Quantification of Polyethylene Wax in Semibatch Laboratory Reactor and a Study of Different Parameters on Wax Production as a By-Product in the Slurry Ethylene Polymerization

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ABSTRACT: In coordination polymerization of alpha-olefins utilizing Ziegler-Natta catalysts via slurry, polyolefin is produced with other by-products such as polyethylene wax. Wax is defined as a linear short chain saturated by hydrocarbons in the relevant industries. Hexane and heptane are two of the most common suspending agents for the slurry process and wax molecules are soluble or swollen in these kinds of liquids. After termination of polymerization, wax separates from the main product by physical processes. A procedure for wax quantification in a laboratory reactor is suggested. Also, impacts of various factors such as reaction duration, pressure, and cocatalyst on wax generation have been investigated. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The application of Ziegler-Natta catalysts, based on transition metals, for the polymerization of olefins has been developed over the last 50 years. Various aspects of these catalysts and their polymerization have been reported in several reports and articles.[1–6]

Wax is low molecular weight tail in the molecular weight distribution of polyolefin, produced as the by-product of ethylene polymerization by Ziegler-Natta catalysts in the slurry phase, and because of the separation costs and decrease in main product yield it is not desirable. Wax generation during polyethylene production using slurry phase is not avoidable though no wax generation happens when different production methods are applied (for example in gas phase/fluidized bed reactor). Waxes have molecular weight in the range of 200–1000 g/mol but the desired polymer is in the range of 10,000–6,000,000 g/mol.[7,8]

Upon the initiation of polymerization, oligomer, wax, and long chain polymers generate. Polyethylene is insoluble in the suspending agent and can easily be separated by filtration. Oligomers separate from the suspending agent simply because of their low molecular weight and exit out along with the unreacted monomer when the reactor depressurizes. Together with the increase in chain length, the melting point increases.

The knowledge of wax content in the mother liquor is an essential criterion for the system to control in industry. Mother liquor is used as a suspending agent which has been recovered from polyethylene by a physical separation and contains wax, cocatalyst, and mainly a suspending agent. The suspending agent is returned to the production line by distillation and the wax remains.

Many different factors are able to change the wax amount in the slurry phase such as temperature, pressure, concentration of molecular weight controlling agents (hydrogen), cocatalyst, type of suspending agent, existence and concentration of electron donor compounds, presence of water, impurities and … .

The kinetic scheme of coordinative polymerization of α-olefins describes other reactions known as chain transfer reactions other than the main reaction.[10,11] Four types of chain transfer reaction include:
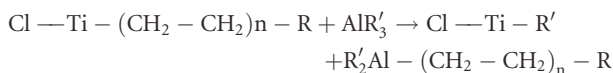
1. Transfer to ethylene by transferring hydrogen from the β-carbon of the propagating chain to the coordinated monomer:

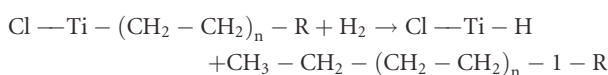$$Cl-Ti-(CH_2-CH_2)_n-R+CH_2=CH_2 \rightarrow Cl-Ti-CH_2CH_3+CH_2=CH-(CH_2-CH_2)_{n-1}-R$$
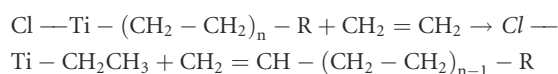
2. Transferring a hydrogen atom from the β-carbon of the propagating chain to the transition metal of the active site (β-hydrogen elimination):

$$Cl - Ti - (CH_2 - CH_2)_n - R \rightarrow Cl - Ti - H$$
$$+ CH_2 = CH - (CH_2 - CH_2)_{n-1} - R$$
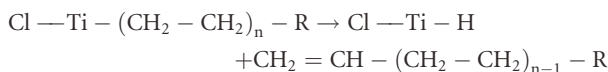
3. Transfer to organoaluminum compound (co-catalyst):

$$Cl - Ti - (CH_2 - CH_2)n - R + AlR'_3 \rightarrow Cl - Ti - R'$$
$$+ R'_2Al - (CH_2 - CH_2)_n - R$$

4. Transfer by molecular hydrogen:

$$Cl - Ti - (CH_2 - CH_2)_n - R + H_2 \rightarrow Cl - Ti - H$$
$$+ CH_3 - CH_2 - (CH_2 - CH_2)_n - 1 - R$$

As it can be seen the scheme also anticipates the generation of lower molecular weight components such as waxes.

With this in mind, a common suspending agent in the slurry process for the production of polyethylene is often Hexane or Heptane. Wax molecules are liquid or solid (against oligomers) and the density is about 0.74–0.85 g/cm^3 that is very near to polyethylene (0.88–0.94 g/cm^3); however, it can be removed by physical operation. Wax is soluble (low molecular weights) or partially soluble (higher molecular weights) in the suspending agent. Higher molecular weight waxes swell in the suspending agent (especially at elevated temperatures); therefore, the density decreases to near the suspending agent and this makes it feasible to separate physically from the polymer along with the mother liquor. The generated wax can be measured after drying by gravimetery and this is the exact procedure that is employed in industry and our base for estimation in a laboratory reactor.

Since polyethylene is the main product of Ziegler-Natta catalyst systems, polyethylene wax is barely applied and mentioned in literatures. In this article, a method for the determination of the total wax is described and then the effect of some of the most important variants (those which are common to consider in Ziegler-Natta type systems and have the most effects on efficiency and the way that reaction continues) on the amount of wax is studied. Although there are several different definitions for wax and in some cases low molecular weight polyethylene is regarded as wax, the by-product of ethylene coordinative polymerization applying the slurry method is considered in this article.

MATERIALS

Ethylene and Nitrogen (purity > 99.99%) were passed through columns packed with moisture and oxygen scavenger, respectively. Hexane (Merck) was dehydrated by refluxing through a distillation column using sodium as a dehydrating agent under dry nitrogen. Then hexane was dried over a molecular sieve of 0.4 and 0.5 nm (same portion) for 24 h to reach less than 5 ppm. Other reagents were used without purification [Hydrogen

(>99.9%), TEAL (Triethylaluminum) solution 1.0M in hexanes (Sigma Aldrich) and TIBAL (Triisobutylaluminum) solution 1.0M in hexanes (Sigma Aldrich)].

Catalyst

A Mg(OEt)$_2$-Supported TiCl$_4$ catalyst was used for this study. The catalyst used contains 2.7% Ti (w/w). The procedure of preparing this type of catalyst has been described in the literature.[12–15] In order to increase the dosage accuracy, the prepared catalyst was diluted 10 times with dried hexane.

EXPERIMENTAL

Polymerization

The polymerization was carried out in a 5 L steel jacket Büchi autoclave reactor fitted with a thermocouple equipped with a mechanical seal stirrer (variable speed, anchor form) in the slurry phase.

After running out of all moisture and air by nitrogen, 2700 mL of hexane and 2.0 mL of TEAL (1.0M in hexane) were added and the mixer was turned on to annihilate any probable contamination. After 5 min, 1.0 mL of the diluted catalyst (containing 0.042 mmolTi) was added by using dried syringe. The reactor was warmed up to 80°C and ethylene was supplied continuously at 6 bars for 1 h. The polymerization was terminated by injecting ethanol while the mixer was working after switch off the ethylene supply and depressurizing the reactor to atmosphere pressure. It has been observed in some literatures that hydrochloric acid was applied to stop the reaction. This procedure is not suitable because hydrochloric acid may solve some titanium in the final product and wash it out so it would interfere in Ti residua determination in the final product.

Wax Determination Procedure

After termination of the polymerization, the reactor cooled down to below 40°C and untreated and generated gases were slowly released by the upper valve and then this valve closed. Hexane was gradually transferred out by the force of nitrogen to a preweighted seal vessel by means of a stainless steel pipe connected to the lower valve (Lower valve should not open too much to avoid outflow of any polyethylene particles along with hexane). After that the lower valve closed and 2700 mL of hexane was ejected and then after closing the valves, the mixer was turned on for 5 min. Hexane was added to the rest and the washing stage was repeated to ensure that the entire wax is extracted from the reactor. The vessel was reweighed to get the net weight of the gathered mother liquor.

Considering that the mother liquor contains cocatalyst (wax carries a high concentration of aluminum, unlike polyethylene) and it partially converts to aluminum oxide (nonvolatile) during the drying stage, and also evaporates along with other volatiles, it should be totally converted to get a repeatable and reliable result. TEAL reacts with water and releases hydrocarbons and short chain alcohols and ultrafine aluminum oxide. After transferring 400 mL of mother liquor and 50 mL of hydrochloric acid (1N) to a screw cap Erlenmeyer, the mixture is exposed to vigorous shaking for 10 min. The suspension was settled down for a night to ensure complete separation of the phases and deposition of aluminum oxide. The upper layer is the modified

Table I. Standard Reaction Condition (Exp No1)

Exp no	Duration (min)	Cocatalyst (mmol)	H_2O ppm in Hexane
1	60	2 (TEAL)	5
Total P (Bar)	Ti Residue in PE (ppm)	Al Residue in PE (ppm)	Al/Ti
6	3	10	48

The reference state which applied for this research and just the targeted item is changed and traced.

mother liquor. For a double determination, two 250-mL conical flasks with ground stopper were preweighted (m_1). To avoid any evaporation during weighting, a 100-mL glass syringe was used. The syringe was filled by the modified mother liquor and was discharged two times. The syringe was filled by the modified mother liquor and then weighted (m_{s1}) and the mother liquor was introduced to a conical flask. The syringe was reweighed (m_{s2}) so the difference is the exact weight of the sample (m_0).

$$m_0 = m_{s2} - m_{s1}$$

The hexane phase was separated off by evaporating and the residue was dried in a vacuum oven in two steps (First stage for about 35 min at 500 mBar at 60°C, the second stage for 20 min more at 20 mbar at 80°C). After cooling to room temperature the remainder was determined by weighing the flasks (m_2) and then the wax percentage was calculated according to the equation below:

$$\text{Wax content } \% = ((m_2 - m_1)/m_0) \times 100$$

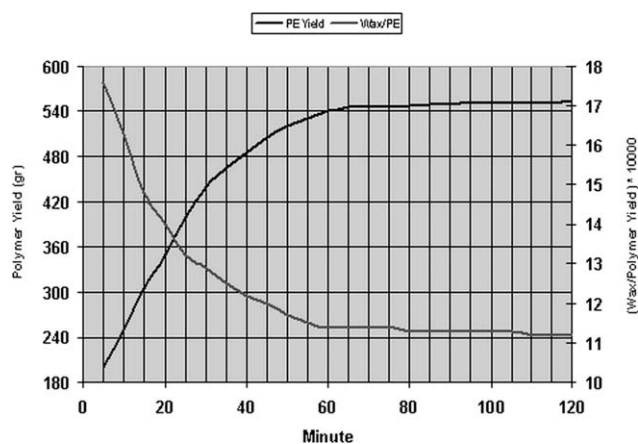And finally the total wax in the batch laboratory reactor:

$$\text{Total wax (g)} = (\text{Wax content } \% \times \\ \text{Total gathered mother liquor (g)})/100$$

CHARACTERIZATION

The total obtained polymer was fully gathered and then washed with ethanol and dried in vacuum at 50°C to a constant weight. The viscosity average molecular weight (M_v) of the polymer was obtained using Ubbelohde suspended level dilution viscometer. The temperature of the viscometry was maintained at 133 ± 1°C by boiling chlorobenzene in the vapor jacket of the viscometer. The M_v was calculated from the intrinsic viscosity using the Mark-Howink Sakurada equation.

Figure 1. The effect of polymerization duration on yield and PE/Wax ratio.

$$[\eta] = K \times M_v^\alpha$$

where K and α are 6.77×10^{-4} and 0.67, respectively.[16]

The amount of titanium in the prepared catalyst and other minerals (Al and Ti) in the final polymer were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Microwave digesting was applied to be decomposed.[17] The number of double bond per chain was calculated by FTIR spectroscopy.[18] Moisture content in applied hexane was quantified by the Karl-Fischer method.[19]

RESULTS AND DISCUSSION

The reference condition for polymerization (standard state) has been described before. Other experiments were done in the same conditions and only the targeted item has been changed [see Table I (experiment No.1)].

The Effect of Polymerization Duration
As shown in Table II and Figure 1, the polymerization yield increases and then reaches a constant level but the wax to polyethylene ratio decreases by increasing the reaction time. This indicates that most of the wax was produced in the early stages of the polymerization, also with regard to the total wax that reached a steady level at the end of the reaction. Another interesting fact deduced from Table II is that the double bonds per each polymer chain increase when reaction time increases. This attests that near the end of the polymerization (when less amount of wax is generated) transfer to monomer and β-hydrogen elimination are the main cause of the chain transfer. These

Table II. Polymerization Duration and Polymer Specifications (Exp No2-6)

Exp no	Minutes	Yield (g)	M_W	Wax (g)	Wax/PE *10000	[C=C]
2	5	239	450,000	0.42	17.6	0.18
3	15	305	560,000	0.45	14.8	0.21
4	30	402	790,000	0.52	12.9	0.24
1	60	545	960,000	0.62	11.4	0.50
5	90	546	950,000	0.60	11.0	0.55
6	120	550	970,000	0.63	11.5	0.63

Table III. Ethylene Pressure Effect on Wax Content and Polymer Specifications

Exp no	Total Pressure (Bar)	Yield (g)	M_W	Wax (g)	Wax/PE *10,000	[C=C]
7	2	84	480,000	0.76	90.5	0.29
8	4	291	890,000	0.62	21.3	0.44
1	6	545	960,000	0.62	11.4	0.50
9	8	577	1,000,000	0.60	10.4	0.52

series of experiments (Exp1-6) also imply that there is more probability to form wax when shorter polymers are being generated. Another interesting fact that may be inferred form these data is that the used catalyst contains several types of active centers (this is why its PDI is higher than 2) therefore the centers that form relatively low molecular weight PE fractions (which contain the largest wax fraction) are unstable and may die after 10–15 min. The centers that produce the high molecular weight polymer are more stable (although they also die after about 60 mininutes). This is why the wax fraction decreases with time.

The Effect of Ethylene Pressure
As it can be seen from Table III, there is a predictable ratio between the ethylene pressure and the final yield. Seeing that the polymerization is supposed to be carried out in the slurry phase, based on Henry's law, ethylene concentration increases in hexane by increasing the pressure. If the polymerization reaction is running at increasing ethylene pressure, the average molecular weight of the polymer increases. Consequently, the fraction of the low molecular weight component in the molecular weight distribution (wax) strongly decreases. In lower pressure, the lessened polymer is yielded with the lower molecular weight. In this case, more wax and a higher ratio of the wax to polymer is obtained.

The Effect of Hydrogen
In these series of experiments, hydrogen was applied as a molecular weight modifying agent loaded at 25°C before ethylene to the defined pressure. After closing the hydrogen valve, the reactor was warmed up to 80°C, and then ethylene was supplied continuously to the reactor to keep the total pressure constant at 6 bars.

As it is shown in Table IV, wax increases significantly when hydrogen is used as the chain-transfer agent. Hydrogen also reduces the double bonds number in each polymeric chain and

Table IV. Hydrogen Pressure Effect on Wax Content and Polymer Specifications

Exp no	Hydrogen PRESSURE (Bar)	Yield (g)	M_W	Wax (g)	Wax/PE *10,000	[C=C]
1	0	545	960,000	0.62	11.4	0.50
10	1	207	230,000	1.24	59.9	0.27
11	2	127	140,000	1.86	146.5	0.16
12	4	43	90,000	2.23	518.6	0.08

Table V. Cocatalyst Concentration and Type (Effect on Wax Content and Polymer Specifications)

Exp no	Cocatalyst (mmol)	Yield (g)	M_W	Wax (g)	Wax/PE *10,000	[C=C]
1	2 (TEAL)	545	960,000	0.62	11.4	0.50
13	4 (TEAL)	511	800,000	0.94	18.4	0.37
14	6 (TEAL)	453	720,000	1.40	30.9	0.25
15	2 (TIBAL)	714	1,180,000	0.57	8.0	0.41

this means when hydrogen is applied, the influence of other transferring agents are negligible. Experiments 10, 11, and 12 demonstrate that the wax generation intensifies with the presence of any molecular weight reducing agent.

The Effect of Cocatalyst
TEAL is one of the most common cocatalysts in these kinds of polymerization systems. Also, it is reported in many papers that the utilization of other types of cocatalyst such as TIBAL are able to change the polymerization path. According to data from Table V, the wax content enhances to the higher level when the cocatalyst concentration (TEAL) increases but the double bonds decrease. Thus, in the absence of hydrogen, the organometallic plays the main role in chain transferring. Regarding the reduction of molecular weight, the polymer yield does not reduce as expected and this means that there is a broadening in molecular weight distribution (higher value for PDI). Therefore, it could be perceived that any chemical agent that is able to broaden the MWD causes more wax generation. In experiment No. 15, another kind of cocatalyst was used. TIBAL had different effects on the polymerization (Table V). Despite it being added in the same molar portion to the reaction medium, a different ratio of the wax to polymer is gained and clarifies the important role of the organometallic compound on the wax generation.

The Effect of External Electron Donor
External donors have been found to play an important role in the coordination polymerization of α-olefins.[20,21] It is well known that external donors affect catalyst activity, MW and MWD. The Ziegler-Natta type catalysts are sensitive to the compounds which have oxygen and nitrogen in their molecular structure.[22,23] THF (Tetrahydrofuran) was used as an external electron donor. By dosing 2 mmol THF, some changes occurred to the reaction route. The expected MW increased in spite of the decrease in the yield of polymerization and meanwhile, the wax content reduced. According to this experiment, an external

Table VI. External Donor Effect (THF - Exp 16) and Impurities Effect (H_2O - Exp 17) on Wax Content and Polymer Specifications[a]

Exp no	THF/H_2O	Yield (g)	M_W	Wax (g)	Wax/PE *10,000	[C=C]
16	50 mmol THF	422	1,050,000	0.35	8.3	0.48
17	45 ppm H_2O[a]	403	590,000	1.05	26.1	0.48

[a]When Fresh Hexane Applied Without Any Pretreatment.

donor can also significantly affect the wax quantity (see Table VI). As the external donor changes, the mechanism of the monomer insertion to the active sites of the transition metal complex even the kinetic of the polymerization changes, therefore the wax content varies.

The Effect of Impurities

Regarding the high sensitivity of Ziegler-Natta catalysts to moisture, hexane and other components are dehydrated before use. In this experiment (Exp. No 17), fresh hexane is used without any pretreatment or dehydration. Other parameters are retained similar to Experiment No. 1 (the standard reaction condition). The initial water content of the fresh hexane was determined (45 ppm). Experimental data shows that less yield and more wax has been obtained (Table VI).

CONCLUSIONS

In the coordination polymerization of ethylene in the slurry phase, wax is an inevitable by-product. This is the integral part of any olefin polymerization and could be defined as the low molecular weight fraction of the combined polymer material. The wax fraction depends on two principal parameters, the average molecular weight of the polymer and the presence of low molecular weight components in the molecular weight distribution. The factors that affect any of these two properties affect the relative content of the wax. It is feasible that the quantification of wax in a laboratory reactor by gravimetery be carried out in order to study different variants in conditions that the total wax is separated and purified. In the semibatch reactor, wax is generated in the early stage of reaction but continuous reactors generate steadily. Several various chemical or physical factors are able to change the wax quantity although in view of the fact that there is a big difference between the molecular weight of wax and the main product, it could be concluded that wax is the result of chain transfer reactions to other reaction components such as cocatalyst and particularly hydrogen. Also, as result of deactivation of the catalyst (catalyst poisons and any impurities) the wax content increases and these kinds of reactions have the most likely portion and were observed to occur at the beginning of the reaction, especially.

On the basis of the results, since physical or chemical parameters are able to vary wax quantity, the lower and constant wax content as a by-product in continuous industrial production is an indication of desirable purity in raw materials. Also, the nonexistence of catalyst poisons enhances minimum fluctuations in physical variants such as temperature, pressure, and et cetera.

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