IN-SITU POLYMER GRAFTING ON ULTRAFINE METAL POWDERS.

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Abstract
Ultrafine aluminum and boron powders have been identified as very promising fuels as part of energetic materials formulations. However, the large specific surface area that gives these powders a high reactivity also makes them particularly difficult to maintain in an unoxidized state. They also agglomerate easily during compounding processes. The coating of the particles by a polymer could offer a solution to these problems. We carried out the in-situ synthesis of crystalline and semi-crystalline polyolefins on the surface of aluminum and boron nanoparticles by the Ziegler-Natta process. The process was found to be flexible enough to control the amount of polymer grafted on the powders. High density polyethylene and polypropylene coatings were successfully obtained. The resulting characteristics of the coated powders are discussed by means of thermogravimetric characterizations and electronic microscopy. The coated powders were also characterized by the means of X-ray photoelectron spectroscopy

Introduction
Ultrafine metal powders (nanometer scaled) are being recognized as very promising materials for diverse combustion applications, such as additives in solid rocket propellants, and metallic fuel in explosive formulations. The aluminum nanopowders have been reported to show burning rates 5 to 10 times greater than microsized ones, and when used in gas generator fuels, they achieve a more complete combustion. These enhanced properties are due to their large specific surface. In spite of the extremely high expectations about the potential use of ultrafine aluminum and boron powders in energetic materials, some problems remained to be overcome fully benefit of their nanometric size: 1) Ultrafine aluminum powders are very reactive and difficult to maintain in an unoxidized state, 2) In either dry or wet processes, they tend to agglomerate. The coating of these powders is a solution to protect them from non-desirable reaction (as oxidation). Several researchers have proposed different coating approaches. Among them are coating by carbon deposition [1], stearic acid and aluminum diboride deposition [2], polyvinylidene fluoride deposition by SCF carbon dioxide [3], and polystyrene polymerization [4]. In a previous work we have investigated several polymer grafting approaches to obtain the desired thin protective layer, such as the *in situ* synthesis of thermoplastics (polyethylene PE, polypropylene PP) by the Ziegler-Natta reaction and surface initiated polycondensation of thermoset polymers [5]. In this paper, we extend this work by conducting the polymerization reaction to graft a layer of polyethylene on nanosize aluminum particles and nanosize boron

particles. Polypropylene grafting was also successfully achieved. The process is conducted in solvent by the means of a Ziegler-Natta polymerization using the hydroxyl sites on the metal particles to attach the coordination catalyst system, i.e. titanium tetrachloride ($TiCl_4$) and an alkylaluminum co-catalyst compound such as $Al(C_2H_5)_3$. The catalyst/co-catalyst solution of the Ziegler-Natta reaction is extremely sensitive to moisture and oxygen and thus, the coating process must be carried out in a controlled environment under inert atmosphere. The main objective of this work is to obtain an evenly thin polyolefin coating on passivated ultrafine aluminum and boron particles. For that purpose we investigated several variables controlling the polymerization, such as catalyst/powder ratio and reaction time and attempt to correlate these parameters with the properties of coated powders, as observed by weight loss analysis, electronic microscopy and X-ray photoelectron spectroscopy (XPS).

Experimental details

Materials

All chemicals used in this study were handled in inert conditions under dry argon or nitrogen blanketing. In order to preserve their efficiency, the catalyst and co-catalyst have to be strictly handled in a medium with no residual water or oxygen. Ultrafine aluminum powders were bought from TECHNANOGY Materials Development, Santa Ana, USA (mean diameter of 120 nm, and a $18.0 m^2/g$ specific surface area) and TEKNA Plasma Systems, Sherbooke, Canada (mean diameter of 120 nm, and a $16.5 m^2/g$ specific surface area). The boron particles (25-40 nm in diameter) were also procured from TEKNA and were found to have a specific surface area of $80.0 m^2/gr$ as measured by BET. The catalyst used for the Ziegler-Natta reaction was pure titanium tetrachloride $TiCl_4$, provided by ACROS ORGANICS (New Jersey, USA). The co-catalyst was triethylaluminium $Al(C_2H_5)_3$ 1M in hexane, and it was provided by ALDRICH. The hexane used as a reaction solvent was dried for at least 24 hours on molecular sieve (silico aluminate zeolite - GRACE Davison, Columbia, USA). All the gases were obtained from Air LIQUIDE CANADA. Argon HP$^+$ grade 2 was used for preparing an inert atmosphere in the glove box. Nitrogen N_2 HP$^+$ grade 2 was used for the purge of the reactor before polymerization. Ethylene grade 2 and propylene grade 2 were used for the polymerization step.

Synthesis procedure for in-situ polyethylene or polypropylene coating

The polymerizations were carried out in thoroughly dried hexane using a 1 liter pressurized glass vessel BUCHI reactor (BUCHI laboratory autoclave BEP 280). The jacketed reactor was heated by an external fluid bath circulator and mixing was provided by a top mounted magnetic drive impeller. A 750W ultrasound probe was also installed on the reactor cover plate and activated before the polymerization process to conduct the dispersion of the metal powders. During the reaction, the 1.25 cm ultrasonic probe (SONICS) was also periodically activated as previously reported [5]. The inert gas blanket and gaseous monomer were brought to the reactor by 2 feeding ports. An additional port, protected by a polymer septum, was put in place to allow for the injection of the catalysts. During a typical polymerization, 20g of previously dried (for 12 hours under vacuum at 70°C) aluminum or boron powders were dispersed in 800 ml dried hexane (~10%w/w) by mechanical agitation (200 rpm) at a mild temperature (60°C) for 30 minutes, under a slight flow of nitrogen. When octadecylamine was used as a surfactant, it was added to the suspension at this stage of the process. Then, the desired "ideal" quantity (440 μl) of catalyst $TiCl_4$ was injected through the

septum feeding port with a syringe and ultrasounds were applied shortly after the first injection, for 3 minutes (power = 375 W, pulse 50%). Ten minutes after the injection of the catalyst, the co-catalyst $Al(C_2H_5)_3$ was injected in an "semi-ideal" or "ideal" quantity of 2ml (see the next paragraph for more information about the signification an "ideal" amount of catalyst). Then, a delay of three minutes was observed so as to be sure that the catalyst and the co-catalyst have formed a complex on the surface of the aluminum powder. After the co-catalyst injection, the polymerizations were conducted under the positive monomer pressure. In the case of ethylene, the pressure was regulated at 30 kPa (gage) while for the propylene, the pressure of monomer was set to 400 kPa (gage). After the desired reaction time, the polymerization was stopped by an injection of 10ml of ethanol. The role of ethanol is to hydrolyze the catalyst complex. At that point, the coated powders were filtered on a Buchner funnel, washed with hexane and dried at 60°C under vacuum to eliminate traces of hexane.

Estimation of the ideal quantity of catalyst

We obtained the best results with an "ideal" amount of catalyst, here defined as the quantity required to cover the total surface of the powder by $TiCl_4$ molecules. The specific surface area of the powders was measured by BET. Most of the experiments were carried out with an "ideal" quantity of catalyst, and a "semi ideal" quantity of co-catalyst. The calculation of the ideal catalyst quantity was made on the following assumption: The $TiCl_4$ molecule is modeled by a sphere with a radius equivalent to the Ti-Cl bond length. The aluminum powders only contain spherical particles. When the $TiCl_4$ molecule reacts with the –OH on the surface of passivated aluminum, it keeps the same tetrahedral geometry. We supposed that the space occupied by every $TiCl_4$ molecule on the surface of an aluminum particle equals the surface of a disc with a diameter equivalent to two times Ti-Cl bond length. Ti-Cl bond length is about 2.18Å. It corresponds to a disc surface of $1.493×10^{-19}$ m^2. For example, a quantity of 20g of aluminum powder represents a total surface of 18m^2/g×20g=360 m^2. As a consequence, the number of molecules required to cover the entire surface of aluminum is 360/$1.493×10^{-19}$ m^2 = $2.41×10^{21}$ molecules. The corresponding number of moles is $4×10^{-3}$, with a mass of 0.759g and a volume of 440 µl ($TiCl_4$ molar mass = 189.9g; $TiCl_4$ density = 1.72g/cm^3). The $Al(C_2H_5)_3$ co-catalyst "semi ideal" quantity is $4×10^{-3}/2 = 2×10^{-3}$ moles.

Characterization

The amount of polymer grafted on Al particles was measured by thermogravimetric (TGA) experiments using a METTLER TOLEDO apparatus operated on a 25°C–800°C temperature range at a 10°C/min heating rate under a flow of argon (inert atmosphere). The SEM images were acquired with a JEOL-JSM 7400F field emission scanning electron microscope (FESEM). The operating conditions for the SEM were: a LEI imaging mode (lower secondary electron image), acceleration voltage of 1 kV and a working distance of 8,5 mm. TEM observations were made with a PHILLIPS CM30 transmission electronic microscope.

Results and discussion

We carried out a series of experiment aimed at evaluating the effect of time of the on the coating process, mainly in terms of the amount of polymer grafted on the surface. The kinetic aspect of the reaction has been discussed in a previous paper [6]. We report in Figure 1 three TGA traces of polymerization reactions conducted for 5 minutes, 15 minutes and 30 minutes

respectively. The plots can be used to evaluate the loss of mass (in percentage) as a function of temperature. One can distinguish several distinct zones on the TGA thermograms. The first one (between 25°C and 100°C) is represented by a very slight and continuous decrease in mass percentage and corresponds to solvent evaporation. The second one, in the interval of temperature between 100°C and 125°C, probably corresponds to the pyrolysis of small oligomers chains. Between 125°C and 370°C, pyrolysis of oligomers chains and a partial thermocracking (about 300°C) of a few quantities of HDPE (high density polyethylene) chains contribute to a slight and continuous decrease of mass. The reaction of thermocracking reduces the molecular weight of HDPE chains and produce vinyl double bonds in polymer chains. Moreover, these chains will be completely burned at a higher temperature range. The most important mass decrease corresponds to the interval of temperature between 370°C and 500°C. This dramatic change corresponds to the complete pyrolysis of HDPE chains in an inert atmosphere (argon). It is also observed that for the 30 minutes polymerization sample, the degradation of oligomers appears to be less pronounced, an indication that the polyethylene obtained after a longer polymerization might have a larger molecular weight.
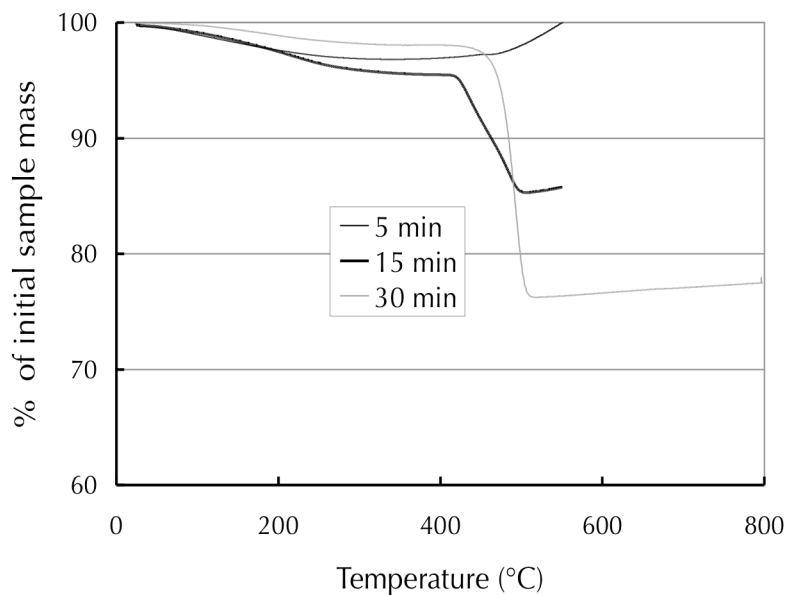

Figure 1 TGA of three PE coated samples

As discussed previously, the Ziegler-Natta polymerization process can be applied to other monomers than ethylene. We attempted the polymerization of propylene under a monomer pressure of 4 to 5 atm for a 30 minutes duration. The Figure 2 shows the thermogram of a sample of polypropylene coated aluminum particles. It is seen that for a longer polymerization time, a smaller amount of polymer is produced than with the polyethylene. Also, an analysis of the curve shows that a more important amount of mass is lost at lower temperature, indicating that a significant quantity of low molecular weight products are obtained by the polymerization process. On the other hand, the weight loss observed beyond 325 °C also confirms that only

about 3-4% of polypropylene is made. In order to improve this result, we choose to use an amine surfactant to not only facilitate the dispersion of the powders in the solvent but also to increase the yield in polypropylene, since Lewis bases are often included in Zeigler-Natta catalyst formulations for polypropylene. The results presented at Figure 3 for a polymerization where 1% w/w of octadecylamine was used show a definitive improvement but a significant loss weight is still observed at low temperature and thus, further investigations are required.
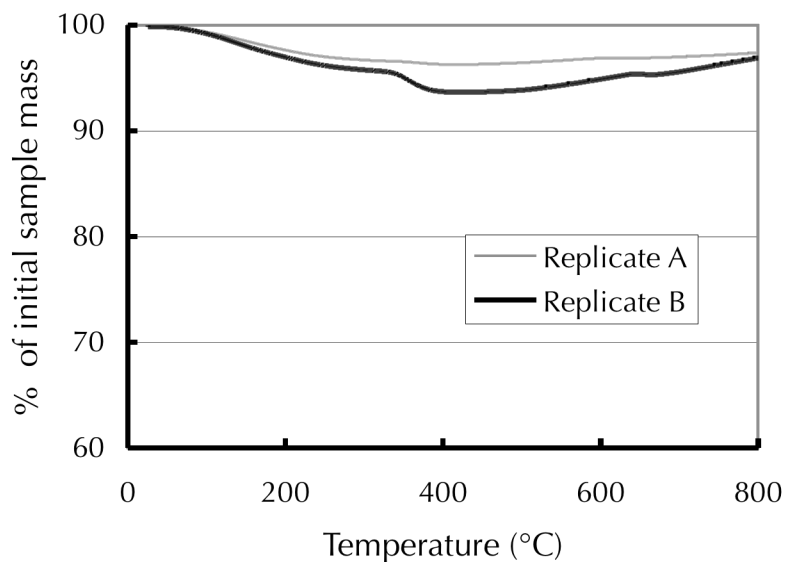
Figure 3 TGA of a PP coated aluminum sample
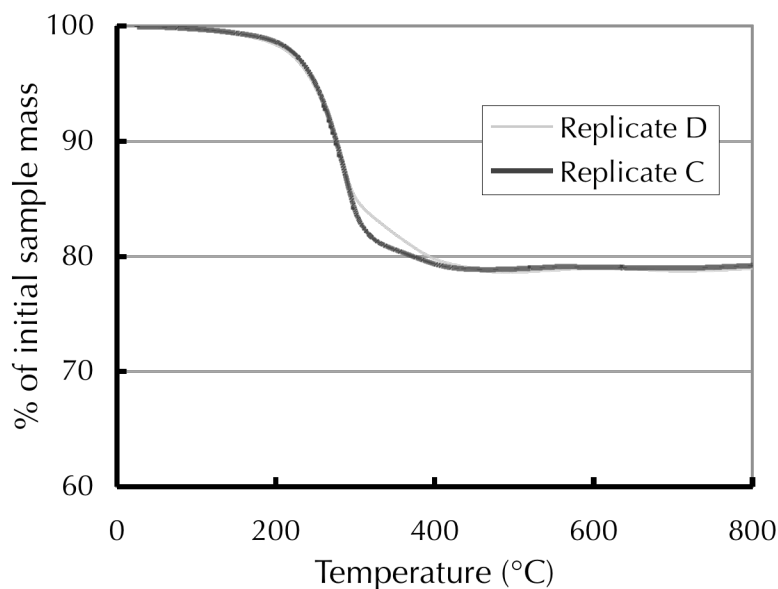
Figure 3 TGA of a PP coated aluminum sample using 1% of octadecylamine

The Zeigler-Natta polymerization of ethylene was also successfully conducted on the surface of the boron particles. Due to their very high specific area, a larger amount of polymers was obtained than with aluminum powders using similar reaction conditions. In Figure 4 we present the TGA curve of a sample of TEKNA boron powders coated by a 30 minutes reaction. It shows that more than 60% w/w of polyethylene is obtained. Moreover, the degradation of the polymer occurs at a high and narrow range of temperature indicating that high molecular weight PE is produced.
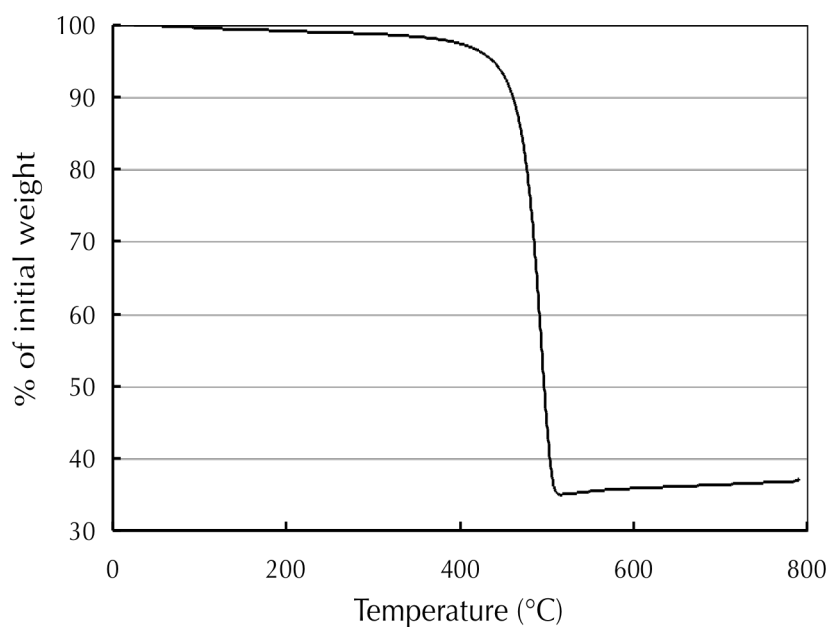
Figure 4 TGA of a PE coated boron sample

The characterization of the aluminum powders was also pursed by a study of their morphology using transmission electronic microscopy (TEM) and scanning electronic microscopy (SEM). TEM observations were carried out on samples of polyethylene coated powders resulting from a 10 minutes synthesis and containing 10 % w/w of PE. Figure 4a presents a 125 nm aluminum particle uniformly coated by a polymer layer about 5 nm thick. Figure 4b presents non coated aluminum particles. No polymer is seen around the surface of aluminum particles and we can distinguish the sharp edge of the particles.
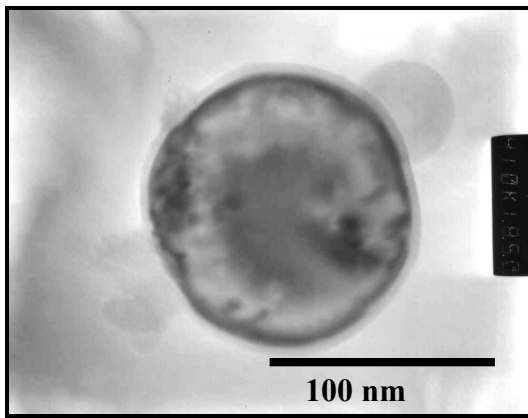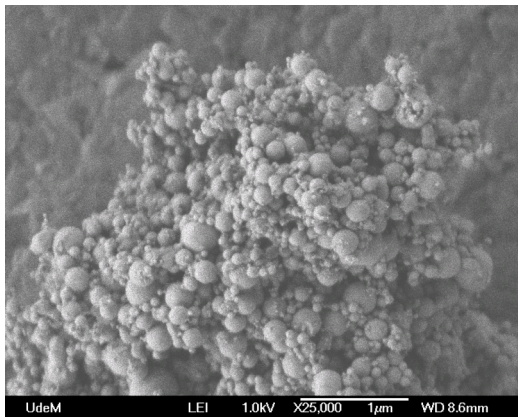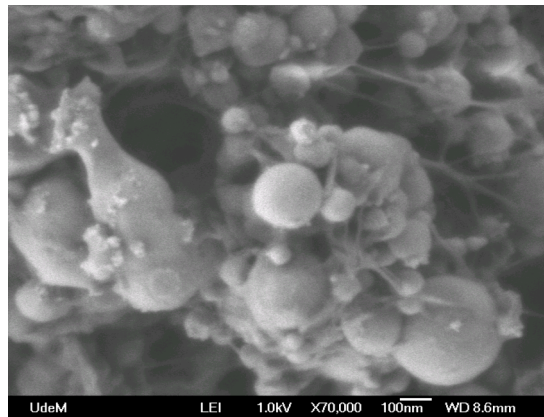
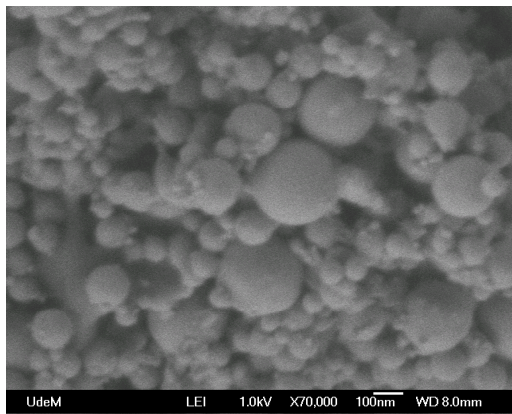a) Polymer coated particles (×410000)   b) Non coated particles (×410000)
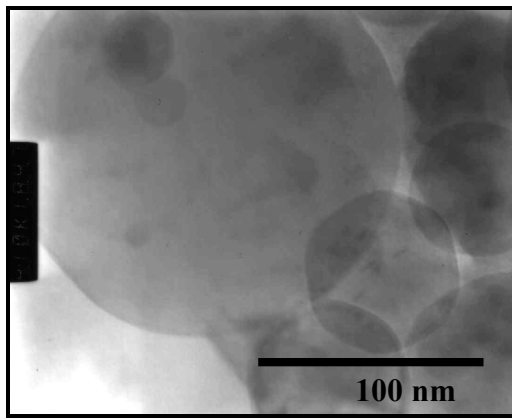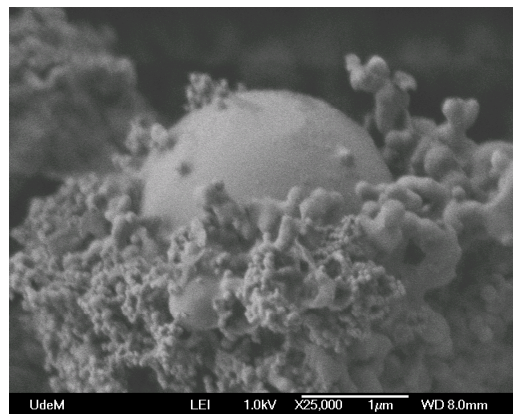
Figure 5: TEM images of aluminum/polyethylene samples

a) Non coated particles (×25000)   b) PE Coated particles (10 % PE) (×70000)

c) PP Coated particles (16% PP) (×70000)   d) PE Coated particles (Technanogy) (×25000)

Figure 6: SEM images of coated and non-coated aluminum particles

Typical SEM observations are shown at Figure 6. In Figure 6a) (magnification ×25000) we see that even non-coated particles are agglomerated in clusters and this may be due to the solvent removal process. A simple visual inspection of the picture also reveals a large size

distribution, ranging from 50 to 400 nm. Figure 6b (magnification ×70000) presents polyethylene coated aluminum particles. While it is seen that particles appear to be individually coated, they retain, after the synthesis, an agglomerated state. One can also see the presence of some very thin bridges of polymer between particles leading to the assumption that too much polymer is made during the reaction. Figure 6c) (magnification x70000) a picture of a sample of polypropylene coated powders is shown. Even if the sample contains more polymer (16%) than the sample presented in Figure 16b), the coating appears to be more uniformly built around the particles and no bridges are found. Finally in Figure 6d) we present a picture of a sample of Technanogy aluminum powders coated with 7% w/w of PE. It is seen that among the nanoparticles very large particles are sometimes found (about 1 μm). Such particles make the process more difficult to control due to their effect on the specific area of powders.

While TGA traces and electronic microscopy provides evidences of polymer at the surface of the powders, they do not give the chemical composition of the coating. In order to obtain a confirmation of the nature of the reaction occurring at the surface, we used XPS analysis. The spectrum presented in Figure 7 shows peaks at binding energy of 475 eV and 200 eV, indicating the presence of titanium and chloride atoms and thus confirming the grafting of the polymerization catalyst.
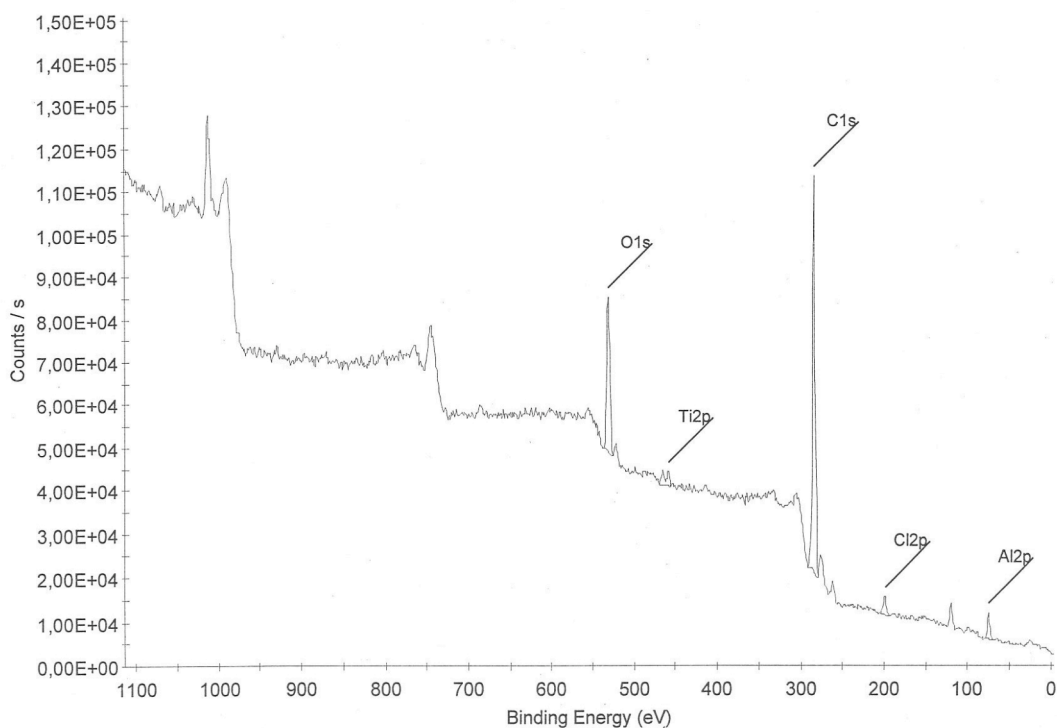

Figure 7 XPS of a 12% PE coated w/w aluminum sample

Conclusions

This project aims at evaluating the Ziegler-Natta reaction as a mean of obtaining a thin polymer film evenly polymerized from the surface of metal particles. For the polymerization of ethylene, it was found that the polymerization conditions can be varied effectively to control the amount of polymer produced on the particles. A characterization of the surface by XPS has confirmed the grafting of the titanium chloride catalyst. In cases where polypropylene coatings were made, it took a longer reaction time and a higher pressure to achieve a significant level of grafting. Moreover, the presence of octadecylamine as a surfactant was found to favour the polypropylene polymerization. For the two processes, the degradation temperatures observed on the TGA measurements confirmed the presence of a non-volatile polyolefin. However, the characterization by SEM/TEM images show that the primary goal is only partially achieved. For polyethylene coatings, it is seen that particles are indeed individually covered but we also observed very thin polymer bridges between some particles, which is clearly an undesirable feature. On the other hand, a sample coated with 16% of PP did not show the same polymer strands. Finally, preliminary work on boron particles proved that these particles can also be treated by a similar process.

Acknowledgments

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