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A Comparative Study of *in situ* and *ex situ* Impregnation for LLDPE/Silica Composites Production

Ekrachan Chaichana[1], Takeshi Shiono[2], Piyasan Praserthdam[3]
and Bunjerd Jongsomjit[3,*]

[1] Chemistry Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand
[2] Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan
[3] Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
E-mail: bunjerd.j@chula.ac.th*

Abstract. The two different kinds of impregnation (*in situ* and *ex situ*) were used in the heterogeneous copolymerization of ethylene and 1-hexene for production of LLDPE/silica composite. For the *ex situ* impregnation, MMAO cocatalyst was immobilized firmly onto the silica support through washing and drying step before introducing the powder of MMAO/silica support into the copolymerization system. For the *in situ* impregnation, MMAO was only contacted with silica support for the short period of time before bringing all of the slurry of MMAO/silica support into the copolymerization system. By comparing the catalytic activity between two methods, it was found that the *in situ* impregnation provided the higher one beneficial from the lower interaction between MMAO and silica due to lower contacting time. The lower interaction enhanced the reactivity of MMAO toward zirconocene catalyst during activation process thus leading to the higher catalytic activity. The said interaction can be proven by thermal gravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) analysis. In addition, the obtained polymers were further characterized by means of scanning electron microscopy (SEM), ^{13}C-NMR spectroscopy (NMR) and differential scanning calorimetry (DSC).

Keywords: Polymers, thermal properties, x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), metallocene.

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1. Introduction

Linear low-density polyethylene (LLDPE) is one of the most widely used polyolefins in many applications, especially for plastic films. However, LLDPE is limited using in some case by its drawbacks such as, low mechanical strength and low thermal resistance. To overcome these problems, some materials (filler) with the properties that can make up for the absent properties of LLDPE are needed. Silica is an inorganic material, which has outstanding benefits of high thermal stability and high strength. Hence, silica is brought to fill into LLDPE to obtain the LLDPE/silica composite with various beneficial properties.

As known that LLDPE can be produced by copolymerization of ethylene and higher 1-olefins with metallocene and MAO catalyst. However, the homogeneous liquid phase reaction of metallocene is lack of morphology control. Therefore, the supported catalytic system (heterogeneous system), which can improve this problem, has been developed [1]. It has been reported that many inorganic supports such as SiO_2, Al_2O_3 and $MgCl_2$ have been extensively studied. SiO_2, particularly, is a main inorganic material often brought into the system as a supporting materials since it can form support having suitable particle-size and porousity properties [2]. The procedure of making supported catalytic system is to immobilize the catalytic species (metallocene or MAO) onto the solid supports (SiO_2) then called supported catalyst and introduced it into the copolymerization system. Therefore, when introducing silica into synthesis of LLDPE, it can act as catalytic supporting material in the supported catalytic system and also as filler in polymer composites as mentioned above.

Presented as a support, silica provides the heterogeneous system with great advantages over the homogeneous system such as, giving the obtained polymer with good morphology and decreasing reactor fouling in the system [3]. Nevertheless, there was a crucial disadvantage in heterogeneous copolymerization that is, supporting material, often declining the catalytic activity of the system. The lower activity probably derives from strong interaction between cocatalyst (MAO) and support that occurred during immobilizing step [4,5]. With this strong interaction, MAO on the support is susceptible not to form bond with the other molecules during copolymerization including monomer and comonomer then decreasing activity. Therefore, in order to retain the high activity in supported system, the additional liquid MAO (or MAO) may be required as performed by many researchers [6,7]. Another method that can be used to retain or even gain the high activity in supported system is to reduce interaction between MAO and support during immobilizing step by using *in situ* impregnation method in preparation of supports, as proposed by Wannaborworn [8]. In this method, only short period of mixing between MAO and support is needed without washing and drying step. Thus, the lower interaction between them is expected and consequently the high catalytic activity for the system could be obtained. However, this method may cause many problems to the obtain polymer such as the leaching of MAO into homogeneous phase, which causes non-uniform properties and a bad interfacial adhesion due to low interaction of MAO and support. Hence, balancing this interaction is very crucial and should be further investigation in the near future.

For this study, we aim to develop a better understanding on how different impregnation methods can influence the copolymerization system on both its catalytic activity and the properties of its obtained polymer, thus, two impregnation methods (*in situ* and *ex situ*) for synthesis of LLDPE/ silica composites with metallocene/MMAO (modified MAO) catalyst were investigated. In addition homogeneous copolymerization will also be conducted for comparison. The catalytic activities of each system and the properties of the entire obtained polymers are carefully considered together.

2. Experimental

2.1. Materials

All operations were manipulated under an argon atmosphere using glove box and/or standard Schlenk techniques. The $[t\text{-BuNSiMe}_2\text{Flu}]\text{TiMe}_2$ (Ti-complex) was synthesized according to the procedure described by Hagihara *et al*. [9]. Ethylene (polymerization grade) was obtained from the National Petrochemical Co. Ltd., Thailand. 1-Hexene (≥ 97%) was purchased from Aldrich Chemical Company, Thailand and further purified by distilling over CaH_2 for 6 h. Modified methyl aluminoxane, MMAO [(Me–Al–O–)*m*-(i–Bu–Al–O–)*n*] having 1.86 M in toluene, was donated by Tosoh Akzo, Japan.

Toluene (commercial grade) was donated by the Exxon Chemical, Thailand Co. Ltd. It was dried over dehydrated $CaCl_2$ and distilled over sodium/ benzophenone.

2.2. Preparing of supported MMAO

2.2.1. *In situ* impregnation method

Silica (0.1 g) was allowed in contact with 4 mmol of MMAO for at least 2 h in a reactor with magnetic stirring, and then the slurry of MMAO/ support was obtained [8].

2.2.2. *Ex situ* impregnation method

The support was reacted with the desired amount of MMAO in 20 ml of toluene at room temperature for 30 min. The solvent was then removed from the mixture by evacuation. This procedure was done only once with toluene (20 ml x 1) and three times with hexane (20 ml x 3). Then, the solid part was dried under vacuum at room temperature. The white powder of supported cocatalyst (MMAO/support) was then obtained.

2.3. Polymerization procedure

Ethylene/1-hexene copolymerization was carried out in a 100 ml semibatch stainless steel autoclave reactor equipped with a magnetic stirrer. At first,

- for the homogeneous system: 4 mmol of MMAO and the toluene were introduced into the reactor;
- for the heterogeneous system with *ex situ* impregnation: about 0.1 g of MMAO/ support and some adding liquid MMAO in toluene (make the total MMAO to 4 mmol) were introduced into the reactor;
- and for the heterogeneous system with *in situ* impregnation the prepared MMAO/support (0.1 g support and 4 mmol MMAO) and the toluene were introduced into the reactor.

The titanium complex in toluene (10 $\mu mol \cdot ml^{-1}$) was put into the reactor to make the $[Al]_{MMAO}/[Ti]cat = 400$. Then, the reactor was immersed in liquid nitrogen. 0.018 mole of 1-hexene was added into the frozen reactor (to stop or prevent possible polymerization of 1-hexene). The reactor was heated up to the polymerization temperature at 70 °C. The polymerization was conducted by feeding ethylene into the reactor for 10 min. The ethylene pressure and reactor temperature were kept constant during the polymerization (pressure in reactor = 50 psi). The reaction was terminated by adding acidic methanol and the material was stirred for 30 min. After filtration, the copolymer obtained was washed with methanol and dried at room temperature.

2.4. Analytical technique

2.4.1. Thermal gravimetric analysis

TGA was performed using SDT Q 600 analyzer (TA instrument, USA). The samples of 10-20 mg and a temperature ramping from 30 to 600 °C at 5 °C/min were used in the operation. The carrier gas was N_2 UHP.

2.4.2. X-ray photoelectron spectroscopy

XPS analysis was performed using an AMICUS photoelectron spectrometer (Shimadzu corporation, Japan) equipped with a MgK_α X-ray as a primary excitation and a KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 eV.

2.4.3. Scanning electron microscopy

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 polymer samples were coated with the platinum prior to observation. The EDX was performed using Link Isis series 300 program.

2.4.4. ^{13}C-NMR spectroscopy

^{13}C-NMR spectroscopy was used to determine the 1-hexene incorporation and copolymer microstructure. Chemical shifts were referenced internally to the $CDCl_3$ and calculated according to the method described by Randall [10]. Each sample solution was prepared by dissolving 50 mg of copolymer in 1,2,4-trichlorobenzene and $CDCl_3$. ^{13}C-NMR spectra were taken at 60 °C using a BRUKER AVANCE II 400 (Bruker corporation, Germany) operating at 100 MHz with an acquisition time of 1.5 s and a delay time of 4 s.

2.4.5. Differential scanning calorimetry

The melting temperature of ethylene/1-hexene copolymer products was determined with a Perkin-Elmer diamond DSC (Perkin-Elmer, USA). The analyses were performed at the heating rate of 20 °C/min in the temperature range of 50–150 °C. The heating cycle was run twice. In the first scan, samples were heated, and then cooled to room temperature. In the second scan, samples were reheated at the same rate, but only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of samples.

2.4.6. Inductive couple plasma-optical emission spectroscopy

ICP-OES was performed using Perkin Elmer model PLASMA-1000 (Perkin-Elmer, USA) to determine the amount of MMAO (Al) on the support. About 50 μg of a sample was digested by sulfuric acid, and then made the volume to 50 ml by ionized water.

3. Results and Discussion

3.1. Catalytic activity

There were three copolymerization systems used for obtaining LLDPE in this comparison. The first was the homogeneous system (HOMO), where all materials: catalyst, MMAO, comonomer and solvent were in liquid phase (excluding ethylene introduced in gas phase). The second and the third (HTRO-*ex* and HTRO-*in*) are the heterogeneous systems, which besides all the materials used in the homogeneous system, silica in solid phase was also introduced into the system as a support. The different between HTRO-*ex* system and HTRO-*in* system is that, in HTRO-*ex* system, the *ex situ* impregnation method was used in preparation of support. In HTRO-*in* system, the *in situ* impregnation was used instead. The *ex situ* impregnation was performed by impregnating MMAO onto silica, and then, washing and drying for 3 times before introducing it into the copolymerization system. The *in situ* impregnation was performed simply by impregnating MMAO onto silica for a certain time after that introducing it (slurry of MMAO/silica) into the copolymerization system immediately without washing and drying. To ensure that all MMAO used in the *in situ* impregnation was completely impregnated onto the support, a pretest for finding the proper amount of MMAO and the proper time in impregnation was performed as the method described by Wannaborworn [8].

It has already been known that for metallocene catalytic system, the heterogeneous reaction usually results in a low activity compared to the homogeneous reaction because of the generation of active sites with lower propagation rates due to interactions with the support surface [11]. This problem may be sorted out by introducing the catalytic species (MMAO or metallocene) in liquid form into the system during reaction to compensate the one that was immobilized on the support surface with strong reaction. Therefore, the heterogeneous system with *ex situ* impregnation (HTRO-*ex*) conducted in this study had been added by the liquid MMAO during copolymerization to make the ratio of MMAO to metallocene catalyst (Al/Ti) about 400 (equally to HOMO system).To detect the amount of aluminium species in the silica/MMAO support, ICP-OES technique was used. In HTRO-*in* system, the ratio of Al/Ti had already been fixed at 400 because, in this method, MMAO will never lose during immobilization process like *ex situ* impregnation. Then, the ratio of Al/Ti was constant during the time of copolymerization. The additional liquid MMAO is needless for this method.

Catalytic activities of all the systems with a titanocene catalyst were investigated during copolymerization of ethylene and 1-hexene, and listed in Table 1. From this table, it can be seen that all activities are roughly similar at about 800 $kg_{pol}/(mol_{Ti}/hr)$. This means that the heterogeneous systems (HTRO-*ex*), which usually give a low activity, had been improved by addition of liquid MMAO as expected. A little increase in activities of the heterogeneous systems compared with the homogeneous system may be come from some advantages of support when introducing it into the system, including decrease in reactor fouling and improvement in stability of the catalyst [12]. When comparing between both of the heterogeneous systems with different impregnation methods, it was found that the system with *in situ* impregnation (HTRO-*in*) gave a slightly higher activity than the system with *ex situ* impregnation (HTRO-*ex*). In order to explain this result, the difference between two impregnation methods should be concerned. The major differences are the amount of MMAO on the surface of silica supports during copolymerization and the strength of interaction between MMAO and the silica surface. Hence, these two factors should be concerned in order to clarify the results.

Table 1. Polymerization activities for different systems.

System	**Reaction**	**Impregnation**	**Yields (g)**	**Activity** [a] **$kg_{pol}/(mol_{Ti}/h)$**
HOMO	Homogeneous	-	1.261	757
HTRO-*ex*	Heterogeneous	Ex situ	1.311	786
HTRO-*in*		In situ	1.474	885

[a] Copolymerization condition: Ti = 10 μmol, Al/Ti = 400, temperature = 343 K, 50 psi of ethylene pressure was applied.

As mentioned earlier that one disadvantage of the heterogeneous system is that the species on the support surface will generate active sites with a low propagation rate. Therefore, with the same amount of the overall active sites, which system has more active sites on the support surface will give a lower activity than the other. However, for these two impregnation methods, it was the *in situ* impregnation method (HTRO-*in*) that should posses more active species on the surface because there were no washing and drying in this method. Therefore, it reduced in the loss of MMAO during preparation and then, providing the higher amount of active species on the support surface. Whereas the *ex situ* impregnation method (HTRO-*ex*) which at first the support in the system was contacted with the same amount of MMAO, gave the finished support exhibited only about 60% of MMAO on it as investigated by ICP-OES technique. It can be seen that the result that *in situ* impregnation provides better activity than *ex situ* impregnation is inconsistent with the presumption that the more active species on the support surface is the less activity for the system obtains. Thus, the other difference between both impregnation systems that is the interaction of MMAO and the support surface, should substitute for the first one to further explain the result.

The stronger interaction of MMAO and silica support can cause lower activity for the system because MMAO with this strong interaction is susceptible not to react with metallocene catalyst during an activation step thus generating less catalytic active spicies [5] (the position of each species can be seen in Fig. 1). This interaction would occur more in *ex situ* impregnation as a result of the fact that with this method, MMAO bound to the support had to involve in washing and drying processes that making some lose during these processes, and then only some with sufficiently strong interaction to the support could exist until the end of the processes. To prove this hypothesis, some parameters obtained from TGA measurement, which normally indicate thermal stability, can also be used to indicate the degree of interaction in polymers and therefore can be used to trace back to the interaction of MMAO and support.

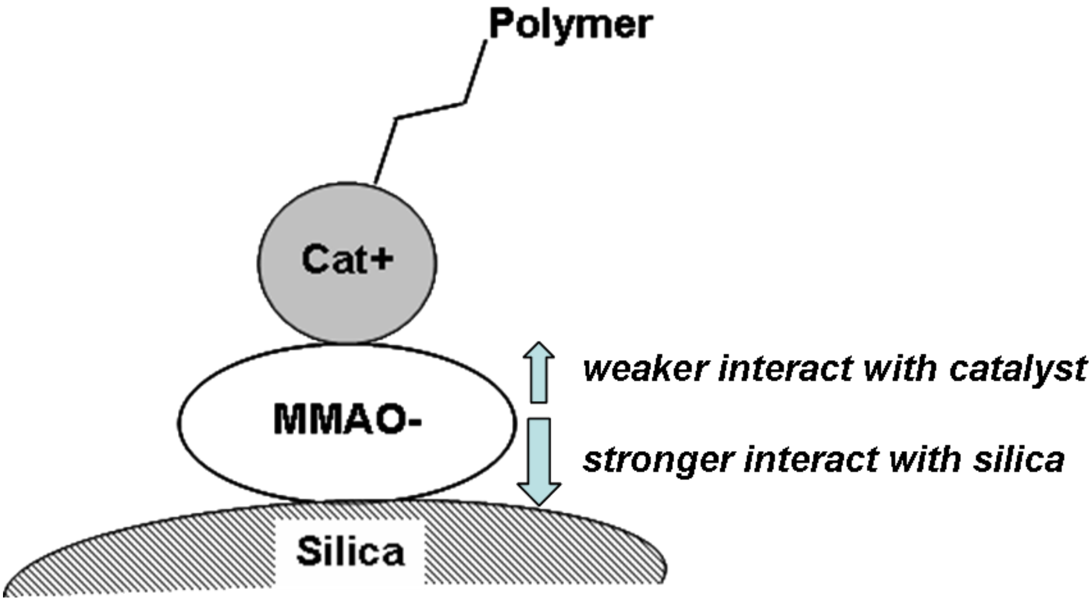

Fig. 1. Conceptual model indicating the position of species in polymer composites.

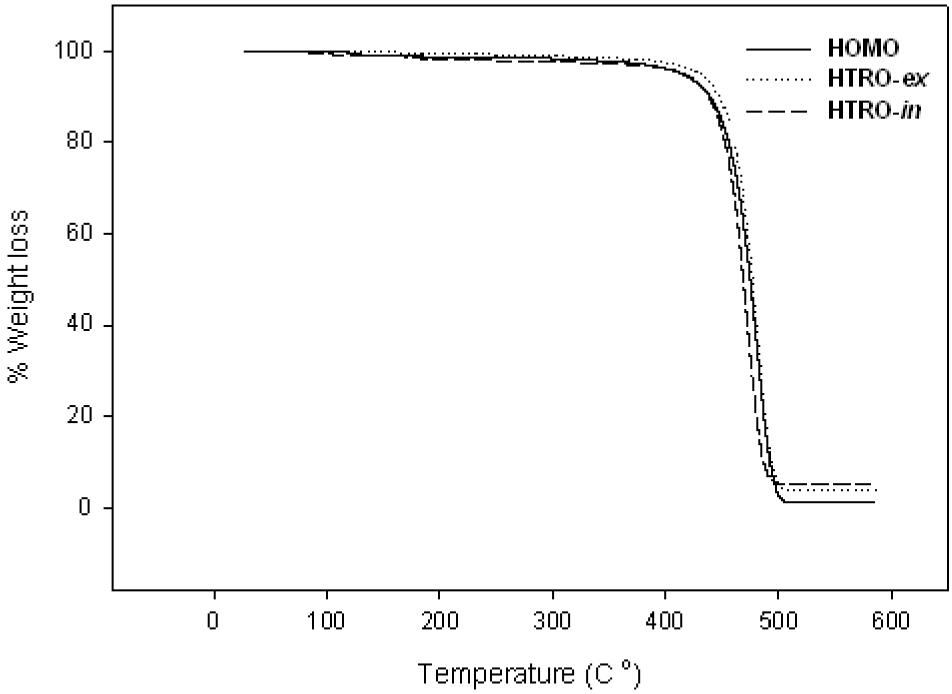

Fig. 2. TGA curves of polymers for different systems.

From Fig. 2, it shows the weight loss profiles of the polymers obtained from different systems. From this figure, all three profiles were similar indicating to the normal profile of LLDPE. The onset temperatures for degradation (temperatures at 5% and 10 % weight loss [13]) are shown in Table 2. The highest onset temperatures for degradation were observed in the polymer obtained from HTRO-*ex* system while HTRO-*in* system exhibited those temperatures nearly to the homogeneous system (HOMO). This suggests that, even polymers with the same type of filler (support) and also with nearly the same amount (about 7 %wt) could differ in thermal stability due to the variation of internal interactions. The better thermal stability may derive from the support particles interacting to polymer stronger through a tighten bond of MMAO and silica. Therefore, the polymer obtained from HTRO-*ex* system showed the better thermal stability than HTRO-*in* system because the first one has stronger interaction between silica and MMAO. This stronger interaction then reduced the activity in HTRO-*ex* as seen in the previous result.

Table 2. The degradation onset temperature for different systems.

System	**Temperature at weight loss** (°C)	
	5%	**10%**
HOMO	414.6	439.6
HTRO-*ex*	433.6	451.7
HTRO-*in*	416.3	438.1

An XPS measurement is one of the methods that can reveal the chemical linkage between the support particles and the polymers [14], so it can be used to further investigate the interaction being discussed. With regard to binding energy values of Si in Table 3 among two heterogeneous systems, the strong interaction between Si atom and adjacent chemical group would belong to HTRO-*ex* system due to the higher binding energy (B.E.) of Si. It has been known that the binding energy of Si (probed atom) would increase when it was bound with the electron withdrawing group. Therefore, MMAO compound which has been found that it presents some relatively Lewis acidity (electron withdrawing) when forming interaction [15], could increase the binding energy of Si when it interacts with Si through Si(–O–MMAO) bond. The stronger interaction between Si and MMAO in HTRO-*ex* system as presumption tends to draw MMAO closer to Si than in HTRO-*in* system. Therefore, MMAO significantly affected binding energy of Si in HTRO-*ex* system than in HTRO-*in* system and then caused binding energy of Si higher. For the binding energies of O and C, they were different among all the samples due to the variation of the chemical environment.

Table 3. Binding energy of the elements measured by XPS.

System	**B.E. (eV)**		
	Si	**O**	**C**
HOMO	-	532.4	285.0
HTRO-*ex*	103.1	534.0	286.5
HTRO-*in*	102.3	532.3	285.0

3.2. Characteristic of polymer

Comonomer contents (1-hexene incorporations) and sequence distributions of each obtained polymer, which can influence on many properties of polymer can be investigated by ^{13}C-NMR technique (Table 4.). From Table 4, it was found that the 1-hexene incorporations of both heterogeneous systems (HTRO-*ex* and HTRO-*in*) were significantly higher than that of the homogeneous system. This is due to good distribution of active sites influenced by the silica particles enhancing 1-hexene accessibility to the active sites and depression in the reactivity of monomer in supported system [16]. The ethylene reactivities showed in Table 4 agree with the suggestion as these values of both heterogeneous systems were less than that of the homogeneous system. The product of reactivity ratio ($r_E r_H$) is one of the parameters which can identify types of copolymer with: a value $rErH > 1$ indicating a block copolymer structure, $rErH < 1$ indicating an alternating copolymer structure and $rErH = 1$ indicating a random copolymer structure. Therefore, the obtained polymers from the heterogeneous systems exhibited block copolymer properties whereas the one from homogeneous system exhibited highly alternating copolymer properties. Melting temperatures (T_m) of polymer obtained from both of the heterogeneous systems were roughly equal but higher than that obtained from the homogeneous system even higher 1-hexene incorporations. This is because the silica particles in the heterogeneous system acted as a nucleating agent during polymerization; consequently, they increase the crystallinity of polymer, and then raising the melting temperature of polymer [17]. Thus, it can be concluded from these results that synthesis of LLDPE with the various phase reaction systems apparently affected the 1-hexene incorporation, the molecular structure and melting temperature of the obtained polymer whereas the various impregnation methods did not.

Table 4. Characteristic of polymers from ^{13}C-NMR.

Entry	**Triad distribution**[a]						**Reactivity**[b]			**H**[c] (%mol)	**T_m**[d] (°C)
	EEE	**EEH**	**HEH**	**EHE**	**EHH**	**HHH**	r_E	r_C	$r_E r_C$		
1	0.611	0.229	0.034	0.126	0.000	0.000	*1.323*	*0.000*	*0.000*	**12.6**	112
2	0.533	0.173	0.036	0.154	0.103	0.002	*0.946*	*1.311*	*1.240*	**27.0**	126
3	0.452	0.230	0.048	0.159	0.108	0.003	*0.754*	*1.208*	*0.910*	**25.6**	122

[a] *Examined by ^{13}C-NMR*

[b] *Relative comonomer reactivities (rE for ethylene and rH for 1-hexene) calculated by*
rE = 2[EE]/[EC]X, rH = 2X[CC]/[EC],
[EE] = [EEE] + 0.5[CEE], [CC] = [CCC] + 0.5[ECC]
[EC] = [CEC] + 0.5[CEE] + [ECE] + 0.5[ECC]

[c] *1-hexene incorporation*

[d] *Melting temperature*

Images of polymer morphologies created from scanning electron microscope (SEM) are shown in Fig. 3. It can be observed that the polymer obtained from HOMO system looked totally different from both of the heterogeneous systems. However, the polymers obtained from the two heterogeneous systems with different impregnation methods (HTRO-*in* and HTRO-*ex*) are also exhibited only a small difference in morphology. This may be due to the different interaction of the silica particles and polymer inside the polymer matrix.

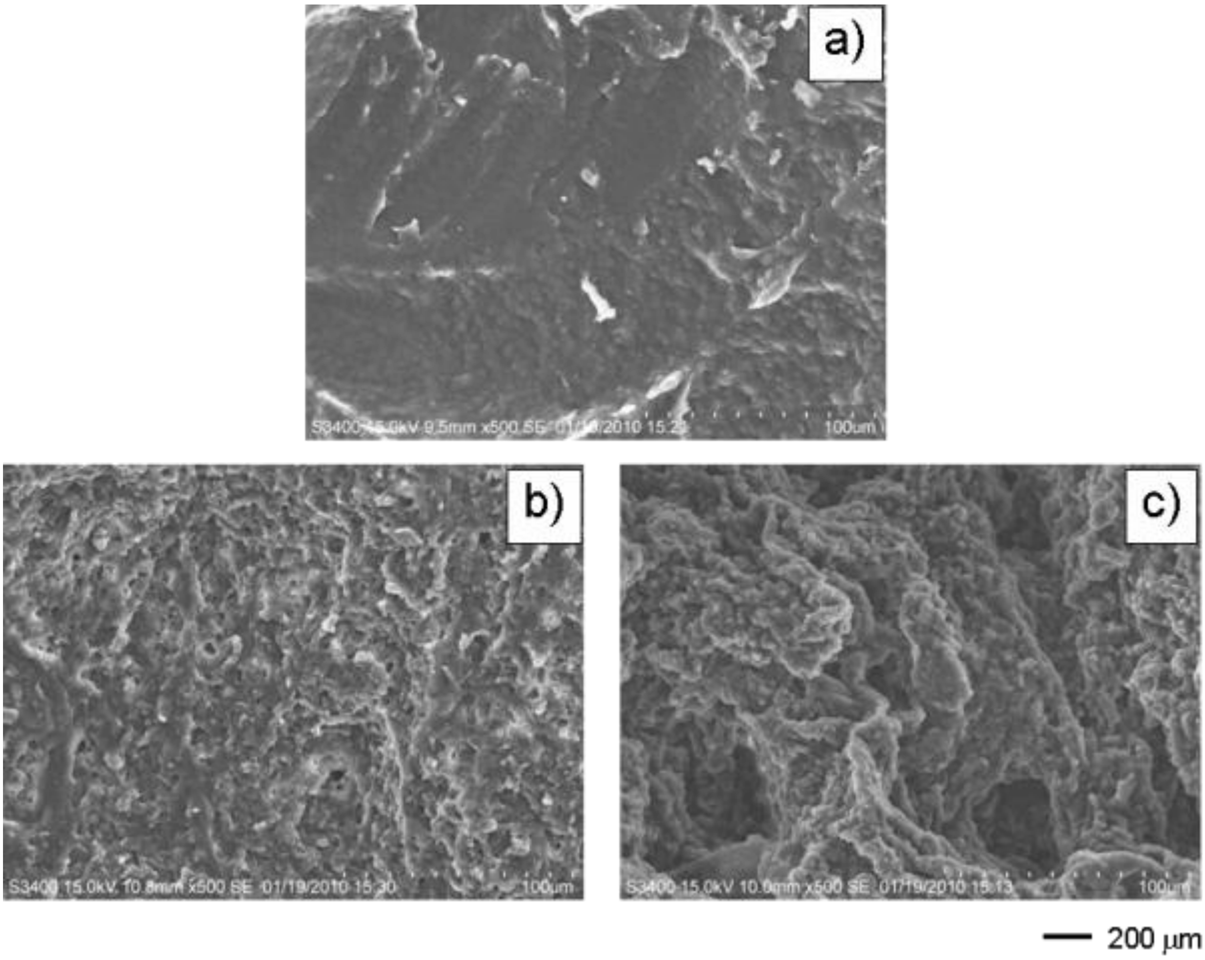

Fig. 3. Morphologies of the polymers obtained from the different systems: a) HOMO, b) HTRO-*ex*, and c) HTRO-*in*.

4. Conclusion

The heterogeneous reaction with *in situ* impregnation revealed here that it is the interesting procedure used to synthesis LLDPE/ composites because it can be performed simply and provided a high catalytic activity. However, as a result of lower interaction between MMAO and support, some properties, such as thermal properties need to be improved. Comonomer contents (1-hexene incorporations) and sequence distributions of the obtained polymers (composite) from both two heterogeneous systems with various impregnation methods were nearly similar, but significantly differed from that of the homogeneous system. This means that the different reaction phases have a greater influence on the microstructure of the obtained polymer than the different impregnation methods.

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References

[1] B. Jongsomjit, S. Ngamposri, and P. Praserthdam, "Observation of bimodal polyethylene derived from TiO_2-supported zirconocene/MAO catalyst during polymerization of ethylene and ethylene/1-hexene," *Catal. Lett.* , vol. 117, no. 3-4, pp. 177-181, 2007.

[2] T. Saudemont, R. Spitz, J. Broyer, J. Malinge, and N. Verdel, *Activator Solid Support for Metallocene Catalysts in the Polymerization of Olefins, a Process for Preparing Such a Support, and the Corresponding Catalytic System and Polymerization Process*, U.S. Patent 6239059, 2001.

[3] K. J. Chu, J. B. P. Soares, and A. Penlidis, "Polymerization mechanism for *in situ* supported metallocene catalysts," *J. Polym. Sci., Part A: Polym. Chem.*, vol. 38, no. 3, pp. 462-468, 2000.

[4] B. Jongsomjit, J. Panpranot, and P. Praserthdam, "Effect of nanoscale SiO_2 and ZrO_2 as the fillers on the microstructure of LLDPE nanocomposites synthesized via *in situ* polymerization with zirconocene," *Mater. Lett.* , vol. 61, no. 6, pp. 1376-1379, 2007.

[5] P. Wongwaiwattanakul and B. Jongsomjit, "Copolymerization of ethylene/1-octene via different pore sized silica-based-supported zirconocene/dMMAO catalysts," *Catal. Commun.* , vol. 10, no. 1, pp. 118-122, 2008.

[6] A. Funck and W. Kaminsky, "Polypropyrene carbon nanotube composites by *in situ* polymerization," *Compos. Sci. Technol.*, vol. 67, no. 5, pp. 906-915, 2007.

[7] Y. S. Ko and S. I. Woo, "Generation of active site confined inside supercage of NaY zeolite on a nano-scale and its ethylene polymerization," *Eur. Polym. J.*, vol. 39, no. 8, pp. 1553-1557, 2003.

[8] M. Wannaborworn and B. Jongsomjit, "Ethylene/1-octene copolymerization over Ga-modified SiO_2-supported zirconocene/MMAO catalyst using *in situ* and *ex situ* impregnation methods," *Iran. Polym. J.* , vol. 18, no. 12, pp. 969-979, 2009.

[9] H. Hagihara, T. Shiono, and T. Ikeda, "Living polymerization of propene and 1-hexene with the $[T\text{-}BuNSiMe_2Flu]TiMe_2/B(C_6F_5)_3$ Catalyst," *Macromolecules*, vol. 31, no. 10, pp. 3184-3188, 1998.

[10] J. C. Randall, "A review of high resolution liquid ^{13}carbon nuclear magnetic resonance characterizations of ethylene-based polymers," *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* , vol. 29, no. 2-3, pp. 201-317, 1989.

[11] F. Silveira, M. d. C. M. Alves, F. C. Stedile, S. B. Pergher, A. Rigacci, and J. H. Z. d. Santos, "Effect of the silica texture on the structure of supported metallocene catalysts," *J. Mol. Catal. A: Chem.* , vol. 298, no. 1-2, pp. 40-50, 2009.

[12] G. G. Hlatky, "Heterogeneous single-site catalysts for olefin polymerization," *Chem. Rev.*, vol. 100, no. 4, pp. 1347-1376, 2000.

[13] Q. Ji, X. Wang, Y. Zhang, Q. Kong, and Y. Xia, "Characterization of poly (ethylene terephthalate)/SiO_2 nanocomposites prepared by sol-gel method," *Composites Part A* vol. 40, no. pp. 878-882, 2009.

[14] J. Che, Y. Xiao, B. Luan, X. Dong, and X. Wang, "Surface structure, grafted chain length, and dispersion analysis of PBT prepolymer grafted nano-silica," *J. Mater. Sci.*, vol. 42, no. 13, pp. 4967-4975, 2007.

[15] V. A. Zakharov, E. P. Talsi, D. E. Babushkin, and N. V. Semikolenova, "Structure of methylaluminoxane and the mechanism of active center formation in the zirconocene/ methylaluminoxane catalytic system," *Kinet. Catal.* , vol. 40, no. 6, pp. 836-850, 1999.

[16] J. T. Xu, Y. B. Zhu, Z. Q. Fan, and L. X. Feng, "Copolymerization of propylene with various higher alpha-olefins using silica-supported " *J. Polym. Sci., Part A: Polym. Chem.*, vol. 39, no. 19, pp. 3294-3303, 2001.

[17] A. S. Luyt, J. A. Molefi, and H. Krump, "Thermal, mechanical and electrical properties of copper powder filled low-density and linear low-density polyethylene composites," *Polym. Degrad. Stab.* , vol. 91, no. 7, pp. 1629-1636, 2006.