

Polymer-Grafted Metal Nanoparticles for Fuel Applications

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Ultrafine metal powders have been identified as very promising fuels for future energetic material formulations. However, the large specific surface area that gives these powders a high reactivity also makes them particularly difficult to remain in a nonoxidized state. They also agglomerate easily during compounding processes due to strong particle-to-particle interactions. The coating of the particles with a polymer may offer a solution to these problems. We investigated two in situ polymerization processes using thermoplastic and thermoset coatings. Polyolefins such as polyethylene and polypropylene were obtained using a modified Ziegler–Natta reaction scheme. This process was found to be flexible enough to control the amount of polyethylene grafted onto the powders. The second type of coating was based on polyurethane chemistry. Nanometric-sized aluminum and boron powders were treated and characterized by means of thermogravimetric analysis, electronic microscopy, and x-ray photoelectron microscopy. The barrier properties of the polymer layer grafted onto the particles were evaluated using a chemical digestion method and thermoanalytical techniques. Polyethylene-coated particles showed a better resistance to early aging under stringent conditions of humidity and temperature and therefore would be expected to demonstrate a longer shelf life in a propellant formulation.

I. Introduction

THE addition of metal particles to solid propellants and fuels can significantly improve the performance of both rocket and airbreathing propulsion systems. However, in both cases, the size of the particles used can have a significant effect on the rates of energy release and combustion efficiency. For example, aluminum is commonly used in solid rocket propellants to boost specific impulse on the order of 10% over nonaluminized formulations. By using nanometric-sized particles, burn rates of the propellant can be enhanced by 5 to 10 times with respect to similar formulations using micron-sized metal powders [1].

For airbreathing propulsion systems such as solid-fuel ramjets and ducted rockets (see Fig. 1), boron is the metal of choice because of its superior gravimetric (58 kJ/g) and volumetric (136 kJ/cc) heats of combustion. Until now, the use of boron has been limited by the difficulty of igniting and burning it efficiently, mainly due to the particular properties of its outer oxide layer. Although combustion efficiency can be enhanced by using nanometric-sized particles, the thickness of the oxide layer can still limit any improvement.

In spite of the previously stated benefits, metal nanoparticles often fall short of delivering the expected performance or, when they do, the result is obtained at the cost of a series of precautions and measures that pose a serious impediment to the regular use of these materials. For example, ultrafine metal powders age rapidly in humid conditions [2–4]. They also react more readily with energetic components, such as cyclotrimethylenetrinitramine (RDX) [5], and produce gas. This minor incompatibility can cause problems in mixes kept in long-term storage. Finally, their electrostatic discharge

sensitivity (ESD), and that of any mixes containing the powders, can be much higher than the ESD of micron-sized powders [6].

One way to solve these problems is to coat the nanoparticles with a protective layer of material. For boron particles, coating the particles with a polymer can prevent excessive oxidation, and the use of an energetic polymer can bring additional heat close to their surfaces and facilitate ignition. Another benefit of the polymer coating is to improve the dispersion of the particles in the polymeric matrix during mixing, and this may also prevent particle agglomeration in the combustion chamber. Cliff et al. [4] demonstrated that a coating of palmitic acid on Alex® nanopowders significantly decreased the sensitivity of the aluminum powder to humid conditions and slowed down the aging of the powders. However, the acidic nature of the coating produced incompatibilities in mixes of energetic materials. Puszynski [2] also demonstrated that silane Z-6124, at a concentration of 5%, protected aluminum nanoparticles from aging. He also showed that the coating had an effect on the ignition delay time. Several other types of coatings have also been studied: carbon deposition [7], stearic acid and aluminum diboride deposition [8], polyvinylidene fluoride deposition by supercritical fluid (SCF) carbon dioxide [9], and polystyrene polymerization [10]. For most of these investigations, the coating process is, in fact, a physical deposition operation in which the monomer or polymer is allowed to coat the nanoparticles, which themselves act as nucleating agents. Because of particle–particle interactions, the metal nanoparticles have a tendency to agglomerate and, as a consequence, the polymer layer applied by deposition can often envelop clusters of particles. A potentially more efficient way to achieve a uniform polymer coating of ultrafine particles is to conduct a so-called in situ polymerization reaction initiated from the surface of the solids. In previous work, this approach was successfully applied for both thermoplastic polyolefins [11] and polyurethane coatings [12].

In this paper, we present recent advances obtained for each approach for both nanometric-sized aluminum and boron particles. The effects of the resulting coatings are also further discussed by considering the morphology and the aging behavior of the coated materials. The underlying objectives of this work were to coat the powders with very thin polymeric coatings and to control their thicknesses. It was hypothesized that these coatings would then protect the powders against premature oxidation, prevent incompatibilities with other energetic materials, and even help

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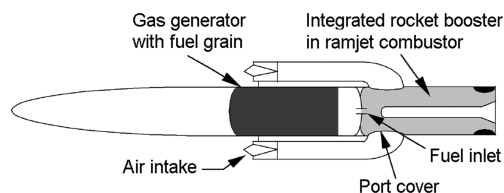
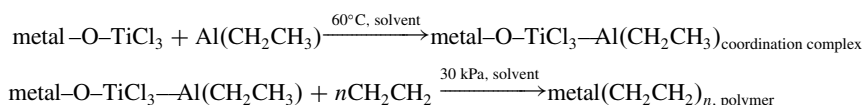


Fig. 1 Schematic of a solid-fuel ducted rocket.

obtain nanoparticles with larger percentages of active aluminum by coating nonpassivated or underpassivated metal particles. In addition, with a small controlled thickness of combustible material, it should be possible to control the burning rate of the coated particles,

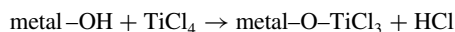
Although the number of hydroxyl functions varies depending of the nature and source of particles used, our experience with aluminum, boron, copper, iron, and stainless steel particles showed that a sufficient number of anchoring points for the catalyst were usually found. The Ziegler–Natta reaction is conducted under mild conditions of temperature and pressure in an organic solvent in which the nanoparticles are put in suspension by mechanical agitation and ultrasonic processing. Once grafted with the catalyst, the particles can act as multiple initiation sites for the polymerization by sequentially introducing in the chemical reactor the coinitiator (triethylaluminum) and the olefin monomer (as a gas):



as Puszyński [2] showed with coatings that increased the burning rate of Al–CuO metastable intermolecular composites (MIC). Finally, mechanical properties of energetic materials containing coated nanoparticles could be enhanced if the surface of the coating has an affinity for the binder system used.

II. In Situ Polymerization Processes

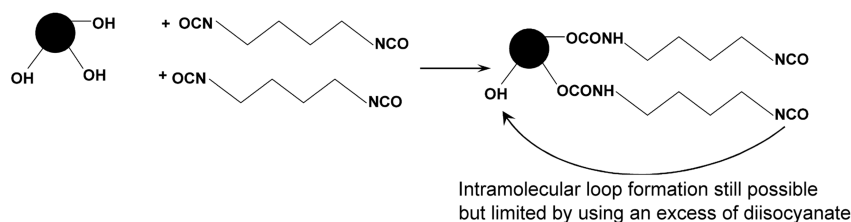
Polymers and plastics are often classified as being either thermoplastic or thermoset materials. In the course of this project, both types of coatings were investigated. For thermoplastic polymers, polyethylene (PE) and polypropylene coatings were obtained using a modified Ziegler–Natta polymerization scheme in which the polymerization catalyst, titanium tetrachloride, was first grafted onto the particle using hydroxyl sites available at its surface:



The catalyst and cocatalyst used in this reaction are both hygroscopic compounds, but the latter is also a very sensitive pyrophoric material. Accordingly, the reaction is conducted under strict conditions of a dry and inert atmosphere. The thickness of the coating is proportional to the reaction time, and the kinetics of the polymerization are affected by the temperature and pressure. In turn, the nature and thickness of the polymer layer will control its permeability and therefore its barrier properties and ability to prevent early aging of the metal powders.

The preparation of particles coated with thermoset polymers was carried out using polyurethane chemistry. This reaction was chosen in light of the fact that many modern solid rocket propellants rely on polyurethane binders, and therefore polyurethane-coated particles should exhibit an improved compatibility with these formulations. As for the thermoplastic coating technique, the reactive sites on the nanoparticle are exploited to initiate the polymerization from the surface, as shown in Fig. 2. The polyurethane reaction is a polycondensation reaction of hydroxyl and isocyanate chemical

Step 1: Grafting a diisocyanate



Step 2: Grafting a diol

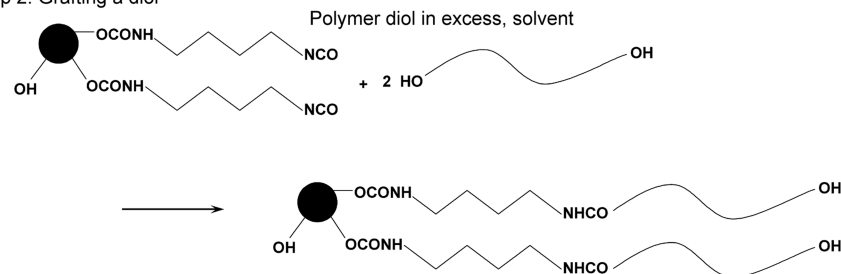


Fig. 2 Reaction scheme for polyurethane coatings.

functions. The first step of the process is therefore to attach one end of a polyisocyanate molecule to the solid particle. The second step involves the reaction of the free ends of the grafted isocyanate with a polyol product, leading to an extension of the molecule. Successive repetitions of the polyisocyanate/polyol reaction are then carried out until the desired molecular weight is achieved. As with the previous process, this reaction is conducted in an organic solvent under an inert atmosphere. Because of the large variety of isocyanates and polyol prepolymers readily available from commercial sources, different types of coatings can be obtained, which allows for a wider spectrum of physical and barrier properties on the particles. In the course of this work, bisphenol-A/toluene diisocyanate (BA/TDI), hydroxy-terminated polybutadiene/toluene diisocyanate (HTPB/TDI), and TDI/Zonyl BA-L systems were investigated. The Zonyl BA-L is a hydroxy-terminated fluorinated aliphatic oligomer commercially produced by Dupont. Interest in this product was motivated by the presence of fluorine atoms in the molecule, which should bring an increased heat of combustion and improved hydrophobic properties for the coated powders.

III. Experimental Methods

A. Materials

All chemicals used in this study were handled in inert conditions under dry argon or nitrogen blanketing. In particular, the catalyst and cocatalyst used for the Ziegler–Natta polymerization have to be strictly manipulated in a medium with no residual water or oxygen, to preserve their efficiency and avoid a pyrophoric ignition. Ultrafine aluminum powders provided by the former Technanogy Materials Development had an average diameter of 43 nm, whereas the powder obtained from TEKNA Plasma Systems had a mean diameter of 120 nm and a specific surface area of 18 m²/g. These powders were slightly passivated during their plasma synthesis with a thin oxide layer of about 2.5-nm thickness. These 120-nm powders were used for all of the syntheses that were carried out for the kinetic study. Ultrafine boron particles were obtained from TEKNA Plasma Systems and were found to have a specific surface area of 80 m²/g.

The catalyst used for the Ziegler–Natta reaction was pure titanium tetrachloride TiCl₄, provided by Acros Organics. The cocatalyst was triethylaluminum [Al(C₂H₅)₃, 1 M in hexane], and it was provided by Sigma-Aldrich. The reagent grade hexane solvent was dried for at least 24 h on a molecular sieve (silico aluminate zeolite produced by GRACE Davison). All of the gases used in the processing were provided by Air Liquide Canada. Argon HP⁺ grade 2 was used for preparing the inert atmosphere in the glove box, nitrogen N₂HP⁺ grade 2 was used for the purge of the reactor before polymerization, and ethylene CH₂ = CH₂ grade 2 was used for the polymerization reaction. The preparation of oligomeric polyurethane coatings used bisphenol-A (C₁₅H₁₆O₂) and toluene diisocyanate (C₉H₆N₂O₂) procured from Sigma-Aldrich. The dibutyltin dilaurate (DBTDL) catalyst (C₃₂H₆₄O₄Sn) was also bought from Sigma-Aldrich. The hydroxy-terminated polybutadiene (HTPB) was obtained from Arco Chemicals under the R-45M designation, and complimentary samples of Zonyl BA-L were provided by Dupont Canada.

B. Preparation of Polyolefin Coatings

The polymerizations were carried out in thoroughly dried hexane using a one-liter pressurized glass vessel Buchi reactor (Buchi laboratory autoclave BEP 280). A simple schematic of the polymerization setup is shown in Fig. 3. The jacketed reactor was heated by an external fluid bath circulator, and mixing was provided by a top-mounted magnetic drive impeller. A 750-W ultrasound probe was also installed on the cover plate and activated before and during the polymerization process. The dispersion of nanosized metal powders carried out by means of a 1.25-cm ultrasonic probe (SONICS) was found to be essential for obtaining a satisfactory suspension [13]. The inert gas blanket and gaseous monomer were brought into the reactor by two feeding ports. An additional port was protected by a polymer septum to allow for the injection of the catalysts. During a typical polymerization, 20 g of previously dried

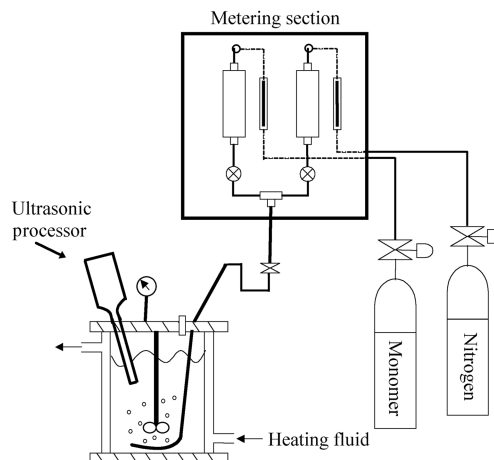


Fig. 3 Experimental setup for polyolefin coatings.

(for 12 h under vacuum at 70°C) aluminum or boron powders were dispersed in 800 ml of dried hexane (~10%w/w) by mechanical agitation (200 rpm) at a mild temperature (60°C) for 30 min, and under a slight flow of nitrogen. Next, the required quantity (a few hundred microliters) of catalyst TiCl₄ was injected through the septum feeding port with a syringe, with ultrasonic vibrations applied shortly after the first injection for 3 min (power is 375 W and pulse is 50%). Ten min after the injection of the catalyst, a quantity of the cocatalyst triethylaluminum was injected (a few milliliters). There was then a delay of 3 min to be sure that the catalyst and the cocatalyst had formed a complex on the surface of the metal powder. After the cocatalyst injection, the polymerizations were conducted in the reactor at low positive pressure (30 kPa for ethylene monomer or 300 kPa for propylene monomer) for the desired duration (between 5 to 20 min) before being stopped by an injection of 10 ml of ethanol. The role of ethanol was to hydrolyze the catalyst complex. At that point, the coated powders were passed through a Buchner filter, washed with hexane, and dried at 60°C under vacuum to eliminate any traces of hexane.

C. Preparation of Polyurethane Coatings

The grafting of urethane oligomers onto metal nanoparticles was conducted in a two-liter glass reactor according to a batchwise process. The multiple-step reactions were carried out in dried acetonitrile at 60°C under a nitrogen atmosphere. Between 20 to 40 g of ultrafine powders, previously dried under vacuum for several hours, were added to the solvent and put in suspension using an impeller-shaped mechanical agitator. At the same time, periodic bursts of vibrations from the ultrasonic processor were applied to enhance particle dispersion. An amount of DBTDL catalyst solution (in methylene chloride) was then injected in the reactor to achieve a 0.05-M concentration, immediately followed by the diisocyanate added with a 30 to 50% molar excess. The reaction with the diisocyanate was allowed to proceed for 2–3 h before the addition of the polyol compound, also in a 30 to 50% molar excess, followed by a similar reaction time. At the end of this cycle, the powders were filtered to remove any unreacted soluble oligomers. The procedure was repeated as needed to promote the progressive growth of the grafted chains on the metal particles.

D. Characterization of Coated Powders

The amount of polymer grafted onto the aluminum particles was measured by thermogravimetric analysis (TGA) experiments using a Mettler Toledo apparatus. It operated at a 25–800°C temperature range with a 10°C/min heating rate under a flow of argon (inert atmosphere). The scanning electron microscope (SEM) images were acquired with a JEOL-JSM 7400F field emission SEM. The operating conditions for the SEM included a lower secondary electron image (LEI) mode, acceleration voltage of 1 kV, and a working distance of 8.5 mm. Transmission electronic microscope

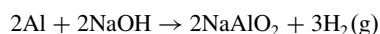
(TEM) observations were made with a Phillips CM30 TEM; x-ray photoelectron spectroscopy (XPS) was carried out on a Phillips model 5500 spectrometer, with a monochromatized aluminum source for x-ray production. The spectra were taken at 300 W, with a neutralizer for insulating samples. Specific surfaces were estimated for BET experiments conducted in a Micromeritics FlowSorb 2300 apparatus.

E. Methods for Aging Studies

Two different methods were used to assess the ability of the coatings to slow down or eliminate the aging of the small aluminum powders. One of them was a direct measurement of the active aluminum content in the powders during accelerated aging tests performed at elevated temperatures. The second one was an indirect measurement of the active aluminum during aging tests at room temperature.

1. Accelerated Aging

The method used to determine the amount of active aluminum in the samples was a simple digestion. This method was inspired by the one used by Cliff et al. [4] for their aging study and is a digestion of the aluminum using a NaOH solution. The reaction produces hydrogen gas according to the reaction:



The volume of gas generated is measured to determine how much aluminum has reacted. An excess of 2M NaOH was used. The reaction was carried out in a 500-ml flask, onto which a pressure transducer was connected. The pressure transducer was a Boc Edwards Barocell 622 capable of measuring 0–1000 mm Hg. The reaction was performed under a small vacuum so that the reaction would end at atmospheric pressure. This was done to minimize any hydrogen leaks from the system. The reaction was performed in a fluid bath and was usually complete within one or two hours. A thermocouple was installed to monitor the temperature of the bath and that of the reaction vessel to allow a precise conversion of gas pressure to the amount of hydrogen liberated. A quantity of approximately 0.25 g of aluminum was used for each test. The accelerated aging of the powders was performed by placing the samples in a desiccator, but replacing the desiccant with water. The desiccator was then placed in an oven at 60°C. This created conditions of almost 100% humidity at 60°C, which are quite extreme for aging. However, they permitted us to run and complete the aging tests in a week.

The aluminum nanopowders selected for these aging tests were the 43-nm powder from Technanogy Materials Development coated with 28% polyethylene, and the 120-nm powder from TEKNA Plasma Systems coated with 18% polyethylene. These correspond roughly to thicknesses of 8 nm and 18 nm, respectively, if the PE was distributed uniformly on the particles. The behavior of the powders was compared with micron-sized powders, H-2 and H-15 from Valimet, with nominal sizes of 2 and 15 μm , respectively. Values for the nanopowder Alex, of 150-nm size, were also included for comparison. The original aluminum content of all of the powders was measured using the digestion equipment and the results are presented in Table 1. It is well known that very small aluminum particles contain less active aluminum than the larger particles

because of the oxide layer that has an almost-constant thickness of 3.5 nm. This layer becomes important for particles smaller than 100 nm. The active aluminum content is then used as the time zero concentration in aging tests. The percentages correspond to what is expected for the particles sizes. However, the 43-nm powder coated with 28% polyethylene contains less active aluminum than the theoretical value. The powders may have lost some of their metal content during the coating process, which was not the case for the 120-nm powder.

2. Aging at Room Temperature

A second method was used to assess the quality and efficiency of the coatings. It consisted of running thermal tests (TG-DTA) on aluminum powders aged at room temperature under humid conditions. The powders, when heated up slowly, will react with the surrounding air to transform into aluminum oxide or aluminum nitride. The weight gain associated with this reaction is quantified and it becomes an indirect measure of the amount of active aluminum. The tests were performed under contract by the Canadian Explosives Research Laboratory. A TA 5200 Thermal Analysis System with a simultaneous TG-DTA 2960 module was used for assessing the thermal behavior of the fresh and the aged samples in air. Equal amounts (10 mg) of the sample and the reference material (platinum foil) were placed in alumina pans and heated at 20°C / min from 30 to 1200°C. Four powders were studied: 120 nm, 120 nm with a 7% polyethylene coating, and Valimet H-2 with and without a 30% polyethylene coating. The samples were placed in a bell jar at a humidity greater than 85% at room temperature. These conditions are representative of the humid conditions experienced in the summer in our area of the globe.

IV. Results and Discussion

A. Polyolefin Coatings

To assess the potential of the Ziegler–Natta polymerization approach as a means of producing uniform polymer coatings on metal nanoparticles, several experimental variables were investigated. The first element to be addressed was the ability of controlling the thickness of the coating as a function of the reaction conditions. For that evaluation, it was found that reaction time is the most important variable affecting the amount of polymer produced. Other parameters, such as catalyst/cocatalyst ratio and pressure, were found to be of lesser importance. Figure 4 presents the amount of polyethylene grafted onto 120-nm Technanogy Materials Development aluminum nanopowders as a function of time. Although a monotonic increase is observed, it is also seen from the error bar that the variability between replicate batches is rather large. This is explained by the small amount of catalyst used for each run (a few hundredths of microliters), which renders the process of its dispersion and grafting onto the outer surface of the particles extremely sensitive to external factors such as orientation of the injection needle, trajectory of the catalyst as it drops into the reactor, etc. The variability induced at the beginning of the reaction will directly affect the number of growing sites for the macromolecules,

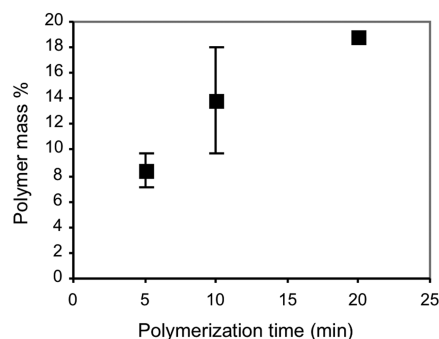


Fig. 4 Effect of the reaction time of polyethylene coating.

Table 1 Active metal content of the aluminum powders

Al powder type	Active Al content(%)
H-15	96.7
H-2	94.5
43 nm	55.4
43 nm with 28% PE	31.9
120 nm	84.0
120 nm with 18% PE	69.0
Alex	81.4

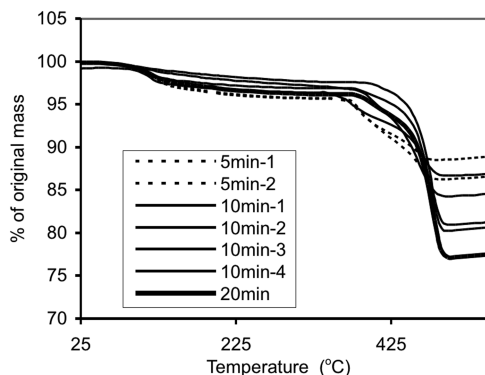


Fig. 5 TGA curves of polyethylene polymerization for several reaction times.

and thus it will increase as the polymerization proceeds because the mass of each molecule also grows with time.

The TGA thermograms corresponding to the set of experiments reported in Fig. 4 are shown in Fig. 5. It presents the mass loss (in percent) for three polymerization times (5, 10, and 20 min, with some replicates). For a given reaction time, the difference in the terminal mass of each replicate is clearly observed. In spite of these variations in the total amount of grafted polymer, each degradation curve exhibits a rather similar shape, which indicates that the nature of the polymer produced is not affected by the polymerization time. However, for the shortest reactions (5 min) the onset of degradation takes place more progressively, on a wider range of temperature, indicating the presence of polyethylene chains of lower molecular weight.

Several distinct zones can be identified on the thermograms. The first one (between 25 and 100°C) is represented by a very slight and continuous decrease in mass percentage and corresponds to residual solvent evaporation. The second one, in the interval of temperature between 100 and 125°C, probably corresponds to the evaporation of small oligomer chains. Between 125 and 370°C, evaporation and pyrolysis of oligomers chains and a partial thermocracking (above 300°C) of a small amount of high-density polyethylene (HDPE) chains contribute to a slight and continuous decrease of the mass (more pronounced for the short reaction time). The reaction of thermocracking reduces the molecular weight of HDPE chains and

produces vinyl double bonds in the polymer chains. Eventually, these chains will be completely pyrolyzed at a higher temperature range. The most important mass decrease corresponds to the interval of temperature between 370 and 500°C. This reflects the final pyrolysis of HDPE chains in an inert atmosphere (argon).

Further evidence of the presence of polyethylene at the surface of the particles is given by the XPS analysis presented in Fig. 6. Among the different peaks identified, binding energies corresponding to titanium and chlorine atoms are found, which confirms the initial grafting of the catalyst on the surface. Moreover, a comparison of the intensity of the peaks associated with carbon and aluminum clearly shows that the former is the dominant species at the surface.

The coating process proved to be fairly flexible and a large variety of powder morphologies were obtained. In spite of the precautions taken to achieve a complete dispersion of the particles during the polymerization reaction, the SEM pictures presented in Figs. 7–10 show that some clusters were obtained, but that single particles were also found. As expected, powders having a larger fraction of polymer are more likely to contain interparticle bridges. It was also observed that the boron nanoparticles had a very high level of reactivity toward the Ziegler–Natta catalyst and therefore, for conditions similar to aluminum particle grafting, a significantly larger amount of polyolefin was obtained. A SEM picture of the raw boron powder is shown in Fig. 9, and the same powders coated with 60% of PE are presented in Fig. 10. The large amount of polymer produced explained the flake shapes of the particle clusters. It is unknown at this point if this higher reactivity can be attributed to the very high specific surface (80 m²/g) of boron powders. On the other hand, no effect of the powder size on the reactivity of 40, 80, and 120-nm powders obtained from Technanogy Materials Development was found.

B. Polyurethane Oligomer Coatings

The grafting of polyurethane oligomers onto the aluminum powders was directly linked to the availability and reactivity of hydroxy functions on the particles. The results of this work show that only a small fraction of these sites, as measured by a gas evolution technique from the reaction of methyl aluminumoxane [14], were able to anchor the first isocyanate-bearing compound. As reported in Table 2, when the TDI-BA and TDI-HTPB coatings are compared, the difference observed in the mass fraction of the grafted chains on

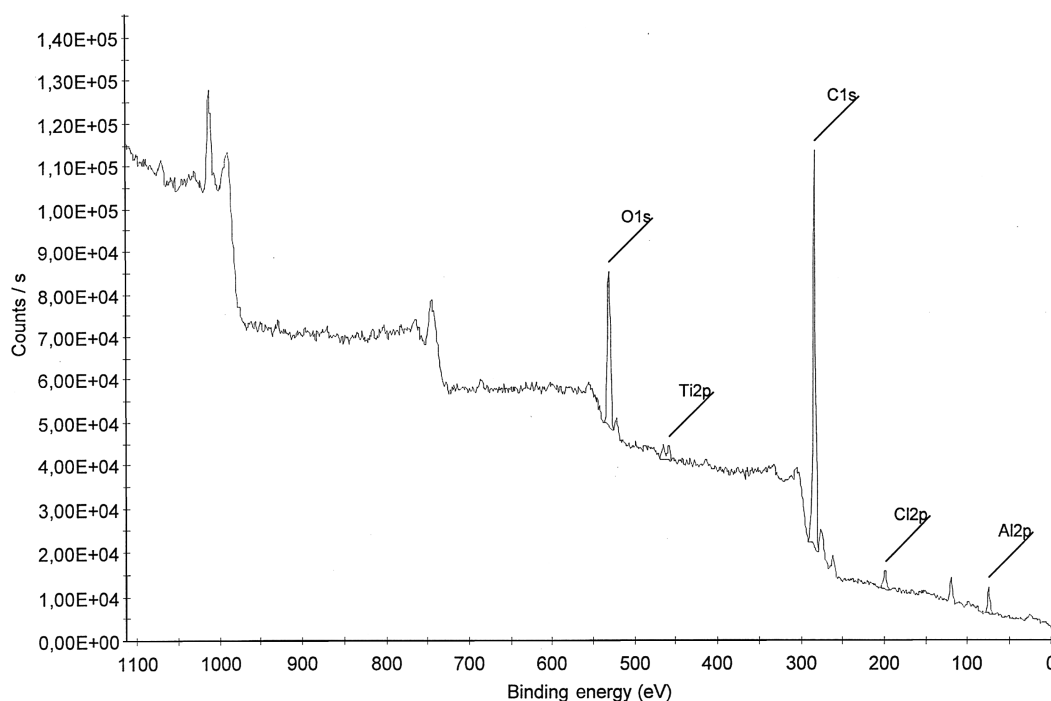


Fig. 6 XPS analysis of a 12% w/w PE-coated Al powders.

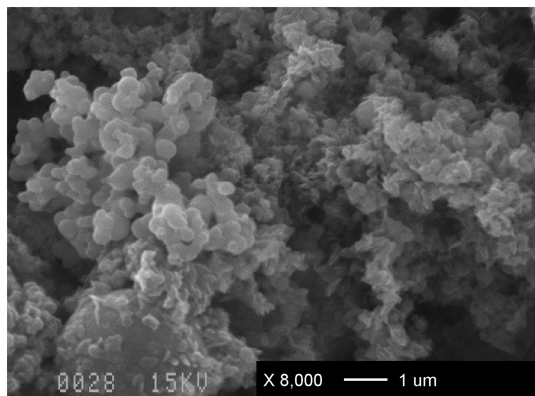


Fig. 7 PE-coated (20%) Al powders (120 nm) from Technanogy Materials Development.

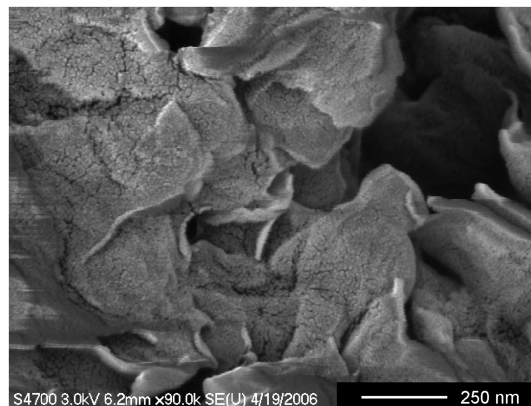


Fig. 10 PE-coated (60%) boron particles.

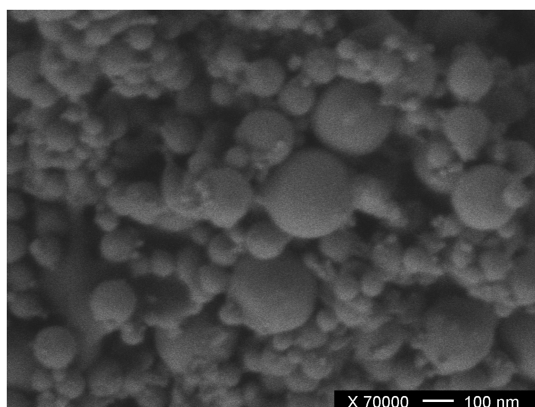


Fig. 8 TEKNA Plasma Systems aluminum powders covered by 16% w/ polypropylene.

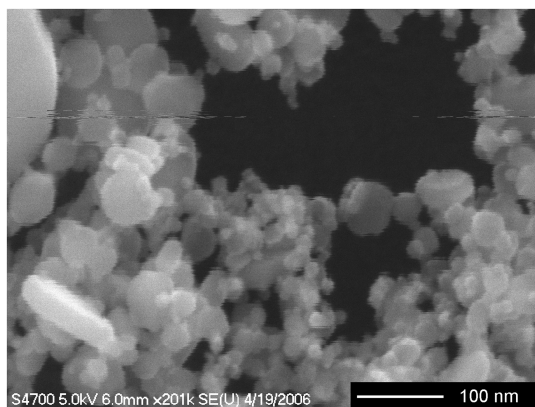


Fig. 9 Noncoated boron particles.

the particles came from the larger molecular mass of HTPB, because the number of grafted chains per unit of particle surface remained the same. Smaller isocyanates and more severe reaction conditions could favor the initial attachment of the oligomers, but these have not been studied yet. On the other hand, TGA analysis conducted on samples taken after the first and second grafting cycle of a TDI-BA coating

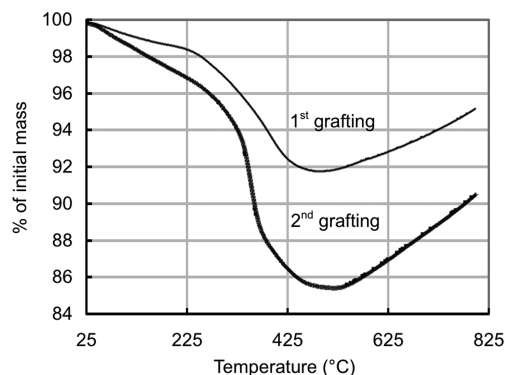


Fig. 11 TGA analysis of consecutive TDI-HTPB grafting.

show that the process takes place in a stepwise manner, unlike the fast pace of the high-molecular-weight polyolefin coating reactions, as found in Fig. 11. The thermal decomposition of TDI-HTPB-Zonyl coatings is shown in Fig. 12. In this particular case, the degradation clearly occurs in two steps and finishes at higher temperatures, which could be an effect of the fluorine groups found in the Zonyl. The morphology of coated particles was studied by SEM. Figure 13 was obtained from a sample of TEKNA Plasma Systems 120-nm aluminum particles coated with 12% TDI-HTPB-Zonyl. The powders appear to be uniformly coated and individual particles are clearly seen. Interparticle polymer bridges observed with polyolefin coatings are absent, even though the mass fraction of coating is quite similar. This is most likely due to the stepwise nature of the coating process, which prevents the type of homopolymerization found with the Ziegler-Natta polymerization reaction.

C. Aging Tests: Accelerated Aging

Figure 14 presents the results for the uncoated aluminum powders. It is clear from the graph that this aging method is very severe. Even the H-15 powder loses more than 30% of its power after 120 h. The nanopowders lose most of their active aluminum within 15 h. They are clearly more sensitive to the test than the micron-sized powders. The 2- μ m powder is an intermediate case, for which a lot of the active aluminum content is lost in 15 h and about 20% remains. This is as if a protective coating had been created over the remaining 20% to prevent it from reacting [4].

Table 2 Initial grafting of the oligomers

Polyol	First TDI-polyol grafting cycle	
	Mass fraction of oligomers (% w/w)	Number of grafted molecules, mol/g
BA	1.7	$6,5 \times 10^{-5}$
HTPB	7.0	$6,2 \times 10^{-5}$

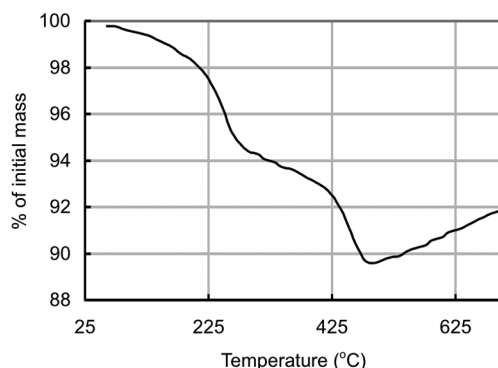


Fig. 12 TGA analysis of a TDI-HTPB-Zonyl-coated powders.

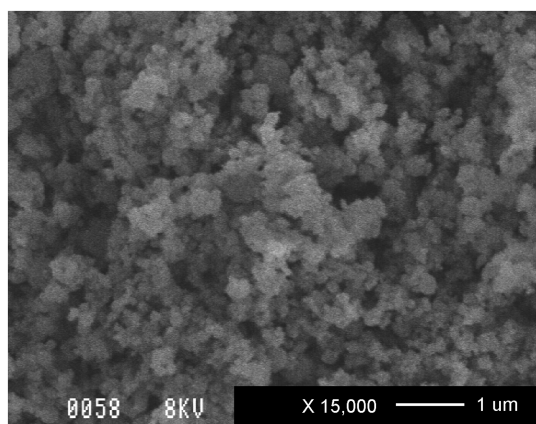


Fig. 13 TEKNA Plasma Systems aluminum powders covered by 8% w/w TDI-BA-Zonyl oligomers.

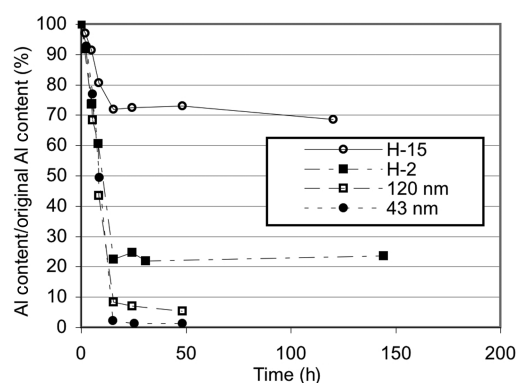


Fig. 14 Accelerated aging (60°C and 100% humidity) of uncoated Al powders.

Figure 15 shows the effect of the polyethylene coatings on the aging of the aluminum powders. The coating on the powders obviously protects the nanopowders in this harsh environment. The 18% PE coating on the 120-nm powders delays the complete loss of active aluminum to more than 120 h, multiplying their resistance by a factor of 8. For the 43-nm powders coated with 28% PE, there remains a large fraction of the original active aluminum after five days. However, this fraction represents only 18% of the total aluminum in the particles, because the original percentage of active aluminum was small at 31.9%. Nevertheless, it is obvious that the PE coating is efficient at protecting the powders.

D. Aging Tests: Room Temperature and TG-DTA

The results from the samples aged at room temperature and evaluated using the TG-DTA technique are presented in Fig. 16. The values reported are the totals of the TGA mass gains below and after

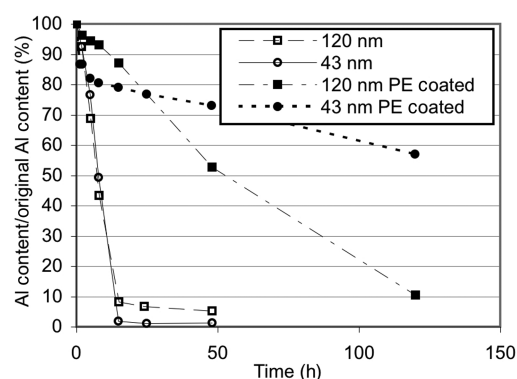


Fig. 15 Comparison of the accelerated aging of coated and uncoated Al nanoparticles.

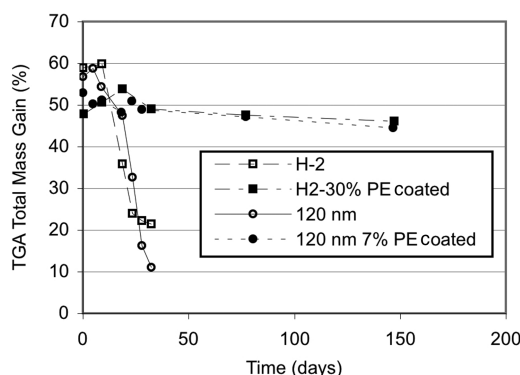


Fig. 16 Results of the aging of the powders at room temperature and greater than 85% humidity.

the melting point, which is an indirect measurement of the active aluminum content of the powders. Actual TG-DTA curves are presented elsewhere [15]. The results show that the uncoated powders aged significantly over a period of seven weeks. The coated powders, on the other hand, remained unaffected for this period, and after more than six months still kept most of their virgin aluminum content. This confirms the results of the accelerated aging tests, specifically, that the polyethylene coatings on the nanoparticles protect the powders from the humidity. It also implies a reasonable shelf life for these products.

V. Conclusions

This work aimed at evaluating two different polymerization processes as a means of obtaining a thin polymer film grafted onto the surface of metal nanoparticles. For polyolefins such as polyethylene and polypropylene, it was found that the Ziegler-Natta polymerization conditions could be varied effectively to control the amount of polymer produced on the particles. In cases in which polypropylene coatings were made, it took a longer reaction time to achieve a significant level of grafting. For both polymers, the degradation temperatures observed on the TGA measurements confirmed the presence of a nonvolatile polyolefin. However, characterization by SEM/TEM images show that the primary goal is only partially achieved, because some clusters of particles were found. The grafting of polyurethane oligomers was also successfully carried out and levels of up to 12% of grafted material were achieved. The polyethylene coating on the aluminum nanoparticles helped to significantly reduce degradation under accelerated aging conditions (60°C and 100% humidity). Although the ordinary nanopowders lost all of their active aluminum content within less than 20 h, the coated powders still had some active aluminum content after 120 h. A similar conclusion can be drawn from the results of aging tests conducted at room temperature, in which it was also found that the polyethylene coating significantly reduces oxidation of the

aluminum. Therefore, this work demonstrates that coating nanometric-sized metal particles with polymers can offer an efficient barrier against aging and degradation of these powders and thus facilitate their use and improve their performance in future fuel and propellant formulations.

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