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Preparation of Ultra High Molecular Weight Polyethylene Using Ziegler-Natta Catalyst System: Optimization of Parameters by Response Surface Methodology

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Abstract

The ultra-high molecular weight polyethylene (UHMWPE) was prepared using titanium tetrachloride ($TiCl_4$) supported by $MgCl_2$ (ethoxide type), accompanied by triisobutylaluminium (TIBA) as co-catalyst. These all constituted the Ziegler–Natta catalytic system. $MgCl_2$ is one of the best supports for Ziegler-Natta catalyst in order to increase its yield.In the present study, the process variables were investigated through response surface methodology (RSM) to optimize the productivity of the catalyst and also the molecular weight of the polymer. Taking this into consideration a three-level Box-Behnken design for three factors with temperature (X_1), monomer pressure (X_2), and [Al]/[Ti] molar ratio (X_3) as the independent variables were selected. Different molar ratio of [Al]/[Ti] is achieved by changing the amount of the co-catalyst.The dependent variables were productivity and molecular weights of the prepared polymers. Specifically, using these three parameters at three levels including 50, 60, and 70°C for temperature; 4, 6, and 8 bar for pressure; and 150, 250, and 350 for [Al]/[Ti] molar ratio. The RSM yielded optimum reaction conditions equal to: temperature of 55°C, pressure of 8 bar, and [Al]/[Ti] molar ratio of 230. Under these optimum conditions, the productivity and molecular weight were 2628 g PE/mmolTi.h and 5.09×10^6 g/mol, respectively.

Keywords: *UHMWPE, Ziegler-Natta, Optimization, Response Surface Methodology*

1. Introduction

Ultrahigh molecular weight polyethylene (UHMWPE) is a unique polymer with outstanding physical and mechanical properties (i.e., high strength and stiffness, good fatigue, and wear characteristics), and is widely used in a wide spectrum of applications such as bearings, pulleys, and joint replacement prostheses in the human body [1-4].

Ziegler-Natta catalyst was one of the most important discoveries in chemistry for its successful synthesis of polyolefin at low pressure and temperature [5,6]. Approximately 50% of all high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) is produced using supported titanium–magnesium catalyst containing titanium chloride in the carrier and activated magnesium chloride [7].

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Modern production of ultrahigh molecular weight polyethylene (UHMWPE) is based on the use of this method as well [8].

In the polymerization, polymerization method, reaction conditions such as temperature, pressure, type of catalyst, cocatalyst, and chain transfer agent can significantly effect the composition, molecular weight and its distribution, degree of branching and the final structure of the prepared polymer [8-10].

Response surface methodology (RSM) is an effective method for optimization and developing regression equations that describe relations between input parameters and output responses [11]. It is well known that molecular weight has a significant effect on the processability and end-use properties of olefin polymers. Therefore, it was necessary to control the molecular weight of polyolefin to produce various grades suitable for the many end-use applications of polyolefin.In this contribution, optimization of process condition such as temperature, monomer pressure and [Al]/[Ti] molar ratio on productivity, and molecular weight was carried out via Box-Behnkendesign.

2. Experimental

2-1. Materials

Ethylene monomer (industrial-grade) was supplied by Amir Kabir Petrochemical Co. (Mahshahr, Iran) and further purified by passing through molecular sieve columns (4A type having a 4-A pore size). High-purity argon (≥99.999%) was used to produce an inert atmosphere for the catalytic system preparation as well as the polymerization. Industrial grade n-hexane was supported by Amir Kabir Petrochemical Co. (Mahshahr, Iran) and dried by a sodium benzo-phenole complex (diphenylketyl). Titanium tetrachloride ($TiCl_4$, Riedel-de Haen Chemical Laboratory) was used as the catalyst while Magnesium ethoxide ($Mg(OEt)_2$, Fluka) and dibutyl phthalate (as an internal donor, Merck) were used for preparation of the catalyst. Triisobutyla-luminium (TIBA, Aldrich) was used as the cocatalyst.

2-2. Catalyst preparation

The preparation of catalyst was carried out according to the method developed by our group [2-3,12-13]. Magnesium ethoxide (8 g) was fed into a triple-necked, round-bottom flask which was equipped with a magnetic stirrer and immersed in an oil bath. Two openings of the flask were equipped with gas valves. One was connected to a vacuum pump while the other was connected to the ethylene monomer cylinder; the third opening was sealed with a rubber septum for further chemical injection. Degassing 3 times and backfilling the flask with high-purity argon caused an inert atmosphere to assure a completely inert condition. After that, 150 mL of n-hexane/ toluene (50/50 wt%) was injected into the flask. The temperature gradually increased to 80°C while the flask contents were vigorously stirred. Upon reaching the desired temperature, $TiCl_4$ (8 mL) and dibutyl phthalate (2 mL) were injected into the flask and its contents were stirred at constant temperature for 2 h. Finally, after cooling the flask contents down to 50°C, they were washed 10 times with n-hexane under an argon atmosphere to assure complete removal of the unreacted residuals from the catalyst complex. At the end, the

flask was cooled down to room temperature; the catalyst was dissolved into 100 mL of n-hexane, and the produced catalyst complex was stored under argon atmosphere for polymerization process. As schematically shown in Fig. 1, the Ziegler-Natta catalyst was supported over Magnesium ethoxide.

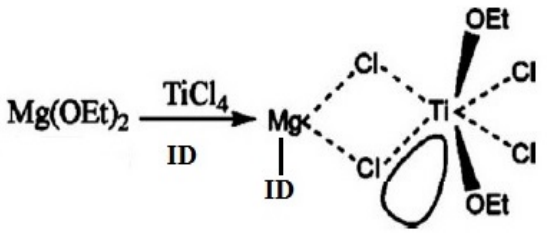

Figure 1. Schematic of the mechanism of supporting Ziegler-Natta catalyst on a $Mg(OEt)_2$.

2-3. Polymerization

A 1 L pressure reactor (versoclave; Buchi AG, Flawil, Switzerland) equipped with a mechanical stirrer, a temperature controller, and a pressure control system was purged with high-purity argon at 1.1 bar at 90°C to assure a completely dry and inert atmosphere. Then, 400 mL of degassed nhexane was transferred to the reactor. Subsequently, while stirring, degassed Triisobutyla-luminium (TIBA) was injected into the reactor. After 5 min, 10 mL of the catalyst complex produced beforehand was added to the mixture and instantly ethylene monomer was introduced into the reactor at different pressure. Finally, after the polymerization was carried out for the desired time, the ethylene inlet was closed, reactor was purged with air, and 10 mL of concentrated HCl was injected into the reactor to deactivate the catalyst and terminate the polymerization. After bringing the reactor temperature down to room temperature, the contents of the reactor were vacuum filtered, washed with ethanol and acetone, and subsequently dried under vacuum at 80°C for 24 h.

2-4. Characterization

The viscosity average molecular weight (M*v*) of the synthesized polyethylene was determined by the Mark-Houwink equatioin [3]: $\overline{M} = 5.37 \times 10^4 [\eta]$ after the measurement of intrinsic viscosity of diluted solutions of UHMWPE in decalin at 135°C.

2-5. Experimental design and data analysis

Response surface methodology (RSM) was used to design experiments and analyze the effects of considered parameters[16]. Monomer pressure, temperature, and [Al]/[Ti] molar ratio were considered as the important parameters that affect Productivity and polyethylene molecular weight. A Box-Behnken design of experiments by each of these parameters at three levels, i.e., polymerization temperatures (50, 60, and 70°C), monomer pressures (4, 6, and 8 bar), and[Al]/[Ti]molar ratio (150, 250, and 350) was used to determine the optimal recipe in preparation of UHMWPE. Box–Behnken experimental design was established using Design Expert software (7.0 trial version). A total of 15 runs were performed to optimize the process parameters and experiments were carried out according to the actual experimental design matrix. Three levels were attributed to each factor, coded as -1 (low), 0 (medium), and +1 (high). The range and levels used in the experiments are listed in Table 1.

Table1. Independence Factors and their Coded Levels used in Box-Behnken design.

Variable	Real Values of Coded Levels		
	-1	**0**	**+1**
Temperature, X_1 (°C)	50	60	70
Monomer Pressure, X_2 (bar)	4	6	8
Al/Ti Molar Ratio, X_3	150	250	350

The mathematical relationship between the three variables and the response can be expressed by the second order polynomial equation:

$$Y\beta = {}_0\beta + {}_1X_1\beta + {}_2X_2\beta + {}_3X_3\beta + {}_{11}X_1{}^2\beta + {}_{22}X_2{}^2 + \beta_{33}X_3{}^2\beta + {}_{12}X_1X_2\beta + {}_{13}X_1X_3\beta + {}_{23}X_2X_3 \quad (1)$$

Where, Y is the response; β_0 is a constant; β_1, $\beta_2\beta$,$_3$ are linear coefficients; $\beta_{11}\beta$,$_{22}\beta$,$_{33}$ are quadratic coefficients, and $\beta_{12}\beta$,$_{13}\beta$,$_{23}$ are cross-product coefficient. X_1, X_2, and X_3 are the factors to be studied.

3. Results and discussion

3-1. Model fitting for productivity and molecular weight

Fifteen experiments were augmented including three replications at the central point for evaluating the pure error. Table 2 lists the Box-Behnken experimental design employed in this work and the obtained results from the experiments.

Table 2. Experimental Box-Behnken design runs and corresponding results.

Run	T(°C)	P(bar)	Al/Ti	Productivity (g PE/mmolTi.h)	MW×10-6 (g/mol)
1	60	8	150	1944	5.34
2	50	8	250	2628	5.1
3	70	4	250	1302	3.86
4	70	6	350	2255	4.12
5	60	4	150	1068	4.4
6	70	6	150	1412	4.78
7	50	6	150	1353	5.11
8	70	8	250	2414	4.63
9	60	4	350	1225	3.72
10	60	6	250	2455	4.57
11	50	4	250	1176	4.11
12	50	6	350	1708	4.46
13	60	8	350	2604	4.62
14	60	6	250	2395	4.54
15	60	6	250	2410	4.61

Analysis of variance (ANOVA) results of the quadratic models are shown in Table 3. ANOVA indicated that the model equations derived by RSM could be adequately used to describe the catalyst activity and molecular weight under a wide range of operating conditions. P-value is the probability value used to determine the effect in the model that was statistically significant. The smaller the value of P, the more significant the corresponding coefficient. For a 95% confidence level, the P-value should be less than or equal to 0.05 for the effect to be statistically significant [17]. After eliminating insignificant parameters, the obtained models in terms of coded parameters were determined as follows:

$$\text{Productivity} = 2420 + 602.38X_2 + 251.88X_3 - 284.12X_1^2 - 255.88X_2^2 - 453.88X_3^2 \quad (2)$$

$$Mw = 4.56 - 0.17X_1 + 0.45X_2 - 0.34X_3 - 0.055X_1X_2 - 0.12X_2^2 + 0.072X_3^2 \quad (3)$$

where X_1, X_2, and X_3 are temperature, monomer pressure, and Al/Ti molar ratio, respectively.

Figs. 2 and 3 show the differences between actual and predicted process productivity and molecular weight, respectively. As can be seen, the predicted values by the models are reasonably close to the actual value obtained by the experiments. However, the actual and predicted values of molecular weight are somewhat closer than those of the productivity because the coefficient of determination (R^2) of the molecular weight model was found to be 0.9974 which is higher than the value of 0.9426 for the productivity model.

Table 3. Analysis of variance results for productivity and molecular weight.

Factor	Productivity		Molecular Weight	
	F-Value	**P-Value**	**F-Value**	**P-Value**
Model	28.56	0.0009	347.58	<0.0001
X_1	1.82	0.2354	262.99	<0.0001
X_2	157.36	<0.0001	1764.07	< 0.0001
X_3	27.51	0.0033	999.65	< 0.0001
X_1X_2	1.57	0.2661	13.18	0.0151
X_1X_3	3.23	0.1324	0.027	0.8754
X_2X_3	3.43	0.1233	0.44	0.5385
X_1^2	16.16	0.0101	2.60	0.1680
X_2^2	13.10	0.0152	60.75	0.0006
X_3^2	41.23	0.0014	19.47	0.0069

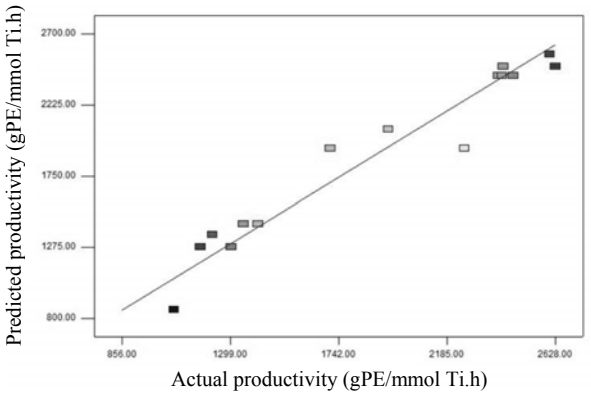

Figure 2. Plot of differences between actual and predicted catalyst productivity.

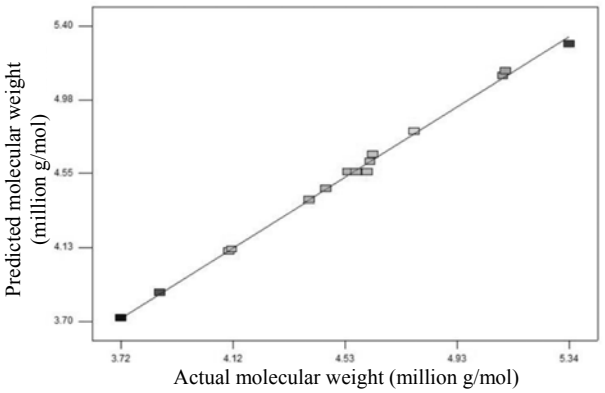

Figure 3. Plot of differences between actual and predicted molecular weight of synthesized polymers.

3-2. Effects of parameters

Figs. 4 and 5 show the surface plot of productivity and molecular weight as a function of temperature and pressure at the middle level of [Al]/[Ti] molar ratio. As seen in the Figures, pressure has positive effects, both on productivity and molecular weight. This could be due to the increasing of the monomer solubility in the solvent and monomer concentration near the catalyst active centers and more fragmentation of the catalyst at higher monomer pressure. Productivity increases as the temperature increases from 50 to 60°C and thereafter decreases further up to 70°C. By increasing of the reactor temperature, alkylation rate, active center formation, and polymerization rate increase, but irreversible deactivation of the active centers may also occur. It is obvious from Fig. 5 that temperature has a negative effect on molecular weight because of an increment in chain transfer reaction rate [14,15].

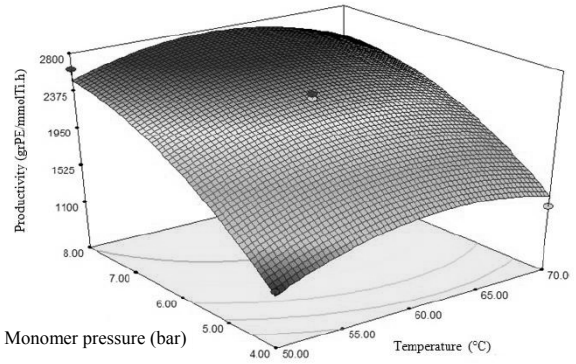

Figure 4. Productivity as a function of monomer pressure and temperature.

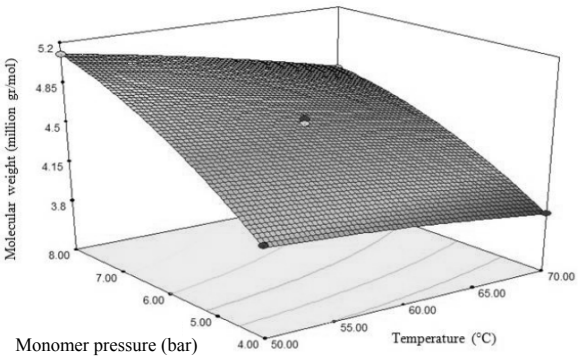

Figure 5. Molecular weight as a function of monomer pressure and temperature.

Figs. 6 and 7 show the surface plot of productivity and molecular weight as a function of [Al]/[Ti] molar ratio and pressure at temperature of 60°C. The plot related to the productivity response is more dome shaped. In these types, in one axis there is a linear increase in the catalyst activity, while in the other axis there is an increase in the catalyst activity only up to a certain extent and a decrease thereafter. This indicates that

there are critical values for [Al]/[Ti]ratio in order to get the maximum catalyst activity. At low concentration of TIBA, the impurity of the system has an influence on productivity and not all active centers were activated. At higher concentration than the optimum value the reduction of Ti^{4+} to Ti^{2+} occurred, which is less active for ethylene polymerization. The molecular weight surface plot shows the molecular weight decreases by increasing the [Al]/[Ti] molar ratio. However, since the reaction rate of chain transfer to cocatalyst compounds increases as the concentration of cocatalyst rises, a reduction in the molecular weight is expected.

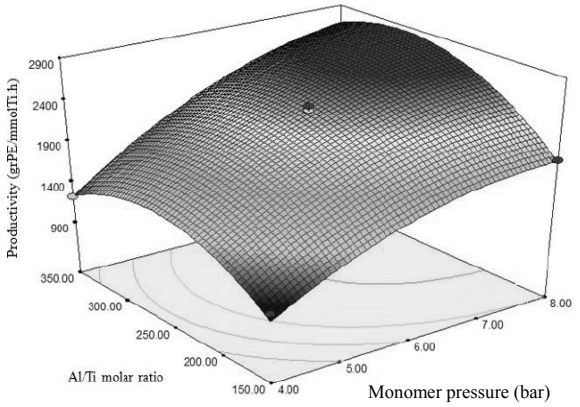

Figure 6. Productivity as a function of monomer pressure and [Al]/[Ti] molar ratio.

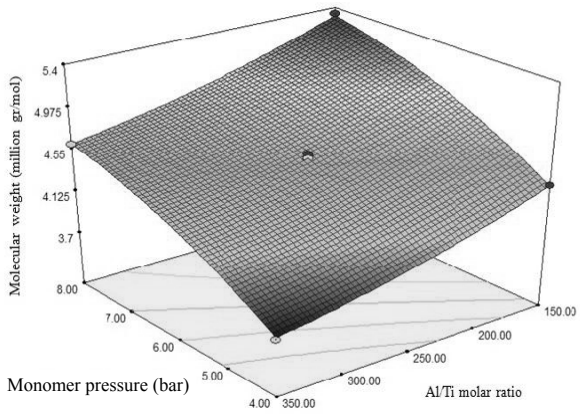

Figure 7. Molecular weight as a function of monomer pressure and [Al]/[Ti] molar ratio.

4. Conclusions

Response surface methodology was used to investigate most affecting parameters on ethylene polymerization catalyzed by Ziegler-Natta catalytic system for preparing ultra high molecular weight polyethylene (UHMWPE). Polymerization temperature, monomer pressure, and [Al]/[Ti] molar ratio were considered as the main process variables. A Box-Behnken design was developed by these three parameters while three levels were considered for each of them through Design-Expert 7 software. Productivity and viscosity average molecular weight were selected as the objective responses. Two empirical models to simulate the catalyst activity and molecular weight were developed in terms of the polymerization conditions by Box–Behnken design and an ANOVA test was performed. The correlation coefficient for the models was evaluated quite satisfactorily. The optimum values for temperature, pressure and [Al]/[Ti] ratio were found to be at 55°C, 8 bar, and 230, respectively.

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