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PE and LLDPE/spherical-silica composite synthesized via in situ polymerization with zirconocene/MAO catalyst

Ekrachan Chaichana[1], Prae Rothakit[2], Piyasan Praserthdam[2]
and Bunjerd Jongsomjit[2,*]

[1]Chemistry Program, Faculty of Science and Technology
Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand

[2]Center of Excellence on Catalysis and Catalytic Reaction Engineering
Department of Chemical Engineering, Faculty of Engineering
Chulalongkorn University, Bangkok 10330, Thailand

Abstract

Polyethylene (PE) and linear low density polyethylene (LLDPE) were filled with spherical-silica during in situ polymerization in the presence of metallocene/MAO catalyst to obtain PE and LLDPE/spherical-silica composites. The particle sizes of the spherical silica introduced into PE and LLDPE productions varied with four sizes; 0.5, 3, 5 and 10 μm. It was found that the catalytic activities of the in situ polymerization systems with the spherical silica increased with particle sizes in the first range and then slightly decreased for both productions. The properties of the obtained polymer composites including melting temperatures, crystallinity and comonomer insertion were investigated by means of X-ray diffractrometer (XRD), differential scanning calorimeter (DSC) and nuclear magnetic resonance (NMR). It was observed that most properties were influenced by the variation in particle sizes of the spherical silica. Considering on the morphologies of the obtained polymer composites, it can see that leaching of the spherical silica existed in both PE and LLDPE composites. The spherical shape and the smooth surface of the silica filler are likely to be the major reason for the leaching.

Keywords: Polymer composites, thermal properties, spherical silica, metallocene

บทคัดย่อ

พอลิเอทิลีน (polyethylene, PE) และพอลิเอทิลีนชนิดความหนาแน่นต่ำเชิงเส้น (linear low density polyethylene, LLDPE) ถูกเติมด้วยซิลากาทรงกลมในระหว่างกระบวนการอินซิทูพอลิเมอร์ไรเซชันโดยมีตัวเร่งปฏิกิริยาเมทัลโลซีนและเมทิลอะลูมิน็อกซีนร่วมด้วยเพื่อผลิต PE และ LLDPE แบบคอมโพสิตด้วยซิลิกาทรงกลม ขนาดของซิลิกาทรงกลมที่ใส่ลงไปใน PE และ LLDPE มีสี่ขนาด ได้แก่ 0.5 3 5 และ 10 ไมโครเมตร จากการทดลองพบว่าความว่องไวในการเกิดปฏิกิริยาของระบบอินซิทูพอลิเมอร์ไรเซชันเพิ่มขึ้นตามขนาดของซิลิกาในช่วงแรกและลดลงเล็กน้อยหลังจากนั้นในพอลิเมอร์ทั้งสองชนิด สมบัติของพอลิเมอร์คอมโพสิตที่ผลิตได้ ประกอบด้วย อุณหภูมิหลอมเหลว ความเป็นผลึก และการแทรกตัวของโคมอนอเมอร์ถูกตรวจวัดด้วยเครื่องเครื่องเอกซเรย์ดิฟแฟรกโตมิเตอร์ (X-ray diffractometer, XRD) เครื่องดิฟเฟอเรนเชียลสแกนนิงแคลอริมิเตอร์ (differential scanning colorimeter, DSC) และ เครื่องนิวเคลียร์แมกเนติกเรโซแนนซ์ (nuclear magnetic resonance, NMR) พบว่าสมบัติส่วนใหญ่ขึ้นกับขนาดของซิลิกาทรงกลม เมื่อพิจารณาลักษณะสัณฐานของพอลิเมอร์คอมพอสิทที่ผลิตได้ จะพบการหลุดออกของซิลิกาทรงกลมอยู่ในทั้งคอมโพสิตของ PE และ LLDPE ลักษณะทรงกลมและความเรียบของพื้นผิวของซิลิกาที่เติมเข้าไปน่าจะเป็นสาเหตุหลักของการหลุดออก

คำสำคัญ: พอลิเมอร์คอมพอสิท, สมบัติทางความร้อน, ซิลิกาทรงกลม, เมทัลโลซีน

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*Corresponding author; e-mail: bunjerd.j@chula.ac.th

1. Introduction

Polyethylene (PE) is known as one of the most popular plastics in the world. It was widely used in production of grocery bags, shampoo bottles, children's toys, and even bullet proof vests [1]. The advantages of PE consisting of light weight, high chemical resistance, low electric constant, good processability etc. However, it still has some drawbacks such as low gas permeability, lack of stiffness and flammability. To overcome these problems, many methods have been introduced including: adjusting the condition of polymerization, irradiating the polymer and adding some filler into the polymer. The last method is the most widely used method due to its convenience and efficiency. After the addition of the filler into the polymer, the obtained material is called a polymer composite. There are many techniques for preparing the polymer composite. However, the technique which is probably considered to be the most powerful one in serving the polymer composite with the uniform properties is *in situ* polymerization. It is due to the direct synthesis via polymerization along with the presence of filler.

Besides the preparation technique, the types and properties of the filler are also crucial in determining the end properties of the polymer composite. Different types of materials have been brought for use as filler such as carbon nanotube (CNT) [2-3], silica (SiO_2) [4-6], alumina ($Al2_2O_3$) [7], and natural clay [8-9]. Silica is one of the most frequently used fillers, since it has relatively high surface area and pore volumes per unit mass leading to good morphological features for polymer particles [10]. However, silica itself can be classified into many types for example nanosilica named for its nanometer size, and spherical silica named for its spherical shape. Spherical silica is superior to non-spherical silica when using as filler benefiting from its narrower particle size distribution, higher bulk density and lower impurity. On account of this benefit, the polymer composite filled with the spherical silica could achieve the better properties than non-spherical silica. Moreover, it was found by Im *et al.* [11] that using spherical silica as a filler could improve processibility and promised additional application for the obtained composites. This is because the spherical shape and smooth surface will have low friction coefficient, therefore acting as a lubricant when exposed to the high shear forces and heat experienced during melt compounding. Another study dealing with spherical silica was also conducted by Yoon [12]. He used spherical silica as a supporting filler for immobilizing the cross-linked methyl aluminoxane (MAO) and then used for polymerization in the presence of bis(n-butylcyclopentadienyl) zirconium dichloride, $(n\text{-}BuCp)_2ZrCl_2$. It was found that the polymer composites could be obtained by this system and the resulting polyethylene particles showed a spherical morphology with very few fine particles.

In this study, the spherical silica with various particle sizes were used as a supported filler for MAO in the *in situ* polymerization of polyethylene composites in the presence of rac-ethylenebis (indenyl) zirconium dichloride ($rac\text{-}Et(Ind)_2ZrCl_2$). Hence, the effect of particle size of the spherical silica was the primary concern. In addition, the productions of linear low density polyethylene (LLDPE) with the spherical silica were also conducted to compare with polyethylene production. The powerful equipment such as scanning electron microscope (SEM), differential scanning calorimeter (DSC) and X-ray photoelectron spectroscopy (XPS) were used to investigate the properties of the obtained polymer and also of the fillers.

2. Materials and Methods

2.1 Materials

All chemicals and polymerizations were manipulated under an argon atmosphere, using a glove box and/or Schlenk techniques. Toluene was dried over dehydrated $CaCl_2$ and distilled over sodium/ benzophenone before use.

The rac-ethylene bis(indenyl) zirconium dichloride ($rac\text{-}Et[Ind]_2ZrCl_2$) was supplied from Aldrich. Methylaluminoxane (MAO) in hexane was donated by Tosoh (Akso, Japan). Trialkylaluminium (TMA, 2 M in toluene) was obtained by Nippon Aluminum Alkyls, Ltd., Japan. Ultrahigh purity argon was further purified by passing it through columns that were packed with BASF catalyst R3-11G (molecular sieved to 3), sodium hydroxide (NaOH), and phosphorus pentoxide (P_2O_5) to remove traces of oxygen and moisture. Ethylene gas (99.96% pure) was donated by the National Petrochemical Co. Ltd., Thailand. 1-Octene (d = 0.715) was purchased from Aldrich. Spherical silica gel with various particle size (3, 5 and 10 μm) were purchased from Ligand Scientific Co., Ltd. Tetramethylorthosilicate, Ethylene glycol ($\geq$ 99.5%), and Sodium hydroxide 1 mol/l were purchased Merck KGaA, Darmstadt, Germany. Dodecyltrimethylammonium bromide, C_{12}TMABr (99%) was purchased from Aldrich Chemical Company, Inc.

2.2 Preparation of spherical silica

Spherical silica was synthesized following procedures as described below. At first, 0.42 g of n-dodecyltrimethylammonium bromide (TMABr), and 0.75 ml of 1 M sodium hydroxide (NaOH) solution were dissolved in 100 g of ethylene glycol/ water (25/75, w/w) solution (weight ratio of co-solvent: 0.25). Then 0.46 g of tetramethylorthosilicate (TMOS) was added to the solution, with vigorous stirring at 25 °C. The composition of the reaction mixture is $1SiO_2$:$0.45C_{12}$TMABr:0.25NaOH: 133ethylene glycol and 1392 H_2O. Following the addition of TMOS, the clear solution suddenly turned opaque, resulting in a white precipitate. After 8 hours of continuousstirring the mixture was aged overnight. The white powder was filtered and washedwith distilled water at least three times, and then dried at 45 °C for 72 hours. Thepowder obtained was calcined in air at 550 °C for 6 hours to remove the organicspecies.

2.3 Preparation of spherical silica/MAO supported filler

All spherical silica including the commercial and the synthesized silica were heated under vacuum at 400 °C for 6 hours prior to use. After that MAO was impregnated onto the support, as follows. One gram of silica was reacted with the desired amount of MAO in toluene at room temperature and stirred for 30 min. The solvent was then removed from the mixture. About 20 mL of toluene was added into the obtained precipitate and the mixture was stirred for 5 min, and the solvent was then removed. This procedure was done for five times to ensure the removal of impurities. Then, the solid part was dried under vacuum at room temperature to obtain white powder of supported filler (MAO/spherical silica).

2.4 In situ polymerization reaction

2.4.1 Linear low-density polyethylene (LLDPE) production

The ethylene and 1-octene copolymerization reaction was carried out in a 100 mL semi-batch stainless steel autoclave reactor equipped with a magnetic stirrer. Using a glove box, 0.1 g. of the supported filler was placed into the reactor. Then, toluene was introduced into the reactor to a total volume of 30 mL. Separately, the desired amount of $Et(Ind)_2ZrCl_2$ (5×10^5 mol/L) and TMA ($[Al]_{TMA}/[Zr]_{cat}$ = 2500) was mixed and stirred in a 5-min aging process at room temperature. This mixture was then injected into the reactor. The reactor was frozen in liquid nitrogen to stop thereaction, and then injected with 0.018 mol of 1-octene. The reactor was evacuated to remove the argon atmosphere, and was then heated up to the polymerization temperature (70 °C). To start the polymerization reaction, 0.018 mol of ethylene (at 6 psi gauge) was fed into the reactor containing the 1-octene and catalyst mixtures. After the ethylene was totally consumed, the reaction was terminated by the additionof acidic methanol, and then stirred for 30 min. The copolymer product (white powder) was filtered, washed with methanol and dried at room temperature.

2.4.2 Polyethylene (PE) production

The same procedure as in the LLDPE production was repeated except no 1-octene comonomerwas introduced into the polymerization system.

2.5 Characterization of spherical silica

2.5.1 X-ray diffraction (XRD)

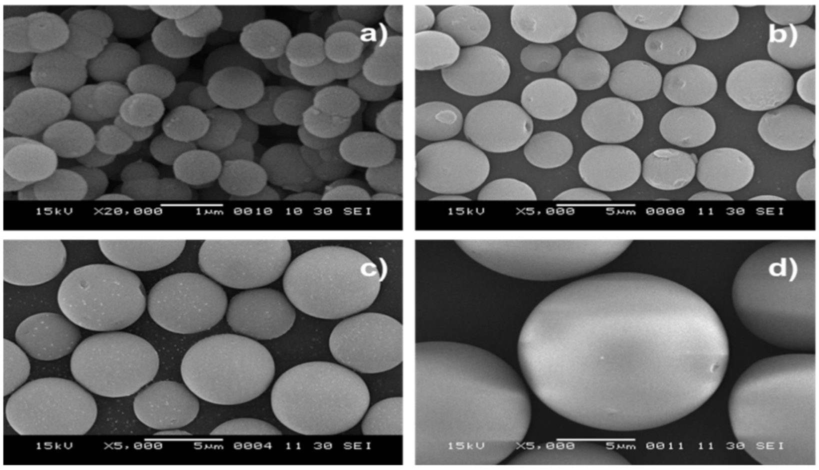
XRD was performed to determine the bulk crystalline phases of the samples using a Siemens D-5000 X-ray diffractometer with CuKα (k =1.54439 Å). The spectra were scanned at a rate of 2.4°/min in the range 2 = 20° - 80°.

2.5.2 BET surface area

Surface area measurement was carried out by low temperature nitrogen adsorption in a MicromeriticChemiSorb 2750 system.

Table 1. BET surface area and pore characteristics of silica.

Silica	BET surface area (m^2/g)	Average pore diameter (Å)	Pore volume (cm^3/g)
SiO_2 (0.5 μm)	1202	26	0.37
SiO_2 (3 μm)	309	86	0.94
SiO_2 (5 μm)	386	56	0.87
SiO_2 (10 μm)	302	88	1.00



a) SiO_2(0.5 μm), b) SiO_2(3 μm), c) SiO_2 (5 μm) and d) SiO_2 (10 μm).

Figure 1. SEM micrographs of spherical silica.

2.6 Characterization of spherical silica/MAO supported filler

2.6.1 X-ray photoelectron spectroscopy (XPS)

XPS was used to determine the binding energy (BE) and the amount of Al on sample surfaces. It was carried out using the Shimazu AMICUS (Japan) with VISION 2-control software. Spectra were recorded at room temperature in high-resolution mode (0.1 eV step, 23.5 eV pass energy) for Al 2p core-level region. The samples were mounted on pieces of adhesive carbon tape as pellets. The energy reference for Ag metal (368.0 eV for 3d5/2) was used for this study.

2.6.2 Scanning electron microscopy (SEM)

SEM was used to investigate the morphology of the silica particle and also the obtained polymer composites. A JEOL mode JSM-5800 LV scanning microscope was employed.SEM was used to determine the morphologies of the polymers.

The SEM of JEOL mode JSM-6400 (JEOL Ltd., Japan) was applied with 15 kV of an acceleration voltage. The samples were coated with the platinum prior to observation.

2.6.3 Thermal gravimetric analysis (TGA)

TGA was performed using a TA Instruments SDT Q-600 analyzer. Samplesof 10-20 mg were examined at a temperature ramping from 25 to 600°C at 2°C/min. The carrier gas was N_2 UHP.

2.7 Characterization of polymer composite

2.7.1 Differential scanning calorimetry (DSC)

DSC was used to determine the melting temperature of products with a Perkin-Elmer Diamond DSC. The analyses were performed at a heating rate of 20°C/min in the temperature range of 50-150°C.

2.7.2 ^{13}Carbon nuclear magnetic resonance (^{13}C NMR)

^{13}C NMR spectroscopy was used to determine 1-hexene incorporationand copolymer microstructure. Each sample solution was prepared by dissolving 50 mg of copolymer in 1,2-dichlorobenzene and $CDCl_3$. The ^{13}C NMR spectra weretaken at 100 °C using a BrukerAvance II 400 operating at 100 MHz with an acquisition time of 1.5 s and a delay time of 4 s.

3. Results and discussion

3.1 Characterization of spherical silica

Spherical silica having sizes of 0.5, 3, 5 and 10 μm were used here. The last three sizes (3, 5 and 10 μm) were commercial silica obtained from the Ligand Scientific, while the first one (0.5 μm) was synthesized using tetramethoxysilane (TMOS) as silica source according to the method described by Yamada and Yano [13]. The smallest one (0.5 μm) was synthesized in order to have the fillers covering the wide range of particle size (0.5 - 10 μm). All spherical silica were characterized by N2physisorption technique to measure BET surface area, average pore diameter and pore size distribution. The results of BET surface area and pore characteristics of various supports are summarized in Table 1. The smallest spherical silica (0.5 μm) as usual appears to have the highest surface area among all the spherical silica. However, for the larger ones (3, 5 and 10 μm), their surface area did not come in descending order. The variation of pore volume and pore diameter of the spherical silica may be the major reason for this phenomenon. The pore size distributions of the spherical silica (not shown) exhibited only unimodal pore size distribution. The images from scanning electron microscope (SEM) in Figure 1 confirm the spherical shape of silica with the particle sizes ranging between 0.5 - 10 μm in accordance with the information from the material provider (3, 5 and 10 μm) and the referred report (0.5 μm) [13].

3.2 Characterization of supported filler

In the production of polymer/spherical silica composites via in situ polymerization, the silica particles were impregnated with MAO cocatalysts prior to introducing them into a polymerization system. Therefore, after the impregnation procedure the finished spherical silica on which the MAO was impregnated named as a supported fillershould be investigated first. Using X-ray diffractometer, the XRD patterns indicating the crystal structure for the entire fillers were obtained (Figure 2). It can be seen that the entire filler exhibited the similar XRD patterns consisting of a broad peak between ca. 20° - 30° assigning to conventional amorphous silica. In addition, no MAO peaks were detected. This suggests that MAO was highly dispersed on the fillers. X-ray photon spectroscopy (XPS) was also used here to study the nature of [Al]MAO on various filler surfaces on which the binding energy (BE) for Al 2p core-level was extended. The typical XPS spectra for the entire filler (Table 2) exhibited the identical BE for Al 2p of cocatalyst at 74.3-75.1 eV. These values were also in accordance with MAO present on the non-spherical silica SiO_2 as reported by Hagimoto *et al.* [14] and Ketloy *et al.* [15]. This suggests that no significant change in the oxidation state of [Al]MAO when presented on the spherical silica employed. The XPS wasused to measure the surface concentration of Al 2p as shown in Table 2. It is indicated that surface concentrations of Al were around 30 wt% and the smallest silica (0.5 μm) gave the highest value likely due to its larger surface area among all the supports.

Because the finished fillers with MAO have to be used in the vigorous conditions of the *in situ* polymerization, their stabilization during the reaction especially thermal stabilization need to be considered. Measuring weight change of the particles upon temperature by thermal gravimetric analysis (TGA) could provide the information related to the trend of the particle behavior under polymerization conditions. The TGA profiles on various fillers are shown in Figure 3. It can be seen that all fillers exhibited similar profiles indicating their similar behavior upon the change of temperature. Nevertheless, there were some differences in the value of weight loss among the entire fillers. The weight loss were in the order of SiO_2 (0.5 μm) 25.85% $>$ SiO_2 (5 μm) 21.60% $>$ SiO_2 (10 μm) 19.17% $>$ SiO_2 (3 μm) 13.74%. The higher weight loss can refer to the lower interaction between MAO and the spherical silica surface, and also lower stability of MAO present on the surface. Therefore, it can be implied from the TGA results that the MAO presented on SiO_2 (3 μm) had the strongest interaction with the silica and has the most stability whereas the smallest SiO_2 (0.5 μm) had the weakest interaction and has the least stability.

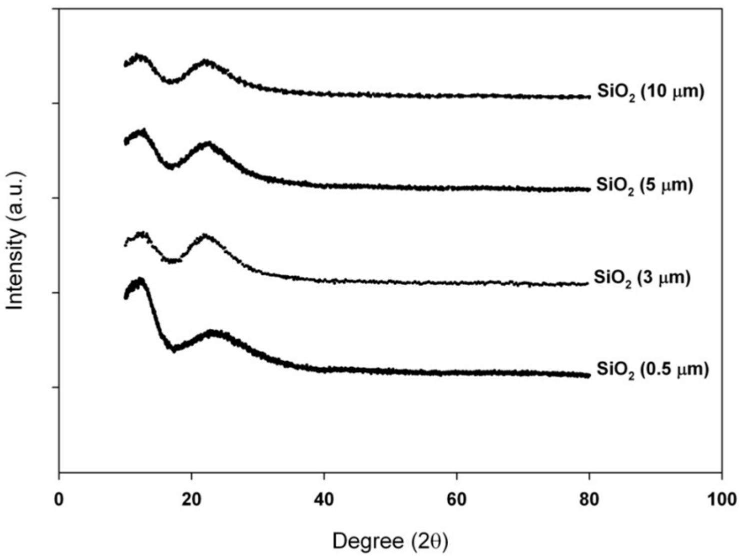


Figure 2. XRD patterns of spherical silica/MAO supported filler.

Table 2. Binding energy and surface concentration for Al 2p obtained from XPS.

Catalyst precursor	BE for Al 2p (eV)	Al mass concentration (wt%)
SiO_2 (0.5 μm) / MAO	74.6	35.07
SiO_2 (3 μm) / MAO	74.5	31.37
SiO_2 (5 μm) / MAO	74.3	34.11
SiO_2 (10 μm) / MAO	75.1	28.42

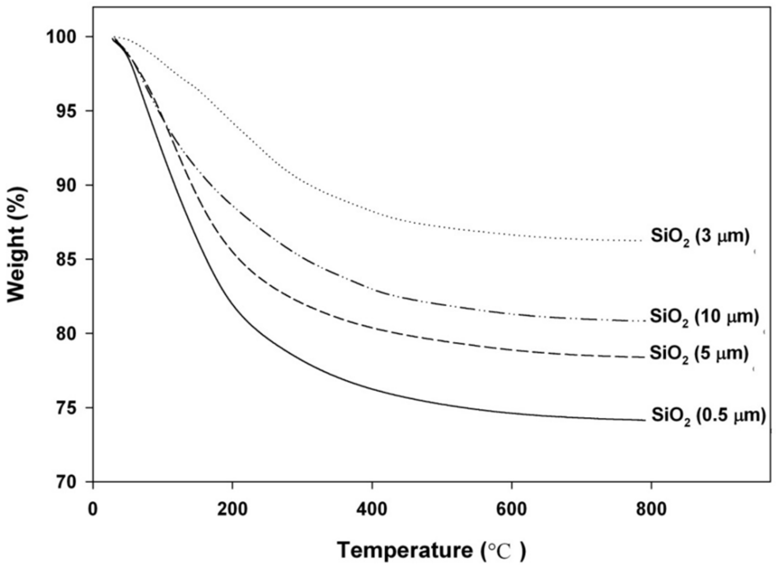


Figure 3. TGA profiles of spherical silica/MAO supported filler.

Table 3. Catalytic activity of *in situ* polymerization with the spherical silica fillers.

Run	System	Fillers	Monomer/ comonomer	Polymerization time (sec)	Yield[a] (g)	Catalytic activity[b] (kg Pol.mol $Zr^{-1}\cdot h^{-1}$)
1	Homogeneous	-	Ethylene	75	0.7318	23,418
2	Heterogeneous	SiO_2 (0.5 μm)	Ethylene	148	0.5199	8,432
3		SiO_2 (3 μm)	Ethylene	105	0.6275	14,343
4		SiO_2 (5 μm)	Ethylene	72	0.6245	20,816
5		SiO_2 (10 μm)	Ethylene	87	0.7406	20,431
6	Homogeneous	-	Ethylene/ octene	71	1.086	36,710
7	Heterogeneous	SiO_2 (0.5 μm)	Ethylene/ octene	131	0.9114	16,697
8		SiO_2 (3 μm)	Ethylene/ octene	113	1.1091	23,556
9		SiO_2 (5 μm)	Ethylene/ octene	94	1.1328	28,922
10		SiO_2 (10 μm)	Ethylene/ octene	84	0.9427	26,935

[a] The polymer yield was fixed and limited by 0.018 mol of ethylene consumption.

[b] Measurement at polymerization temperature of 70 °C, [Ethylene] = 0.018 mole, [1-octene] = 0.0045 mole, [Zr]cat = 5×10^{-5} M, $[Al]_{MAO}$ /$[Zr]_{cat}$ = 1135, $[Al]_{TMA}$ /$[Zr]_{cat}$ = 2500 in toluene with total volume = 30 ml.

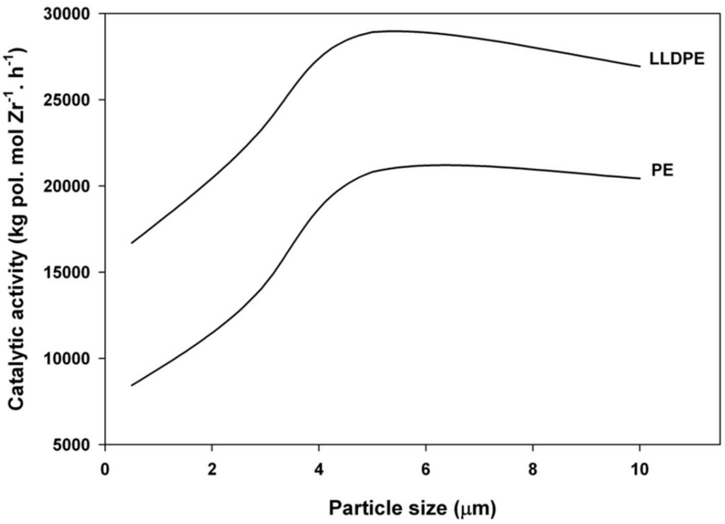


Figure 4. Catalytic activity profile for PE and LLDPE production.

3.3 Catalytic activity performance

The 4 different sizes of spherical silica were introduced as a supported filler into *in situ* polymerization to perform the production of polymer/ spherical silica composites. Each size was used to produce 2 types of polymers: 1. polyethylene (PE) and 2. linear-low density polyethylene (LLDPE). For LLDPE production, 1-octene comonomer was added together with ethylene monomer during polymerization. The polymerization time, polymer yield and catalytic activity for each system were measured as shown in Table 3. It can be seen that the heterogeneous systems (run 2-5, 7-10) in which the spherical silica was added provided lower catalytic activities than that of the homogeneous systems (run 1, 6) for both PE and LLDPE productions. This can be attributed to negative supporting effects such as inaccessibility of MAO cocatalyst to metallocene catalyst, generation of active sites with lower propagation rates due to interactions with the support surface and restrictions of the monomer access to the active sites [16]. The catalytic activities of the heterogeneous systems were plotted against the particle size as shown in Figure 4. It can be observed that the changes of catalytic activity upon the particle size for PE and LLDPE productions are similar.

The catalytic activities increased with increasing the particle size until 5 μm and then slightly decreased at 10 μm.

However, if MAO concentrations on the surface of each filler (based on the XPS result) are considered, it can be seen that they are non-linearly related to the catalytic activity. In fact, the greater amount of MAO should result in more active species present during polymerization and then enhance the catalytic activity [17-18]. Therefore, there should be other factors that affect the polymerization system more than the MAO concentration.

The difference in catalytic activity may rely mainly on the difference of the particle size of spherical silica present in the polymerization system. It was observed that the improved catalytic activity lies in the polymerization system with the larger particle size, probably due to the larger particle sizes providing the larger bulk space for monomer/comonomerto attack the catalytically active sites on the particle surface. In addition, the agglomerated particles usually occur in the smaller particle sizes. This leads to the loss of catalytically active sites in the polymerization system. The low stability of MAO (catalytically active sites) on the smallest particle size (0.5 μm) as observed by TGA may be one of the reasons that reduce the catalytic activity. This is due to the lower stability causing less efficiency to those sites in catalytic manner [19]. Nevertheless, having too many of the larger particle sizes with small surface area results in the poor distribution of the catalytically active sites on the particle, leading to the lower catalytic activity as seen in the case of 10 μm-spherical silica.

Comparing the catalytic activities between PE and LLDPE productions, it is common that the higher values belong to the LLDPE production. This is generally because of a comonomer effect attributing to the easier monomer diffusion due to crystallinity reduction of the growing polymer when a small amount of comonomer is added [20].

3.4 Polymer composite properties

To ensure that the composites obtained were PE and LLDPE as expected, the proper equipments, *i.e.*, XRD and ^{13}C-NMR were used here. Besides confirming the types of the composites obtained, this equipment can provide further details of the composites which give a better understanding on the polymerization systems with various particles. From XRD patterns, the characteristics of PE polymer particularly its crystallinity can be distinguished. As seen in Figure 5, two peaks at 21.8° and 24.3° are clearly shown. These peaks corresponded to the crystalline form of PE, thus confirming that the obtained composites in run 1-5 were PE. Due to LLDPE having low crystallinity, the XRD cannot give a noticeable detail for this type of polymer. The ^{13}C-NMR, which can provide information of comonomer insertion into the polymer chain, was used instead for confirming the characteristic of LLDPE. The spectra obtained from ^{13}C-NMR (not shown) suggested that the introduced 1-octene comonomer into the polymerization system was present in the obtained composites, thus indicating the typical characteristic of LLDPE. In addition from the ^{13}C-NMR spectra, the quantitative analysis of comonomer insertion can be obtained as in the method described by Randall [21]. The comonomer insertions were in the order of; no silica 8.5%, SiO_2 (0.5 μm) 12.2% $>$ SiO_2 (3 μm) 11.8% $>$ SiO_2 (5 μm) 12.8% $>$ SiO_2(10 μm) 30.4%. As observed, the polymerization systems with spherical silica can increase the comonomer insertion for the obtained polymer compared to the system without it. This was due to a good distribution of catalytically active sites influenced by the silica particles, then enhancing comonomer accessibility and depressing the reactivity of monomer in supported system [22]. There was no significant difference in comonomer insertions among various particle sizes. This suggests that the difference of particle size did not affect the mechanism of comonomer insertion.

Thermal properties of the obtained composites can be evaluated in terms of melting temperature (T_m), crystallization temperature (T_c) and percentage of crystallinity by using the differential scanning calorimeter (DSC) as shown in Table 4. It can be observed that the melting temperatures of the samples inrun 1-5 were in the range of 130-135 °C, which are the characteristic melting temperature of polyethylene. Therefore, this result were in agreement with the XRD result. Only minor alteration of the melting temperature upon the various particles size was observed. It was not directly related to the particle sizes of the fillers. Therefore, the particle sizes do not affect the melting temperature of the obtained polyethylene. Nevertheless, the crystallization of polyethylene was affected by the particles size. It decreased with increasing the particle size. Moreover, introducing the spherical silica into the polyethylene matrix (run 2-5) caused noteworthy reductions of the polymer crystallinity. To explain this result, the crystallization kinetics of polymer should be reviewed here. In general, polymer crystallization occurs through 2 main processes, nucleation and growth [23]. Nucleation can be divided into homogeneous and heterogeneous nucleation, the former being the sporadic formation of critical nuclei from the pure phase, the latter occurring at the surface of impurities within the system. In high, polymers heterogeneous nucleation dominates in most cases [24]. Comparing with this study, the spherical silica introduced during polymerization in run 2-5 can act as impurities (heterogeneous nucleation) and then should enhance the nucleation process. However, it should be noted that the surface qualities such as, roughness and smoothness of the impurities can play important role in the nucleation. In general, the rough surface is more efficient for nucleation than the smooth surface because of the easier stress relaxation for rough surface structures, thus clusters having potential to be a crystal being preferentially formed [25]. On this account, the spherical silica with a smooth surface as used in this study had low capability in nucleation.

Growth processes can be categorized into interface-controlled growth and diffusion-controlled growth. Diffusion-controlled growth is the rate of transport of heat and mass, to or from the growth front that limits the rate of growth. Interface-controlled growth is the actual process of attaching and detaching molecules at the surface that controls the growth rate. Although it is hard to identify how the spherical silica affects growth, a plausible explanation for its drawback is that the spherical silica may inhibit the rate of transportation and also with the smooth surface the process of attaching may be interrupted. To conclude, it can be said that the presence of the spherical silica in the PE production deteriorated the crystallization process and therefore decrease the amount of crystallinity in the obtained composites.

For the effect of particles size on the crystallization, it should be noted that differences in the particle sizes also come with differences in surface areas. The smaller the surface area in the larger particle provides less nucleating sites, consequently less nucleation occurred. Therefore, decreasing in crystallinity took place when increasing the particle size. However, as observed in BET surface area, SiO_2 (3 μm) having smaller surface area than SiO_2 (5 μm) provided more crystallinity. Hence, there should be other factors affecting the crystallization process besides the surface area. The particle size itself may be a crucial factor. The larger particle can cause a greater obstacle to folding polymer chains to form a lamellae layer, which develops into a crystal structure. Combining with the courtesy of smaller surface area, the larger particle therefore provided less crystallinity to the obtained polyethylene than the smaller one.

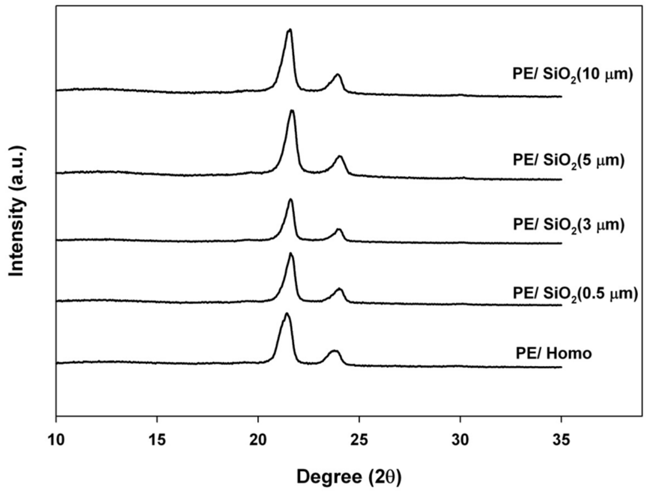


Figure 5. XRD patterns of PE with various fillers.

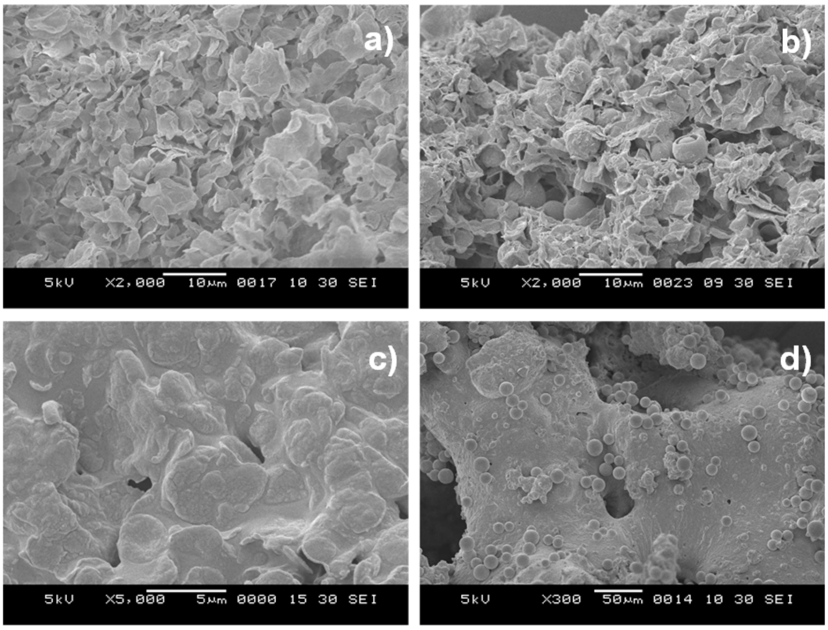
Table 4. Thermal properties of the polymer composites.

Run	Melting temperature, T_m (°C)	Crystallization temperature, T_c (°C)	Crystallinity (%)
1	131.3	115.5	68.8
2	132.7	116.5	53.6
3	132.4	116.8	52.2
4	134.7	115.8	48.1
5	132.4	116.5	46.8
6	117.4	98.8	4.7
7	111.7	95.3	1.8
8	113.2	98.6	1.9
9	111.6	95.2	1.7
10	113.9	99.4	3.1

For the LLDPE production (run 6-10), the melting temperatures of the obtained LLDPE composites varied between 111-118 °C, which were slightly lower than that of a commercial LLDPE reported (about 120 °C) [26]. This may arise from the large comonomer fraction in the samples. The crystallinties of the obtained LLDPE were all lower than the obtained PE as expected. This is because the long side chains of comonomer slow a chain folding process. In addition, the polymers with a complex structure cannot easily rearrange themselves to form a crystalline structure. The LLDPE production with spherical silica filled (run 7-10) provided less crystallinity to the obtained polymer than the homogeneous system (run 6) as happened as in the PE production. This means that the spherical silica also deteriorates the crystallization process for the LLDPE production. However, the effect of particle size was not clearly shown in this production. This is probably because the mechanism of crystallization in LLDPE is more complex than that in PE. The amount of comonomer side chain and even the uniformity of it can strongly influence the crystallization process [26], thus the effect of particle size may be less profound.

The morphology of the polymer products was examined by the scanning electron microscope (SEM). The SEM micrographs are shown in Figure 6. Figure 6 a) and 6 c) are the morphologies of the polymer obtained from the homogeneous polymerization system; a) for the PE production and b) for the LLDPE production. It was obvious that they were totally different. The PE polymer exhibited a plate-like structure, in which each individual plate was not strongly linked together, whereas the LLDPE polymer revealed the continuous phase surface where no individual plate was observed. This result is probably due to the difference in the crystallinity between two products. The lower crystallinty in the LLDPE likely causes more amorphous material that behaves similarly to the liquid but with higher viscosity. Therefore, the LLDPE molecules can easily be gathered together like liquid, as observed from the SEM micrographs.

The morphologies of the composites obtained from both PE and LLDPE productions are also shown in Figure 6 b) and 6 d) respectively. Considering the polymer matrix part of the PE and the LLDPE composites, it was found that both still retained the structure of the host polymer. The plate-like structure was still observed in the PE composites while the LLDPE composite still exhibited the continuous phase surface. This suggests that the spherical silica did not affect the morphology of the polymer products. The leaching of the silica particles from the polymer matrix can be found in both PE and LLDPE composites. This was an unusual case because with the same polymerization system but difference in the type of a filler (*e.g.* non-spherical silica [27-28], titania (TiO_2) [29], zirconia (ZrO_2) [30]) the leaching never occurred. Therefore, the properties of the used filler particularly its spherical shape and its smooth surface should be taken into account. In fact, in the polymer production used here leaching can exist for 2 reasons: 1)leaching of MAO from the catalytic filler, and then run homogeneously leaving the bare particles without the ability to form the polymer on them, and 2) a leaching of the growing polymer from the particles during polymerization. The first reason is less likely to happen because it is unlikely that the entire MAO molecule will leach the particles. There should be some remaining on the particles, thus forming the polymer on them. Nevertheless, the bare particles could be present if the remaining MAO molecules were in an inactive form. The second reason may be true if the adhesion force between the particles and the polymer is weak. This may have resulted from the silica particles with spherical shape and smooth surface having lower coefficient of friction [31], thus lower interfacial adhesion in a polymer matrix. In addition, the spherical particles particularly ones with a broad size distribution are usually packed densely in the polymer matrix, and consequently having low space for the attachment between particles and polymer. It was found that the more dense particles in the polymer matrix also cause the reduction of the other crucial properties such as a modulus [32], which strongly depends on local polymer-filler interaction. Therefore, all the disadvantage of the spherical particles mentioned above could lead to the leaching of the particles from the polymer matrix as seen in the SEM micrographs.



a) PE, b) PE/ spherical silica composite, c) LLDPEand
d) LLDPE/ spherical silica composite.

Figure 6. SEM micrographs of polymer composites.

4. Conclusions

Based on this study, it was found that the catalytic activity of the *in situ* polymerization systems increased with the particle size of the spherical silica filler in the first range and then slightly decreased. This is because the larger particle size provides the larger bulk space for monomer/comonomerto attack the catalytically active sites on the particle surface, then increasing the catalytic activity. Nevertheless, too many of larger particle size comes with smaller surface area, thus resulting in the poor distribution of the catalytically active sites on the particle, and consequently leading to the lower catalytic activity. The crystallinity of the PE composite decreased with the filler particles size, while in the LLDPE composite, the change in crystallinity was not relating to the filler particle size. This was due to more complexity in the crystallization mechanism in the LLDPE composites. The leaching of the spherical silica fillers occurred in both PE and LLDPE composites. Therefore, the modification by the spherical silica needs further investigation.

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