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ORIGINAL PAPER

Ultra-high molecular weight polyethylene synthesis using externally modified Si-Mg-Ti Based Z-N catalyst system

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ABSTRACT

Ultra-high molecular weight polyethylene (UHMWPE) was synthesized using Bi-supported $SiO_2/MgCl_2/TiCl_4$ (Si-Mg-Ti) Ziegler-Natta catalyst in conjugation with triethyl aluminum (TEA). The impact of temperature and the presence of a chain-terminating agent were examined in the context of ethylene polymerization. The findings showed that as temperature decreases, the activity of the polymerization decreases, and the molecular weight of the polymer increases. Conversely, in the presence of a chain-terminating agent, the molecular weight of the polymer decreases. The introduction of triethyl borate (TEB) and tetraethoxy silane (TEOS) as an external donor has a pronounced effect on the catalyst activity, causing a significant decrease, while simultaneously leading to a substantial increase in the viscosity average molecular weight (M_v). Additionally, when a chain-terminating agent is added along with triethyl borate (TEB) in the system, it results in a significant decrease in molecular weight, albeit with a slight increase in activity compared to a system without a donor. The crystallinity, particle size and bulk density of the polymer synthesized with and without external donor have been also investigated. **Polyolefins J (2024) 11: 61-70**

Keywords: Si-Mg-Ti Ziegler-Natta catalyst; UHMWPE; ethylene polymerization; external donor.

INTRODUCTION

Ziegler-Natta (Z-N) catalysts have had a significant impact on various aspects of human life over the past few decades, mainly due to their role in the production of high-strength, low-cost, and lightweight polyolefin materials. These materials have contributed to advancements in technology, sustainability, and everyday convenience [1,2]. Polyethylene (PE) and polypropylene (PP) are most common and widely used polyolefin commodity plastics. The combination of their affordability, versatility, and outstanding physical properties has rendered them indispensable across various industries. Moreover, the continuous increasing demand for polymers in specialty applications has driven scientists and researchers to pursue advanced developments in polymer science and technology [3-5]. In general, advanced Z-N catalyst consists of magnesium dichloride ($MgCl_2$) support, titanium tetrachloride ($TiCl_4$) active catalyst, Lewis's base mainly internal donors and external donors and alkyl aluminum activator [6]. Currently, several grades of PP

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*Corresponding Author - E-mail: Virendrakumar.Gupta@ril.com (homo, random, and impact co-polymer-ICP) and PE (high-density polyethylene-HDPE, liner low-density polyethylene-LLDPE, and ultra-high molecular weight polyethylene (UHMWPE)) are commercially producing, by selecting the appropriate components of the Z-N catalyst.

UHMWPE is a liner long chain high molecular weight polymer. It is more commonly used in a specialty application due to its excellent mechanical, chemical, and physical properties. The superior properties of UHMWPE make it comparable to engineering plastics [7-14]. UHMWPE is generally synthesized via several catalyst systems Mg-Ti [15-16], Si-Mg-Ti [17], metallocene [18-19], and post-metallocene [20-23]. However, at commercial scale $MgCl_2$ supported Z-N catalyst is more popular due to better activity and providing superior product properties [24-26]. Despite, many advantages of Mg-Ti catalyst at the commercial scale, major drawbacks are attrition of catalyst during synthesis which, resulted in fines generation in polymerization, and also poor bulk density which, severely affects plant process [27].

These phenomena were reported in many articles by different scientists. Hence, to overcome the said issue, recently silicon dioxide (SiO_2) and $MgCl_2$ bi-supported Z-N catalysts reported in many articles for polyethylene synthesis. This catalyst is very much suitable for controlling the particle size of polymers [28-32], which improves catalyst activity as well as morphology significantly [33-36]. Generally, proper selection of catalyst and cocatalyst, donors, plant process parameters and reaction conditions are necessary for the production of UHMWPE [37-39]. Nowadays, internal and external donors play important roles in the polymerization of ethylene and propylene as its greatly influence catalyst activity, hydrogen response, tacticity and end-product properties. Mg-Ti and Si-Mg-Ti-based supported catalyst with internal donor have been reported in many articles for HDPE and UHMWPE synthesis [38-40] but the effect of external donor is still less explored for UHMWPE synthesis.

In this study, we employed a Si-Mg-Ti catalyst for the polymerization of ethylene. This process was conducted in the presence of TEOS within TEB as an external donor, at varying concentrations. Subsequently, we analyzed the influence of these varying concentrations on the polymer resin's molecular weight, thermal behavior, and bulk density.

EXPERIMENTAL

Materials

The silica-supported magnesium titanium Bi-supported $SiO_2/MgCl_2/TiCl_4$ catalyst (Si-Mg-Ti), with Ti of 2.0 wt.%, Mg of 2.2 wt.%, and mean particle size (D_m) of 9.1 μm, was obtained from Grace and employed without modification for the polymerization of ethylene. n-Decane (99.5 wt.%) and n-hexane (99.5 wt.%) utilized in the polymerization process were sourced from Labort Chemicals in Surat, India. All the solvents were used after drying over a molecular sieve. Co-catalyst triethylaluminium (TEA, 99.5 %) was received from Gudbranson, India. The co-catalyst was used after dilution to 10 v/v%. triethyl borate (TEB, 99 wt.%) and tetraethoxy silane (TEOS, 98.5 %) from Labort Chemicals, India, Surat, were used as external donors for ethylene polymerization. External donors were used after drying over a molecular sieve. Ethylene (purity > 99.9%) for polymerization was obtained from RIL, a commercial polypropylene plant. All the polymerization experiments were carried out in a nitrogen atmosphere.

Polymerization

Ethylene polymerization was conducted in a 4 L high-pressure Parr reactor equipped with a magnetic overhead stirrer, pressure regulator, safety valve, and heating and cooling jacket. A 4 L reactor was heated to 120°C under a nitrogen atmosphere for 2 h, the reactor was evacuated and purged with nitrogen several times and then cooled to 30°C. The reactor was filled with 2 L pre-dried n-hexane as reaction media followed by a small amount of 10 diluted TEAL to kill the moisture in the hexane. To saturate the solvent, the reactor was filled with ethylene for 10 minutes and then discharged. After reducing the pressure of ethylene gas from the reactor, the calculated amount of catalyst, TEAL and charged external donor were injected into the reactor. The polymerization was carried out for 1h with monoester and 2h with a diester catalyst system under 400 rpm stirring and a constant feed of ethylene. The polymer was filtered out and dried at room temperature after the completed reaction.

Characterizations

Molecular weight and viscosity average molecular weight

The polymer's viscosity-average molecular weight (M_v) was determined in decalin at 135°C, following the methodology outlined in the literature [41]. The calculation of M_v was based on the intrinsic viscosity, employing the Mark-Howink formula mentioned as Equation 1:

$$M_v = 5.34 \times 10^4 [\eta]^{1.49} \quad (1)$$

Thermal analysis

The thermal analysis of the variously synthesized polyethylene samples, employing different catalysts and donors, was carried out using a Differential Scanning Calorimetry (DSC) instrument in a nitrogen atmosphere. Samples weighing between 5 and 8 mg were carefully placed in alumina pans. The temperature was then increased from 30°C to 200°C at a heating rate of 10°C/min, utilizing the Perkin-Elmer model, USA. Additionally, during the cooling phase, the crystallization temperature was recorded, and the cooling rate was maintained at 10°C/min. The crystallinity of polymers was calculated by the following equation [38]:

$$X_c = \Delta H / \Delta H^\circ \times 100 \quad (2)$$

In this context, ΔH signifies the fusion heat for the polyethylene specimen, whereas ΔH° stands for the fusion heat of linear polyethylene, with a value of 290 J/g.

RESULTS AND DISCUSSION

A silica-supported magnesium Ti (Si-Mg-Ti)-based catalyst has been investigated for ethylene polymerization at different temperatures with and without external donors. TEOS and TEB were used as an external donor as shown in Scheme 1. The study included the use of a silica-supported magnesium titanium (Si-Mg-Ti) catalyst for the polymerization of ethylene at varying temperatures, both with and without the inclusion of external donors. Two specific external donors, namely TEOS and TEB are depicted in Scheme 1.

Silicon tetraethoxide, TEOS   Triethyl borate TEB

Scheme 1. External donor used with Si-Mg-Ti catalyst for UHMWPE synthesis.

The results of ethylene polymerization using Si-Mg-Ti catalyst in Al/Ti-100 with keeping different temperatures in n-hexane solvent indicate that with increasing temperature, the activity of the catalyst increases significantly. The catalyst activity at 80, 75, 70, 60, and 50°C temperatures was found 10.4, 10.1, 9.7, 4.4, and 2.5 kg_{PE}/g_{cat}, respectively, as shown in Table 1. The observed increase in catalyst activity at higher temperatures can be attributed to the more availability of active centers for polymer growth. This is a common phenomenon in catalysis, where elevated temperatures can enhance the rate of reactions by providing more energy for reactants to interact. However, interesting observation was that at temperatures of 70°C to 80°C, the catalyst activity remains relatively stable, while at temperatures below 70°C, it decreases drastically. This indicates that there might be a temperature threshold or an optimal temperature range at which the catalyst exhibits its highest activity, and beyond which further increases in temperature do not yield significant improvements in activity. This trend revealed that optimal temperature is required to activate the catalyst by alkyl aluminum cocatalyst. The high activity of the catalyst was found for ethylene polymerization due to enough stabilization of Ti^{+3} from Ti^{+4} at temperatures between 70 to 80°C.

The molecular weight of the polymer synthesized at 80, 75, 70, 60, and 50°C was determined as 2.3, 2.8, 5.4, 6.1, and 8.8 million, g/mol, respectively, which shows that the molecular weight decreases with increasing temperature. Higher temperature is attributed to the strong chain transfer reaction during polymerization [42-44]. The data in Table 1 reveals an interesting trend, at lower temperatures, specifically at 60°C and 50°C, there is a significant increase in molecular weight, reaching 6.1 and 8.8 million g/mol, respectively. This phenomenon can be attributed to the decrease in temperature in the process of ethylene polymerization using Si-Mg-Ti catalyst, and in this regard, it was found that the molecular weight of the resulting polymer increases significantly due to the lower rate of chain termination compared to chain growth. At reduced temperatures, the catalyst's active sites are more stable, and the slower monomer diffusion to and from these sites allows polymer chains to grow longer before termination. Meanwhile, the overall catalyst activity drops because the diminished thermal energy slows down the reaction kinetics, leading to fewer successful collisions between ethylene molecules and active sites, thereby slowing the rate of polymer formation.

Table 1. Ethylene polymerization using Si-Mg-Ti catalyst at different temperatures in hexane medium[(a)].

Run No.	Temp. (°C)	Activity (kg_{PE}/g_{cat})	M_v[(b)] (million g/mol)[(b)]	BD (T) (g/cm^3)	APS (µm)	Mp (°C)	X_c[(c)] (%)
1	50	2.5	8.8	0.40	210	135.5	51
2	60	4.4	6.1	0.40	229	134.6	56
3	70	9.7	5.4	0.44	191	134.2	52
4	75	10.1	2.8	0.44	200	133.9	54
5	80	10.4	2.3	0.46	209	133.4	51

(a) Polymerization conditions: polymerization, time = 2 h, C_2 Pressure = 6 kg/cm^2, [Al]/[Ti] = 100, Catalyst amount = 70mg, Hydrogen = 0 kg/cm^2

(b) Solution viscosity method using Ubbelohde viscometer

(c) Crystallinity percent from DSC

Polyethylene produced with the Si-Mg-Ti catalyst exhibits a trend in which the melting point decreases with an increase in the polymerization temperature. Specifically, when polymerization occurred at the low temperature of 50°C, the melting point was observed to be 135.5°C. In contrast, at a higher polymerization temperature of 80°C, the melting point dropped to 133.4°C. The decrease in melting temperature as the polymerization temperature increases is primarily due to the production of polymer chains with lower molecular weights and less regularity in their structure at higher temperatures. Elevated polymerization temperatures can accelerate the reaction kinetics, leading to a higher frequency of chain termination events. This results in shorter polymer chains that are less tightly packed and exhibit a reduced degree of crystallinity and resulted as lower melting temperature. The polymer synthesized using Si-Mg-Ti at different temperatures showed a crystallinity percent between 51 to 56. However, interesting observation was at lowest crystallinity observed at both the highest and lowest polymerization temperatures may be a consequence of different mechanisms. At high temperatures, fast polymerization kinetics prevents the formation of a highly ordered crystalline structure. At low temperatures, the slow polymerization process allows for longer, entangled chains but limits the formation of crystalline regions due to the lack of energy for chain alignment. Lower temperatures typically lead to slower polymerization rates, allowing more time for the polymer chains to grow longer and become entangled with one another. At higher temperatures, polymerization occurs more rapidly, leading to better-organized structures and higher crystallinity. The tapped bulk density of the polymer slightly decreases as molecular weight increases, which is also a reflection of more entanglement in the polymer. At higher temperatures, crystal alignment in the polymer is more regular compared to entangled higher molecular weight polymer at all temperatures of polymer resin synthesized by modified catalyst system. The average particle size of the polymer resin was found between 190-230 µm (Table 1).

As previously established, hydrogen serves as a widely recognized and effective chain transfer agent for reducing the molecular weight of polymers in olefin polymerization [45-46]. In the catalytic process of ethylene polymerization using Si-Mg-Ti catalysts at an Al/Ti ratio of 100 and 70°C, the incorporation of hydrogen has a marked impact on both the catalyst activity and the molecular weight of the polyethylene produced. The catalytic activity demonstrated a downward trend from 9.7 kg_{PE}/g_{cat} in the absence of hydrogen to 5.0, 5.1, and 0.3 kg_{PE}/g_{cat} as hydrogen concentrations were increased to 240, 320, and 480 ml, respectively (Table 2). The diminishing activity with rising hydrogen levels points to the blocking of active sites by hydrogen, which in turn, limits the availability of ethylene monomers to these sites and promotes the termination reactions [47]. This behaviour is

Table 2. Effect of chain transfer agent in Si-Mg-Ti catalyst for ethylene polymerization at 70ºC[(a)].

Run No.	Chain transfer agent (Hydrogen, ml)	Activity (kg_{PE}/g_{cat})	M_v^{b} (million g/mol)[(b)]	BD (g/cc)	APS (µm)	Mp (°C)	X_c[(c)] (%)
1	0	9.7	5.4	0.44	191	134.2	52
2	240	5.0	1.8	0.46	175	133.5	48
3	320	5.1	1.4	0.44	235	132.9	50
4	480	0.3	1.1	0.42	75	132.8	52

(a) Polymerization conditions: polymerization temperature = 80°C, time = 2 h, C_2 Pressure = 6 kg/cm^2, [Al]/[Ti] = 100, Catalyst amount = 70mg

(b) Solution viscosity method using Ubbelohde viscometer

(c) Crystallinity percent from DSC

indicative of the formation of Ti-H bonds, which are characteristically less reactive, and predispose the catalyst to form stabilized Ti-C_2H_5 bonds [46]. Particularly, the catalytic activity remains relatively constant at hydrogen concentrations of 240 and 320 ml, suggesting a partial site blockage by Ti-H bonds [48-51]. However, as hydrogen increases more the activity suddenly decreases drastically, revealing that, Ti-H bond quantity increases significantly and availability of monomer to active site decreases, which suppresses the reaction resulting in lower activity. Parallel to the effect on catalytic activity, the molecular weight of the polymer shows a direct correlation with hydrogen concentration. Absent hydrogen, the molecular weight stands at 5.4 million g/mol, while the introduction of hydrogen at concentrations of 240, 320 and 480 ml results in a reduction of molecular weight to 1.8, 1.4, and 1.1 million g/mol, respectively (Table 2). This decrease in molecular weight confirms the role of hydrogen as a chain transfer agent. Concurrently, the polymer crystallinity was observed to increase a phenomenon attributable to the blocking of catalyst sites by hydrogen [52-53]. This increase in crystallinity could potentially explain the enhanced bulk density of the polymer resin, which was found to be in the range of 0.40 to 0.46 g/cm^3 (Table 2). The simultaneous examination of the effects of hydrogen reveals a complex interplay between its inhibitory action on the catalyst active sites, reducing polymerization activity, and its function as a chain transfer agent, diminishing molecular weight. This balance between site-blocking and chain transfer roles of hydrogen is a critical factor in controlling the polymerization process.

In the advance generation Z-N catalysts, internal and external donors play an important role as they control stereo selectivity, catalyst activity, and final polymer properties, which decide end-use applications [6,38-40]. The high-performance internal donor-based catalysts have gained extensive use in ethylene polymerization processes nowadays. However, it is important to take note that the use of external donors in the context of ethylene polymerization is an area that has not yet received extensive study and investigation. However, some reports [39,54] mentioned the importance of external donors, which influence the molecular weight of the resultant polyethylene, activity of the catalyst, altered the polymer properties, etc. The key working mechanism of external donors is as it alters the electronic and steric environment of the active sites. This modification can lead to a change in the polymer chain growth rate, resulting in longer polymer chains and thus forms higher molecular weights of the polymer. On the other hand, if the external donor suppresses chain transfer reactions, the polymer chain continues to grow longer, leading to increased molecular weight. Additionally, sometimes external donors can reduce the number of active sites available for polymerization by blocking or deactivating them. This leads to decreased catalyst activity since fewer sites are available for ethylene coordination and insertion. The effectiveness of ethylene polymerization employing the Si-Mg-Ti catalyst, in combination with TEOS and TEB external donors, was studied across various donor concentrations. In the absence of an external donor, the catalyst demonstrated an activity of 9.7 kg_{PE}/g_{cat} and a viscosity average molecular weight of 5.4 million g/mol. However, when TEOS external donor was introduced at Al/D ratios of 30, 10 and 2, the activity notably declined to 2.6, 1.0 and 0.5 kg_{PE}/g_{cat}, respectively. A similar observation was found with TEB external donor at Al/D 40, 30 and 10 activities, showing 4.2, 3.0, and 0.2 kg_{PE}/g_{cat}, respectively (Table 3, Figure 1). The decrease in activity indicated that the

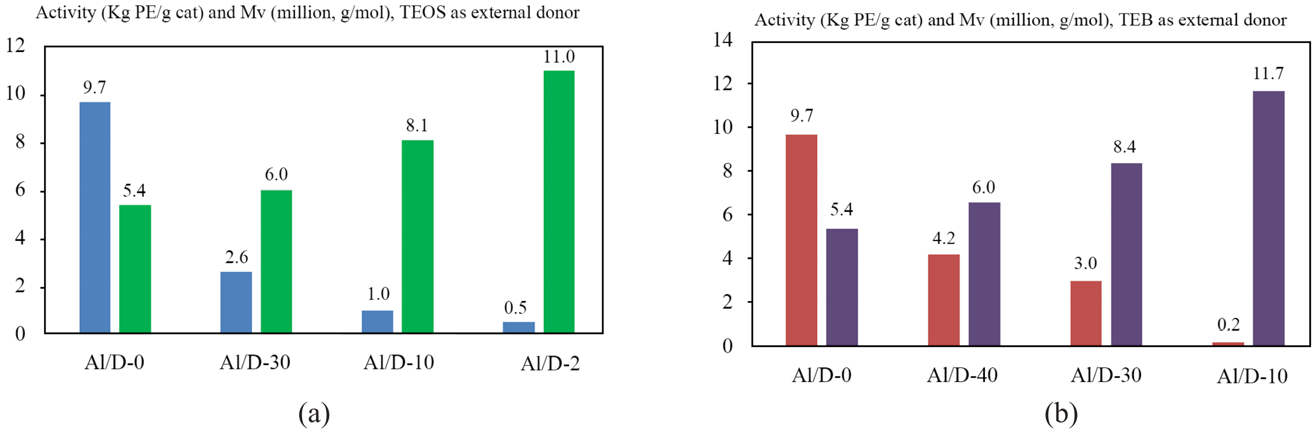
Table 3. Effect of external donor on ethylene polymerization using Si-Mg-Ti catalyst at 70ºC(a).

Run No	ED	H2(ml)	Al/D Molar ratio	Activity (kg_{PE}/g_{cat})	M_v b (million, g/mol)(b)	BD (T) (g/cm^3)	APS (µm)	Mp (°C)	X_c(c) (%)
1	-	0	0	9.7	5.4	0.44	191	134.2	52
2	TEOS	0	30	2.6	6.0	0.45	185	134.3	51
3	TEOS	0	10	1.0	8.1	0.37	216	135.1	48
4	TEOS	0	2	0.5	11.0	0.29	240	135.7	47
7	TEB	0	40	4.2	6.6	0.45	190	134.3	50
6	TEB	0	30	3.0	8.4	0.36	183	135.2	50
5	TEB	0	10	0.2	11.7	0.30	222	135.7	47
8	TEB	240	10	1.1	1.9	0.40	160	133.4	50
9	TEB	480	10	0.4	1.7	0.41	166	133.2	48

(a) Polymerization conditions: polymerization temperature = 70°C, time = 2 h, C_2 Pressure = 6 kg/cm^2, [Al]/[Ti] = 100, Catalyst amount = 70 mg

(b) Solution viscosity method using Ubbelohde viscometer

(c) Crystallinity percent from DSC



(a) (b)

Figure 1. Effect of TOES and TEB external donor on Si-Mg-Ti catalyst activity and molecular weight of UHMWPE.

external donor blocks the active site of the polymer. In addition, due to their bulky group molecular structures, TEOS and TEB introduce steric hindrance a phenomenon where bulky groups within a molecule block the active sites by their sheer size. This hindrance leads to less frequent successful additions of ethylene units, thereby decreasing the catalyst's overall activity in forming polyethylene. Such steric limitations can slow down the rate of polymer formation and alter the polymer's structure and properties. By fine-tuning the concentration of these external donors, the catalytic process can be fine-tuned, and the properties of the polyethylene produced can be customized [55-57]. Moreover, the configuration of the external donor is a crucial factor influencing the activity of the Si-Mg-Ti catalyst. In the case of TEOS, where four ethoxy groups are connected to silicon, it exhibited lower activity in comparison to TEB, which has three alkoxy groups linked to boron (B). This observation suggests that a higher number of alkoxy groups effectively deactivate the active centers of the catalyst [58].

The molecular weight of the polymer synthesized with and without external donor results shown in Table 3 indicate that external donor significantly affects the molecular weight of polyethylene. In ethylene polymerization without a donor, the molecular weight was determined to be 5.4 million g/mol. However, when using TEOS as the external donor at Al/D ratios of 30, 10 and 2, the molecular weight increased to 6.0, 8.1, and 11.1 million g/mol, respectively. Similarly, with TEB as the external donor at Al/D ratios of 40, 30, and 10, the molecular weight was measured at 6.6, 8.4 and 11.7 million g/mol, respectively (Table 3, Figure 1). These results demonstrate the significant influence of external donors on the molecular weight of the synthesized polyethylene. The significant increases in molecular weight and simultaneously decreases in activity observed in the presence of external donors indicate a reduction in chain termination as the donor concentration increases. An interesting observation showed that with TEOS as the external donor, the molecular weight was extremely high, reaching 11.0 million g/mol with an Al/D ratio of 2. Conversely, when TEB was used as the external donor at an Al/D ratio of 10, the molecular weight reached 11.7 million g/mol. This showcases the remarkable impact of external donors on increases of the molecular weight of the polymer. The higher molecular weight and lower activity with lower donor consumption in the case of TEB compared to TEOS revealed that TEB required less amount of donor to block the active sites on the catalyst after a certain concentration of donor. Also, during the polymerization reaction, external and co-catalyst make complex and bind to the catalyst surface, which reduced the active center on the catalyst surface compared to the ‘donor-free’ system, which reflected a reduction in catalyst activity [59]. Interestingly, at the same time external donors were not allowed chain termination faster, which resulted in a higher molecular weight polymer generation.

The bulk density results of the polymer synthesized using TEOS and TEB external donor shown in the table indicate that as molecular weight increases, the bulk density decreases significantly compared to donor-free system. The bulk density without donor was found 0.45 g/cm^3, whereas, with increased concentration of TEOS, it was observed between 0.45 to 0.29 g/cm^3, and in the case of TEB it was between 0.45 to 0.30 g/cm^3. The results clearly indicate the relation between molecular weight and bulk density of polymer resin. A decrease in the bulk density of the high molecular weight polymer occurred due to greater entanglement of the polymer chain compared to chain alignment in the donor-free polymer. The APS of the resin synthesized with TEOS and TEB donor increases with increasing donor concentration and is higher compared to the resin was prepared by the donor-free catalyst system. The crystallinity percent of the polymer decreases as donor concentration increases in both TEOS and TEB external donors. The results shown in Table 3 indicate that there is a relation between crystallinity percent and molecular weight, as molecular weight increases the crystallinity percent decreases. The results exhibited that donor-free catalyst system has a short polymer chain compared to a polymer synthesized using an external donor. The long chain always has more entanglement compared to the short chain polymer, which reflects a lowering of the crystallinity compared to with donor system (Table 3).

The effect of different concentrations of chain-terminating agents during ethylene polymerization was investigated with Si-Mg-Ti catalyst and TEB external donor. The results shown in Table 3 indicate that at 240 ml and 480 ml hydrogen concentration, activity increases slightly 1.1 and 0.4 kg_{PE}/g_{cat} compared to without hydrogen 0.2 kg_{PE}/g_{cat}. However, molecular weight decreases significantly from 11.7 million g/mol to 1.9 and 1.7 million g/mol, respectively. This is due to the higher hydrogen response of the catalyst, as well as the increased rate of chain termination in the active center, which is reflected in the decrease in the molecular weight of polyethylene. [60]. The crystallinity percent of the polymer was found 50% and 48% which is slightly higher compared to the polymer synthesized without hydrogen. The bulk density of the polymer increases as chain transfer agent concentration increases.

CONCLUSION

In conclusion, the Si-Mg-Ti catalyst for ethylene polymerization at different temperatures provides polyethylene with different scales of higher molecular weight polyethylene. The molecular weight increases with decreases in the polymerization temperature. However, Si-Mg-Ti is highly active for ethylene polymerization between 70 to 80°C, below that activity decreases drastically. The utilization of TEOS and TEB as external donors at different concentrations with Si-Mg-Ti catalyst for ethylene polymerization leads to decreases activity but at the same time increases viscosity average molecular weight significantly. The catalyst's responsiveness to hydrogen is marked, evidenced by a considerable reduction in molecular weight when a chain-terminating agent is present, as opposed to molecular weight without chain terminating agent. The bulk density of polyethylene is higher in cases without a donor, and it decreases with increases in the molecular weight of polymer. The modification of the catalyst with external donors for ethylene polymerization provides a straightforward and cost-effective method for producing very high molecular weight polyethylene. This advancement opens opportunities for niche applications.

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CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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