher pre-polymerization yields (>1 g PP /g-cat). This can be attributed to the sticky nature of polypropylene thus leading to some agglomeration during main polymerization, just like polyhexene. This behaviour is however not observed at Ultra Low yield pre-polymerization (0.14 g PP/g-cat) where the particle (catalyst / support) is still pre-dominantly $MgCl_2$ *and follows the normal fragmentation behaviour.*

7.4 Conclusion

From *Case1*, *Case2* and *Case3* we can conclude that 1-hexene pre-polymerization can lead to complete fragmentation of the catalyst as observed in literature[9,12]. This pre-polymerization step determines the morphology and the particle size distribution of the polymer produced during subsequent main polymerization, leading to the production of predominantly fines. At the same time, this type of polymerization demonstrates the high brittleness of the carrier in the earlier polymerization stages. Pre-activation of the catalyst and the fragmentation of the catalyst during the pre-polymerization step lead to the higher observed polymerization rates. The high polymerization rates leads to high growth stresses in the growing particles contributing further to external fragmentation. The increase in the polymerization rate is predominantly due to the physical fragmentation of the catalyst in the case of 1-hexene pre-polymerizations. An important message from these experiments is that PSD cannot always be used as a measure to interpret particle disintegration. As shown in this study, it is possible to have agglomeration due to particle disintegration. Hence, care must be taken to interpret particle disintegration / agglomeration directly from the PSD.

In the case of propylene pre-polymerizations (*Case4*) the increase in the reaction rate is due to a chemical effect as reported in literature. There is however no observable difference in the morphology or in the particle size distribution of the final polymer after main polymerization in the presence or absence of this pre-polymerization step. The key take out from this entire study is that the early stages of polymerization are extremely critical (nearly all the important things / steps happen during this stage) and determines the final product morphology.

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Chapter 8: Fragmentation – Influence of Temperature

8.1. Introduction

In gas phase polymerizations an overlapping of different influences has been described in the previous chapters of this thesis, namely, influence of monomer pressure (chapter 4), hydrogen pressure (chapter 6), fragmentation (refer chapter 2) and particle overheating , thus making it an extremely complex process. A lot of work has been done in academia and industry to investigate the influence of heat and mass transfer effects on local particle overheating predominantly for gas phase polymerizations and has been reported in Appendix 2.

The experiments in this study have been performed in slurry to completely eliminate the influence of local particle overheating. We can consider the particle temperature to be the same as the bulk temperature.

Changing the temperature impacts the following parameters / properties in the reacting polymeric system, for instance:

- *Reaction Kinetics*: With increasing temperature it is well known that the reaction rate increases[1-3].
- *Molecular weight (MW)*: With increasing temperature, transfer reactions are accelerated faster than propagation leading to the formation of shorter chains and production of polymers with a lower MW and higher crystallinity.
- *Micro-viscosity*: At higher temperature, the micro-viscosity of the polymer matrix decreases.
- *Transport properties*: The softer matrix also influences the transport properties (chain mobility and diffusion, sorption, swelling, etc.) within the growing polymer particle. For instance, n-hexane sorption in the polymer increases in a closed system such as this, thus leading to a more swollen polymer matrix.
- *Material* properties: The softer matrix also means the visco-elastic properties (brittleness / ductility) of the polymer particle are different at higher temperatures.

Particle fragmentation and the evolution of the polymer morphology depend on the stress generation and relaxation[4,5]. The rate of the buildup of the stress depends on the rate of polymerization reaction and inherits its Arrhenius dependence on temperature as well as the effects of intra-particle transport of monomer and temperature dependent sorption of monomer in the polymer[5]. The rate of stress generation is clearly dependent on the polymerization rate which in turn is deeply influenced by the polymerization temperature.

With the above explanations one could expect the following:

- At low temperatures the reaction is relatively slow and hence would have lower stress accumulation in the particle, provided the relaxation of the stress is sufficiently fast. However, it must be noted that at lower temperatures the polymer is more brittle and could form micro-cavities and disintegrate into fines[6]

- At higher temperatures, and higher polymerization rates the stress relaxation becomes the dominant factor for the evolution of the polymer morphology. With higher temperatures, the relaxation time for the stress decreases (due to reduction in the local intrinsic viscosity[4]). The faster relaxation time at higher temperatures, implies the stress is also relaxed quickly thus preventing high energy accumulation and external particle fragmentation.

8.2. Experiments and Materials

The experiments were performed in a 1.6*l* jacketed Buchi reactor, for slurry ethylene polymerizations[7]. The details of the experimental setup and the experimental protocol are as explained in Chapter 3. The temperature was the only parameter that was adjusted according to the required set point. In this investigation, the temperature was varied from 60°C to 85 °C. All other variables were kept constant.

8.3. Results and discussion

The influences of temperature on the polymerization kinetics and particle size distribution are as shown in *Figure 1* and *Figure 2* respectively. The experimental conditions and the physical properties of the final polymer, i.e. molecular weight, crystallinity, etc. are given in *Table 1*. It is clear that the polymerization rate decreases strongly with decreasing temperature. However, at higher temperatures (>80°C) it seems that the influence of temperature is limited or significantly low.

It can be observed from *Table 1* that with increasing temperature **the molecular weight (MW) decreases** and the crystallinity of the polymer increases. This is expected, as increasing the temperature of reaction accelerates chain transfer reactions, which have higher activation energy, than chain propagation reactions leading to shorter chains and hence **lower MW**. This consequently leads to the higher crystallinity of the polymer. However, it must be noted that the overall increase in the crystallinity from 60°C to 85°C is small (<10%) and is not in the critical range (% critical crystallinity >75%) where it could have a major influence on particle disintegration.

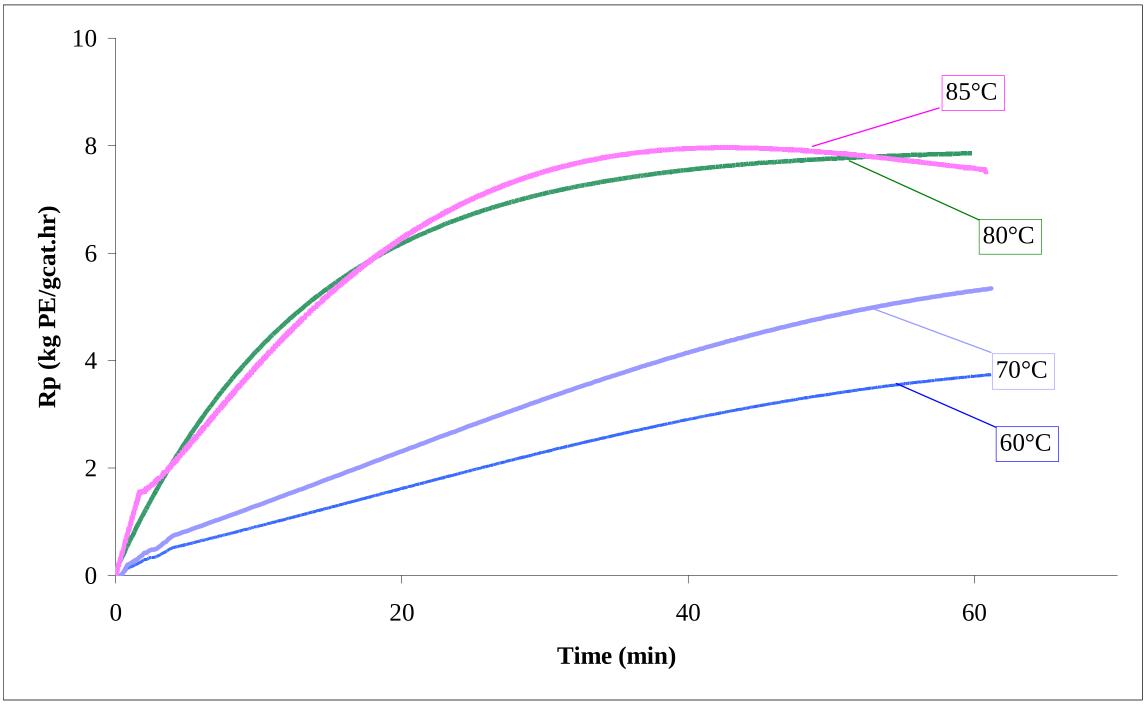

Figure 1: Influence of temperature on the polymerization kinetics at 2 bars ethylene partial pressure

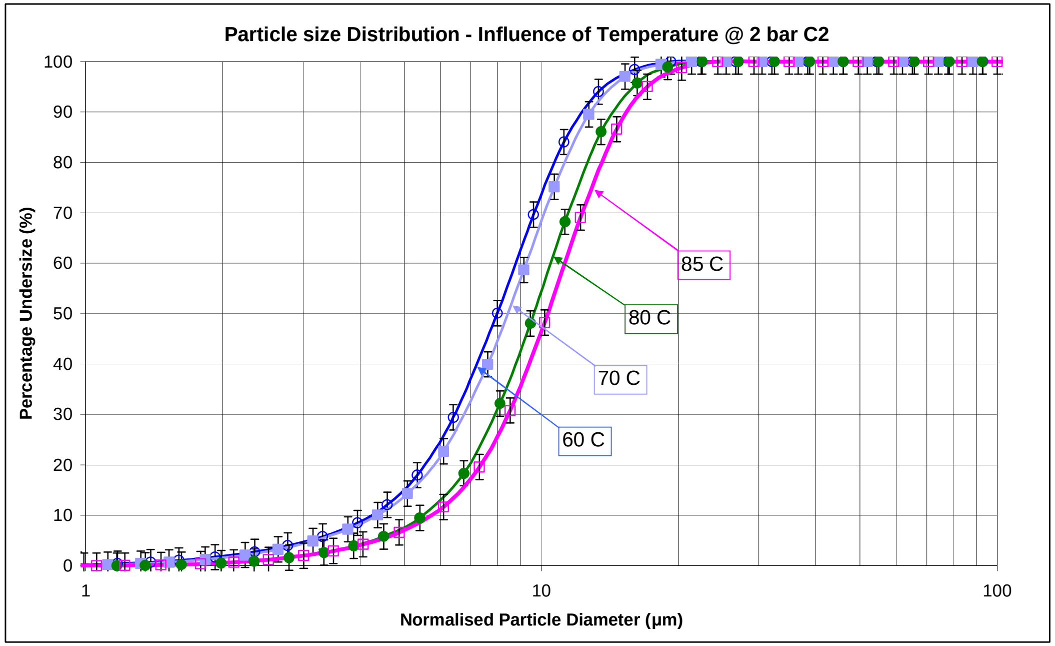

Figure 2: Influence of temperature on the particle size distribution at 2 bars ethylene partial pressure

T (°C)	Rpmax (kg PE /gcat hr)	Yield (g PE / gcat)	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w / \overline{M}_n$	% Crystallinity
60	3.7	2857	1375000	280600	4.9	45.1
70	5.3	3309	601100	131100	4.6	47.6
80	7.8	6230	485600	98000	5.0	52.9
85	8.0	6470	492500	90000	5.5	52.7

Table 1: Influence of temperature on maximum polymerization rate, yield, MWD at 2 bars ethylene partial pressure

The lower MW at higher temperatures also implies a reduction in the micro-viscosity within the growing polymer particle. This reduction in micro-viscosity would lead to higher chain mobility. In addition, n-hexane also contributes to the swelling of the polymer at higher temperatures leading to a softer polymer matrix. This changes the solubility of monomer / hydrogen and could lead to **a slightly higher molecular weight with increasing temperature.** It can be seen from *Table 1* that at 85°C the molecular weight is slightly higher or similar to that at 80°C but has nearly the same crystallinity.

Looking at the PSD (*Figure 2*) it can be observed that with increasing temperatures the **Particle Size increases**. The **particle size is smaller** at lower temperatures i.e. 60°C and 70°C respectively. For example, for a normalized particle diameter of 10μm, there is a 30% reduction in the fines or particles with lower PSD at 85°C as compared to 60°C.

The stresses (growth stress in combination with thermal stress) generated within the growing polymer particle are more at higher temperatures. It must be noted that at temperatures >80°C, swelling of the polymer due to n-hexane and local particle temperature contribute to softening of the polymer matrix. This softer polymer matrix makes the particle more sensitive to shear and normal stresses.

The key factor to particle fragmentation (external) and morphology of the polymer particle is the relaxation of these stresses[5]. With higher temperatures, the relaxation time for the stress decreases due to the reduction in the local intrinsic viscosity[4] (lower MWD). The faster relaxation time at higher temperatures, implies the stress is also relaxed quickly thus preventing external particle fragmentation. At lower temperatures (60°C-70°C), the reaction is relatively slow and hence stress buildup or accumulation within the growing particle is not as fast as at higher temperatures, but the relaxation of the stress is obviously slow . From *Figure 2* it can be seen that the PSD shifts to the left (towards fines) at lower temperatures. A similar result was also obtained by Llinas et al when they found more fines at lower temperatures[6]. The reasoning for this is straightforward. The temperature affects the stress-strain relationship of the polymeric material. At low temperatures, the polymer is brittle. Hence, micro-cavities could develop within the particles due to the longer relaxation times and over time, these cracks lead to the disintegration or external fragmentation of the particle. This is plausibly the reason why we observe more fines at lower temperatures in our study. It must be noted that the fragmentation behaviour differs for each catalyst/support system. It depends a lot on the type, mechanical strength, porosity and the catalyst loading of the support. Hence, observations always refer to the particular catalyst system in use.

The influence of temperature on the maximum polymerization rate is as shown in *Figure 3*. The well known dependency of the polymerization rate (Rp) on the monomer concentration (C_m), concentration of the active sites (C^*) and the propagation rate constant (k_p) is given by *Equation 1*[1]. In a wide range, the propagation rate shows an exponential dependency on the activation energy and the bulk temperature as shown in *Equation 2*.

$$R_p = k_p \left[C_m\right]\left[C^*\right] \qquad (1)$$

$$kp = k_{p0} \cdot e^{Ea/RT} \qquad (2)$$

Substituting, $R_p = k_{p0} \cdot e^{Ea/RT} \left[C_m\right]\left[C^*\right]$ (3)

Re-arranging and simplifying *Equation 3* gives the Arrhenius plot of propagation in slurry ethylene polymerizations (as shown in *Figure 4*). The activation energy for propagation (E_a) as can be seen in *Figure 4* was found to be ~ 30-40 KJ/ mol and compares well with data reported in literature[7-11]. From a closer examination of *Figure 4* it can be observed that at temperatures greater than 80°C, there is no significant influence of temperature on the overall activation energy.

A similar behaviour at higher temperatures has been previously reported by Pater et al[3] for propylene polymerizations. They found that deactivation of the catalyst at higher temperatures was the reason for this reduced increase in the reaction rate at higher temperatures. For this study and this catalyst system (Cat1), the first signs of deactivation were observed only at 85°C. No deactivation was observed for the standard one hour experiments at other temperatures.

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[1] Assumptions: (i) the polymerization rate depends directly on the monomer concentration and the active site concentration in the bulk / slurry (ii) the growing polymer particle is assumed to be devoid of temperature or monomer concentration gradients.

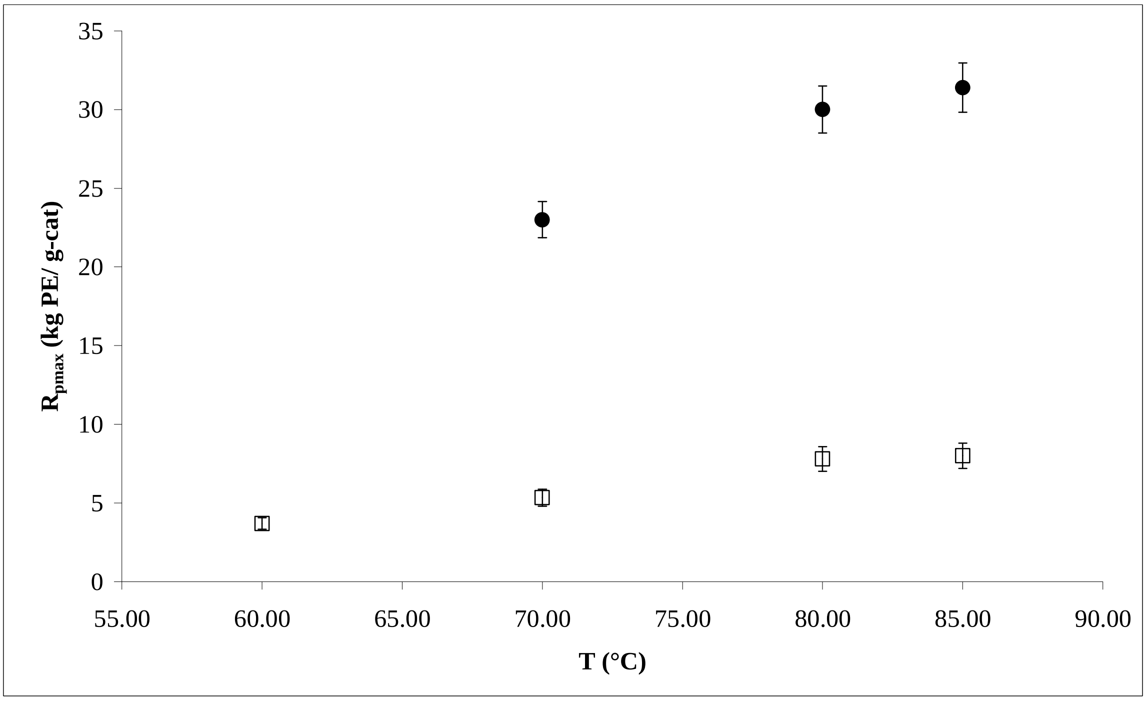

Figure 3: Influence of Temperature on maximum polymerization rate (R_{pmax}) at (□) 2 bars and (●) 5 bars ethylene partial pressure

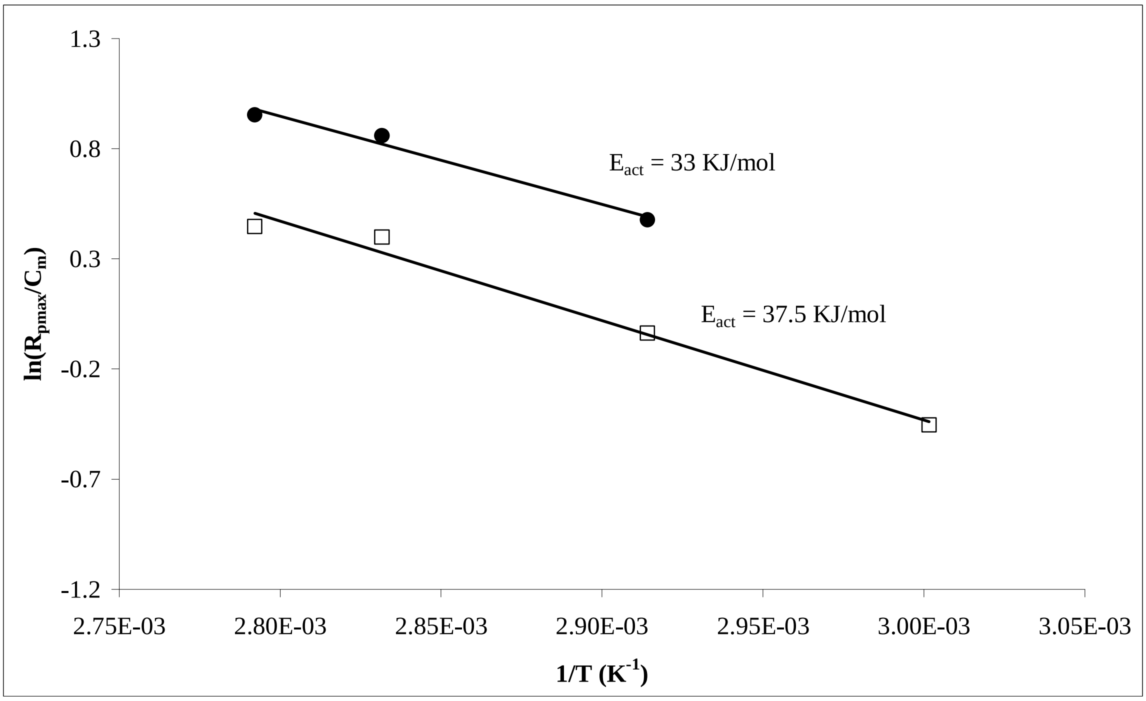

Figure 4: Arrhenius plot of propagation in slurry ethylene polymerizations (between 60°C and 85°C) at (□) 2 bars and (●) 5 bars ethylene partial pressure.

8.4. Conclusion

The influence of temperature on the kinetics of slurry ethylene polymerization was investigated in this study. It was observed that the reaction rate increased with increasing temperature and the activation energy is nearly constant in the temperature and pressure range investigated. This increase is only up to a certain temperature (80°C for this catalyst system). At temperatures higher than this, the influence on the polymerization rate was not found to be significant. The activation energy for propagation was found to be ~ 40 KJ/mol and compares well with that obtained in literature. Temperature had a reverse influence on the particle size distribution in slurry ethylene polymerizations. The normalized PSD shifted towards the right (away from fines) with increasing temperature. This is expected, due to a combination of both faster stress relaxation (facilitated by reduction in the local intrinsic viscosity) and a softer polymer matrix at higher temperatures. These influences could however be drastically different for gas phase polymerizations because of the different matrix properties.

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Chapter 9: Summary and Recommendations

9.1. Summary

The main objective of this thesis was to develop a semi-quantitative method for characterization of fines generation in ethylene polymerization[*] using $MgCl_2$- supported Ziegler-Natta catalysts based on a detailed analysis of:

- Polymerization rate profiles
- Molecular weight
- Crystallinity
- Particle growth and particle size distribution
- Pre-polymerization and Catalyst pretreatment

and their impact on

- Internal and external fragmentation[1]

This was done by systematically varying the key reaction parameters that influence particle fragmentation and kinetics in slurry ethylene homo-polymerizations (using an industrial Ziegler-Natta catalyst on $MgCl_2$ support), such as:

1. Ethylene pressure from 2 bars to 20 bars.
2. Co-catalyst concentration from 60mg TEA (with and without pre-contacting) to 180mg TEA.
3. Hydrogen partial pressure (at a constant ethylene pressure of 2 bars) from 2 bars to 18 bars.
4. By introducing a pre-polymerization step (using 1-hexene – no outer skin and propylene – with outer skin) prior to main polymerization in the presence and absence of hydrogen.
5. Temperature from 60°C to 85°C.

Polymerization rate profiles (reflecting the growth stress within a growing polymer particle), crystallinity (an indirect measure of the brittleness of the produced polymer), particle size distribution (gives a direct measure of the particle disintegration) and molecular weight (MW) of the produced polymer (determines the intrinsic viscosity of the polymer matrix) were

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[*] main focus on slurry polymerization, but gas phase polymerization effects are taken into account

[1] „internal“ stands for fragmentation without fines formation, the number of particles does not change

measured to quantify and understand the degree, extent and mechanism of particle disintegration during polymerization.

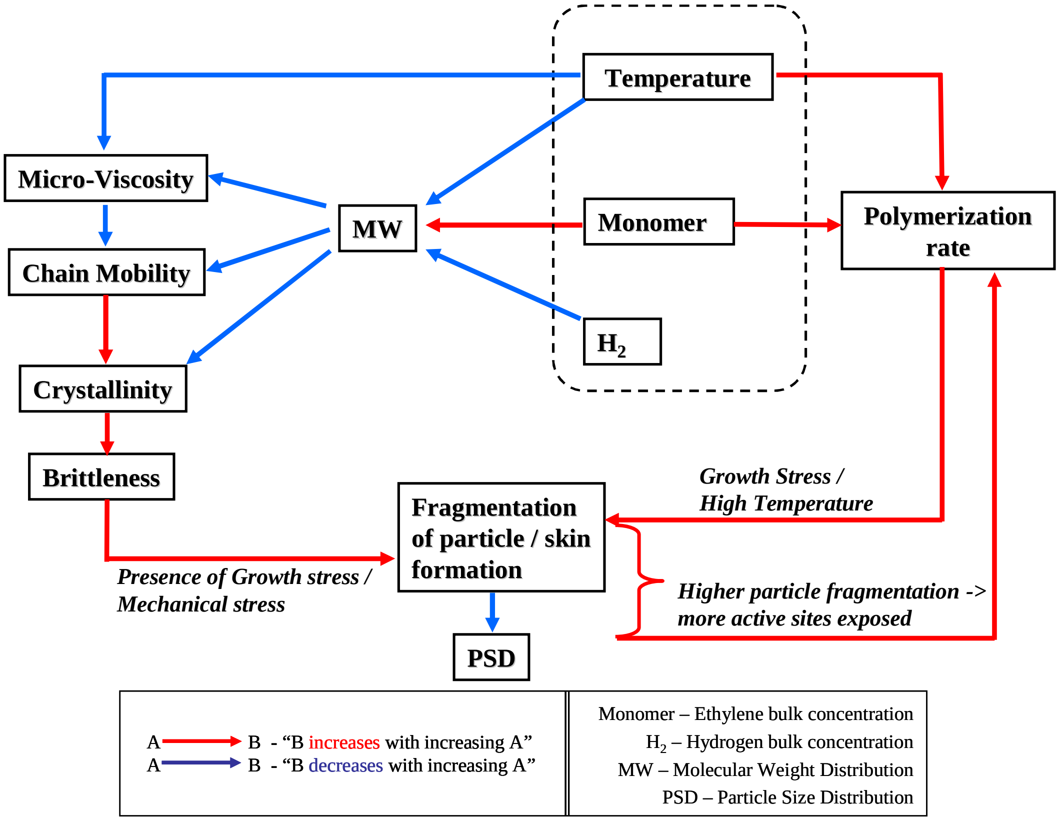

*Figure 1: **GRAF-S**, a semi-quantitative theory of fines generations and the various factors influencing particle fragmentation and fines generation.*

How do we quantify these interactions? Which processes contribute to particle disintegration and under what conditions and how can they be characterised? In this work we have developed a comprehensive semi-quantitative theory for fines generation (refer *Figure 1*) that clearly illustrates the underlying processes and their influences on the properties of the produced polymer and consequently on the final morphology of the particle during polymerization. We shall now proceed to summarise each of the chapters individually.

"Chapter 2 – Mechanism of Fines generation"

It discusses the issues of fines in industry, the various methods that have been employed to reduce the same and the current state of art and understanding of the mechanism of fines generation. Our hypothesis was developed based on the state of art and conclusions obtained from our well designed experiments. The main factors that determine fines generation were identified to be

- Intra-particle stress composed of two components;
    - the growth stress which builds up with increasing polymerization rate
    - mechanical / external stress; although it is out of the scope of this work, a method was developed to quantify the same (refer Appendix 1)
- Brittleness of both the support (during the first seconds of polymerization) and of the polymer particle during polymerization
- The importance of the outer polymer skin during the early stages of polymerization
- Influence of the solvent / slurryfying agent (n-hexane) on the polymer matrix
- Homogeneous polymerization on unsupported catalysts, which has not been dealt with in this work

The most important and critical of these are the growth stress, the brittleness of the polymer (the more crystalline the polymer the more brittle it is and hence more fragile) and the presence of an outer polymer skin that holds the micro-grains within a growing polymer particle together. Once the basic factors were identified, the next step was to segregate the individual influences by recognizing key reaction parameters that control the same. They are as listed below:

- Monomer (ethylene in this case): The monomer pressure directly correlates to the growth stress generated within a growing polymer particle at an almost constant crystallinity, which means, the brittleness of the polymer remains nearly unaltered with increasing molecular weight of the produced polymer.

- Co-catalyst: The amount of co-catalyst would change the Al/Ti ratio, thus influencing the kinetics. In addition, pre-contacting the catalyst with the co-catalyst would change the activation state of the active sites. Both cases would lead to a faster activation profile during polymerization, thus leading to higher growth stresses and at almost constant crystallinity.
- Hydrogen: It is well known that hydrogen is a good chain transfer agent. Addition of hydrogen in the reaction system decreases the molecular weight of the polymer. The higher the hydrogen content, the lower would be the molecular weight. This would also mean higher crystallinity of the produced polymer and hence higher brittleness of the system thus facilitating fragmentation in the presence of a critical growth stress.

- Importance of the Outer Polymer Skin: In the absence of an outer polymer skin, the micro-grains of a growing polymer particle would continue to polymerize independently leading to the production of predominantly fines. This can be done by performing a 1st step low yield pre-polymerization using 1-hexene, followed by main ethylene homo-polymerization. The converse would be the presence of the thick polymer ductile skin, preventing particle fragmentation. Both these influences were clearly established in this work.

- Temperature: Temperature influences all the parameters mentioned above. Changing the temperature changes the following: the catalyst activation profile, the kinetics of polymerization (and hence the growth stress), the molecular weight distribution, the crystallinity of the produced polymer (although not to a great extent), the intrinsic viscosity within the polymer matrix (which would influence mobility of the polymer chains and all other transport properties of monomer / hydrogen / co-catalyst within the polymer matrix),

According to the above understanding a complete experimental plan was designed to illustrate each of individual influences and their combined effect on particle disintegration and fines generation.

"Chapter 3 – Experimental"

Precise measurements of polymerization rate profiles, the characterization of the brittleness of the growing polymer particles, and the quantification of the disintegration of the particles are prerequisites for understanding the mechanism of fines generation.

The 1.6-L stainless steel jacketed reactor, fully automated and operating at pressures up to 40 bar and temperatures up to 120°C, was selected for slurry experiments. n-Hexane was used as medium for the slurry. The reaction temperature and pressure were adjusted and controlled in the both isothermal (within 0.2 C) and isobaric (within 0.15 bar) modes. A heterogeneous Ziegler-Natta (Z-N) catalyst system, which is used in slurry-phase industrial ethylene polymerizations, was used in all experiments. The catalyst had an average particle size of around 10-15µm. Due to high sensitivity of the Z-N catalyst, all gases and liquids used were of 'polymer grade' and were purified in a series of purification columns. The instantaneous polymerization rate was measured by measuring the fed ethylene into the reactor via a mass flow meter for maintaining a constant reactor pressure during the polymerization.

The polymerization kinetics was found to be reproducible with maximum deviations of ±5%. The normalised particle size distribution was effectively used to determine the influence and extent of particle disintegration during polymerization. The crystallinity was effectively used as a measure to quantify the brittleness of the produced polymer and the molecular weight distribution (MWD) reflected the intrinsic viscosity of the polymer matrix. To study the influence of particle disintegration especially during pre-polymerisations with 1-hexene and propylene, SEM (Scanning Electron Microscopy) measurements were used to study the particle morphology. The ethylene bulk concentrations in slurry at different temperatures were obtained from PC-SAFT calculations. The hydrogen bulk concentration in slurry was computed precisely using Aspen Polymer Plus.

"Chapter 4 – Fragmentation: Influence of Monomer Pressure"

The chapter illustrates the role of growth stress and the formation rate of the outer polymer skin on particle disintegration during ethylene polymerizations. As per our hypothesis, we observed the following:

- By changing the monomer pressure the polymerization rate increased almost linearly (especially at higher pressures) thus implying higher growth stress at higher ethylene pressures without changing the crystallinity (~46%) and hence the brittleness of the produced polymer. As expected the molecular weight of the produced polymer increased with increasing monomer pressure.

- At low ethylene pressures the outer polymer skin is not thick enough to withstand the growth stress and hold the micro-particles together, thus displaying a decrease in particle size.

- For this catalyst system, it was found that 8 bars ethylene pressure seemed to be the critical limit (under these conditions), where the polymer and the catalyst support along with the outer skin, are able to counter balance the internal growth stresses due to polymerization thus exhibiting a PSD shifting away from fines.

- Above this critical pressure, the internal growth stress due to polymerization is much higher that critical strength of the outer skin thus leading to particle disintegration. This disintegration leads to further increase in the polymerisation rate, due to the increased exposure of active sites to the monomer as explained in detail in Chapter 2 of this thesis.

- Incomplete fragmentation at low pressures could be the reason for the observed broken dependency of the polymerization rate on the bulk monomer concentration.

“Chapter 5 – Fragmentation: Influence of co-catalyst”

This chapter discusses the influence of catalyst pre-contacting (with co-catalyst) and co-catalyst concentration on the kinetics of polymerization and particle disintegration.

Case 1: Pre-contacting catalyst

- Pre-activation of the catalyst leads to higher initial polymerization rate and also significantly reduced the initial activation period for this catalyst.

- The higher initial polymerization rate implies high growth stress during the early stages of polymerization thus leading to particle disintegration (at the same crystallinity / brittleness of the polymer). The percentage undersize almost doubled for the same normalized particle diameter (for example, the % undersize at a normalized particle diameter of 10μm without pre-contacting was 35% and the same was 70% when catalyst pre-activation was performed).

- The maximum polymerization rate with and without pre-contacting remained the same in both experiments.

Case 2: Influence of co-catalyst concentration

- In-situ activation of the catalyst always displays a slower activation profile than pre-activated catalyst. This means a gradual build up of the stresses due to slower reaction kinetics primarily due to slower diffusion of the TEA into the growing polymer particle. However, the polymerization rate and consequently the stress buildup within the particle, is also higher at higher co-catalyst concentrations.

- At high TEA concentrations it was observed that there is a greater stress on the outer skin due to the counterbalance of the TEA/activation front and the expanding polymer / reaction front leading to a greater production of polymer in the outer shell of the macroparticle vis-à-vis the inner core, thus leading to rupture of the outer shell and hence fines generation

“Chapter 6 – Fragmentation: Influence of hydrogen”

The influence of hydrogen partial pressure on the kinetics and particle disintegration, especially internal fragmentation in slurry ethylene polymerizations was comprehensively examined in this study. Introduction of hydrogen not only alters the chemistry but also the physics during polymerization.

- Addition of hydrogen leads to the production of a polymer with lower MW (as is well known).

- Lower MW implies, shorter chain lengths, with lower local micro-viscosity, consequently facilitating higher chain mobility and faster crystallisation kinetics.

- This in turn leads to the higher crystallinity of the polymer and consequently the higher brittleness of the polymer, which in the presence of a critical growth stress leads to particle disintegration.

- The particle disintegration in turn leads to the higher observed polymerisation rate as explained in detail in our theory in Chapter 2.

- Particle disintegration could occur internally within a particle, with the outer skin holding the fragmented grains up to a certain crystallinity (< 76%). The importance of the outer polymer skin in the presence of hydrogen is more clearly established in Chapter 7, with the so-called "1-Hexene" effect.

- The above observations clearly imply that polymerization kinetics cannot be interpreted correctly without considering the physical influences, i.e. particle disintegration, that is occurring simultaneously during the polymerization reaction. A higher polymerization rate is not always due to a chemical effect.

"Chapter 7 – Influence of pre-polymerization: the counterbalance of fragmentation and agglomeration"

In this chapter, the influence of a low / ultra low yield pre-polymerization step with an alfa-olefin (1-hexene and propylene), prior to main homo-polymerization was investigated. The alfa-olefins being more bulky should show a different fragmentation behaviour, crack propagation and skin formation. The high solubility of polyhexene in alkanes (n-hexane in this case) implies no skin formation. Four cases were studied in this investigation.

Case1: Influence of 1-hexene pre-polymerization with different yields

— 1-hexene pre-polymerization led to complete disintegration of the particle after main homo-polymerization at 5 bars C2. This was clearly observed in the PSD as well as in SEM.

— This was clearly due to the absence of an outer polymer skin during main polymerization (as PH is extremely soluble in n-hexane), as well as the high initial growth stresses during early polymerization (high polymerization rate).

— The particle morphology of the homo-polymer with 1-hexene pre-polymerization is distinctly different (no fibrous interconnections, holding the macro-particles together).

Case2: Influence of 1-hexene pre-polymerization time

— When the pre-polymerization time was long ~ 90 minutes, it was observed that the PSD shifted completely to agglomerates.

— Agglomeration is predominantly due to a higher surface concentration of sticky polyhexene, which bonds the disintegrated macro-particles together like an adhesive.

— At higher PH yields, the slower diffusion causes a higher stress at the shell of bigger macro-particles thus leading to fracture / disintegration. These smaller disintegrated particles, stick to other particles, thus forming agglomerates. This effect was also clearly visible with the top end of the particle size distribution shifting towards agglomerates even at short pre-polymerization times.

— An important learning from this experiment was the PSD alone cannot be used to quantify or interpret particle agglomeration / disintegration.

Case3: Influence of 1-hexene pre-polymerization in the presence of hydrogen

— The importance of the outer polymer skin is clearly established in the experiments performed in this investigation especially in the presence of hydrogen.

— These set of experiments comprehensively establish the presence of internal fragmentation observed at 10 bars hydrogen in Chapter 6. The absence of the outer skin lead to a further increase in the polymerization rate, as well as an increase in the crystallinity of the polymer formed. This obviously led to complete disintegration of the particle leading to the production of mostly fines.

Case4: Influence of propylene pre-polymerization

- Pre-polymerization with propylene led at ultra-low to low yields led to significant increase in the polymerization rate, during main ethylene homo-polymerization.
- However, this was clearly due to a chemical influence (reported previously in literature), as no difference could be observed either in the PSD or in the particle morphology (SEM images).
- The thick polypropylene skin holds the growing macro-particles together, thus preventing particle fragmentation despite the high polymerization rate (read growth stress).
- The stickiness of polypropylene also leads to agglomeration, although not as much as polyhexene. This could clearly be observed from the upper end of the PSD.

"Chapter 8 – Influence of Temperature"

Changing the temperature, has a deep influence on the reaction kinetics, molecular weight distribution, micro-viscosity, the crystallinity of the produced polymer, material and transport properties within the polymer matrix and also the visco-elastic behaviour of the polymer particle. With increasing temperature the following was observed:

- The reaction rate increases with rising temperature, demonstrating the Arrhenius-type temperature dependency over the whole temperature range and displaying an almost constant activation energy of 40KJ/mol for the temperature and pressure ranges investigated in this study.
- This increase in the polymerization rate was only up to a certain temperature (80°C), after which it was relatively constant.
- Temperature had an inverse influence on the PSD with the PSD shifting away from fines with increasing temperature. A 30% reduction in fines was observed at 85°C as compared to that at 60°C (for $d_{\text{normalised}} = 10\mu m$). This shift in the normalised PSD is due to a combination of both faster stress relaxation (facilitated by reduction in the local intrinsic viscosity) and a softer polymer matrix at higher temperatures.

- The higher the temperature, the lower the molecular weight follows the well-known rule: transfer reactions increase more rapidly than propagation due to their higher activation energy.

- The lower molecular weight, and the higher chain mobility (due to reduced micro-viscosity) leads to a higher crystallinity of the produced polymer, however, the change in the crystallinity (<10%) is not in the critical range (75%) in order to have any impact on particle disintegration.

9.2. Recommendations

A considerable amount of work has been done in our group in the last 4 years with the GRAF[1] and the GRAF-S (this work) theories that have been simultaneously developed, for particle disintegration in ethylene polymerizations using completely different (gas phase catalyst vis-à-vis slurry catalyst) Ziegler-Natta catalysts. The ***GRAF-S*** theory (***G*****rowth Rate** ***A*****ccelerated** ***F*****ragmentation –** taking into account the role of the outer polymer ***S*****kin**) contributes deeply to a more complete understanding of different mechanisms in play, taking into account many influences (individual and combined) and the key influence of the role of the outer polymer skin, during polymerization. This understanding could lay foundation for future research work in the field of polyolefins, such as:

- Extension of the theory for ethylene co-polymerizations, which would be interesting as the presence of a co-polymer completely changes the inherent properties of the final polymer.

- Studying particle disintegration using catalysts on other supports (SiO_2, for instance) which should exhibit completely different fragmentation behaviour.

- During the first seconds of polymerization there is a complete phase transition from a ~ 95% $MgCl_2$ system to one with > 99% polymer. The mixing rules of the polymer and $MgCl_2$ during this phase transition are not clearly understood. This understanding would enable one to develop a global Brittleness Model taking into account the brittleness of the support, the polymer and the outer polymer skin. The kinetics of in-situ crystallization would also greatly help in obtaining a deeper understanding of the mechanisms in play, taking into account the influence of MW and PDI.

- Investigations on understanding the kinetics of activation and co-catalyst back diffusion and activation of “new site” would also be worthwhile and contribute to the growing knowledge.

- Comparison of slurry and gas phase ethylene polymerization using a gas phase catalyst has been simultaneously developed in our group[1] during the same time as this work. However, some of the influences like for instance, a low yield pre-polymerization step prior, to main homo-polymerization could be performed to understand the effects better.

- The development of a comprehensive mathematical model for particle fragmentation, taking into account changes in monomer pressure, hydrogen concentration, monomer/H_2 ratio, temperature and their influences on the polymerization rate (internal growth stress), the crystallinity (brittleness of the polymer), the MWD, sorption, transport and visco-elastic properties in both slurry and gas phase.

Other interesting experiments that could be performed to add more to our understanding would be:

- To check the influence of high co-catalyst concentrations at high ethylene pressures. Would the relatively slower diffusion of the co-catalyst and the faster production of polymer in the outer shell lead to rupture of the polymer layer by layer from the outside?

- An interesting experiment would be to pre-contact the catalyst with the co-catalyst for a short time, followed by washing of the catalyst completely to remove any free co-catalyst prior to injection into differently scavenged reaction masses. Would we have the same maximum polymerization rate? Would we notice a lower polymerization rate due to starvation of potential active sites / new sites from the co-catalyst, during main polymerization?

- A 1-hexene pre-polymerization step in the presence of hydrogen. Would it lead to a production of low molecular weight poly-hexene which can diffuse out faster, thus preventing unbalanced stress development in the shell of the particle during main polymerization, thus preventing fragmentation?

- Multistage polymerizations could also be helpful in tailoring pre-polymer / polymer properties.

- The influence of pre-treating the catalyst, with say hydrogen, or other fillers would also be interesting to study.

Reference List

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Appendix -1 – Testing method for single particle shooting & breakage, simulating conditions of transfer between reactors / flashing

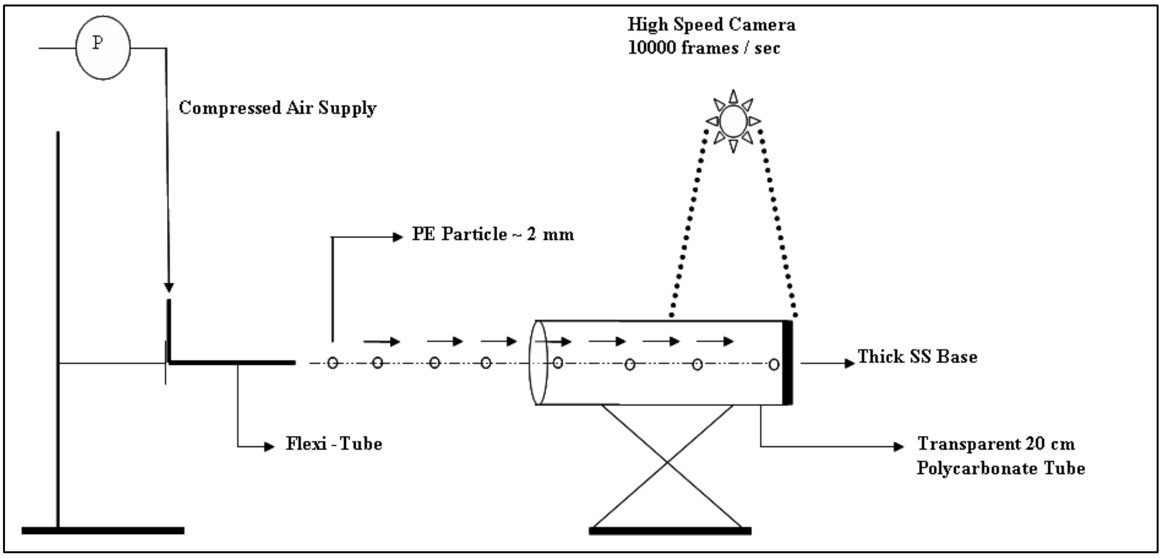

Figure 1: Experimental set-up for single polymer particle shooting

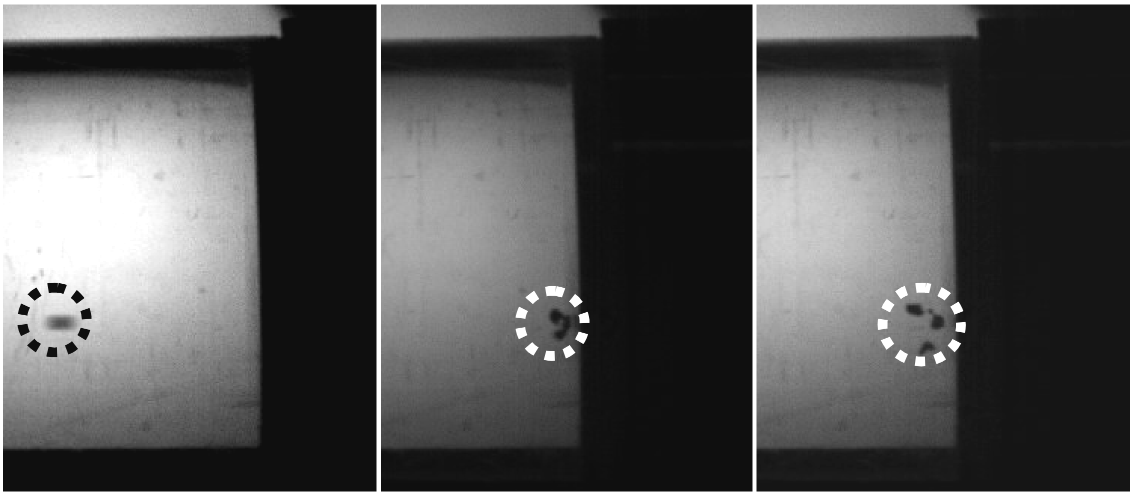

Figure 2: Results of single particle (HDPE ~ 2mm) shooting as observed using a high-speed camera. Minimum particle velocity required to break this PE sample particle was > 47 m/s.

A method was developed where a single PE particle of mass ‘m’, diameter ‘d’ was accelerated to a velocity ‘u’ m/s, using compressed air and allowed to impinge on a hard surface - Stainless Steel (refer *Figure 1*). The particle velocity is reduced from ‘u' m/s to zero, when it impinges against the surface. The energy of the particle can be calculated and it was observed that a given (high-crystalline) particle begins to break at a velocity of 50 m/s. Such velocities in processes are encountered during transfer of polymer between rectors, in cyclones, during flashing in some processes, etc. The method can be used to estimate the averaged brittleness in terms of the fracture energy. This has been clearly illustrated in *Figure 2*, which shows the fragmenting of a PE particle at a velocity of 50 m/s.

Such velocities in processes are encountered during transfer of polymer between reactors, in cyclones, during flashing in some processes, etc. The method can be used to estimate the averaged brittleness in terms of the fracture energy (*Figure 3*).

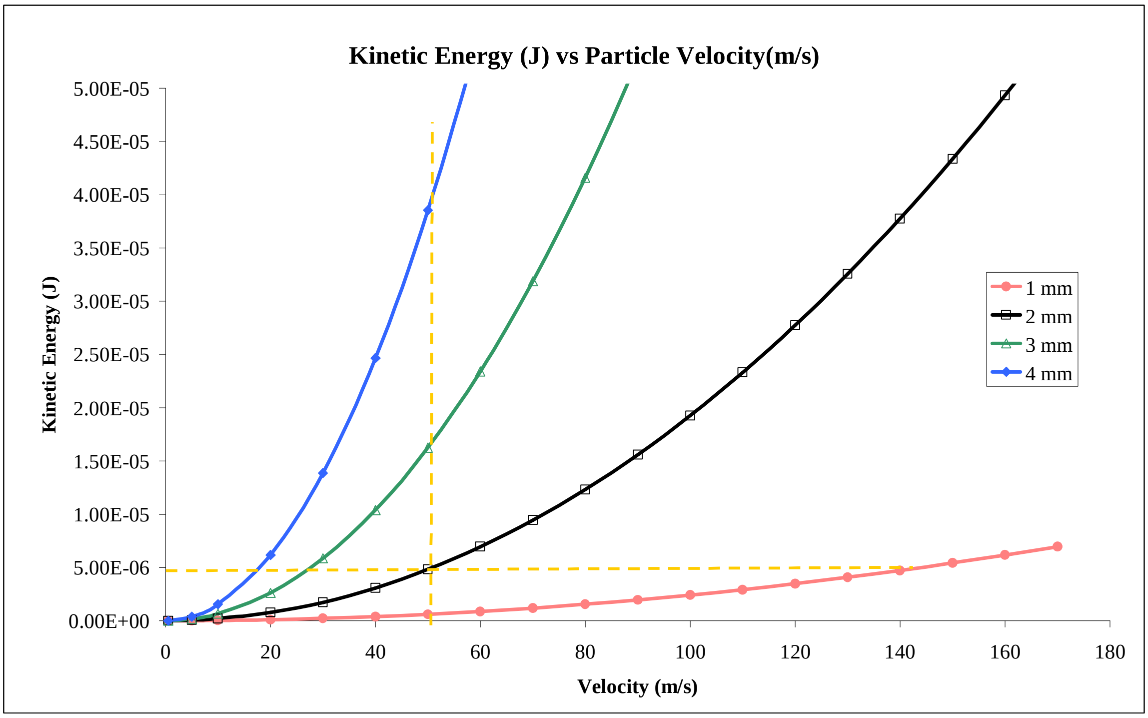

Figure 3: Kinetic Energy calculations for a typical spherical PE particle of 2mm diameter. The calculations for 1mm, 3mm & 4mm are theoretical calculations. The cross wire, defines the energy required to break the particle calculated from experiments.

Appendix 2 – Local particle overheating in olefin polymerizations

Work	Observation / Remarks	Citation
First model to explain local particle overheating and its influence on particle growth and morphology	Particle agglomeration - related to mass and heat transfer limitations which occurred during the growth of the polymer particle.	Floyd et al[1,2]
Single particle stability analysis	Model to establish conditions under which a growing polymer particle overheats	Hutchinson et al[3]
Using existing heat and mass transfer models to predict particle growth in modern industrial catalysts	It was not possible to use existing models "as-is" to model highly active catalysts, ($\geq$ 50kg gcat^{-1} h^{-1}) as they predicted prohibitively large concentration gradients inside the growing particles during slurry polymerizations, and temperature gradients outside the particles during polymerization in the gas phase.	Mckenna et al[4]
Computational f1uid dynamics to study the heat transfer from catalyst to polymer particles during ethylene polymerization in a gas phase reactor	The importance of conductive heat transfer, particle–particle and particle–wall interactions was raised.	Mckenna et al[5,6]
Particle-overheating in olefin polymerizations	Modeled and studied particle-overheating phenomena for an entire population of particles for different residence times and catalyst particle size distributions.	Zacca et al[7]
Influence of catalyst particle size on overheating for gas phase polymerizations using computation fluid dynamics	The larger the initial catalyst particle size, the higher the temperatures inside the particle. Further it was shown that particle interactions play a large role in the heat transfer, due to which both convection and conduction are important	Eriksson et al[8]

Work	Observation / Remarks	Citation
Morphogenesis model and Viscoelastic model	Discussed the influence of local particle overheating and temperature on the visco-elastic properties as well as the stress (and relaxation time) for a growing polymer particle	Grof et al[9], Kittilsen et al[10]
Partial melting of polymer occurred at high temperatures in gas phase polymerizations	This partial melting lead to a diffusion limitation which was found to be partially responsible for an observed decrease in the polymerization rate at elevated temperatures (>99°C).	HanAdebekun et al[11]
Optical and infrared imaging of growing polyolefin particles	The local particle surface temperature rise could be as high as 20K-30K depending on the reaction rate and particle size	Pater et al[12], Banat et al[13]
Polymerization at higher temperatures	Reduction in fines at higher temperatures during both pre-polymerization and polymerization due to a softer polymer matrix	Banat et al[13], Llinas et al[14]

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Acknowledgements

Life during my PhD, as with most people, has been very interesting, fascinating, demanding and challenging on many an occasion. During this period I came across a number of people in academia, industry and personally as well, who have contributed in some way or the other to my success and my progress as an individual. Reflecting back, I would like to take this opportunity to express my gratitude to all who have helped me during this interesting phase of my life.

Special thanks to my supervisor, Prof. Günter Weickert, who gave me this wonderful opportunity to work in his group, in the field of polyolefins. Thanks Gunter! It was indeed a pleasure working with you and I sure did learn a lot from you during this time. Your inquisitiveness, enthusiasm, passion for the field and attention to finer details are some of things that I admire and would like to imbibe in my career.

I would also like to express my gratitude to my committee members Prof. K-H. Reichert (TU Berlin), Prof. Cor Koning (TuE), Prof. W.P.M. van Swaaij (University of Twente), Dr. Martin van Sint Annaland (University of Twente), Dr. Erik van Praet (Borealis) and Dr. K.D. Hungenberg (BASF SE). I am very grateful to Dr. John Chadwick (TuE) for all his valuable inputs and Dr. Sascha Kersten (University of Twente) for his help.

I would also like to take this opportunity to thank the Dutch Polymer Institute (DPI) for funding my project “Fines generation in ethylene polymerizations” and the University of Twente for the excellent facilities and atmosphere during my entire stay in Enschede, the Netherlands. I would like to thank Borealis for helping me with their catalyst and Dr. Michiel Bergstra (Borealis) for all the good discussions, valuable inputs and ofcourse friendly advice during my masters and PhD. I would also like to express my gratitude to my group leader Dr. Achim Stammer (BASF SE) for his support and guidance since the time I joined BASF SE.

It was indeed fantastic to work in the High pressure lab (HDL) in Twente and I wish to acknowledge the technical assistance of Geert Monnink, Fred ter Borg, Karst van Bree, and Johan Agterhorst for helping me with my setup. I wish to also thank my colleagues from the former IPP (Industrial Polymerization Processes) group - Michiel, Inge, Yahya, Ravi, Makarand, Ide, Majid, Peng Fei, Jing Yu - for all the nice discussions and the enjoyable hours.

Personal thanks are due to my friends - Balaji, Ragav, Anand, Jiten, Vishnu, Manish, Charu, Vinay, Ganesh and the rest - for all the good times we spent together. A special thanks to all members of my cricket team from Hengelo-1 (Andrew, John, Johan, Didi, Rob, Wilhem, Rulof, Rahim). I thoroughly enjoyed playing league cricket for Hengelo for 4 years and also managing to win the Championship in 2006. I had great fun playing badminton for DIOK 13 during the winter of 2005-2006 along with my team mates Ambatti and Ramkrishna. Many thanks to my colleagues in BASF SE – all the desi junta (Sachin, Vinit, Mano, Karthik, Vijay, Ketan, Ravi, Sameer and their families), Gimmy, Mohammed, Ali, Tobias, Fatemeh, Brian – for all the good times (*coffee!*) that we have had together during the last 2 years. I would also like to express my gratitude to my ex-bosses at Unilever Research India (Bangalore) – Rajan, Kartik, Narayanan, Maltesh, Glyn, Benji – for all the support and motivation.

Most importantly, I would like to convey my deepest appreciation to my parents. “Thanks” would be too small a word to acknowledge what they have done for me over the years and enabled me to become what I am today. I hope I have made them proud in whatever little way I could. Special thanks to my sister, Jayanthi, for being a real inspiration to me during my early student days. Many thanks to her family too. I also wish to express my gratitude to my in-laws for their continued support and encouragement and many thanks to my father-in-law for making it to my defence. I would also like to thank all my other relatives for their constant motivation in some way or the other. Last, but not the least, my deepest appreciation also goes to my wife, Archana, for her patience, support, and encouragement during the last 3 odd years. Thanks so much for standing by me at all times and helping me through some difficult phases.

Finally, I would like to thank all the people who were not mentioned but have helped me in some way or the other to complete my work successfully.

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Shankara Narayanan Keelapandal Ramamoorthy (Shankara Keelapandal) was born on the 28th of January 1979, in Madras (Chennai), India. He did his schooling in Bangalore, and went on to receive his Bachelors in Chemical Engineering from the Bangalore University (B.M.S. College of Engineering, Bangalore) in September 2000. His dissertation was titled the "*Design and Optimization of a Compact Heat Exchanger*" and the project was carried out in association with Aeronautical Development Agency (ADA) under the guidance of Dr. C. Ranganayakulu and Dr. Shiny Joseph. He then proceeded to work with Unilever Research India (URI, Bangalore) for 2 years as a Research Officer / Consultant, focusing on the processing of detergent bars and the evaluation of new detergentless washing techniques. In January 2003, Shankara Keelapandal joined the International Masters Programme at the University of Twente, the Netherlands, in the Industrial Polymerization Processes (IPP) group of Prof. G. Weickert. In March 2004, he graduated with a Masters in Chemical Engineering from the University of Twente. His masters dissertation titled "*Gas phase co-polymerizations of Ethylene/1-Hexene with heterogeneous metallocene catalyst* " was done under the guidance of Prof. G. Weickert and supervision of Dr. Michiel Bergstra. In April 2004, he started with his PhD project in the same group under the able guidance of Prof. G. Weickert to study the mechanism of fines generation in ethylene polymerizations. The author has been working as a Research Scientist in the Process Development Group for Global Polymer Research at BASF SE, Ludwigshafen, Germany since July 2007.