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Synthesis of polyethylene/exfoliated MoS₂ nanocomposites by *in situ* exfoliation polymerization using Ziegler–Natta catalyst intercalated MoS₂†

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A new synthetic route for polyethylene (PE)/exfoliated MoS₂ (EMoS₂) nanocomposites using novel Ziegler–Natta catalyst intercalated MoS₂ was designed. The catalyst was synthesized by the intercalation of MoS₂ with a Grignard reagent, followed by anchoring of TiCl₄ into the MoS₂ galleries. The intercalated MoS₂ was exfoliated to form PE/EMoS₂ nanocomposites during *in situ* ethylene polymerization. The resultant PE/EMoS₂ nanocomposites had a layered morphology, and they were well dispersed in the PE matrix. In addition, the thermal stability and mechanical properties of PE were significantly enhanced with the introduction of EMoS₂. Thus, this work provides a facile approach to the production of PE/EMoS₂ nanocomposites.

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Introduction

Polyolefins are the most widely used materials, because of their excellent combination of chemical and physical properties, along with low production cost, superior processability and good recyclability. However, for advanced applications, it is necessary to improve the performance of polyolefins, such as stiffness and rigidity. Over the past decades, the study of polyolefin nanocomposites has attracted considerable attention, because of their high potential as materials with improved properties, such as mechanical and thermal stability, flame resistance, and thermal and electrical conductivities.

Two-dimensional (2D) nanomaterials, including graphite, graphene, and inorganic graphene analogs, have been drawing tremendous attention for many potential applications due to the fascinating properties associated with their ultrathin layer structures.^{1–4} Among the layered nanomaterials, molybdenum disulfide (MoS₂) is one of the most attractive; it has a structure similar to that of graphite.^{5–9} It has been reported that a monolayer of MoS₂ has extraordinarily high breaking strength (~23 GPa) and Young's modulus (~300 GPa), which are higher than those of chemically reduced graphene.^{10,11} The aforementioned

fascinating properties make MoS₂ an attractive substitute in the fabrication of high-performance organic–inorganic polymer nanocomposites. For example, Hu *et al.* reported a solution blending method to prepare EMoS₂-based nanocomposites of polymethyl methacrylate, polystyrene, and polyvinyl alcohol.^{12–14} The resultant polymer/EMoS₂ nanocomposites exhibited enhanced mechanical properties, thermal stability, and fire resistance properties. The uniform dispersion of EMoS₂ in the polymer matrix can be achieved by solution mixing, which is the ideal strategy, wherein these polymers are dissolved in common organic solvents. However, the solution mixing process is difficult and uneconomical in the case of polyolefin, since polyolefin are soluble in limited solvents, such as xylene and trichlorobenzene, at high temperature. In our previous reports,^{15,16} the PE/EMoS₂ nanocomposites were prepared through an *in situ* polymerization of ethylene using EMoS₂ containing Ziegler–Natta catalyst. The resulted nanocomposites exhibited enhanced physical properties than neat PE. However, the catalyst preparation process are very complicate, including use excess amount of *n*-butyl lithium to lithiation of MoS₂, the longtime lithiation reaction, violent exfoliation reaction, waste too much water to remove lithium salt and longtime vacuum freeze-dried process, and so on.

Therefore, in this research, we reported a Ziegler–Natta catalyst intercalated MoS₂. The catalyst preparation process is very simple, including intercalation of a Grignard reagent into MoS₂ galleries and anchoring of TiCl₄. During the ethylene polymerization, the intercalated MoS₂ layers are *in situ* exfoliated and dispersed in the polymer matrix (no need additional exfoliation process), producing PE/EMoS₂ nanocomposites directly.

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Experimental

Materials

Molybdenum disulfide (MoS_2 , $\sim 6 \mu\text{m}$), *n*-butylmagnesium chloride (BuMgCl , 2.0 M in THF) triethylaluminum (TEA, 1.0 M in hexane), and titanium tetrachloride (TiCl_4 , >99%) were purchased from Sigma-Aldrich and used as received. Polymer-grade ethylene was provided by Korea Petrochemical Ind. Co. Ltd., Korea. *n*-Hexane was distilled from sodium/benzophenone under N_2 prior to use.

Preparation of Ziegler–Natta catalyst intercalated MoS_2

1 g of MoS_2 was first placed in the autoclave and 20 mL of BuMgCl was added. The autoclave was heated at 150°C for 12 h under argon atmosphere. After that, the autoclave was cooled to room temperature and the product was filtered, and washed with anhydrous *n*-hexane. The resulting powder was suspended in *n*-hexane (200 mL). Then, TiCl_4 (10 mL) was added dropwise to the suspension of MoS_2 – MgCl at 0°C , after which the temperature was increased to 80°C (2°C min^{-1}) and the suspension stirred for 4 h. The mixture was filtered to remove the unreacted TiCl_4 and then washed several times with hot *n*-hexane. The obtained powdery catalyst was dried under vacuum at 60°C for 3 h. The contents of MoS_2 , Mg and Ti in the resultant catalyst as determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis were: MoS_2 – 44.7 wt%, Mg – 6.6 wt% and Ti – 7.4 wt%. The catalyst was also synthesized without the addition of MoS_2 for comparison. For this, a similar procedure was followed to prepare the catalyst without including MoS_2 . The contents of Mg and Ti in the resultant catalyst determined by ICP analysis were: Mg – 2.3 wt%, Ti – 14.1 wt%.

Ethylene polymerization

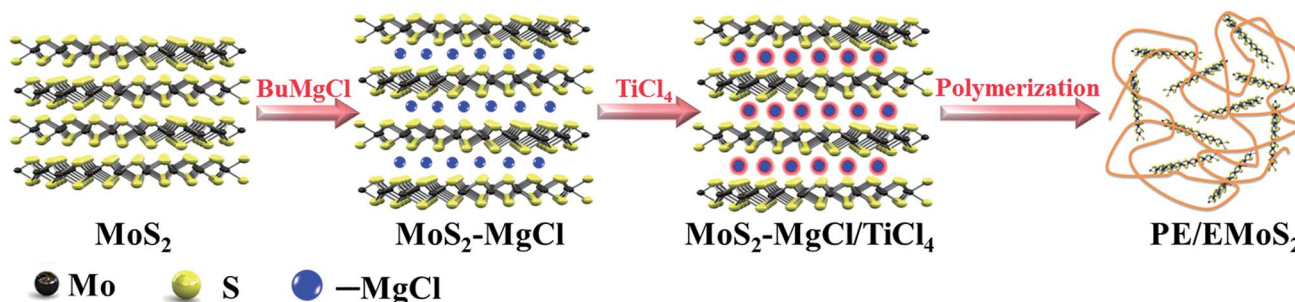
Ethylene polymerization was performed in a three-neck glass reactor (300 mL). The reactor was thrice back-filled with N_2 and charged with 100 mL distilled *n*-hexane. The reaction solution was stirred at 40°C under 1 bar of ethylene for 5 min, followed by addition of the TEA cocatalyst. Subsequently, the catalyst was added into the reactor, and polymerization was started under a continuous feed of ethylene (1 bar). After 0.5 h polymerization, 10 mL HCl-methanol solution (10%) was

added to the suspension to terminate to polymerization. The mixture was poured into large quantity of methanol (500 mL) to precipitate the polymer. The product was collected by filtration, and washed with methanol. Then, the product was dried under vacuum at 60°C until a constant weight was achieved.

Characterization

The contents of Mg and Ti in the catalyst were determined using inductively coupled plasma-atomic emission spectroscopy (PerkinElmer, Optima 7300DV). Scanning electron microscopy (SEM) images were recorded using a JEOL JSM-6380LV microscope. The morphologies of the support and the catalyst were studied by an optical microscope (ANA-006, Leitz, Germany) equipped with a charge coupled device-based camera for recording the images. The X-ray diffraction patterns were obtained on a Philips X-Pert PRO MRD diffractometer using Cu-K α radiation.

The melting temperature (T_m) of the obtained polymer was determined using differential scanning calorimetry (DSC; DSC131evo, Setaram) at a heating rate of $10^\circ\text{C min}^{-1}$. The sample was heated to 200°C and held in the molten state for 3 min to eliminate the influence of the thermal history. The polymer melt was cooled to 30°C at the rate of $10^\circ\text{C min}^{-1}$. The melting point was determined in the second scan. The analysis of the decomposition temperature was conducted under N_2 atmosphere using a thermogravimetric analyzer (TGA; Setaram Labsys evo) from 30 to 800°C with a programmed heating rate of $10^\circ\text{C min}^{-1}$. The tensile mechanical properties of the polymers were measured using a universal testing machine (Instron M4465). The sample sizes for the tensile drawing experiments were $5.0 \times 75.0 \times 1.0 \text{ mm}^3$. The sample gauge length was 25.0 mm, and the crosshead speed was 50.0 mm min^{-1} . The preparation process of Ziegler–Natta catalyst intercalated MoS_2 (MoS_2 – $\text{MgCl}/\text{TiCl}_4$ catalyst) and PE/ EMoS_2 nanocomposites are illustrated in Scheme 1. In the first step, the Grignard reagent (BuMgCl) was intercalated into the MoS_2 galleries and obtained MoS_2 – MgCl support, and then treatment with excess TiCl_4 to generate Mg/Ti catalyst species between MoS_2 layers. During the ethylene polymerization process, the layered MoS_2 will *in situ* exfoliated by the polymerization force arising from the propagation of PE chain.



Scheme 1 Preparation of MoS_2 – MgCl -supported Ziegler–Natta catalyst and PE/ EMoS_2 nanocomposites.



Results and discussion

The preparation process of Ziegler–Natta catalyst intercalated MoS₂ (MoS₂–MgCl/TiCl₄ catalyst) and PE/EMoS₂ nanocomposites are illustrated in Scheme 1. In the first step, the Grignard reagent (BuMgCl) was intercalated into the MoS₂ galleries and obtained MoS₂–MgCl support, and then treatment with excess TiCl₄ to generate Mg/Ti catalyst species between MoS₂ layers. During the ethylene polymerization process, the layered MoS₂ will *in situ* exfoliated by the polymerization force arising from the propagation of PE chain.

The morphologies of the pristine MoS₂ sample and the MoS₂–MgCl/TiCl₄ catalyst were studied by SEM analysis. It could be clearly seen from Fig. 1(a), the pristine MoS₂ sample contains a large number of tightly stacked MoS₂ layers and the diameters are in the range of several micrometers. As shown in Fig. 1(b), after reacted with Grignard reagent and TiCl₄, the sheet structure remained and the tightly stacked MoS₂ layers cannot be observed on the edge of MoS₂. This could be corresponding to the intercalation of Ziegler–Natta catalyst into the MoS₂ galleries that blocked the edge of MoS₂. The MoS₂–MgCl/TiCl₄ catalyst was also characterized by SEM-EDS (Fig. S1†). It was found that the catalyst not only covered the surface of MoS₂, but also the galleries of MoS₂. Concerning the catalyst in the absence of MoS₂ (BuMgCl/TiCl₄), the morphology were exhibited as irregular particles.

XRD analyses were conducted for the pristine MoS₂, MoS₂–MgCl–TiCl₄, and BuMgCl–TiCl₄ catalyst to confirm the successful intercalation of the catalyst into the gallery of MoS₂. As shown in Fig. 2, an intense reflection at $2\theta = 14.3^\circ$ (the corresponding interlayer distance was 0.62 nm) was observed for pristine MoS₂, which was attributed to the (002) plane of MoS₂. After the treatment with the Grignard reagent and TiCl₄, a new peak at $2\theta = 11.2^\circ$, which correspond to the layer distances of 0.8 nm, respectively were observed. This clearly indicated that the expansion of the interlayer space is due to the successful intercalation of the Ziegler–Natta catalyst into the MoS₂ galleries. Although the reflection at $2\theta = 14.3^\circ$ was observed after the intercalation, the peak became very broad and the intensity was drastically reduced compared to that of the pristine MoS₂. This phenomenon also proves that MoS₂ was successful intercalated by Ziegler–Natta catalyst.

After activation with the TEA cocatalyst, the ethylene polymerization behaviors of the catalysts in the absence and the presence of MoS₂ were evaluated. As shown in Table 1, the catalyst activity of BuMgCl–TiCl₄ catalyst were much lower than those with the MoS₂–MgCl–TiCl₄ catalyst. When the equivalent

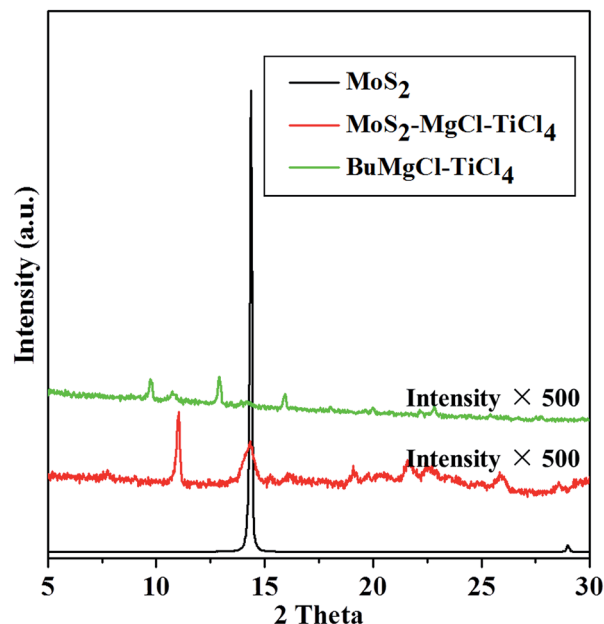


Fig. 2 XRD patterns of pristine MoS₂, MoS₂–MgCl–TiCl₄ and BuMgCl–TiCl₄ catalyst.

weight of catalyst was added (entry 1 vs. 4), the catalyst activity of MoS₂–MgCl–TiCl₄ is 3.6 times the catalyst in the absence of MoS₂. This phenomenon may be due to the fact that MoS₂ act as a template to provide a large specific surface area for the Ziegler–Natta catalyst. The PE/EMoS₂ nanocomposites with EMoS₂ content of 0.4–3.1 wt% were obtained in this research by changing the feed weight of the catalyst and [Al]/[Ti] ratio.

As shown in Fig. 3, PE obtained using the BuMgCl–TiCl₄ catalyst comprised irregularly shaped white particles, while the PE/EMoS₂ nanocomposites showed layered shapes (1–3 mm) with homogeneous gray color. This could be ascribed to the morphology of the resultant PE and the PE/EMoS₂ nanocomposites directly mirror the morphology of the catalyst.

In order to investigate the dispersion of EMoS₂, the resultant PE and PE/EMoS₂ nanocomposites were hot-pressed into films. The polymer films were characterized by optical microscope in the transparent mode; the micrographs are presented in Fig. 4. It was found that the EMoS₂ fillers were well dispersed in the PE matrix.

The dispersion of EMoS₂ in the PE/EMoS₂ nanocomposites was further confirmed by XRD analyses and the data are presented in Fig. 5. The XRD data of PE/EMoS₂ nanocomposites showed the presence of two diffraction peaks at 21.4° and 23.8° , which correspond to the (110) and (200) planes of PE (Fig. 5). The peak due to intercalation (11.2°) disappeared completely for PE/EMoS₂ nanocomposites. The disappearance of these peaks is ascribed to the complete exfoliation of the intercalated EMoS₂ by the chain propagation force of propylene polymerization. No conspicuous diffraction peaks were observed in addition to the ones of crystalline PE, indicating that no obvious stacking of EMoS₂ sheets occurs in the PE/EMoS₂ nanocomposites and that the stacked MoS₂ sheets of the catalyst are completely exfoliated.

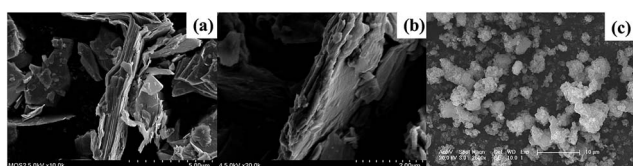


Fig. 1 SEM images of (a) pristine MoS₂, (b) MoS₂–MgCl/TiCl₄ catalyst and (c) BuMgCl/TiCl₄ catalyst.



Table 1 Results of ethylene polymerization by $\text{MgCl}_2/\text{TiCl}_4$ and $\text{ODA-MoS}_2/\text{MgCl}_2/\text{TiCl}_4$ catalysts^a

Entry	Cat.	Cat. (mg)	[Al]/[Ti]	Activity ($\text{kg mol}_{\text{Ti}}^{-1} \text{ h}^{-1}$)	ODA-MoS ₂ (wt%)	<i>T</i> _m (°C)	<i>T</i> _c (°C)	<i>X</i> _c (%)
1	BuMgCl/TiCl ₄	100	50	17.3	—	133.2	116.2	52.5
2	MoS ₂ -MgCl-TiCl ₄	25	200	129.7	0.4	136.0	118.0	60.9
3		50	100	85.6	0.7	135.8	118.3	62.6
4		100	50	62.3	0.9	135.4	118.3	68.9
5		200	25	29.8	2.0	135.5	118.6	71.9
6		300	17	19.5	3.1	135.2	119.1	78.5

^a Polymerization conditions: 100 mL *n*-hexane, TEA co-catalyst, 0.5 h, 1 atm, 40 °C.

**Fig. 3** Optical images of PE and PE/EMoS₂ nanocomposites.

The effects of the EMOs₂ fillers on the melting temperature, degree of crystallinity of PE was characterized using DSC; the typical DSC curves are summarized in Fig. S2.† As shown in Table 1, the *T*_m of PE prepared by MoS₂-free catalyst was 133.2 °C. Upon the introduction of the EMOs₂ fillers, the values of *T*_m and *X*_c of PE gradually increased with the EMOs₂ amount. The increase in *T*_m may be due to the interaction between the EMOs₂ and the PE matrix, which restricts the motion of the PE chain.¹⁷ As compared to the neat PE sample, the *T*_c also increased with the introduction of MoS₂ fillers, which demonstrates that the EMOs₂ fillers can act as nucleating agents to induce PE crystallization.

The thermal degradation of PE and the PE/EMoS₂ nanocomposites with different weight fractions of EMOs₂ fillers were investigated by TGA under N₂ atmosphere. The results are given in Table 2, and the TGA curves are shown in Fig. S3.† In comparison to the case of neat PE, the thermal degradation temperatures are linearly shifted to the higher-temperature

region with the introduction of the EMOs₂ fillers, indicating significant improvement in the thermal oxidation stability of PE. This enhancement of polymer thermal stability upon incorporation of the EMOs₂ filler has already been reported by both ourselves and other groups.^{11–16} With the incorporation of EMOs₂, the value of *T*_{dmax} of the PE/EMoS₂ nanocomposites increased to ~486.5 °C, which is 17.3 °C higher than that of the pure PE. The significant enhancement in the thermal stability of PE after the incorporation of EMOs₂ could be ascribed to the good dispersion of EMOs₂ in the PE matrix, which may act as an insulator between the heat source and the polymer surface where combustion occurs. In addition, the char yield of virgin PE is 0.9 wt% at 600 °C, and those of all the PE/EMoS₂ nanocomposites are higher than that of the virgin PE. It is clear that the EMOs₂ can catalyze the char formation of PE during the process of thermal degradation. These results are not unusual because the transition metal, molybdenum, can catalyze the char formation of polymers and sulfur can improve the flame retardancy of the polymers.^{14,18} Considering the above results, it is believable that the introduction of inorganic components into organic polymers, such as PE, can improve their thermal stabilities on the basis of the fact that EMOs₂ fillers have good thermal stability due to the heat insulation effect of the EMOs₂

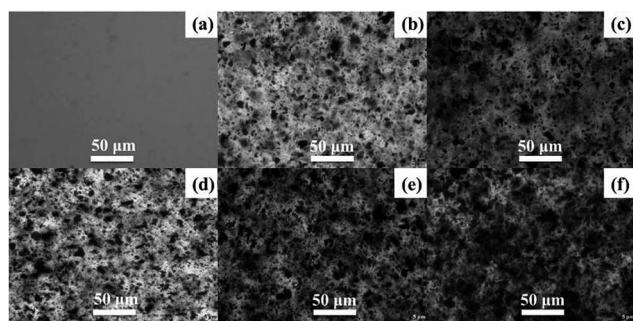
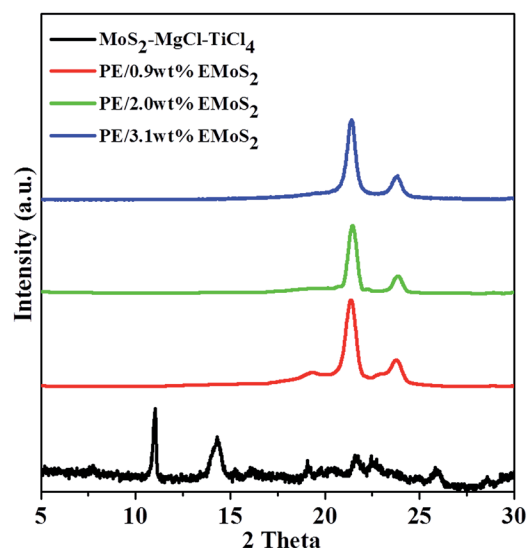
**Fig. 4** Optical micrographs of (a) PE and PE/EMoS₂ nanocomposites with EMOs₂ contents of (b) 0.4, (c) 0.7, (d) 0.9, (e) 2.0 and (f) 3.1 wt%.**Fig. 5** XRD spectra of PE and PE/ODA-MoS₂ nanocomposites.

Table 2 Effect of EMOs₂ content on the thermal stabilities of PE/EMOs₂ nanocomposites

EMOs ₂ content (wt%)	<i>T</i> _{d5%} (°C)	<i>T</i> _{dmax} (°C)	Char yield (wt%)
—	399.8	469.2	0.9
0.9	430.9	485.3	4.8
2.0	430.1	482.5	5.9
3.1	431.8	486.5	7.8

Table 3 Mechanical properties of PE and PE/EMOs₂ nanocomposites with various EMOs₂ contents

	EMOs ₂ content (wt%)	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)
Neat PE	—	25.6 ± 1	480 ± 20	1000 ± 80
PE/EMOs ₂	0.9	32.3 ± 2	720 ± 30	1600 ± 90
nanocomposites	2.0	35.4 ± 2	780 ± 30	1500 ± 90
	3.1	39.5 ± 2	1050 ± 40	1000 ± 80

layers and to the mass transport barrier to the volatile products generated during decomposition.

The mechanical properties of PE and the PE/EMOs₂ nanocomposites with various EMOs₂ loadings were investigated by tensile tests and the results are presented in Table 3. The values of the tensile strength, the modulus, and the elongation at break for the resultant PE nanocomposites are significantly enhanced even at very low EMOs₂ nanofiller loadings. With increasing the EMOs₂ loading, the tensile strength and modulus drastically improved. The elongation at break value was also increased with the introduction of relatively lower amount of EMOs₂. The maximum increase in tensile strength, modulus, and elongation at break value is 54%, 119% and 60%, respectively. Hu *et al.*¹⁹ reported that the largest increase in tensile strength and modulus was 16.8 and 37.5% for PE/MoS₂ nanocomposites that prepared from solution mixing method, which is much lower than our results. These results indicate that the PE/EMOs₂ nanocomposites obtained by *in situ* polymerization with the MoS₂-MgCl-TiCl₄ catalyst, exhibit remarkable combination of stiffness and toughness.

Conclusions

A new concept for ethylene polymerization using MoS₂-MgCl-supported Ti-based Ziegler-Natta catalyst was successfully established by the intercalation of Ziegler-Natta catalyst into MoS₂ galleries. After the *in situ* polymerization of ethylene, PE/EMOs₂ nanocomposites with well-dispersed EMOs₂ nanofillers were fabricated. The resultant PE/EMOs₂ nanocomposites displayed enhanced thermal stability as compared to PE obtained from the MoS₂-free catalyst system. The mechanical properties of PE were enhanced significantly even with a very small amount of the EMOs₂ nanofiller. Thus, this work provides

a facile approach for the production of high-performance PE with good thermal stability and excellent stiffness-toughness balance.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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