LLDPE/nano-silica composites synthesized via *in situ* polymerization of ethylene/1-hexene with MAO/metallocene catalyst

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It is known that the copolymerization of ethylene with higher 1-olefins is a commercial importance for productions of elastomer and linear low-density polyethylene (LLDPE). LLDPE (density 0.920 to 0.940) is one of the most widely used polyolefins in many applications, especially, for plastic films. However, in some cases, the use of polyolefins or LLDPE is limited by their drawbacks such as low mechanical strength, low thermal resistance, poor optical properties and so on. Thus, in order to improve the specific properties of these polymers, some additives need to be blended with them.

It has been reported that blending polymer with inorganic materials is considered as a powerful method to produce new materials called polymer composites or filled polymers. However, due to the significant development in nano-technologies in the recent years, nano-inorganic materials such as SiO_2, Al_2O_3 and TiO_2 have brought much attention to this research field. Therefore, the polymer composites filled with nano-inorganic materials are well recognized as polymer nano-composites. Essentially, addition of the nano-materials into polymers may lead to overcome the drawbacks and produce new materials, which are considered to be robust. Basically, there are three methods used to produce the filled polymer; (i) melt mixing, (ii) solution blending, and (iii) *in situ* polymerization. Due to the direct synthesis via polymerization along with the presence of nano-materials, the *in situ* polymerization is perhaps considered to be the most powerful techniques to produce polymer nano-composites with good dispersion of the nano-particles into polymer matrix. Although, many authors [1–6] have studied LLDPE composites only synthesized via melt mixing and solution blending, no further reports have been done on synthesizing polymer nano-composites via the *in situ* polymerization with metallocene catalysts.

In the present study, LLDPE/nano-SiO_2 composites synthesized via the *in situ* polymerization with MAO/metallocene catalyst was investigated for the first time. The nano-SiO_2 and nano-SiO_2 doped Al_2O_3 filled materials were synthesized using sol-gel method [7] to obtain the nano-SiO_2 with particle size of ca. 50 nm. The amounts of nano-materials filled were also varied. Yields, activities, and polymer morphologies were discussed.

The preparation of LLDPE/nano-composites via *in situ* polymerization was performed as follows; all chemicals [nano-SiO_2, nanoSiO_2 doped Al_2O_3, toluene, rac-ethylenebis (indenyl) zirconium dichloride [$Et(Ind)_2ZrCl_2$], methylaluminoxane (MAO), trimethylaluminum (TMA) and 1-hexene] were manipulated under an inert atmosphere using a vacuum glove box and/or Schelenk techniques. The nano-materials were heated under vacuum at 400 °C for 6 hr prior to impregnation with MAO. In order to impregnate MAO onto the nano-materials, the method was described as follows. One gram of the nano-materials was reacted with the desired amount of MAO 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, the mixture was stirred for 5 min, and then the solvent was 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 nano-materials/ MAO.

Polymerization was conducted upon the methods as follows. The ethylene/1-hexene copolymerization reaction was carried out in a 100-ml semi-batch stainless steel autoclave reactor equipped with a magnetic stirrer. At first, 0.1, 0.2, and 0.3 g of the nano-materials/MAO ($[Al]_{MAO}/[Zr]$ = 1135, 2270, and 3405) and 0.018 mole of 1-hexene along with toluene (to make the total

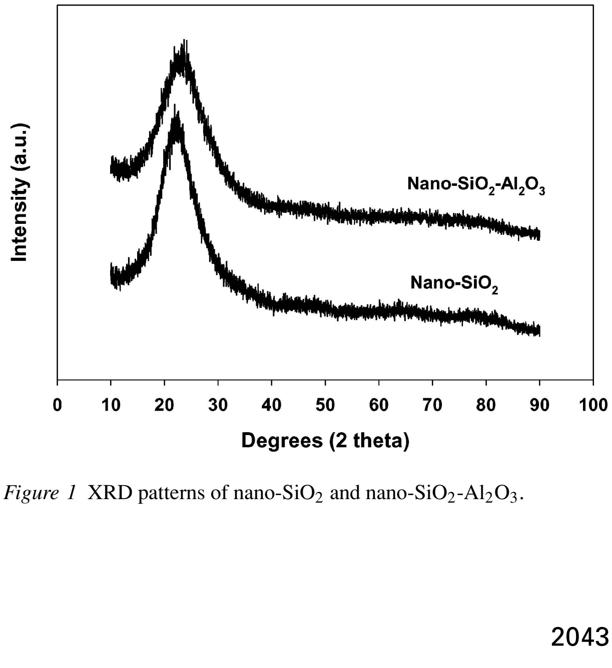

Figure 1 XRD patterns of nano-SiO_2 and nano-SiO_2-Al_2O_3.

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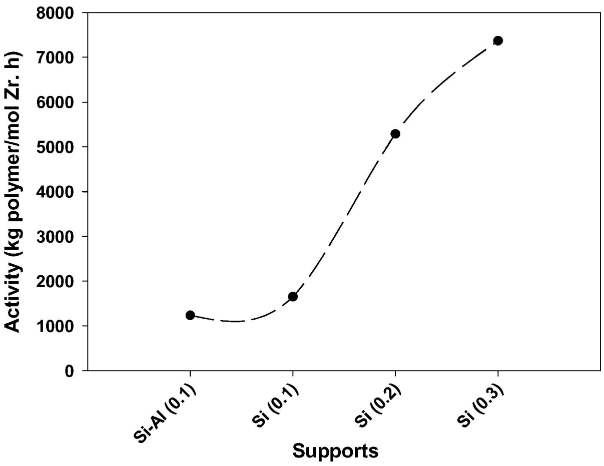

Figure 2 Activity profile with various amounts of support used.

volume of 30 ml) were put into the reactor. The desired amount of $Et(Ind)_2ZrCl_2$ (5×10^{-5} M) and TMA ($[Al]_{TMA}/[Zr] = 2500$) was mixed and stirred for 5-min aging at room temperature, separately, and then was injected into the reactor. The reactor was frozen in liquid nitrogen to stop reaction for 15 min and then the reactor was evacuated to remove argon. The reactor was heated up to polymerization temperature (70 °C). To start reaction, 0.018 mole of ethylene was fed into the reactor containing the comonomer and catalyst mixtures. After all ethylene was consumed, the reaction was terminated by addition of acidic methanol (0.1% HCl in methanol) and stirred for 30 min. After filtration, the obtained copolymer (white powder) was washed with methanol and dried at room temperature. The LLDPE/nano-SiO_2 composites obtained were characterized using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) to study morphologies and elemental distribution, respectively.

TABLE I Activity and yield of LLDPE/nano-composites via *in situ* polymerization with metallocene catalyst

Nano-filled	Amounts/Run (g)	Yield (g)	Time (s)	Activity (kg pol./mol. Zr.h)
SiO_2–Al_2O_3	0.1	0.2006	450	1234
SiO_2	0.1	0.2147	360	1652
SiO_2	0.2	0.6070	318	5288
SiO_2	0.3	0.8382	315	7369

XRD patterns of nano-SiO_2 and nano-SiO_2-Al_2O_3 are shown in Fig. 1. It was found that XRD patterns for both materials exhibited similar patterns assigning to amorphous silica. No XRD peaks of Al_2O_3 were detected indicating highly dispersed forms of it. After impregnation of MAO onto the nano-particles, copolymerization of ethylene/1-hexene was performed with various conditions based on changing types and/or amounts of the nano-particles used. Activities and yields of LLDPE/nono-composites are shown in Table I. It was observed that activities and yields dramatically increased with increasing the amounts of SiO_2 particles used due to increased MAO as a cocatalyst. However, at the same amount (0.1 g) of particles, the SiO_2-Al_2O_3 exhibited the lowest yield and activity of any other samples. A comparison of activities is also shown in Fig. 2. It should be noted that activities of LLDPE/nano-SiO_2 composites obtained in this present study were much lower (about three times) compared to the LLDPE/micron-SiO_2 composite as reported by our group [8]. This was probably due to more steric hindrance arising from the nano-particles. Morphologes of LLDPE/nano composites are shown in Fig. 3.

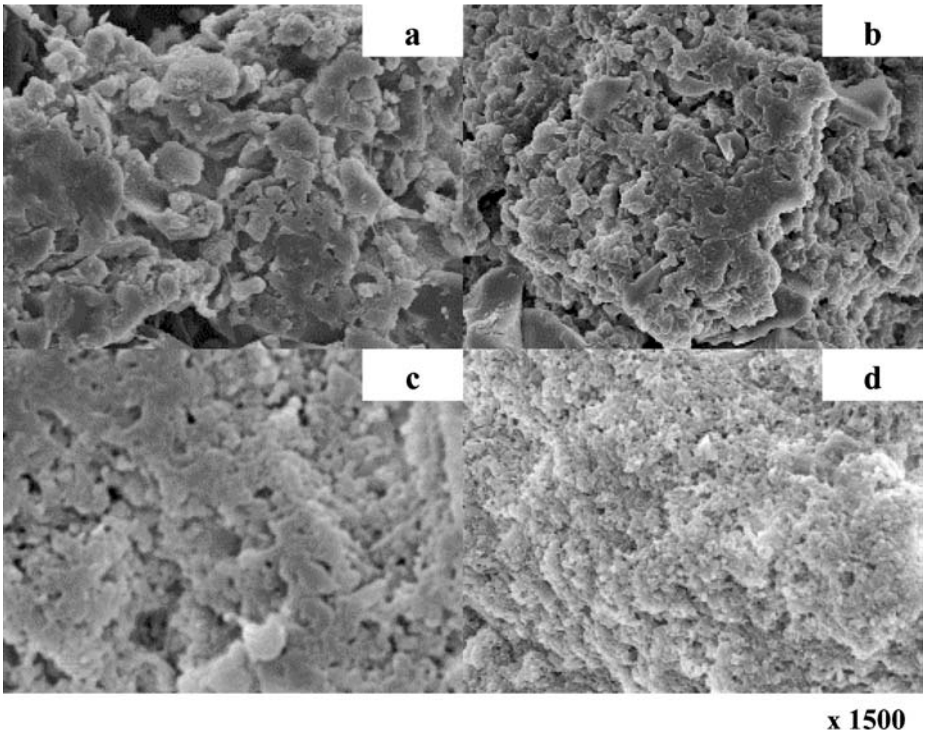

Figure 3 Morphologies of LLDPE/nano composites with: (a) SiO_2–Al_2O_3 (0.1 g), (b) SiO_2 (0.1 g), (c) SiO_2 (0.2 g), and (d) SiO_2 (0.3 g).

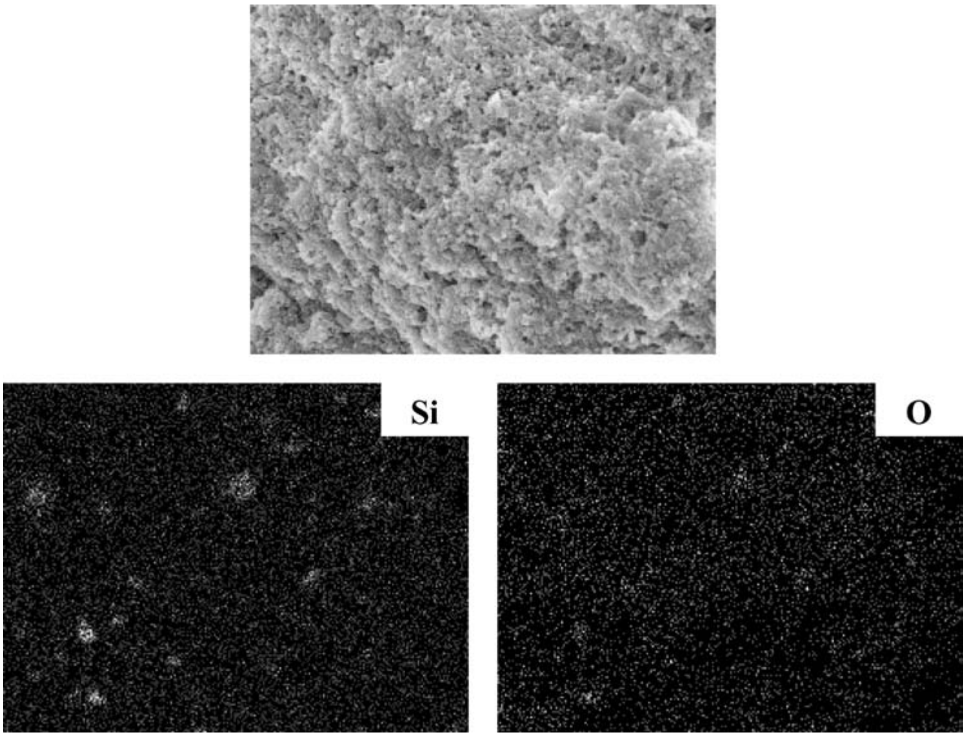

Figure 4 EDX mapping of LLDPE/nano-SiO_2 composite with SiO_2 (0.3 g) indicating distribution of Si and O.

It can be observed that with using SiO_2-Al_2O_3 (0.1 g), SiO_2 (0.1 g), and SiO_2 (0.2 g), morphologies [Fig. 3a–c] were found to be similar indicating only the polymer texture as seen in ref. [8]. However, with increasing the amount of nano-SiO_2 to 0.3 g, the morphology as shown in Fig. 3d was significantly changed indicating better combination between the silica and polymer textures. This was suggested that the LLDPE/nano-SiO_2 composite can be obtained at a certain amount of the nano-SiO_2 particles used. In order to identify the distribution of SiO_2 particles in the polymer matrix, EDX mapping was performed on the distribution of Si and O elements as shown in Fig. 4. It can be observed that Si and O elements exhibited good distribution all over the polymer matrix indicating good dispersion of nano-SiO_2 particles.

In summary, LLDPE/nano-SiO_2 composites can be obtained via the *in situ* polymerization with MAO/metallocene catalyst. It was found that silica particles were well dispersed in the polymer matrix at some certain amounts of them. However, activities and yields of polymerization were apparently low probably due to more steric hindrance arising from the nano-particles. Thus, polymerization conditions, catalysts used, and types of nano-particles need to be further investigated in order to increase productivity.

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