

# Effect of nanoscale SiO<sub>2</sub> and ZrO<sub>2</sub> as the fillers on the microstructure of LLDPE nanocomposites synthesized via *in situ* polymerization with zirconocene

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## Abstract

In the present study, the nanoSiO<sub>2</sub> and nanoZrO<sub>2</sub> were used as the fillers for linear low-density polyethylene (LLDPE) nanocomposites. In fact, the LLDPE nanocomposites were synthesized via the *in situ* polymerization of ethylene/1-octene with a zirconocene/MAO catalyst in the presence of the fillers. The LLDPE–nanocomposites were further characterized by means of TEM, DSC, <sup>13</sup>C NMR and XPS. It was found that productivity increased more when the nanoZrO<sub>2</sub> filler was applied. The similar distribution for both fillers was observed by TEM. Based on the <sup>13</sup>C NMR results, it appeared that the LLDPE nanocomposites obtained from both fillers were random copolymer. In particular, the resulted binding energy and elemental concentration at surface obtained from XPS measurement were further discussed in more details.

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**Keywords:** Polymer nanocomposite; Nanofillers; Metallocene; LLDPE; XPS

## 1. Introduction

Polymer composites are important commercial materials with various applications. It is known that materials or fillers with synergistic properties can be selected to create the polymer composites with desired properties. However, upon the significant development of nanoscience and nanotechnology in the recent years, nanoscale fillers have brought attraction to research in polymer composite. As known, polymers filled with nanoscale fillers are recognized as polymer nanocomposites. Apparently, with addition of nanoscale fillers into polymers, robust materials can potentially be produced due to the synergistic effects (cooperating for enhanced effects) arising from the blending process. In general, there are technically three methods used to produce a polymer composite; (i) a melt mixing [1–5], (ii) a solution blending [6] and (iii) *in situ* polymerization [7]. Due to the direct synthesis via polymerization along with the presence of fillers, the *in situ* polymerization is perhaps considered the most promising technique to produce

polymer nanocomposites with homogeneous dispersion of nanoscale fillers inside the polymer matrix. Based on the commercial interest of using metallocene catalysts for olefin polymerization, it has led to an extensive effort for utilizing metallocene catalysts efficiently [8–11]. With a combination of knowledge in nanotechnology, polymerization, and metallocene catalysis, a promising way to synthesize the polymer nanocomposites using a metallocene catalyst is captivating.

In our previous work [12], we revealed that LLDPE nanocomposites could be synthesized via the *in situ* polymerization with a zirconocene/MAO catalyst. However, our present study focussed on further development in order to give a better understanding on how different nanoscale fillers could interact inside the polymer matrix. Obviously, this can result in different properties of polymer nanocomposites obtained.

## 2. Experimental

All chemicals [ethylene (99.96%) donated by the National Petrochemical of Thailand, toluene (Exxon), *rac*-ethylenebis(indenyl) zirconium dichloride [*rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>] from Aldrich, methylaluminoxane (MAO, 2.67 M in toluene) donated by the

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Table 1  
Characteristics of LLDPE nanocomposites

Characteristics	LLDPE–nanoSiO <sub>2</sub>	LLDPE–nanoZrO <sub>2</sub>
1) Productivity (kg polymer/mol cat. h)	1319	6924
2) Melting temperature, $T_m$ (°C)	90	94
3) Copolymer type (obtained from <sup>13</sup> C NMR)	Random	Random
4) C 1s binding energy (eV)	286.5	285.7

Tosoh Akso, Japan, trimethylaluminum (TMA, 2.0 M in toluene) from Nippon Alkyls, Japan, 1-octene (98%, Aldrich), nanoSiO<sub>2</sub> (Aldrich) and nanoZrO<sub>2</sub> fillers] were manipulated under an inert atmosphere using a vacuum glove box and/or the Schlenk techniques. 1-Octene was purified by distilling over sodium under argon atmosphere. Toluene was dried over dehydrated CaCl<sub>2</sub> and distilled over sodium benzophenone under argon atmosphere prior to use.

The nanoZrO<sub>2</sub> filler was synthesized by flame spray pyrolysis (FSP) as described by Mueller et al. [13]. The primary particle size of ZrO<sub>2</sub> was in the range of 6–35 nm. The crystal structure consisted of the tetragonal/monoclinic phase (95/5 by mol%). The nanoSiO<sub>2</sub> filler was obtained from Aldrich (30–40 nm). First, 1 g of the filler reacted with a desired amount of MAO in toluene at room temperature and was 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 5 times to ensure the removal of impurities. The white powder of nanoscale filler-impregnated MAO was obtained.

The ethylene/1-octene copolymerization reaction on the filler-impregnated MAO was carried out in a 100-ml semi-batch stainless steel autoclave reactor equipped with a magnetic stirrer. At first, 0.3 g of the nanoscale filler-impregnated MAO ([Al]<sub>MAO</sub>/[Zr]=3405) and 0.018 mol of 1-octene along with

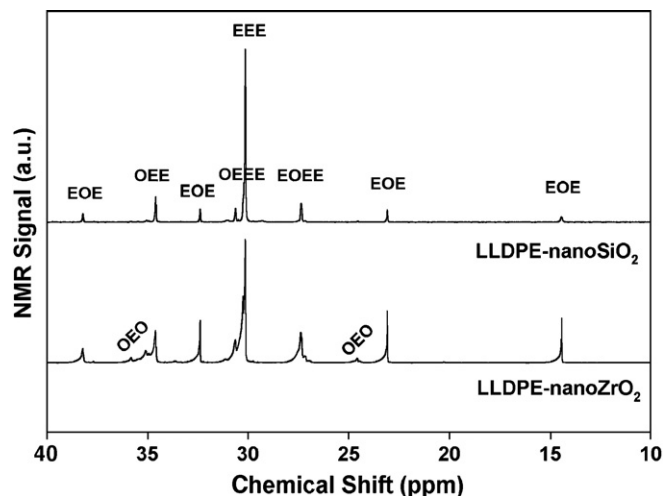


Fig. 2. <sup>13</sup>C NMR spectra of the LLDPE–nanoSiO<sub>2</sub> and LLDPE–nanoZrO<sub>2</sub> and their triad distribution identification (E refers to the ethylene sequence and O refers to the 1-octene sequence).

toluene (to make a total volume of 30 ml) were put into the reactor. The desired amount of *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> ( $5 \times 10^{-5}$  M) and TMA ([Al]<sub>TMA</sub>/[Zr]=2500) was mixed and stirred for 5 min aging at room temperature, separately, then was injected into the reactor. The reactor was heated up to polymerization temperature at 70 °C. To start reaction, 0.018 mol of ethylene was fed into the reactor. After, all ethylene was consumed, the reaction was terminated by addition of acidic methanol. After filtration, washing with methanol and drying at room temperature, white powder of nanoZrO<sub>2</sub> (SiO<sub>2</sub>)-filled polymer was obtained.

The polymer sample was then characterized using the differential scanning calorimetry; DSC (NETZSCH DSC 200), transmission electron microscopy; TEM (JEOL-TEM 200CX), X-ray photoelectron spectroscopy; XPS (Shimadzu AMICUS with VISION 2 control software), and <sup>13</sup>carbon nuclear magnetic resonance; <sup>13</sup>C NMR (JEOL JMR-A500).

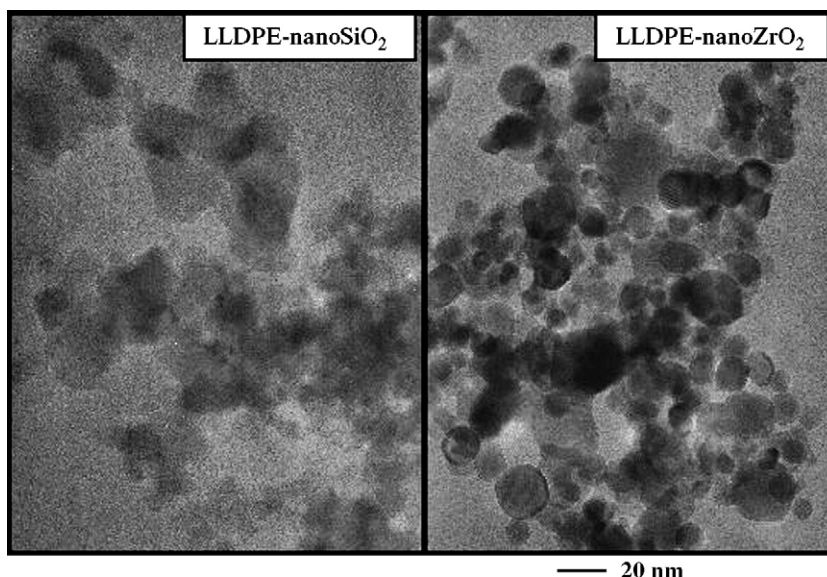


Fig. 1. TEM micrographs of the LLDPE–nanoSiO<sub>2</sub> and LLDPE–nanoZrO<sub>2</sub>.

### 3. Results and discussion

In the present study, we synthesized the LLDPE–nanoSiO<sub>2</sub> and LLDPE–nanoZrO<sub>2</sub> composites via the *in situ* polymerization with a zirconocene/MAO catalyst. At low amounts of the MAO impregnated-fillers, the activities of catalyst were very low. Hence, the amount of filler at 0.3 g which was corresponding to the ratio of  $[Al]_{MAO}/[Zr]=3405$  was applied. After polymerization, the white powder of LLDPE nanocomposites was obtained. The characteristics of LLDPE nanocomposites are shown in Table 1. It was found that the productivity of LLDPE–nanoZrO<sub>2</sub> synthesized via this specified condition was much higher than that of the LLDPE–nanoSiO<sub>2</sub> about 5 times. This was probably due to the strong interaction between MAO and the nano-SiO<sub>2</sub>. The melting temperature ( $T_m$ ) obtained by DSC showed only slight difference in  $T_m$  of the two samples. As known, images from high resolution transmission electron microscopy (TEM) are an essential component of nanoscience and nanotechnology, therefore, TEM was performed in order to determine the distribution and dispersion of fillers. The TEM images of the LLDPE–SiO<sub>2</sub> and LLDPE–ZrO<sub>2</sub> are shown in Fig. 1. As seen from both two images, the nanoscale fillers appeared as a group of spherical-like particles indicating the agglomeration of the primary particles. It only indicated that the nanoscale fillers were well distributed inside the polymer matrix, but somehow were poorly dispersed due to the agglomeration. There was no significant difference based on the TEM images for the LLDPE–nanoSiO<sub>2</sub> and LLDPE–nanoZrO<sub>2</sub>.

Among a number of important aspects for making a polymer composite, one has to mention how the microstructure of polymer is altered with the addition of nanoscale fillers. Technically, the nanoscale fillers added should not affect the polymer microstructure, but only change the physical properties based on the macroscopic point of view. It has been known that up to now <sup>13</sup>C NMR is one of the most powerful techniques used to identify the microstructure of polymer, especially polyolefins. The <sup>13</sup>C NMR spectra obtained from LLDPE–nanoSiO<sub>2</sub> and LLDPE–nanoZrO<sub>2</sub> are shown in Fig. 2. The resulted <sup>13</sup>C NMR spectra were assigned typically to the LLDPE obtained from the copolymerization of ethylene/1-octene. The triad distribution was identified based on the method reported by Randall [14] where **E** refers to the ethylene sequence and **O** refers to the 1-octene sequence. It can be observed that both samples exhibited the similar <sup>13</sup>C NMR patterns indicating the similar molecular structure. Upon the calculation described by Galland et al. [15], the distribution of comonomer was random as also shown in Table 1. This was similar to what we have found in our previous work when no filler was added [10]. However, as

Table 2

Elemental distribution on the surface of LLDPE nanocomposite and the binding energy measured by XPS

Polymer nanocomposite	Peak	B.E. (eV)	FWHM (eV)	Atomic conc. (%)	Mass conc. (%)
LLDPE–nanoZrO <sub>2</sub>	O 1s	533.3	1.386	1.79	2.37
	C 1s	285.7	1.419	98.19	97.47
	Zr 3d	185.7	0.756	0.02	0.16
LLDPE–nanoSiO <sub>2</sub>	O 1s	534.3	2.368	29.99	32.35
	C 1s	286.5	1.740	59.90	48.50
	Si 2p	104.6	1.944	10.11	19.15

seen from Fig. 2, it showed that the degree of 1-octene incorporation for LLDPE–nanoZrO<sub>2</sub> was slightly higher.

Although <sup>13</sup>C NMR showed that the molecular structure of polymer did not change upon the addition of the nanoscale fillers, it cannot differentiate interaction arising from different fillers inside the polymer matrix. Hence, a more powerful characterization technique was necessary for such a purpose. Here, we used the X-ray photoelectron spectroscopy (XPS) to identify different interactions inside the polymer matrix. Since XPS is one of the most powerful techniques used for many applications in surface analysis, so it is also interesting to extend the use of XPS in order to probe the different interactions of the polymer nanocomposites. A plot of the binding energy (BE) for C 1s obtained from XPS for both LLDPE–nanoSiO<sub>2</sub> and LLDPE–nanoZrO<sub>2</sub> is shown in Fig. 3. BE for the LLDPE–nanoSiO<sub>2</sub> was found to be 286.5 eV whereas the BE for LLDPE–nanoZrO<sub>2</sub> was 285.7 eV (Table 1). Obviously, as seen from Fig. 3, the shift of BE was observed with different nanoscale fillers due to perhaps a different interaction between the fillers and polymer matrix. In fact, the binding energy between 285.7 and 286.5 eV was assigned to the C–C bond in the polymer chain under a different environment. It must be noted that the samples used in this study are insulators. The insulators are always a problem in XPS due to the sample charging. The problem can be partially alleviated, but shifts in BE of several eV can still occur in the presence of charging. To overcome the charging problem, the samples must be coated with a very thin layer of gold by sputtering. It is common practice in XPS to refer the BE to the C 1s electrons that are to be measured. Hence, the energy reference for Ag metal (368.0 eV for 3d<sub>5/2</sub>) was used in this study. Besides the BE obtained from XPS, the amounts of Si and Zr atomic and mass concentrations at surface (the depth for XPS is ca. 5 nm) were also determined as shown in Table 2. Surprisingly, with the same amount (0.3 g) of the nanoscale fillers added to the polymer, the penetration of them was totally different. As seen in Table 2 for the mass concentrations, it can be observed that only 0.16% of Zr was found at the surface. This indicated that the ZrO<sub>2</sub> filler penetrated more deeply into the polymer matrix. In contrast, it was found that 19.15% of Si was present at the surface. It was suggested that the SiO<sub>2</sub> filler preferred to be located on the surface more. Therefore, a different location of fillers in the polymer matrix would result in a different interaction indicating the slight shift of BE of the C–C bond in the polymer chain as seen by XPS.

### 4. Summary

In summary, the LLDPE–nanoSiO<sub>2</sub> and LLDPE–nanoZrO<sub>2</sub> were synthesized via *in situ* polymerization using a zirconocene/MAO catalyst. With the use of nanoZrO<sub>2</sub>, the productivity increased more pronouncedly about 5 times. The distribution of both nanoscale fillers obtained from TEM was similar. It also

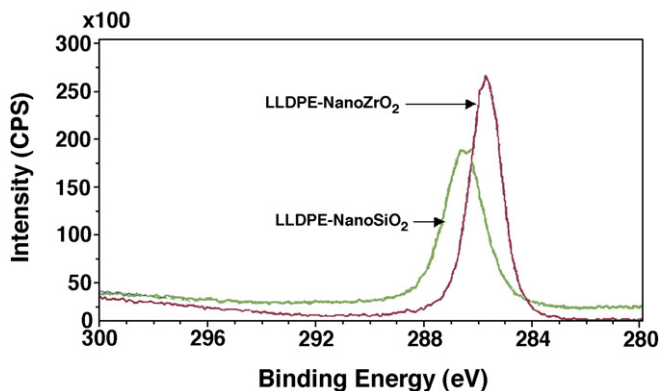


Fig. 3. A plot of binding energy for C 1s obtained from XPS of LLDPE–nanoSiO<sub>2</sub> and LLDPE–nanoZrO<sub>2</sub>.

showed that both LLDPE–nanocomposites exhibited the similar  $^{13}\text{C}$  NMR spectra indicating that only random copolymer was obtained. In particular, the XPS measurement indicated only a slightly different interaction for those LLDPE–nanocomposites. It was found that the different location of the nanoscale fillers rendered the BE shift of the C–C bond in the polymer chain.

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