DOI: 10.1002/masy.200651125

Polymerization Compounding on the Surface of Zirconia Nanoparticles

*Babak Esmaeili, Jamal Chaouki, Charles Dubois**

Summary: Zirconia nanoparticles were encapsulated by polyethylene via a polymerization compounding method using a Ziegler-Natta catalyst. The chemical reaction was carried out in an organic solvent under moderate pressure of ethylene monomer. Transmission electron microscopy (TEM) indicated the presence of a thin layer of polymer, about 6 nm, uniformly applied around the particles. However, the thickness of coating layer can be controlled as a function of time and operating conditions of the process. The morphology study using scanning electron microscopy (SEM) as well as TEM revealed that although the nanoparticles seem to be coated individually, some agglomerates, encapsulated by a polymer film, could be observed. The grafting of the catalyst to the original surface of particles was further confirmed by X-ray photoelectron spectroscopy (XPS).

Keywords: encapsulation; polymerization compounding; Ziegler-Natta catalyst; zirconia nanoparticles

Introduction

Coating or encapsulating nanoparticles by polymers is desirable in many applications in order to improve their chemical stability, to reduce their toxicity, and to facilitate their storage, transport, and processing. Over the recent years, several methods and approaches have been investigated to carry out polymer coating of nanoparticles. Among them, we note melt mixing, solvent dispersion and precipitation.[1–4] However, not all of these methods provide the modified particles with the properties required to obtain high performance composite materials. The mechanical properties of polymer composites greatly depend on the combined behavior of particles (filler), the polymer matrix, and, most importantly, the interface between them. The latter is readily affected by any change to the particles surface, such as a polymer coating of the same nature of the polymer matrix. Under such a configuration, the quality of the interactions between the particles and encapsulating polymer becomes an important factor favorably affecting the nanocomposite performance. If a catalyst supported on the surface of particles gets involved in a polymerization reaction, a very intimate contact between the particle surface and polymer will be established, bringing improved interfacial properties, and consequently enhanced properties of the nanocomposite. Polymerization compounding (PC) is an approach in which the polymer is forced to grow from the surface of the solid using catalyst sites covalently bonded to the particles.

The PC technique have been developed and extensively studied by Ait-Kadi and his coworkers for polyethylene and nylon coating applications on the surface of fibers.[5–10] When incorporated in composite materials, they observed that the surface of fibers having received the grafted polymerization catalyst were completely covered, while ungrafted fibers, where no catalyst was grafted on, were only scattered by polymer after polymerization.[7] Therefore, when the catalyst was chemically

---

Département de Génie Chimique, École Polytechnique de Montréal, C.P. 6079, succ. Centre-ville, Montréal, Québec, H3C 3A7, Canada
E-mail: charles.dubois@polymtl.ca

bonded to the fibers, the monomer was polymerized from the fibers surface forming a polymer coating of each fiber, which ensured their dispersion in the polymer matrix and good wetting of fibers surfaces by polymer. Also, solvent extraction experiments confirmed the strong adhesion between the fibers surface and polymer obtained by the polymerization process.[5] Moreover, SEM images of fractured composites revealed a smooth surface of fibers with no polymer on for untreated fibers, while adhered polymer was clearly observed on the treated fibers surface.[9] Recently, Rajabian and Dubois applied PC approach to make a HDPE coating on the Kevlar pulps to be used as reinforcement in polyethylene matrix.[11] Composites with fibers contents as high as 15% were successfully obtained, owing to the improved adhesion and dispersion of the treated fibers. All of the results mentioned above confirmed that catalyst-grafted polymerization provides an excellent dispersion of solid in the polymer binder, wetting of solid substrate by polymer, and interaction between the solid substrate and encapsulating polymer, which are not always well satisfied by conventional methods of composite preparation such as melt mixing.

In the field of nanoparticle fillers and substrates, several recent investigations were devoted to applying the PC approach to nanocomposites preparation and fine particles encapsulation.[12–19] Kasseh et al conducted free radical polymerization of styrene on the surface of ultrafine silica to prepare highly filled composite.[12] They obtained highly loaded composites (77.9%) which could not be otherwise achieved by techniques such as mechanical mixing, solvent dispersion and precipitation. Roy et al carried out the in-situ synthesis of high density polyethylene on the surface of aluminum nanoparticles using Ziegler-Natta catalyst.[14] They applied a thin polymer layer, in the order of a few nanometer, around particles in a process which was flexible enough to control the amount of polyethylene grafted on powders up to 25% w/w. He et al deposited a thin layer of polyethylene film on zirconia nanoparticles by inductively coupled plasma polymerization and the covalent bond between the substrate and polymer was confirmed by XPS.[17] Rovira-Bru et al treated zirconia nanoparticles to first modify the density of hydroxyl group at the particle surface and then carry out vinylpyrrolidone polymerization.[18] They claimed that the surface was fully covered by a well-dispersed polymer coating of about 20 nm in thickness. Recently, Dubois et al incorporated fumed silica ultrafine particles into polyurethane at concentrations as high as 25% via PC approach.[19] They explained that the enhancement in water absorption, thermorheological and mechanical properties was due to improved bonding between the solid substrate and the binder.

In this research, we apply the polymerization compounding process to encapsulate zirconia nanoparticles by polyethylene. The objective of the present work is to investigate the feasibility of ethylene polymerization on zirconia powder via a Ziegler-Natta catalyst system to obtain zirconia nanoparticles whose surface is uniformly modified by a layer of polyethylene in the scale of a few nanometers. As mentioned earlier, Ziegler-Natta catalysts were successfully used for encapsulation of aluminum nanoparticles and Kevlar pulps by high molecular weight polyethylene via PC approach.[11,14] The polymerization reaction, based on coordination polymerization, starts from the surface of nanoparticles so that ethylene monomers are sequentially grafted to substrate. It is proposed that Ziegler-Natta catalyst, $TiCl_4$, reacts with hydroxyl groups on zirconia particles surface as shown in following equation.[5]

$$-OH + TiCl_4 \rightarrow -O-TiCl_3 + HCl \quad (1)$$

Therefore, there is a covalent bond established between the catalyst and the particles, and consequently, the polymerization is initiated from the surface of the particles, which favors their encapsulation. Although the chain transfer termination usually occurs in Ziegler-Natta polymerization systems, an appropriate interaction will be established between the polymer and substrate. Since polymerization reaction starts from the surface and monomers are consecutively added to polymer chains, the diffusional limitations and steric hindrance effects are greatly lower than in the case where polymer chains are simply brought to the surface by the substrate nucleating action. Therefore, appropriate wetting of solid surface by polymer, and consequently, high interfacial interactions are achieved via polymerization compounding process.

Experiments

Materials

The zirconia powder of 250 nm average particle size was used for all coating experiments. Figure 1 shows the SEM image of original particles. Ethylene gas with purity of 99.5%, supplied by Canadian Liquid Air, was used as monomer for polymerization reaction. The Ziegler-Natta catalyst system, consisting of titanium tetrachloride ($TiCl_4$), manufactured by Acros, as catalyst, and triethylaluminum ($AlEt_3$) obtained from Sigma-Aldrich, as co-catalyst, was stored and handled in a glove box in order to protect them from moisture and oxygen. Methylaluminoxane (MAO) also procured by Sigma-Aldrich was employed to determine the hydroxyl group density on particles surface.

Quantification of Hydroxyl Chemical Groups on Nanoparticles

The polymerization process used in this work necessitates the anchoring of the catalyst to the particles using the OH sites on their outer surface. Accordingly, appropriate amounts of catalyst and co-catalyst needed to be estimated from the OH group density on nanoparticles surface. To carry out this quantification,[20] a small amount of nanoparticles, about 0.5 g, is agitated and heated in 5 ml of toluene in a lab test tube where a flow of dry nitrogen and vacuum conditions are first applied to remove oxygen and humidity from the system. After 1 hr, the lab test tube is cooled to ambient temperature, and subsequently, 1 ml of methylaluminoxane

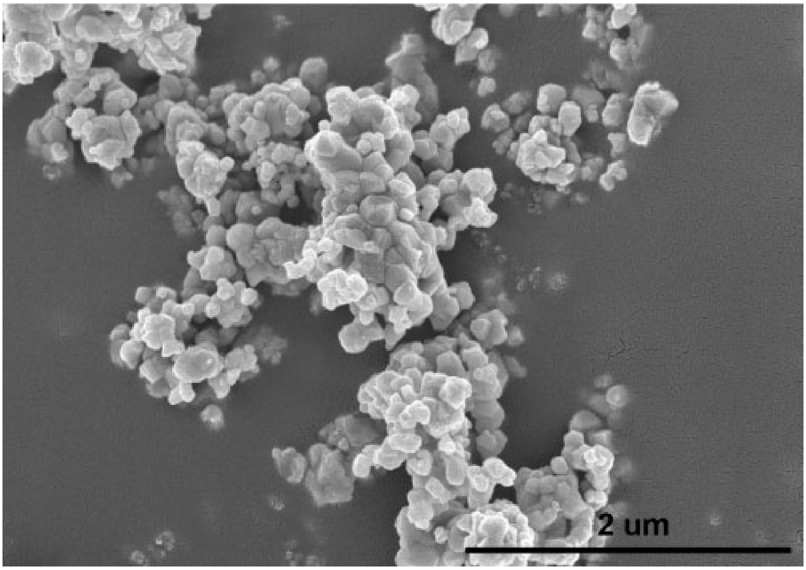


Figure 1.
SEM image of original zirconia nanoparticles.

Table 1.
Catalyst and co-catalyst calculated based on OH concentration.

Pressure rise	50.7 mmHg/gr zirconia
OH concentration on the surface of particles	$1{,}9 \cdot 10^{-4}$ mole/gr zirconia
$TiCl_4$ (pure catalyst)	0.02 ml/gr zirconia
$AlEt_3$ (1 Molar solution in Hexane)	0.19 ml/gr zirconia

(MAO) is injected in the closed tube through a septum. As a result of the reaction between each mole of MAO and hydroxyl groups of the surface, one mole of methane is released. Consequently, the hydroxyl group density is calculated by determination of methane gas evolved in the process using a pressure monitoring setup. An example of the use of the observed pressure rise to determine the amount of catalyst and co-catalyst employed for a particular polymerization is given in Table 1.

Synthesis

The polymerization reaction is carried out in a 1 liter pressurized glass vessel BUCHI reactor (BUCHI laboratory autoclave BEP 280) as shown in Figure 2. The jacketed reactor is heated to 65 °C by an external oil bath circulator and mixing is provided by a top mounted magnetic drive impeller. The pressure of reactor is measured by a pressure gauge located on the top of reactor. In a typical polymerization process, the previously oven-dried zirconia powder is dispersed in dried hexane by mechanical agitation at the reaction temperature. The dried nitrogen with a low flow rate is purged to remove oxygen and any trace of water. An ultrasonic processor is mounted on the top of the reactor and periodically activated to facilitate the dispersion of nanoparticles in the hexane during degassing. After an hour, the desired quantity of catalyst $TiCl_4$ is injected through a septum feeding port, and 15 minutes later, co-catalyst $AlCl_4$ is injected through the same port. The reaction of polymerization starts once nitrogen is replaced by ethylene monomer and continues under a moderate overpressure of 30 kPA for desired time duration before being stopped by an injection of ethanol.

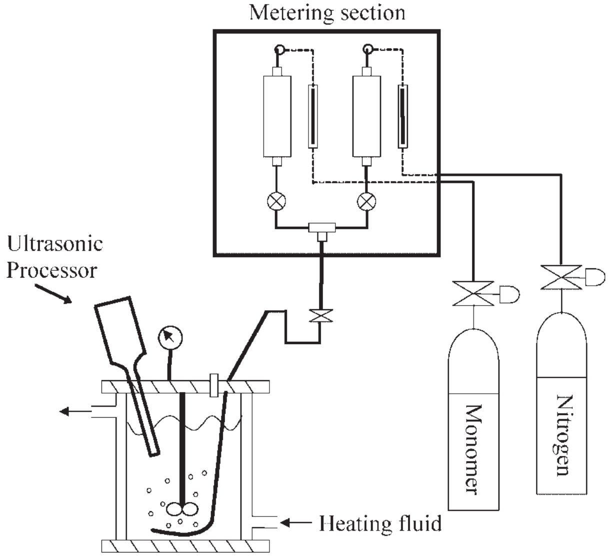


Figure 2.
Schematic of the reactor setup.

Characterization

The amount of polymer on the zirconia particles was determined by thermogravimetry analysis (TGA) using a METTLER TOLEDO apparatus operated on a 25–800 °C temperature range at a 10 °C/min heating rate under a flow of argon. The thickness of polymer layer on the surface of nanoparticles was observed using Jeol JEM-2100F Transmission Electron Microscope (TEM). The morphology of coated particles was investigated using Hitachi S-4700 scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) is applied to study the interface of grafted polymer and the original surface of particles.

Results and Discussion

A typical thermogravimetry analysis (TGA) of coated zirconia particles is presented in Figure 3. One can see that a sharp weight loss appears at 450 to 500 °C, and since it is known that the pyrolysis of high molecular weight polyethylene (HMWPE) occurs in that region,[14] this confirms presence of HMWPE on the surface of nanoparticles.

The characterization of the coated particles was continued by a morphology study using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM observations carried out on original and coated nanoparticles are presented in Figure 4. As shown in Figure 4-a, the surface of non coated particles possesses a sharp edge and no other phase is distinguished. On the other hand, as shown in Figure 4-b for a coated particle, an image contrast is found that corresponds to polyethylene layer of about 6 nanometer thick uniformly applied around the particle.

Although these results confirm that zirconia nanoparticles were individually coated by polyethylene, the coating of particles agglomerate is also possible. Figure 5-b shows an agglomerate of nanoparticles which is probably coated by a layer of polyethylene. If so, it demonstrates that the dispersion of original zirconia nanoparticles (Fig. 5-a) in hexane at the beginning of the polymerization process is a crucial factor that should be considered to avoid the presence of these agglomerates in

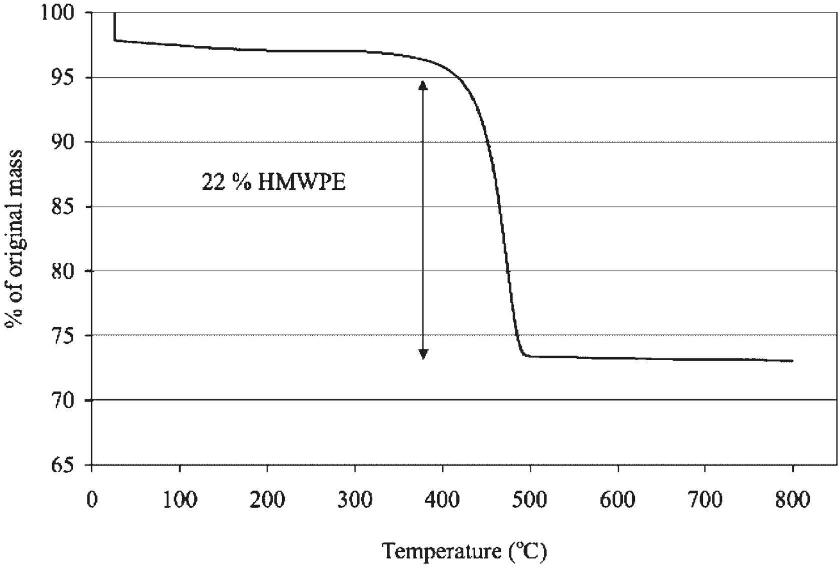
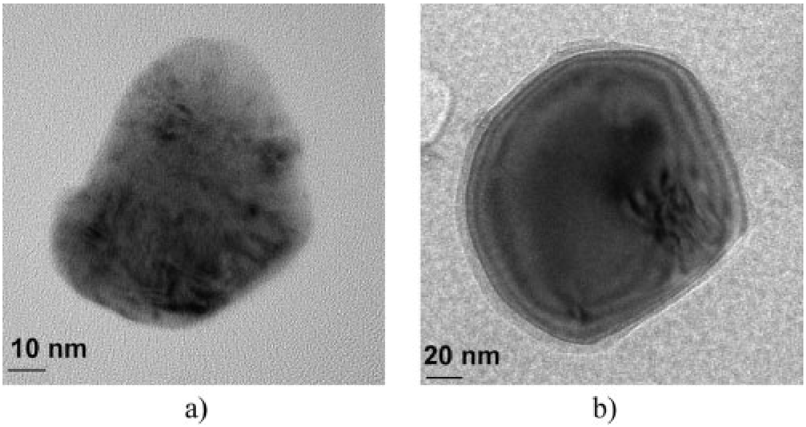


Figure 3.
TGA graph of coated zirconia nanoparticles.



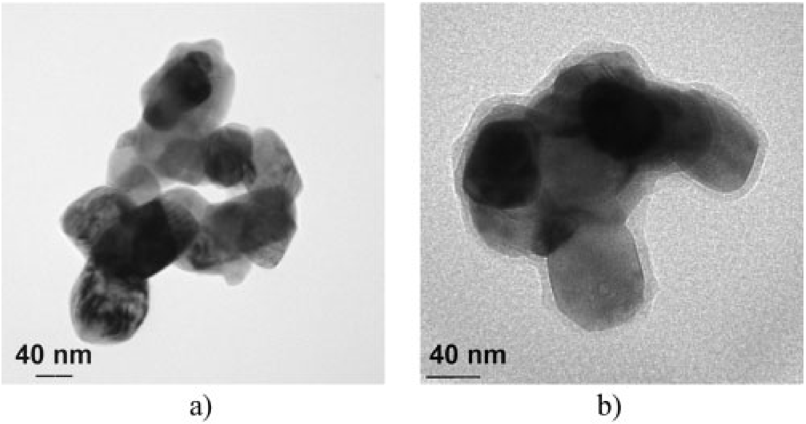
a) b)

Figure 4.
TEM images of a) original and b) coated zirconia nanoparticles.

the final products. However, Figure 5-b might also be the result of agglomeration of individually coated particles.

As shown in Figure 1, a simple visual observation of SEM image of original zirconia particles reveals a wide distribution of particles sizes, ranging from few ten to few hundred nanometers so that the surface average particle size, reported by the supplier, is 250 nm. Moreover, the particles are in a compact agglomerate state according to the high cohesivity of zirconia powder. However, in the process, agglomerates are broken and particles are dispersed in the solvent by means of stirring and ultrasound processor. On the other side, Figure 6 illustrates the coated particles in agglomerate structure as well. While particles had been dispersed in solvent, they retained an agglomerate state after the synthesis. Furthermore, the surface of particles seems to be uniformly coated by polymer after the process, as shown in Figure 6.

The XPS analysis reported in Figure 7 further confirms the grafting of the catalyst on the surface of particles. As shown in Figure 7, the relative intensity of zirconium and oxygen peaks, representing the original surface of particles, is significantly reduced



a) b)

Figure 5.
TEM images of a) original and b) coated zirconia agglomerate.

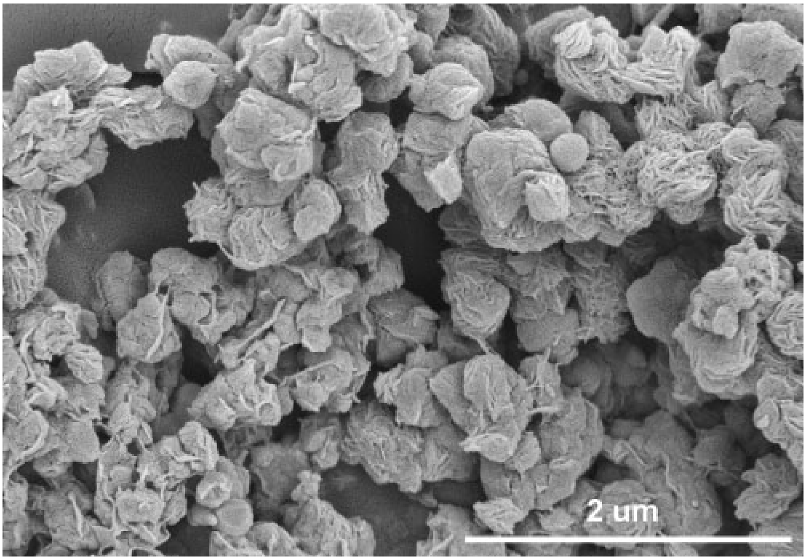


Figure 6.
SEM image of original zirconia nanoparticles.

after the polymerization. In addition, the relative intensity of carbon peak, associated to the presence of a hydrocarbon based polymer coating, increased significantly after the polymerization in comparison with original particles. The results mentioned above are summarized in Table 2. One can see the weight percentage of

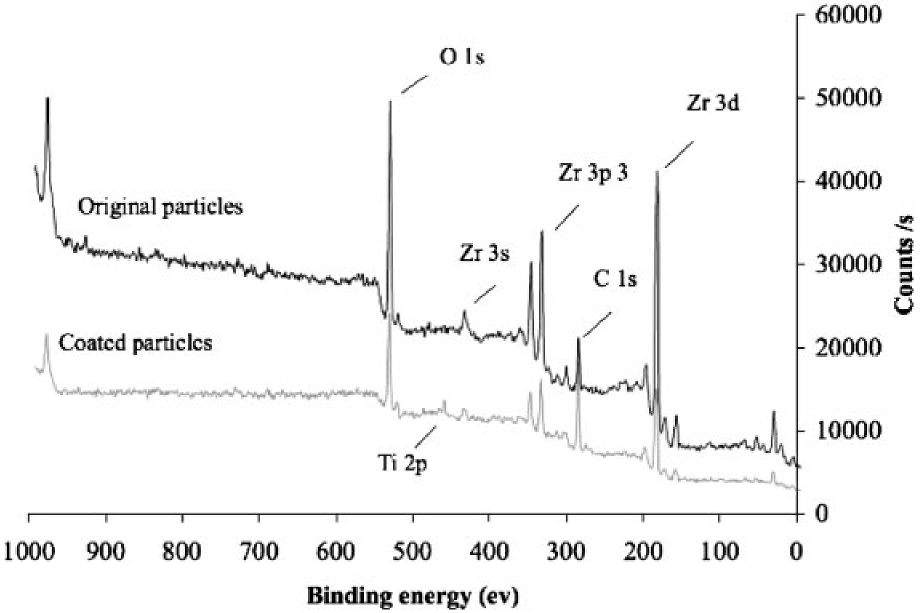


Figure 7.
XPS graphs of original and coated zirconia nanoparticles.

Table 2.
XPS data for original and coated zirconia nanoparticles.

Name	Peak BE	Height cps (original)	Area (p) cps.ev (coated)	Height cps (original)	Area (p) cps.ev (coated)	At. % (original)	At. % (coated)
C 1s	284	5817.20	18175.5	10637.3	32532.3	27.45	58.76
O 1s	530	25448.2	81156.7	11168.4	38540.2	51.02	28.94
Zr 3d	183	28648.8	123389.0	9602.14	50822.6	21.53	10.61
Ti 2p	454	–	–	2.74	6146.33	–	1.64

zirconium and oxygen elements are considerably lower for coated particles compared to non coated particles. Instead, carbon content augments from 27.45% for non coated particles to 58.76% for coated particles. The initial amount of carbon for non coated particles, detected by XPS, is due to the sample contamination by atmospheric carbon (CO2). Furthermore, two different coated particles with respect to amount of polymer on their surface are compared in Figure 8. It is evident that for the sample with high amount of polymer (22%), no other high intensity peak is observed except for the carbon peak related to polyethylene. The reason is that XPS experiment is capable to detect only a few nanometers in depth of sample from the free surface. Therefore, if the thickness of polymer layer exceeds that limit, XPS can not detect the interface of substrate and polymer coat. On the other hand, the titanium peak, associated with the Ziegler-Natta catalyst, is detected in the case where the amount of polyethylene is low (4%). These results indicate that the catalyst exists only on the surface of original particles and not in the core of the grafter

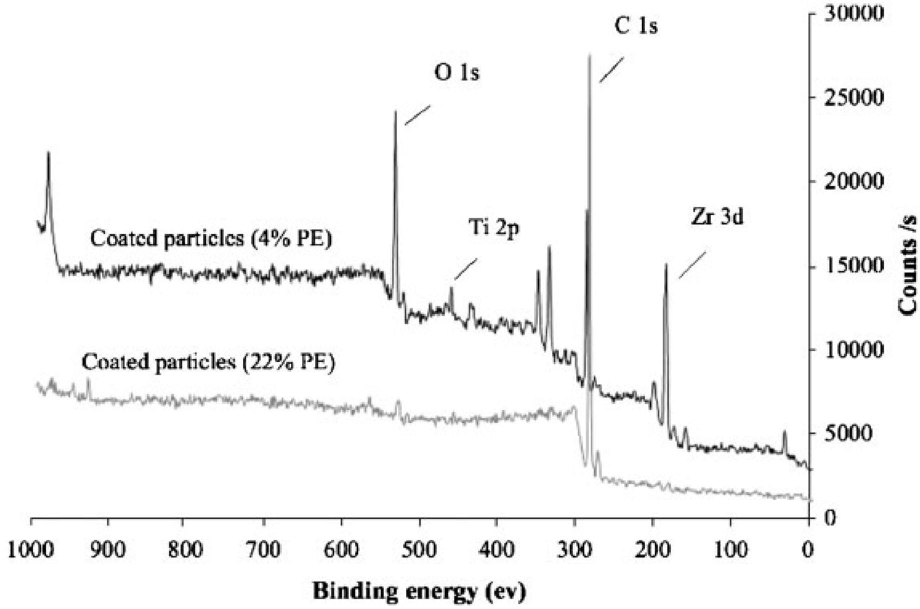


Figure 8.
XPS graphs of two different coated zirconia nanoparticles.

polymer layer. Therefore, the polymerization reaction can only start from the surface of original particles.

Conclusions

It has been shown that the polymerization compounding technique can be used to encapsulate zirconia nanoparticles by high molecular weight polyethylene using surface-grafted Ziegler-Natta catalysts. XPS results confirmed that the polymerization reaction started only from the original surface of particles, generally leading to a uniform polymer layer applied around nanoparticles. As observed from electron microscopy images, the process is capable of coating individual particles by a polymer film of a few nanometers in thickness. However, it was also revealed that some agglomerates were encapsulated by the polymer, which is obviously not desirable. To limit the extent of this agglomerates coating phenomenon, the dispersion of nanoparticles in the polymerization solvent is an important factor which must be taken into account. As future work, the effects of process conditions i.e., temperature and pressure will be investigated in order to obtain a better understanding of the reaction kinetics and therefore to achieve a more reliable control of the thickness of the resulting polymer layer.

[1] M. Avella, M. E. Errico, G. Gentile, *Macromol. Symp.* **2006**, 234, 170.

[2] W. H. Ruan, X. B. Huang, X. H. Wang, M. Z. Rong, M. Q. Zhang, *Macromol. Rapid Commun.* **2006**, 27, 581.

[3] S. Stolnik, M.C. Davies, L. Illum, S. S. Davis, M. Boustta, M. Vert, *J. Controlled Release* **1994**, 30, 57.

[4] J. L. Zhang, Z. M. Liu, B. X. Han, J. C. Li, Z. H. Li, G. Y. Yang, *J. Nanosci. Nanotechol.* **2005**, 5, 945.

[5] Q. Wang, S. Kaliaguine, A. Ait-Kadi, *J. Appl. Polym. Sci.* **1992**, 44, 1107.

[6] Q. Wang, S. Kaliaguine, A. Ait-Kadi, *J. Appl. Polym. Sci.* **1992**, 45, 1023.

[7] Q. Wang, S. Kaliaguine, A. Ait-Kadi, *J. Appl. Polym. Sci.* **1993**, 48, 121.

[8] H. Salehi-Mobarakeh, A. Ait-Kadi, J. Brisson, *Polym. Eng. Sci.* **1996**, 36, 778.

[9] H. Salehi-Mobarakeh, J. Brisson, A. Ait-Kadi, *J. Mater. Sci.* **1997**, 32, 1297.

[10] H. Salehi-Mobarakeh, J. Brisson, A. Ait-Kadi, *Polym. Compos.* **1998**, 19, 264.

[11] M. Rajabian, C. Dubois, *Polym. Compos.* **2006**, 27, 129.

[12] A. Kasseh, A. Ait-Kadi, B. Riedl, J. F. Pierson, *Polymer* **2003**, 44, 1367.

[13] Y. Wang, X. Pei, K. Yuan, *Mater. Lett.* **2005**, 59, 52.

[14] C. Roy, C. Dubois, P. Lafleur, P. Brousseau, *Mater. Res. Soc. Symp. Proc.* **2004**, 800.

[15] D. Shi, S.X. Wang, W.L. van Ooij, L.M. Wang, J. Zhao, Z. Yu, *Appl. Phys. Lett.* **2001**, 78, 1243.

[16] X. Ding, J. Zhao, Y. Liu, H. Zhang, Z. Wang, *Mater. Lett.* **2004**, 58, 3126.

[17] W. He, Z. Guo, Y. Pu, L. Yan, W. Si, *Appl. Phys. Lett.* **2004**, 85, 896.

[18] M. Rovira-Bru, F. Giralt, Y. Cohen, *J. Colloid Interface Sci.* **2001**, 235, 70.

[19] C. Dubois, M. Rajabian, D. Rodrigue, *Polym. Eng. Sci.* **2006**, 46, 360.

[20] M. Sato, T. K Norio Kobayashi, Y. Shima, *J. Catal.* **1967**, *7*, 342.