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Article

Preparation of graphene/MgCl₂-supported Ti-based Ziegler-Natta catalysts by the coagglomeration method and their application in ethylene polymerization

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ABSTRACT

We report a facile coagglomeration method for preparing graphene (G)/MgCl₂-supported Ti-based Ziegler-Natta catalysts. The effects of graphene feed ratio on catalyst morphology and ethylene polymerization behavior were examined. The synthesized catalyst exhibited very high activity for ethylene polymerization. The resultant polyethylene (PE)/G nanocomposites showed a layered morphology, and the graphene fillers were well dispersed in the PE matrix. In addition, the thermal stability and mechanical properties of PE were significantly enhanced with the introduction of a very small amount of G fillers (0.05 wt%). This work provides a facile approach to the production of high-performance PE.

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1. Introduction

Polyethylene (PE) is one of the most widely used commercial polymers because of its excellent chemical and physical properties, low production cost, superior processability, and good recyclability [1]. However, for advanced applications, it is necessary to improve the performance of PE in terms of its stiffness and rigidity in forming nanocomposites. Thus, PE nanocomposites have attracted considerable attention, especially those containing carbon additives (graphene (G) and carbon nanotubes), because of their high potential as materials with improved properties, such as mechanical and thermal stability, flame resistance, and thermal and electrical conduc-

tivities [2–5].

Several groups have used prototypes of graphene and graphite to prepare polyolefin-based nanocomposites. Ramazani's group [6] reported a PE/graphene oxide (GO) nanocomposite prepared by in situ polymerization using a TiCl₄/Mg(OEt)₂-GO or TiCl₄/GO catalyst. The resultant PE/GO showed an improvement in Young's modulus and tensile strength, and almost 50% reduction in its elongation at break. Mülhaupt's group [7] reported a one-step mechanochemical process to synthesize PE/edge-carboxylated G nanocomposites that exhibited a markedly improved modulus and a significant decrease in elongation at break, but these were achieved only at very high graphene loadings (5 wt%). Zhao's group [8] pre-

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pared PE/GO composites using liquid phase ultrasonication mixing, followed by hot-pressing. Complicated chemical reactions are required for introducing functional groups on the surface of G, and consequently, the π -electron system of G is destroyed, reducing the effects of any improvements to the physical properties in the resultant polymer/G nanocomposites [9,10]. Some studies have compared the reinforcement between G and GO, confirming that the enhancing effect of G is more prominent than that of GO [11,12]. Therefore, PE/G nanocomposites are expected to have high potential for advanced applications. However, the major challenge in the preparation of PE/G is to overcome the easy agglomeration resulting from the strong van der Waals interactions and π - π stacking between the individual G layers.

Therefore, in this research, a novel G/MgCl₂-supported Ti-based Ziegler-Natta catalyst was synthesized through a coagglomeration method. The possible aggregation between the individual G layers was prevented by the MgCl₂ support during the catalyst preparation. After polymerization, G should be well dispersed in the PE matrix. Thus, this study provides a facile method to prepare PE/G nanocomposites with well-dispersed G sheets in the PE matrix.

2. Experimental

2.1. Materials

A few layers of (≈ 5 μm , Mote Technology Co., Ltd., Changchun, China), 2-ethyl-1-hexanol (>99.6%, Sigma-Aldrich, St Louis, MO, USA), anhydrous magnesium chloride (>98%, Sigma-Aldrich), triethylaluminum (TEA, 1.0 mol/L in *n*-hexane, Sigma-Aldrich), and titanium tetrachloride (>99%, Sigma-Aldrich) were used as received. Polymerization grade ethylene was provided by Korea Petrochemical Ind. Co., Ltd., Ulsan, Korea. *n*-Hexane was distilled from sodium/benzophenone under N₂ prior to use.

2.2. Preparation of G/MgCl₂-supported Ziegler-Natta catalysts

The G/MgCl₂-supported Ziegler-Natta catalyst with well dispersed G sheets was prepared through a coagglomeration method. One gram of MgCl₂ and the selected amount of G were added to 9.9 mL 2-ethyl-1-hexanol at 20 °C under N₂. The reaction medium was heated to 160 °C to obtain a homogeneous solution. After 2 h at this temperature, the reaction solution was cooled to 30 °C, and 50 mL *n*-hexane was added. Then, 15 mL TiCl₄ was added dropwise to the reaction medium, and a precipitation was observed. After 2 h, the precipitate was filtered to remove the unreacted TiCl₄, and a second portion of TiCl₄ (20 mL) was placed into the reactor directly. The reaction proceeded to completion after stirring for 2 h at 30 °C. The reaction mixture was filtered, and the precipitate was washed several times with hot *n*-hexane and restored in *n*-hexane. The resultant product was used as the catalyst for ethylene polymerization.

2.3. Ethylene polymerization

Polymerization was performed in a 300-mL glass reactor equipped with a magnetic stirring bar. The reactor was back-filled thrice with N₂ and charged with the required amount of *n*-hexane. At the stipulated temperature, the reaction solution was stirred under 1 atm of ethylene for the desired period of time, and the co-catalyst (TEA) was added to the reactor. After co-catalyst addition, the catalyst was injected into the reactor, and polymerization was initiated under a continuous feed of ethylene. The ethylene pressure was kept constant throughout the polymerization with the use of a bubbler. After 30 min, the polymerization was terminated by adding 10% HCl-methanol solution. The mixture was poured into methanol (500 mL) to precipitate the polymer, and then dried under vacuum at 60 °C until a constant weight was achieved.

2.4. Characterization

The Mg and Ti contents in the catalyst were determined using inductively coupled plasma atomic emission spectroscopy (PerkinElmer, Optima 7300DV, Waltham, MA, USA). The chemical structure of the catalyst was characterized using FTIR spectroscopy (Jasco 4100, Tokyo, Japan). Scanning electron microscopy images were recorded on a JEOL JSM-6380LV microscope (Tokyo, Japan).

The melting temperature (T_m) of the obtained polymer was determined using differential scanning calorimetry (DSC; DSC131evo, Setaram) at a heating rate of 10 °C/min. The sample was heated to 200 °C and held in the molten state for 3 min to eliminate any influence of the thermal history. The polymer melt was cooled to 30 °C at a rate of 10 °C/min. The melting point was determined in the second scan. Decomposition temperature analysis was conducted under N₂ atmosphere using a thermogravimetric analyzer (TGA; Setaram Labsys evo, Caluire, France) with a programmed heating rate of 10 °C/min from 30 to 800 °C. The tensile mechanical properties of PE and PE/G nanocomposites were measured with a universal testing machine (Instron M4465, High Wycombe, UK). The sample sizes for the tensile drawing experiment were 5.0 mm $\times$ 75.0 mm $\times$ 1.0 mm. The sample gauge length was 25.0 mm, and the cross-head speed was 50.0 mm/min.

3. Results and discussion

The preparation of the G/MgCl₂-supported Ziegler-Natta catalysts and PE/G nanocomposites with well-dispersed G fillers is illustrated in Fig. 1. The G/MgCl₂-supported Ziegler-Natta catalyst was synthesized through a coagglomeration process in *n*-hexane. During this step, the surface of G was covered by MgCl₂-TiCl₄ catalyst, preventing aggregation between the G layers. In addition, the G fillers served as a template to assist MgCl₂-TiCl₄ catalyst aggregation onto the G surface and afford a layered structure. The resultant G/MgCl₂-supported Ziegler-Natta catalyst was used in ethylene polymerization to prepare PE/G nanocomposites.

The morphologies of untreated G and G/MgCl₂-supported Ziegler-Natta catalysts with different G contents were studied by scanning electron microscopy analysis. As shown in Fig.

Fig. 1. Preparation of G/MgCl₂-supported Ziegler-Natta catalyst and PE/G nanocomposites.

2(a), G with a sheet structure and a diameter of less than 5 μm , was observed. For the MgCl₂-supported Ziegler-Natta catalyst without G, the irregular particle shape catalyst was obtained (Fig. 2(b) and (c)). Upon the introduction of G, a catalyst with layered morphology was formed. This finding was because of the induced molding during the solidification of MgCl₂ by G. At relatively low G feed ($G/\text{MgCl}_2 = 0.1/1$), several G sheets were embedded in one catalyst particle and were well dispersed in the entire catalyst. The solid-state catalyst prevented the aggregation of the G fillers. With an increase in G feed ratio, the G filler became more independent, and the surfaces of individual G sheets were covered by MgCl₂-supported TiCl₄.

The composition of G/MgCl₂-supported Ziegler-Natta catalysts with different G contents was further characterized by inductively coupled plasma atomic emission spectroscopy (Table 1). The G content was calculated using the G/MgCl₂ feed

Table 1
Elemental composition of prepared catalysts.

G/MgCl ₂ (g/g)	Mg (wt%)	Ti (wt%)	Ti/Mg	G (wt%)
-/1.0	17.9	5.3	0.30	—
0.1/1.0	14.8	5.6	0.38	5.9
0.5/1.0	10.1	5.2	0.51	20.0
1.0/1.0	8.4	4.9	0.58	33.3
1.5/1.0	8.2	2.5	0.30	48.7
2.0/1.0	6.9	1.1	0.15	54.6

ratio and mass of MgCl₂. The Mg and Ti contents of the catalyst decreased with the increase in the G feed ratio, whereas the G content undoubtedly increased. This finding was because of the decrease in the Mg content, lowering the number of sites for TiCl₄ anchoring. As shown in Table 1, the Ti/Mg ratio increased with the increase in G feed ratio at first, causing a decrease in the Ti/Mg ratio. The increased Ti/Mg ratio may be because of the increased surface area of the catalyst upon the introduction of G. However, a further increase in the G feed ratio will hinder TiCl₄ anchoring and result in a reduced Ti/Mg ratio.

The ethylene polymerization behavior of the catalysts in the absence and presence of G was evaluated after activation with the TEA cocatalyst. As shown in Table 2, the yields obtained with the MgCl₂/TiCl₄ catalyst were higher than those with the

Fig. 2. Scanning electron microscopy images of (a) G and G/MgCl₂-supported Ziegler-Natta catalyst with different G contents. G/MgCl₂ mass ratio: (b, c) 0/1, (d, e) 0.1/1, (f, g) 0.5/1, (h, i) 1.5/1.

Table 2Ethylene polymerization by G/MgCl₂-supported Ziegler-Natta catalysts with different G contents.

Entry	G/MgCl ₂	Catalyst (mg)	Activity (kg mol ⁻¹ h ⁻¹)	G (wt%)	T _m (°C)	T _c (°C)	X _c (%)
1		20	607	—	136.2	116.8	60.5
2	—/1.0	50	261	—	136.0	116.9	63.1
3		20	514	0.02	136.4	117.2	68.6
4	0.1/1.0	50	213	0.05	136.6	118.2	72.9
5		20	332	0.11	136.4	118.7	63.3
6	0.5/1.0	50	177	0.21	136.3	118.3	59.4
7		20	323	0.20	136.7	118.6	51.3
8	1.0/1.0	50	204	0.32	136.9	118.6	53.0
9		20	461	0.40	136.4	119.1	50.6
10	1.5/1.0	50	284	0.65	136.3	119.5	54.8
11		20	829	0.57	136.5	119.6	53.2
12	2.0/1.0	50	716	0.66	136.5	119.5	49.8

Polymerization conditions: 100 mL *n*-hexane, TEA cocatalyst, [Al]/[Ti] = 100, 0.5 h, 0.1 MPa, 40 °C.

G/MgCl₂/TiCl₄ catalyst when the same weight of catalyst was added. This difference was attributed to relatively lower Ti content of the G/MgCl₂/TiCl₄ catalyst compared with that of the G-free catalyst. However, the activity revealed a slight increase in catalyst activity with increasing G feed. This increment in catalyst activity implies efficient utilization of the Ti space in the presence of G, which results from the high surface area of the G/MgCl₂/TiCl₄ catalyst.

Because of the morphology replication characteristic of the supported Ziegler-Natta catalyst, the polymer morphology can be controlled by modifying the morphology of the catalyst [13,14]. Therefore, the morphology of the resultant PE and PE/G nanocomposites will directly mirror the catalyst morphology. As shown in Fig. 3, PE obtained using the MgCl₂/TiCl₄ catalyst (Fig. 3(a)) comprises small, irregularly shaped white particles (≈ 1 mm), whereas the PE/G nanocomposites (Fig. 3(b)) show a layered shape (2–4 mm) with homogeneous gray color. Additionally, no high-contrast black color G filler was

Fig. 3. Optical images of (a) PE and (b) PE/G nanocomposites.

observed. Thus, G nanofillers are homogeneously dispersed in the PE/G nanocomposites.

To investigate the dispersion of G in the PE matrix, the resultant PE and PE/G nanocomposites were hot-pressed into films. The film was observed under an optical microscope in transparent mode. The obtained micrographs are summarized in Fig. 4. G nanofillers were highly compatible with the PE ma-

Fig. 4. Optical micrographs of (a) PE and PE nanocomposites with different G contents (b) 0.05 wt%, (c) 0.11 wt%, (d) 0.20 wt%, (e) 0.40 wt% and (f) 0.66 wt%.

Fig. 5. DSC (a) cooling and (b) heating curves of PE and PE/G nanocomposites with different G contents.

trix. Although only 0.05 wt% G was added, the G nanofillers were clearly observed in the PE/G nanocomposites. With an increase in the G feed ratio, a large amount of G nanofillers were seen in the PE matrix. A good dispersion of G in the PE matrix was also observed. The dispersion of G in the PE matrix was further examined by XRD analysis. No diffraction peaks except the crystalline diffraction peaks of the PE matrix were recorded. Thus, we expect that PE/G nanocomposites to exhibit improved thermal and mechanical properties.

The effect of G on the crystallization of PE was investigated using DSC, and the representative DSC curves are summarized in Fig. 5. As shown in Table 2, the melting temperature (T_m) of PE produced with the G-free catalyst was 136.2 °C (Entry 1). Upon the introduction of G, T_m was unchanged and the degree of crystallinity (X_c) gradually decreased with the G content increasing for the PE/G nanocomposites. This finding may be ascribed to the random distribution of G in the PE/G nanocomposites, which hinders the crystallization of PE, resulting in a large number of faults and imperfections. Compared with the neat PE sample, the non-isothermal crystallization peak temperature (T_c) gradually increased with increasing G content in PE/G nanocomposites, which demonstrates that the G fillers can act as nucleating agents to induce PE crystallization. Al-Harthi's group [15] also reported a similar result for PE/G nanocomposites produced by in situ polymerization using a metallocene catalyst. The incorporation of G into PE significantly lowers the effective activation energy for crystallization,

confirming nucleation. In addition, the DSC traces were smooth curves with relatively sharp endothermic peaks, which reflected the overall homogeneity of the PE/G nanocomposites.

Thermal stability is an important property for polymers, because it is often the limiting factor in both polymer processing and end-use applications. The thermal degradation of neat PE and PE/G nanocomposites with different weight fractions of G nanofillers was investigated by TGA under N_2 atmosphere. The results are shown in Table 3, and the TGA curves are shown in Fig. 6. The addition of G nanofillers greatly improved the thermal stability of PE. As shown in Fig. 6, all the TGA curves indicate a single degradation process. Compared with neat PE, the thermal degradation temperatures are linearly shifted to higher temperatures with increasing G content, indicating a significant improvement in the thermal oxidation stability of PE. The enhancement of the thermal stability of polyolefin upon the incorporation of carbon-based materials has been already reported by us and other research groups [16–19]. After the incorporation of 0.05, 0.20, and 0.66 wt% G into the PE/G nanocomposites, the degradation temperature at 5 wt% loss increased by 22.7, 44.1, and 54.0 °C, respectively.

Table 3
Effect of G content on the thermal stabilities of PE/G nanocomposites.

Entry	G content (wt%)	$T_{d 5\%}$ (°C)	Char yield (wt%)
1	—	385.6	0.3
4	0.05	408.3	1.0
5	0.11	426.5	0.8
7	0.20	429.7	1.9
9	0.40	428.8	3.6
12	0.66	439.6	4.7

Fig. 6. TGA curves of PE and PE/G nanocomposites.

Table 4

Mechanical properties of PE and PE/G nanocomposites with various G contents.

Sample	G content (wt%)	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)
Neat PE	—	20.0±1	515±20	720±50
PE/G nanocomposites	0.05	25.5±1	730±20	760±50
	0.11	26.4±1	610±20	820±50
	0.20	25.8±1	530±20	680±50
	0.40	26.4±1	530±20	690±50
	0.66	27.1±1	570±20	750±50

These significant enhancements in the thermal stability of PE after the incorporation of G were ascribed to the good dispersion of G in the PE matrix, which may act as an insulator between the heat source and the polymer surface where combustion occurs. In addition, the G nanofillers with a layered morphology may prevent the diffusion of volatile decomposition products into the PE/G nanocomposites by promoting char formation. Therefore, the char yields of the PE/G nanocomposites increased with the increase in the G content.

The mechanical properties of PE and PE/G nanocomposites with different G contents are presented in Table 4. The tensile strength, modulus, and elongation at break values of the resultant PE nanocomposites are significantly enhanced even with very low G nanofiller loadings (0.05 wt%), i.e., by 28%, 42%, and 6%, respectively. These results indicate that the PE/G nanocomposites obtained by in situ polymerization with the G/MgCl₂/TiCl₄ catalyst, which was prepared by coagglomeration method, have a remarkable stiffness-toughness balance.

4. Conclusions

A novel G/MgCl₂-supported Ti-based Ziegler-Natta catalyst

was prepared through the coagglomeration of MgCl₂ and G in *n*-hexane medium. Using in situ polymerization, we successfully fabricated PE/G nanocomposites with well-dispersed G nanofillers. The resultant PE/G nanocomposites displayed enhanced thermal stability compared with that of PE obtained from the G free catalyst system. The mechanical properties of PE were enhanced significantly even with a very small amount of G nanofillers (0.05 wt%). Thus, this work provides a facile approach to the production of high-performance PE with good thermal stability and an excellent stiffness-toughness balance.

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Graphical Abstract

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Preparation of graphene/MgCl₂-supported Ti-based Ziegler-Natta catalysts by the coagglomeration method and their application in ethylene polymerization

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A facile coagglomeration method for preparing graphene/MgCl₂-supported Ziegler-Natta catalyst was reported. After in-situ ethylene polymerization, the resultant polyethylene/graphene nanocomposites exhibited enhanced thermal stability and mechanical properties than neat polyethylene.

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石墨烯/二氯化镁负载钛系齐格勒-纳塔催化剂制备及其乙烯聚合性能

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摘要: 石墨烯自2004年发现以来, 由于其独一无二的优异性迅速成为科学家们的研究热点. 由于石墨烯具有极其优异的电学、力学和热学等性能, 因此被广泛应用于高性能聚合物基复合材料的制备. 众所周知, 纳米填料在聚合物中的分散状态以及与其基体间的界面作用是构筑高性能聚合物纳米复合材料的关键因素. 由于石墨烯极易团聚, 难以通过传统的熔融共混法制备均匀分散的石墨烯增强-聚烯烃纳米复合材料. 另一方面, 聚烯烃通常需要在较高温度下才能溶于部分有毒溶剂(如: 三氯苯和二甲苯等), 因此溶液共混法也不适用于聚烯烃-石墨烯纳米复合材料的制备.

有鉴于此, 本文开发了一种共沉淀法制备石墨烯/二氯化镁负载钛系齐格勒-纳塔催化剂的路线. 通过原位聚合直接制备出石墨烯均匀分散的聚烯烃/石墨烯纳米复合材料. 考察了石墨烯的加入量对催化剂形态及其催化乙烯聚合行为的影响. 当石墨烯加入量较低时, 多个石墨烯片被包裹于较大的催化剂粒子中. 随着石墨烯加入量的增加, 催化剂趋向于在石墨烯表面聚集. 继续增加石墨烯量将导致石墨烯包裹催化剂粒子, 降低过渡金属钛的负载效率. 通过三乙基铝活化后, 所制备的催化剂具有非常高的乙烯催化活性, 所生成的聚乙烯/石墨烯纳米复合材料复制了催化剂的片状结构. 同时, 通过对所制备的聚乙烯/石墨烯纳米复合材料进行电子显微镜和X射线衍射分析可知, 石墨烯均匀分散于聚乙烯基体中, 并且没有任何团聚现象发生. 该复合材料的热重分析表明, 仅加入非常少量的石墨烯就可以使其具有比纯聚乙烯更高的热稳定性, 当石墨烯加入量为0.66 wt%时, 其5 wt%热分解温度较纯聚乙烯升高了54 °C. 同时, 所制备聚乙烯/石墨烯纳米复合材料具有更优异的机械性能. 因此, 本研究提供了一个简单高效的高性能聚烯烃/石墨烯纳米复合材料的制备方法.

关键词: 齐格勒-纳塔催化剂; 聚乙烯; 石墨烯; 纳米复合材料; 原位聚合

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