

Characteristics of LLDPE/ZrO₂ Nanocomposite Synthesized by In-situ Polymerization using a Zirconocene/MAO Catalyst

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ABSTRACT

In the present study, the linear low-density polyethylene (LLDPE)/ZrO₂ nanocomposites were synthesized via in-situ polymerization with *rac*-Et(Ind)₂ZrCl₂/MAO catalyst. First, the nano-ZrO₂ filler was impregnated with the desired amount of MAO. Then, copolymerization of ethylene/1-octene was performed in the presence of nano-ZrO₂/MAO filler to produce the LLDPE/ZrO₂ nanocomposites. The amounts of nano-ZrO₂ filler employed were varied at 0.1 and 0.3 g corresponding to [Al]_{MAO}/[Zr] ratios=1135 and 3405, respectively. It can be observed that the polymer yield increased with increasing the ratios of [Al]_{MAO}/[Zr]. However, the observed polymer yields were much lower (about 5-30 times) compared to the yield with no filler addition. The filler contents in polymer were in the range of 23-25 wt%. The characteristics of LLDPE/ZrO₂ nanocomposites obtained were determined by means of DSC, SEM/EDX, TEM, ¹³C NMR, and XPS. It was observed that the LLDPE/ZrO₂ nanocomposites exhibited slightly lower melting temperature (T_m) and crystallization temperature (T_c). SEM Micrographs demonstrate the homogeneous matrix of the samples. In addition, with EDX mapping technique, it was also revealed that the nano-ZrO₂ filler was well distributed over the polymer matrix. Based on the TEM result, it was also revealed that the smaller and more uniform particles can be observed after polymerization. These observations suggested that the fragmentation of nano-ZrO₂ particles or segregation of the secondary particles could occur resulting in good dispersion of the particles. The distribution of comonomer was studied by ¹³C NMR. It was shown to be random as seen in the similar catalytic system without filler addition. The binding energy (BE) for C 1s obtained from XPS to be 285.7 eV indicating no significant change in the polymer microstructure with the addition of nano-ZrO₂ filler.

Key Words:

polyolefins;
metallocene catalysts;
nanocomposites;
NMR;
TEM.

INTRODUCTION

It is known that blending the polymers with inorganic materials as fillers can be recognized as a way to produce filled polymers or polymer composites. However, upon some significant developments of nanoscience and nanotechnology in

recent years, nanofillers such as silica, alumina, titania, and so on have brought much attraction to research in filled polymers. As known, polymer composites filled with nanofillers are so-called polymer nanocomposites.

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Apparently, with an introduction of nanofillers into polymers, robust materials can potentially be produced due to the synergetic effects arising from the blending process. In general, there are technically three methods used to produce a filled polymer; (i) melt mixing [1-5], (ii) 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 nanofillers inside the polymer matrix. Based on the commercial interest of using metallocene catalysts for olefin polymerization, an extensive effort has been made for efficient utilization of metallocene catalysts [8-12]. 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. Therefore, the main objective of this present study was to investigate, for the first time, the feasibility for making polymer nanocomposites and their characteristics via the in-situ polymerization with a metallocene catalyst.

EXPERIMENTAL

All chemicals (ethylene, toluene, *rac*-ethylenebis(indenyl) zirconium dichloride [*rac*-Et(Ind)₂ZrCl₂], methylaluminoxane (MAO), trimethylaluminum (TMA), 1-octene and nano-ZrO₂ filler) were manipulated under an inert atmosphere using a vacuum glove box and/or the Schlenk techniques.

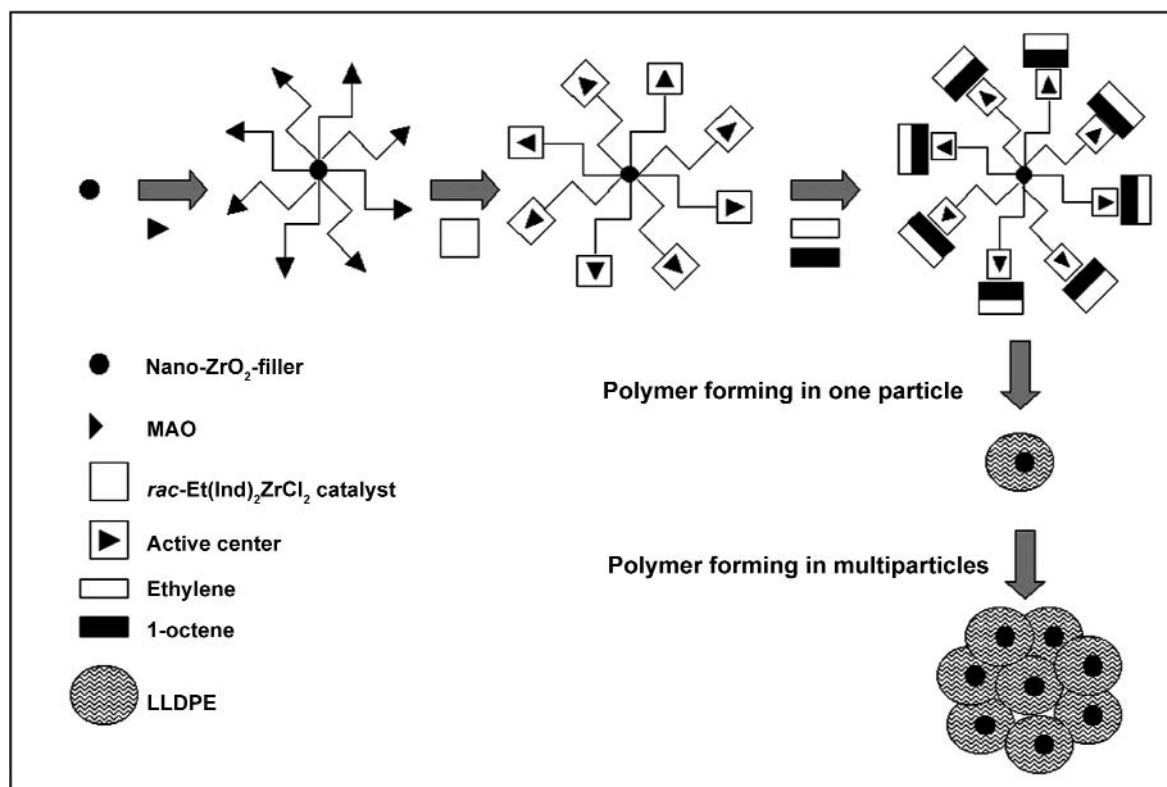
The nano-ZrO₂ filler was synthesized by flame spray pyrolysis (FSP) as described by Mueller et al. [13]. The primary particle size of ZrO₂ was in the range of 6-35 nm. The crystal structure consisted of the tetragonal/monoclinic phase (95/5 by mol%). First, 1 g of the filler was reacted with a desired 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, the mixture was stirred for 5 min, and then the solvent was removed. This procedure was performed 5 times to ensure the removal of impurities. The white powder of nano-

ZrO₂ 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, 0.1 and 0.3 g of the filler ([Al]_{MAO}/[Zr]=1135 and 3405, respectively) and 0.018 mol of 1-octene along with toluene (to make a total volume of 30 mL) were put into the reactor. The desired amount of *rac*-Et(Ind)₂ZrCl₂ (5×10⁻⁵ M) and TMA ([Al]_{TMA}/[Zr]=2500) was mixed and stirred for 5 min aging at room temperature, and then it 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 the full consumption of all ethylene, the reaction was terminated by addition of acidic methanol. After filtration, it was washed with methanol and dried at room temperature and a white powder of nano-ZrO₂-filled polymer was obtained.

The polymer sample was then characterized using the differential scanning calorimetry, DSC (NET-ZSCH DSC 200), scanning electron microscopy, SEM (Jeol-JSM-5800LV), energy dispersive X-ray spectroscopy, EDX (Link Isis series 300), transmission electron spectroscopy, TEM (Jeol-TEM 200CX), X-ray photoelectron spectroscopy, XPS (Shimadzu AMICUS with Vision 2 control software), and ¹³C NMR (Jeol JMR-A500).

RESULTS AND DISCUSSION

In the present study, the nano-ZrO₂-filled linear low-density polyethylene (LLDPE) was synthesized via copolymerization of ethylene/1-octene using *rac*-Et(Ind)₂ZrCl₂/MAO metallocene catalyst. It is known that the copolymerization of ethylene with higher 1-olefins is of commercial importance for production of LLDPE. In this study the nano-ZrO₂ particle, synthesized by flame spray pyrolysis (FSP) [13], was used as a filler due to its narrow particle size distribution, weak agglomeration of single crystal, high thermal resistance, high mechanical resistance and high corrosive resistance. Thus, the physical properties of LLDPE can be escalated with the addition of nano-ZrO₂ filler. In order to synthesize the nano-ZrO₂-filled LLDPE, first, the filler was impregnated



Scheme I. Conceptual model for polymer forming on the nano-ZrO₂-filler via in-situ polymerization by a metallocene catalyst.

with MAO (as a cocatalyst). Then, the in-situ polymerization was conducted while the filler-impregnated MAO was present. It was proposed that polymer was formed at the surface of filler-impregnated MAO as shown in Scheme I suggesting that highly dispersed filler inside the polymer matrix could be achieved. The yield, filler content, melting tempera-

ture (T_m) and crystallization temperature (T_c) are shown in Table 1. It can be observed that the polymer yield increases with increasing the amount of filler from 0.1 to 0.3 g. This was due to an increase in the $[Al]_{MAO}/[Zr]$ ratio from 1135 to 3405. It should be noted that the filler contents in the obtained polymer nanocomposites were found to be within the range of

Table 1. Results of the amount of polymer obtained, filler content, yield, melting temperature (T_m) and crystallization temperature (T_c) of samples.

Nano-filler (g)	Polymer obtained ^a (g)	Filler content (wt%)	Polymerization time ^b (s)	Yield ^c (kg Pol./mol Zr.h)	T_m^d (°C)	T_c^d (°C)
No filler	1.1	0	87	31.000	104	86
0.1	0.3	25	605	1.209	93	85
0.3	1.0	23	352	6.924	94	79

(a) Weight excluding the filler; (b) a period of time used for the total 0.018 mol of ethylene was totally consumed; (c) measured at polymerization temperature of 70°C, $[ethylene]=0.018$ mol, $[1-octene]=0.018$ mol, $[Al]_{MAO}/[Zr]=1135$, $[Al]_{TMA}/[Zr]=2500$, in toluene with total volume=30 mL, and $[Zr]$ of $Et[Ind]_2ZrCl_2=5 \times 10^{-5}$ M; (d) measurement error $\pm 1^\circ C$.

23-25 wt%. However, considering the yield without any filler added, the yield was substantially higher (~5-30 times) than that with the filler added. It was proposed that the low yield as a result of the filler addition could be due to more steric hindrance arising from the nanoparticles. Thus, in order to improve the yield, the modification of nanofiller requires further work. DSC Analysis was performed in order to determine the thermal properties of samples. The temperature range of -10 to 120°C at the heating rate of 20°C/min was employed. The heating cycle was twice operated. In the first scan, the sample was heated up to 120°C, then cooled down to the ambient temperature. In the second scan, the sample was reheated at the same condition. The melting temperatures at the second scan were reported whereas the crystallization temperatures were obtained during the cooling process. Based on DSC results, it is shown that DSC patterns for all samples were similar. The T_m and T_c of samples obtained are also shown in Table 1. The results indicate that the nano-ZrO₂-filled LLDPE exhibits slightly lower T_m and T_c than those of pure LLDPE. It was suggested that addition of nano-ZrO₂ filler rendered lower crystallinity in the LLDPE/ZrO₂ nanocomposites.

In order to identify the morphologies of samples, SEM was performed. It can be observed that the polymer formed has covered the filler as noticed by SEM (Figure 1). As shown in Figure 1a, prior to polymerization, the nano-ZrO₂ filler appeared in white powder as flat sheets of secondary particles. However, after polymerization, the nano-ZrO₂-filled LLDPE was obtained as shown in Figure 1b indicating a homogeneous matrix of filled polymer (not PE particles). In order to determine the location of ZrO₂ in the polymer matrix, EDX mapping technique was also performed (not shown due to low resolution). However, it was suggested that the filler apparently exhibited good distributions inside the polymer matrix. As mentioned, an image from the high-resolution transmission electron microscopy (TEM) is an essential component of nanoscience and nanotechnology. Therefore, TEM was performed in order to determine how the nanofiller behaved before and after the in-situ polymerization. TEM Images of the nano-ZrO₂ filler before and after polymerization are shown in Figures 2a and 2b, respectively. As seen in Figure 2a,

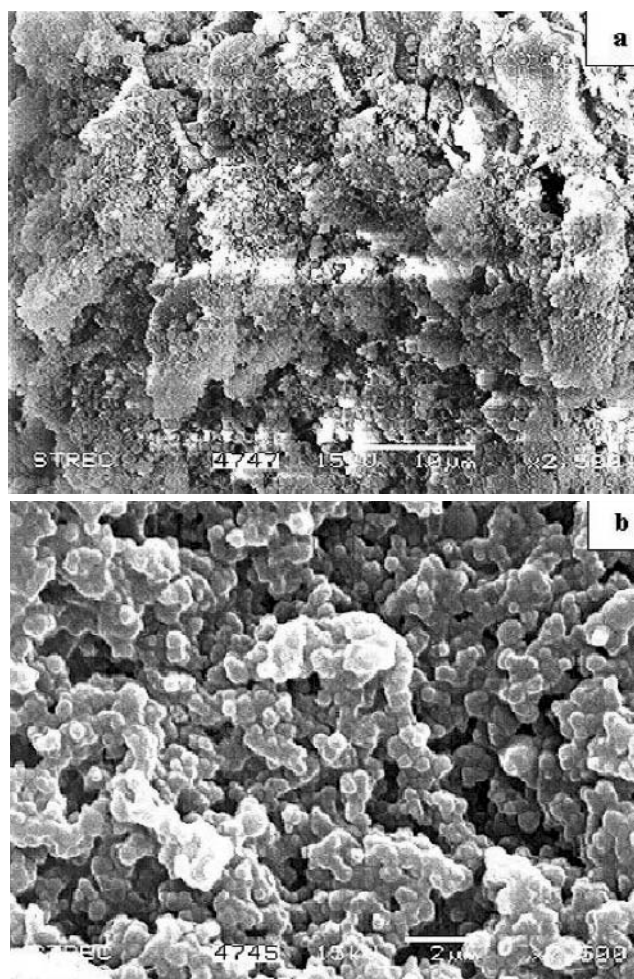


Figure 1. SEM Micrographs of (a) nano-ZrO₂ filler at x 2,500 magnification and (b) nano-ZrO₂-filled LLDPE composite at x 2,500 magnification.

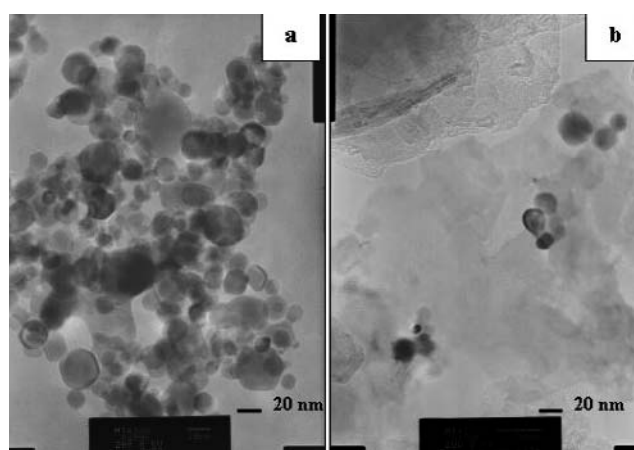


Figure 2. TEM Images of (a) nano-ZrO₂ filler at 200,000 magnification and (b) nano-ZrO₂-filled LLDPE composite (0.1 g of filler) at 150,000 magnification.

prior to polymerization, the nano-ZrO₂ filler appeared in a bunch of spherical-like particles indicating the agglomeration of primary particles. The primary particle size of nano-ZrO₂ filler was in the range of ca. 6-35 nm. However, after polymerization was done on the filler, it can be observed from Figure 2b that the nano-ZrO₂ filler was well dispersed inside the polymer matrix. Apparently, the smaller and more uniform particles were noticed after polymerization. It was suggested that the fragmentation of nanofiller probably occurred as also reported by Fink et al. [14-17]. They found that the fragmentation of a particle such as microsilica, used as a metallocene catalyst support or a carrier, occurred essentially under some specific conditions. In particular, the hydraulic forces of the growing polymer, which may be observed in the case of nano-ZrO₂ filler, induced such a fragmentation of filler as well. However, the segregation of secondary particles from the primary particles was also the case for the nanofiller.

Among various important aspects for making a polymer nanocomposite, one should also mention how the microstructure of polymer is altered with the addition of nanofiller. Technically, the filler added should not affect the polymer microstructure, but only change the physical properties based on macroscopic points of view. It is known that ¹³C NMR is one of the most powerful techniques used to identify the microstructure of polymer, especially, polyolefins. ¹³C NMR Spectra obtained from the nano-ZrO₂-filled LLDPE samples (0.1 and 0.3 g of filler) are shown in Figure 3a,b, respectively. ¹³C NMR Spectra were assigned to the typical LLDPE obtained from the copolymerization of ethylene/1-octene. Based on calculation described by Galland et al. [18], the distribution of comonomer was considered random and similar to what we found in our previous work without any filler added [10]. Since XPS is one of the most powerful surface analysis techniques, so it is also interesting to use the XPS to identify the microstructure of the polymer nanocomposites. A plot of the binding energy (BE) for C 1s obtained from XPS for both nano-ZrO₂-filled LLDPE samples with 0.1 and 0.3 g of filler are shown in Figure 4a,b, respectively. The binding energy for both samples was found to be 285.7 eV. It is suggested that the microstructure has not changed upon the presence of nanofiller. Besides

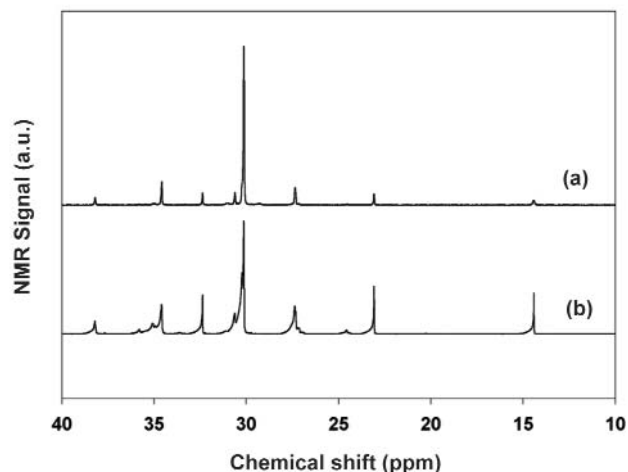


Figure 3. Typical ¹³C NMR spectra of ethylene/1-octene copolymer obtained with the nano-ZrO₂-filled LLDPE samples: (a) 0.1 g of filler and (b) 0.3 g of filler.

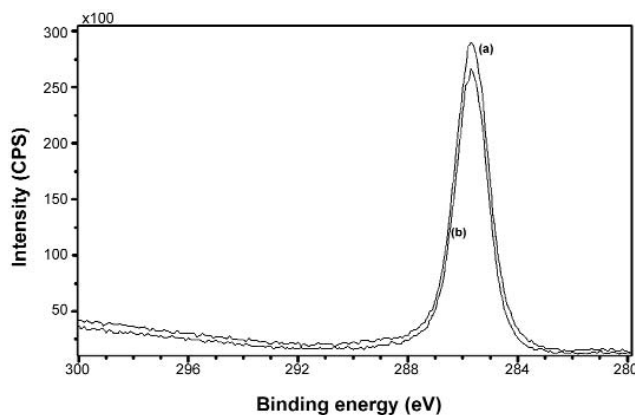


Figure 4. A plot of binding energy for C 1s obtained by XPS of the nano-ZrO₂-filled LLDPE samples: (a) 0.1 g of filler and (b) 0.3 g of filler.

the binding energy for C 1s, the amounts of Zr atomic concentration at surface (the depth for XPS analysis is ca. 5 nm) was also determined by XPS and only 0.02% of Zr was found at the surface for both samples. This could be an indication that the ZrO₂ filler deeply penetrated into the polymer matrix resulting in the highly dispersed nanofiller as examined by TEM. Therefore, based on the ¹³C NMR and XPS data, it can be concluded that the addition of nano-ZrO₂-filler has not changed the microstructure of LLDPE significantly.

CONCLUSION

In summary, the nano-ZrO₂-filled LLDPE can be synthesized via the in-situ polymerization using *rac*-Et[Ind]₂ZrCl₂/MAO catalyst. In particular, the nano-ZrO₂ filler exhibited good distribution and dispersion inside the polymer matrix as observed by TEM. No significant change in the microstructure of polymer was observed by means of XPS and ¹³C NMR. However, the melting temperature (T_m) and crystallization temperature (T_c) were found to decrease slightly with the addition of nano-ZrO₂ filler due to decreased crystallinity. Besides the characteristics of LLDPE nanocomposite produced, it should be mentioned that a decreased yield was more pronounced when the nanofiller was added compared to when nanofiller was absent. Therefore, in order to elevate the polymer yield, some developments of process and modification of the nanofiller need to be further investigated. In addition, a rheological characterization would be very useful for explaining the very large reduction in productivity in the future research consideration.

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