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Treball Final de Grau

Ceramic - polymer composites obtained by milling processes.
Obtenció de compostos ceràmic - polímer per processos de mòlta.

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January 2015

Universitat de Barcelona

Dos campus d'excel·lència internacional

B:KC Barcelona Knowledge Campus

HUBc Health Universitat de Barcelona Campus

Agrair a les persones que m'han donat suport i m'han ajudat en la realització d'aquest projecte, en especial a Marco Robotti, al meu tutor Sergi Dosta i a la meva família.

Gràcies

REPORT

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1. SUMMARY

Ceramic-polymer composites are formed by a polymeric matrix with ceramic nanoparticles. In this case, ECTFE will be used as polymer, which will be joined with titanium oxide using a metallic bond. It is important to keep the crystalline phase of TiO_2, anatase, throughout the process for preserving their properties, especially photocatalytic properties that are the most important. The mechanical anchoring is a strong physical interaction between the two compounds and is carried out by milling mechanisms. However, the processes that will be studied will not exactly mill the particles, because it will work with low energetic conditions in order to get only a composite powder, with not much fractionated particles. The mechanisms that will be studied are Atrittor Milling and Atrittor Cryomilling, which consist in introducing a certain number of balls in a container and, using a blade, push these balls obtaining collision among the balls with the particles, between the walls and the particles and among the particles. The difference between one and the other is that the Cryomilling will work with cryogenic temperatures, below the ductile-brittle transition point of the material. These mechanisms will allow study the behavior of particles with different characteristics as the parameters of milling and the particle size, since the purpose is to form coatings using the spraying technique of projection cold gas spray. Previous studies have shown that the optimal size of the particles by the use of this technique is 40μm.

The best conditions found for obtaining the optimal mixture have been at 1 hour milling process by Atrittor mill, which has done the ball milling, with an initial size of ECTFE particles between 63-80μm. Other parameters are 1:1 ratio between the material and the number of balls and a 75 rpm speed. It has been observed that a length of 30 minutes was too short and with 4 hours the material had been fractured too much, showing that the milling process has started. At the same time, Cryoatrittor has worked below the ductile-brittle point and that has fractured too much the mixture. Atrittor allows more deformation and a fewer number of particles fractured, obtaining a good anchoring between polymer and ceramic materials.

Keywords: Atrittor Milling, Atrittor Cryomilling, mechanical anchoring, ECTFE, titanium oxide, Milling.

2. RESUM

Els compostos ceràmic-polímer estan formats per una matriu polimèrica amb nanopartícules d'un ceràmic. En aquest cas, s'utilitza l'ECTFE al qual se li uniran, mitjançant l'enllaç metàl·lic, nanopartícules d'òxid de titani. Aquest, mantindrà la seva fase cristal·lina, l'anatasa, al llarg de tot el procés, conservant així les seves propietats, especialment les propietats fotocatalítiques que són les més importants. L'enllaç mecànic consisteix en una forta interacció física entre ambdós compostos i es portarà a terme per mitjà de mecanismes de mòlta. No obstant, en els processos que s'estudiaran no es molturaran exactament les partícules, sinó que es treballarà en baixes energies per arribar solament a obtenir una mescla amb partícules poc fraccionades. Els mecanismes que s'estudiaran seran el *Atrittor Milling* i el Atrittor *Cryomilling*, que consisteixen en introduir un nombre de boles determinat en un recipient i, mitjançant unes aspes, impulsar aquestes boles donant així col·lisions entre les boles i les partícules, entre les parets i les partícules i entre les mateixes partícules. La diferència entre l'un i l'altre és que en el *Cryomilling* es treballarà a temperatures criogèniques, per sota del punt de transició dúctil-fràgil del material. Aquests mecanismes permetran estudiar el comportament de les partícules en diferents temps de mòlta i mida de les partícules, ja que la finalitat del compost és la realització de recobriments mitjançant la tècnica de la projecció en fred. Estudis previs han revelat que la mida òptima de les partícules per a la utilització d'aquesta tècnica és de 40μm.

S'ha trobat que les millors condicions per a obtenir la mescla desitjada han estat un procés de molturació d'una hora mitjançant l'*Atrittor*, eina amb la qual s'ha portat a terme el *Atrittor Milling*, amb una mida inicial de les partícules de ECTFE entre 63-80μm, una relació 1:1 entre el volum de material i el nombre de boles i a una velocitat de 75 rpm. S'ha observat que un temps de 30 minuts era massa poc i que un temps de 4 hores fracturava massa el material, fet que indica que ja s'iniciava el procés de molturació. Alhora, s'ha escollit l'*Atrittor* perquè el fet de treballar per sobre la temperatura dúctil-fràgil permetia menys fractura i més deformació de les partícules; i alhora es produïa una bona unió entre el polímer i el ceràmic.

Paraules clau: Atrittor Milling, Atrittor Cryomilling, aliatge mecànic, ECTFE, òxid de titani, mòlta.

3. INTRODUCTION

Polymers that contain inorganic nanoparticles are very important in the nanocomposites group that uses a polymer matrix. Nanoparticles are attractive for their extremely high surface area because it facilitates the creation of strong interaction (mechanical anchoring) between the polymer matrix and the nanoparticles, creating a good interphase in the composite. That kind of composites usually combines the best properties of the polymer matrix with the characteristics of the inorganic nanoparticles.

However, there is a general tendency to produce agglomerations. This means that nanoparticles do not have good adhesion with the polymer matrix and they remain separate in different parts. Therefore, different strategies will be studied to avoid the agglomeration problems. Those treatments will be atrittormilling and cryomilling.

Atrittormilling and cryomilling are techniques used for mechanical anchoring between nanoparticles and polymer. Those techniques are used to synthesize different kind of materials, like nano-crystalline materials, stable and metastable materials, amorphous alloys and intermetallic compounds, for example. In addition, those methods have been chosen as a potential process for simple blending solid-state powered technique which could produce nano-crystalline powder. However, it must be careful with the amount of energy that will take place during the process. High energy milling processes reduce the particle size because the particles collide with the internal wall of the milling machine and between themselves. Due to reduction of the particle size, experiments will be done with a low-energy atrittormilling and cryomilling. The advantages of low-energy processes are reported as simply and efficient. The differences between ball milling and cryomilling are that in the second one we will use Liquid Nitrogen (N_2) as gas inside the mixing vessel. It has better advantages in comparison to a traditional room-temperature milling techniques, including relatively high strain rates, large cumulative strains, uniform particle size distribution and the relatively low level of milling energy. Moreover, the milling time needed for acquire the same nanoparticles size is less than traditional ball milling. That is attributed to the effect of the cryogenic temperatures.

In this project we will use a fluoropolymer, Ethylene-chlorotrifluoroethylene (ECTFE). ECTFE is a clear, semi-crystalline, melt processable and fluorinated resin copolymer. It has many features, like very good chemical resistance and thermal properties, optimum permeation resistance and outstanding flame resistance too. ECTFE will be blending with TiO_2 nanoparticles. TiO_2 has been chosen because it is currently one of the most widely used materials due to its distinguished properties including wide optical bang gap, strong ultraviolet absorptivity, non-toxicity, and the most important in this case, good photocatalysis and high efficiency. As well as, improving TiO_2 nanoparticles in form of inorganic-organic hybrid nanocomposite is one of the effective techniques.

The fundamental properties of the nanocomposite were thoroughly investigated by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Laser Scattering (LS) to determine the Particle-size distribution (PSD) of the materials, differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) to examine the influences of the atrittormilling and cryomilling processes and the distribution of TiO_2 nanoparticles in the polymer matrix. Also, the presence of TiO_2 on the crystallinity, morphology and the non-isothermal crystallization and fusion behavior, will be studied.

To obtain a good results and non-agglomeration particles, the polymer must be previously sieved in a selected size of particles in order to achieve more homogeneous blend and after that, it will take place the atrittormilling or cryomilling process, anchoring the nanoparticles with the polymer matrix. The final objective of this nanocomposite is to achieve a recovering with the ECTFE and TiO_2 properties combined for allowing to be applied with cold-gas spray technique.

4. OBJECTIVES

- The principal objective of this project is to study the mechanisms of anchoring between polymer and ceramic materials during two different milling processes.
- Once carried out the milling processes, it is important to characterize the composite powders and to understand and become familiar with SEM, TGA, DSC and LS techniques in order to observe evolution and changes in the particles.
- It is also important to comprehend if there are changes in the crystalline phase, particle size and shape of the new compounds.
- The last purpose is to find and define the optimal parameters to develop a well-bonded composite mixture which can be sprayed by Cold Gas Spray CGS technique.

5. MILLING PROCESSES

Mechanical anchoring is a technique that allows production, by elemental powders, of a homogeneous mixture. It exactly describes the process when the mixtures of powders are milled together to obtain a homogeneous anchoring. However, these mixtures will be done with low energies. Therefore, it will not be exactly milled because the objective is to obtain a well-bonded compound for the cold gas spray projection.

Atrittormilling is the mechanical anchoring process that will be used. That consists in a solid-state reaction and it is milled without the aid on any process control agent to procedure fine dispersions of oxide in the polymer. The type of ball milling that will be used it is Atrittor milling, whose name is attributed to the container that the milling will be done. In addition, Cryomilling, a variety of ball milling, that consists in carrying the milling operation at cryogenic temperatures with liquid nitrogen.

First of all, mechanical anchoring starts choosing the correct parameters to achieve the atrittormilling and cryomilling. However, the correct proportion powders mix should be added into the milling machines with a grinder medium. The grinder medium that will be used is alumina balls. Also, the important characteristics of the process are raw materials, the mill and the process variables.

5.1. PROCESS VARIABLES

Due to the fact that mechanical anchoring is a complex process, many parameters are involved, but only the most important will be described, as raw materials, type of mills, milling time, grinding medium and the temperature of milling. Annex 1 shows a process variables table.

5.1.1. Materials

The powders that will be used are a polymer, ECTFE, and an oxide, TiO_2. Materials and sizes have been chosen in order to obtain a compound suitable for being sprayed by cold gas spray CGS technology. In addition, oxides are the most common and these anchoresses are known as oxide-dispersion strengthened. Although the size of the particles is not the most important parameter, it must be smaller than the grinding balls. The polymer has passed a sieving process, separating the particles in different sizes: > 80 μm, 80 – 63 μm, 63 – 40 μm, 40 – 20 μm and < 20 μm. However, only 80 – 63 μm and 40 – 20 μm portions will be used. The reason is because the optimal size to project the material is like 40 μm, so, with the milling mechanisms the particle size will be reduced. For this, 80 – 63 μm sizes are chosen, and if the particle size is not reduced, that it is not a problem because the polymer can be deposited by cold gas spray technique too. The 63 - 40μm is not selected to see better the differences between the particle sizes. The sieve process should not be underestimated as it is a parameter to consider; because as bigger the polymer particles are, less the titanium oxide particles adhere.

Ethylene-chlorotrifluoroethylene is a thermo-polymer, semicrystalline, 1:1 alternate copolymers and also it is a fluoropolymer, that means it has an excellent resistance to most corrosive chemicals or organic solvents at most operating temperatures and it has an excellent resistance to UV. ECTFE has a greater strength, wear and cut resistance, and creep resistance than PTFE, PET, and PFA. It can be processed using normal electrostatic powder coating techniques. Generally the procedure involves substrate preparation, spray coating, baking and cooling.

Titanium oxide is obtained directly from the mines or volcanic rocks sand. Generally it is not pure, so previously must remove impurities. TiO_2 is a semiconductor n-type light-sensitive absorbing electromagnetic in the radiation UV region, is amphoteric and very stable chemically. For these features it is the most used photocatalyst, also to nano-reinforce the polymer matrix. The powder charge will consisted in 10 vol% of the oxide.

5.1.2. Type of mills

Different types of mills are used to produce mechanically anchored powders. In this project Atrittor mill and Cryoatrittor mill are the types of millers that will be used.

5.1.2.1. Atrittor mill

Atrittor mill consists in a vertical steel tank with a steel shaft as an impeller. As the tank rotates the balls drop on the powder that is beginning ground. A powerful motor rotates the impellers, which in turn agitate the steel balls in the drum. The centrifugal force of the shaft acting on the balls, and the balls are pinned to the wall of the drum and to the dust. A powder size reduction is produced by the impact between balls, between balls and the container wall, between particles and with the agitator shaft.

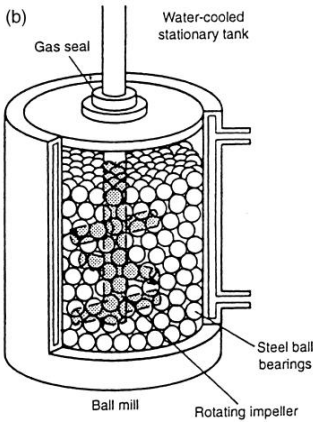

Figure 1. *Arrangement of rotating arms on a shaft in the attrition ball mil (image from C. Suryanarayana **2001**, 46, 80401-1887)*

5.1.2.2. Cryoatrittor mill

Cryoatrittor mill it is the same than Atrittor, the powder is milled in a stationary tank, but in this case it changes the media. It works with a medium of liquid nitrogen and below the ductile-brittle transition temperature.

5.1.3. Milling time

The lengths that will be used are 30 minutes, 1 hour and 4 hours for each atrittor. These times are chosen because it has previously seen that the milling starts with a milling length higher than 4 hours, and it is only important to have a mixed process, because the target is not to reduce so much the particle size.

In conclusion, these lengths have been chosen in order to have a state of equilibrium between the fracture of the particles and the anchor with titanium oxide. The interest is to acquire the best conditions of these composites. However, the characterization will focus on polymer or mixture mixed during 1 hour. This is because it has been observed that in previous studies, the results after 1 hour experiments are better.

5.1.4. Grinding medium

The grinding medium will be composed by 120 Al_2O_3 balls, maintaining a 1: 1 ratio with the volume of the compound, since it will work with 120 ml of ECTFE or ECTFE with titanium oxide in the case of mixtures. It should be noted that the grinding medium influences directly the milling efficiency. The size of the balls is an important parameter too, because as smaller are the balls, more friction is produced, which promoted the amorphous phase formation.

5.1.5. Speed

The rotational speed of the blades will be 75 rpm. This is the minimum speed that the atrittor and cryoatrittor can support. The minimum rotation speed will be applied because the interest is not in a milling process itself, it is in a mixing process.

5.1.6. Temperature of milling

The temperature is another important parameter, especially working with an atrittor that works in temperature between 20ºC – 25ºC controlled by water refrigeration, and the cryoatrittor, that works in a cryogenic temperatures, less than -76ºC. It is important that the cryoatrittor must be less than -76ºC because that is the ductile-brittle transition temperature of the polymer.

From this temperature it can be observed if the polymer is more likely to fracture or to deform, and thus allow observing if a greater number of particles can reduce his size compared to the temperature of 20ºC – 25ºC.

5.1.7. Analysis post milling

The analysis that will be done after de atrittor milling and cryoatrittor milling are , X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Laser Scattering (LS) In order to establish the particles distribution size (PSD), flow index (FI), differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA).

5.1.7.1. X-ray diffraction (XRD)

X-rays are generated in a cathode ray tube by heating a filament that produces electrons acceleration. When electrons have sufficient energy, they are bombarded to a bull's eye, and characteristic X-ray spectra are produced.

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information about dimensions.

5.1.7.2. Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) is use to revel information about the sample, like external morphology, crystalline structure, chemical composition and the orientation of the materials in the mixtures.

SEM consists in using a focused beam of high-energy electrons to generate a variety of signals at the surface of specimens. The signals that derive from electron-sample interactions reveal the information that we are interested.

5.1.7.3. Laser Scattering (LS)

The particle-size distribution (PSD) presents the particle-size distribution of a powder as its name indicates. It presents a list of values or a mathematical function that defines the relative amount, typically by mass or volume, of particles present according to size. PSD will be done by Laser Scattering to get to determine the size distribution profile.

5.1.7.4. Flow index (FI)

The flow index (FI) is a measure of the ease of flow of the particles in a thermoplastic polymer. It is defined as the mass of polymer, in grams, flowing in a known time through a capillary of a specific diameter.

5.1.7.5. Differential scanning calorimeter (DSC)

Differential scanning calorimetry or DSC is used to generate information in order to understand amorphous and crystalline behavior, polymorph and eutectic transitions, fusion point and many other material properties used to design, manufacture, and test products.

It is a thermoanalytical technique in which the difference between the amounts of heat required to increase the temperature of a sample and the reference is measured as a function of temperature.

5.1.7.6. Thermogravimetric analysis (TGA)

Thermogravimetric analysis is based in a gradually raising the temperature of a sample in a furnace measuring gradually his weight. This system allows to observe the mass loss if the thermal event involves loss of a volatile component.

Chemical reactions, such as combustion, involve mass losses, whereas physical changes, such as melting point, do not. The weight of the sample will be plotted against temperature or time to show thermal transitions in the material.

6. CHARACTERIZATION

6.1. ECTFE

As mentioned previously, ECTFE is a 1:1 alternating copolymer. Figure 2 shows the particle size distribution of the ECTFE. It presents that most of the particles have a size between 30µm to 110µm. LS analysis, together with SEM images, is interesting to observe how particles are deformed or if there is any union between them, when grinding processes such as Atrittor mill or Cryoatrittor mill are carried out. During this experimental work, the polymer has been sieved in order to be able to understand in a deeper way the deformation of the polymer powder in its different sieved portions. The experiments will be focused on 63-80µm and 20-40µm sizes as mentioned before.

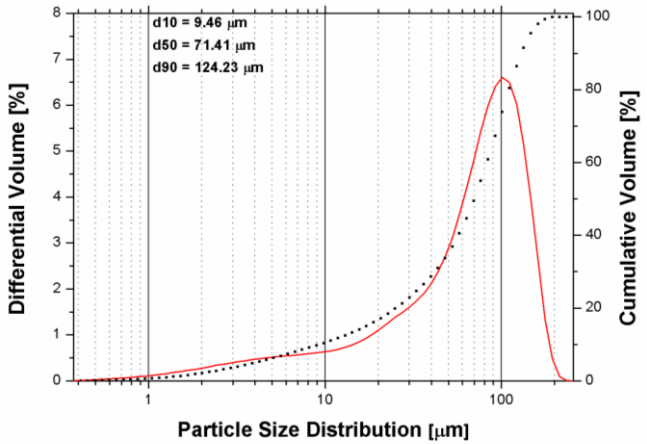

Figure 2. Particle size distribution of ECTFE

Figure 2 also shows that 75% of the volume of the polymer particles have a particle size distribution less than 100µm. There is a small amount of them with a size less than 10µm too,

the 10% of the volume. Therefore, it is necessary to sieve the polymer, to see the exact behavior of the particles

6.2. TITANIUM OXIDE (TiO_2)

The titanium oxide, thanks to its photocatalytic properties, has been chosen as nano-ceramic structured.. As already mentioned, the objective of the mixtures is to have the proper flowablity to be sprayed by CGS and this way develop a new generation of coatings with interesting properties. TiO_2 can be found in five different ways, and in this case anatase will be used, that is also known as octahedral for her morphology. The TiO_2 as anatase, is the form that gives the best properties in the mixture. This way of TiO_2 is important to be present throughout the process, from the titanium oxide before mixing until to obtain coatings by projection with cold gas spray.

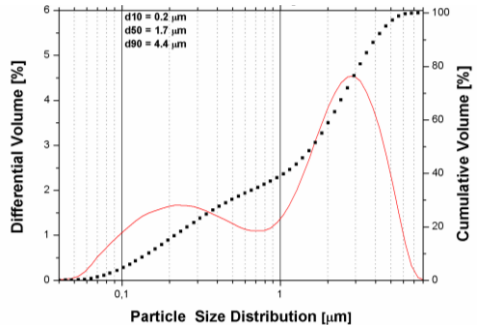

Figure 3. Particle size distribution of Titanium Oxide

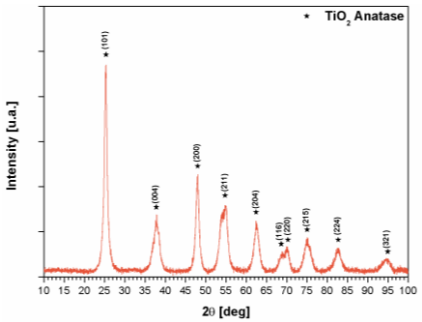

Figure 4. X-Ray Diffraction of Titanium Oxide

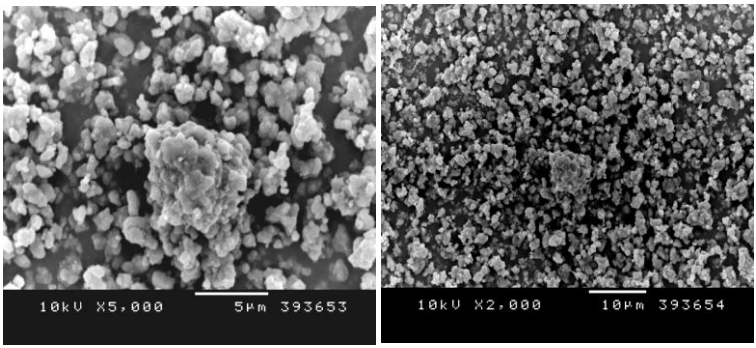

Figure 5. *Morphologies of Titanium Oxide in different magnifications*

Figure 3 shows the distribution of particle sizes of titanium oxide. They have a size between 0,01µm to 6µm, finding most of them between volume and 0,1µm - 3µm and 1µm - 4µm. The size it is fine for the mixtures, because with these sizes the titanium dioxide can cover the polymeric particles and create this way the desired composite powder. Figure 4 shows the X-Ray diffraction of titanium dioxide. This, will be useful to verify that the titanium oxide maintain its anatase phase and does not become rutile, brookite or other crystalline forms due to an increase of temperature caused by energy of the process or other factors. While brookite is unstable, at room temperature, the most stable form of TiO_2 is rutile; however, anatase can exist alone or with rutile in a metastable state. In XRD analysis (Figure 4), peaks at 2θ = 27'4º and 48º are associated with anatase phase.

Finally, Figure 5 shows the morphology of anatase. It is observed that most of the volume of particles has a size less than 5µm, as already shown in Figure 3. Figure 5 it also shows the octahedral morphology of this, which it must not change in the course of the experiments.

6.3. MIXTURES

Next, the results from the mixing of different durations will be shown: 30 minutes, 1 hour and 4 hours. The results are basically focused in 1 hour experiments, because, as mentioned previously, they are the ones which have offered better results in previous tests when the target has the objective to project the mixtures with the cold gas spray technique.

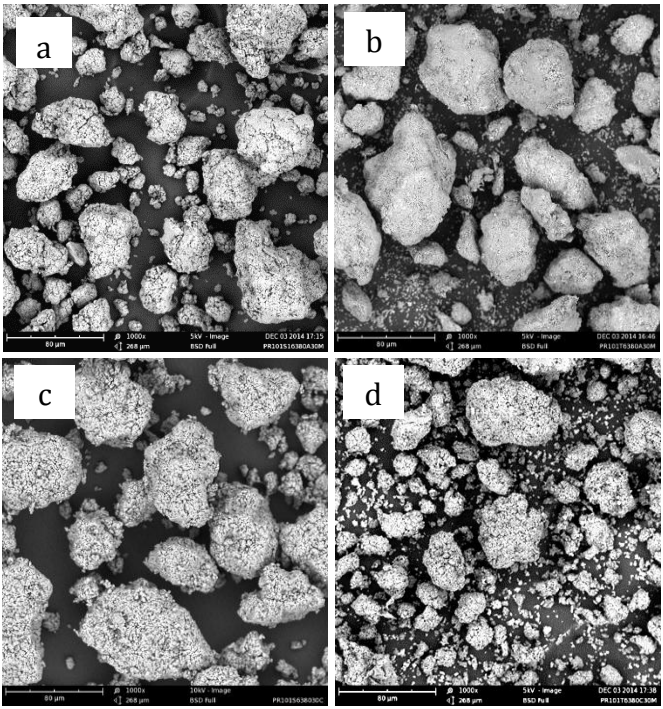

Figure 6. *Morphologies of ECTFE63-80µm powder mixed 30 minutes as Atrittor (a), 30 minutes as Cryoatrittor (b); and ECTFE with TiO_2 63-80µm powder mixed 30 minutes as Atrittor (c), 30 minutes as Cryoatrittor (d).*

The images (a) and (b) of Figure 6 show some particles that are fractured, while (c) and (d) images of the same Figure 7, besides some fractured particles, also show TiO_2 particles that have not joined with the ECTFE. This means that the time used to milling is not enough. However, experiments with a very long time cannot be performed because there would be too fractured particles. Appendix 3 shows more figures.

Next, the 4 hours experiments results that are the images obtained by scanning electron microscope (Figure 7).

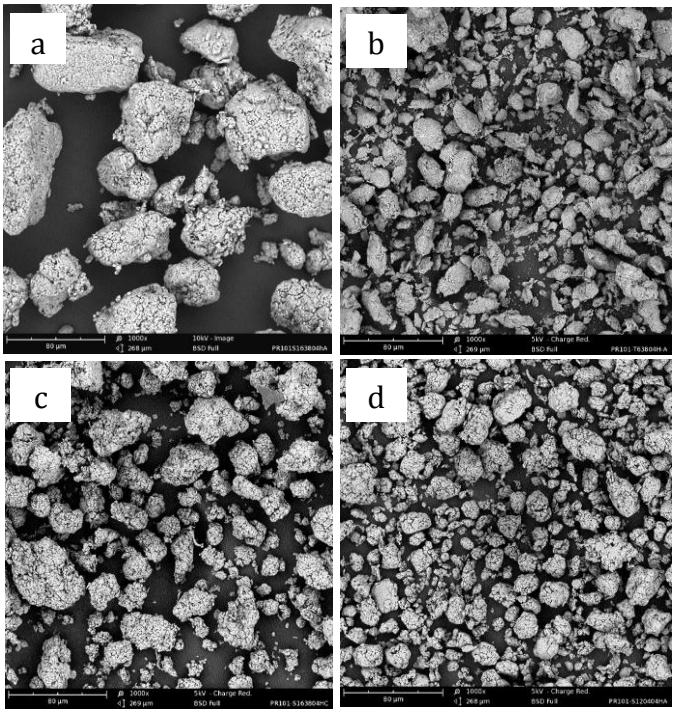

Figure 7. *Morphologies of ECTFE 63-80μm powder mixed 4 hours as Atrittor (a), 4 hours as Cryoatrittor (b); and ECTFE with TiO_2 63-80μm powder mixed 4 hours as Atrittor (c)and ECTFE 20-40μm powder mixed 4 hours as Atrittor (d).*

Figure 7 shows, the particles that have been 4 hours in the mills. These particles are too broken. The particles as much are broken in the Atrittor as in the Cryoatrittor. These experiments, as it would start the milling process itself. For this reason, these compounds are dismissed because they are not suitable for projection spraying.

As previously mentioned, characterization will focus on polymer or mixture mixed 1 hour. Then, after the Atrittormilling and Cryomilling processes are made, the results of the analysis can be observed.

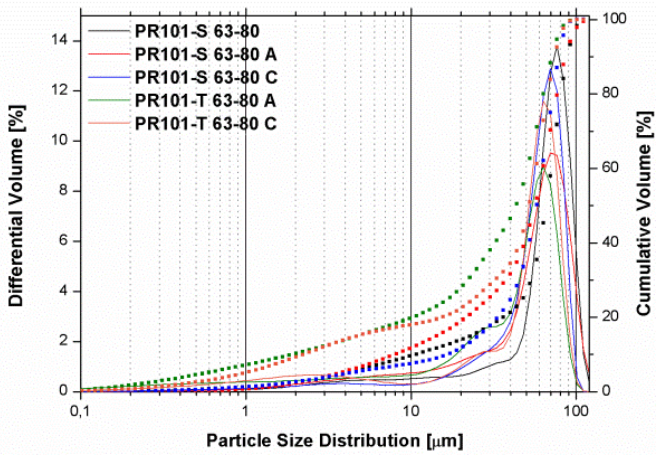

Figure 8. Particle size distribution obtained for the sample of ECTFE or ECTFE with TiO_2 63-80μm mixed with Atrittor or Cryoatrittor for 1 hour.

Figure 8 shows the distribution range of the particles. The particles of the polymer that had been sieved (PR101-S 63-80) are mainly distributed between 63 to 80μm. The ones that have been treated with Cryoatrittor (PR101-S 63-80 A and PR101-T 63-80 C) have more 1-100μm particles than the polymer just sieved. However, the most part of the volume of the particles obtained by Atrittor (PR101-S 63-80 A and PR101-T 63-80 A) are out of range sieve, especially between 10-50μm. Despite that, in all cases the most volumetric amount is in the 63-80μm range. The mixtures were prepared with Cryoatrittor, as can be seen; between 20% and 25% of the volume of particles has a size less than 10μm. However, in the mixtures obtained by Atrittor, approximately 12% of them have a size less than 10μm, as the polymer just sieved. This indicates that due to the Cryoatrittror works a temperature below the ductile-brittle point of material, a greater number of particles are fractured. In both cases, besides the particles that are fractured, there are also polymer particles which have joined between themselves in the respective processes.

Flow index in general is bad, but the flowability that could be observed is better in the case of Atrittor than in the post-sieve polymer, and greater in the case of Cryoatrittor. However, it could not be considered a polymer or a mixture flowing optimally, but it can be used to project with cold-gas spray because it also relies on air pressure.

The density has not changed in the case of Atrittor and the polymer just sieved, and decreased in the case of Cryoatrittor. It adds to the TiO_2, the density has increased compared to the polymer in Atrittor and Cryoatrittor. The higher is the milling time, the higher is the density in both milling methods.

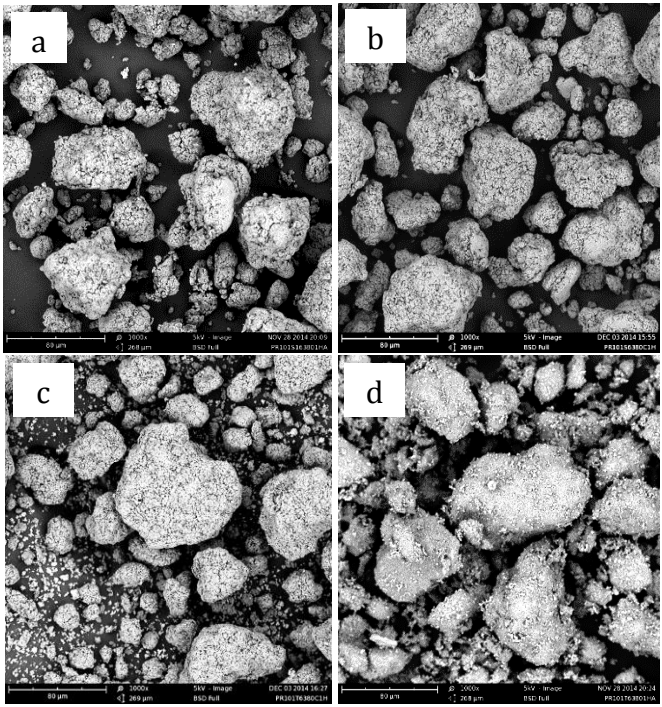

Figure 9. *Morphologies of ECTFE 63-80μm powder mixed 1hour as Atrittor (a), 1hour as Cryoatrittor (b); and ECTFE with TiO_2 63-80μm powder mixed 1hour as Atrittor (c), 1hour as Cryoatrittor (d).*

Figure 9 (a) and (b) shows that the particles tend to be spherical, despite their irregular shape. There are a lot of particles with a size less than 63-80μm and some with a superior size.

There are no significant differences and shape when the polymer particles have been 1h in the Cryoatrittor and in the Atrittor.

At the images (c) and (d) of the figure, it can be observed that in the case of Cryoatrittor there are more fractured particles than with Atrittor. Also, it can be observed that the volume of particles of TiO_2 that anchored with the polymer is greater than in mixtures of 30 minutes and similar than mixtures of 4 hours.

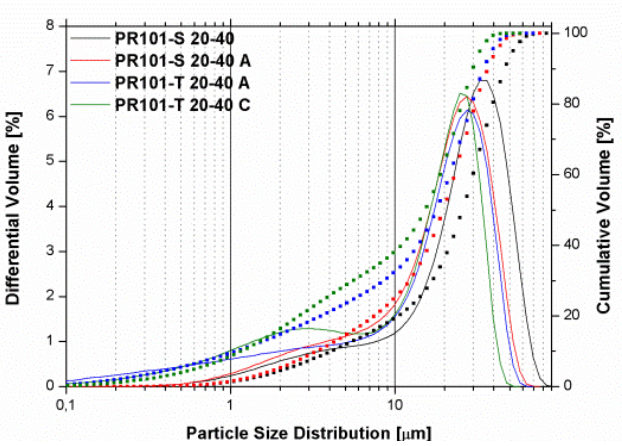

Figure 10. Particle size distribution obtained for the sample of ECTFE or ECTFE with TiO_2 20-40μm mixed with Atrittor or Cryoatrittor for 1 hour.

Figure 10 shows the PSD of the polymer and mixture of 20-40μm and the polymer just after sieved. In post-sieved particles (PR101-S 20-40), it can be seen how the curve of PSD is shifted slightly to a particle size greater, especially compared with the Cryoatrittor (PR101-S 20-40 C and PR101-T 20-40 C). It also shows how approximately 40% of the mixture of polymer particles with titanium oxide mixed with cryoatrittor has a size less than 10μm. In the Atrittor's case (PR101-S 20-40 A and PR101-T 20-40 A) it is not too different, so it has about 35% of the volume of particles with a size less than 10μm. In the case of polymer with no TiO_2 by Atrittor, Cryoatrittor and the polymer just sift: 25% and 20% respectively. This means that Atrittor and Cryoatrittor have decreased the size due to shocks, both among particles, at the wall or with the balls. The fact because this has happened in this case but in 63-80μm not, it is because these particles are smaller and more fragile despite the same energy has been used, and they break much more easily.

The flow rate is likely as with particles 63-80µm, a little better, but it is still bad, somewhat improved in the case of Atrittor and slightly better in the Cryoatrittor. The density is also following the same trend, increasing slightly with the Atrittor and Cryoatrittor, although it does little more in the case of Cryoatrittor.

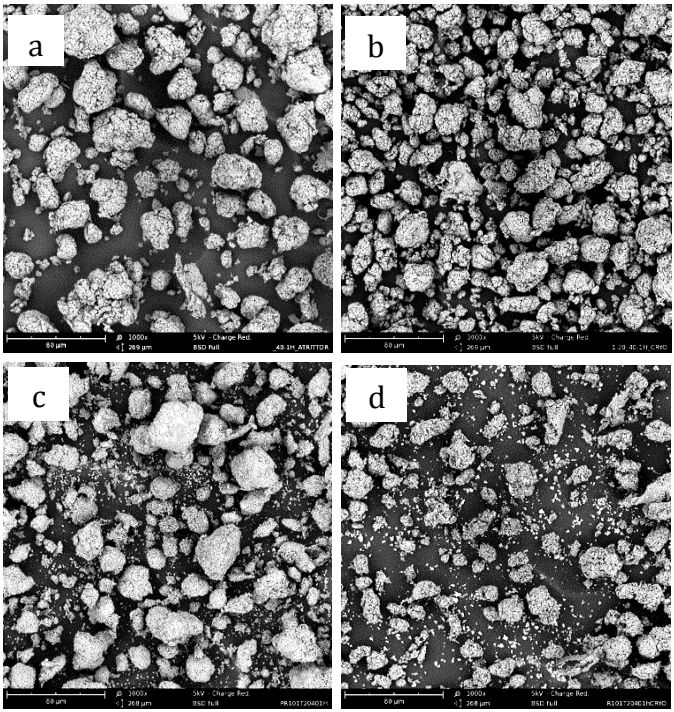

Figure 11. *Morphologies of ECTFE 20-40µm powder mixed 1hour as Atrittor (a), 1hour as Cryoatrittor (b); and ECTFE with TiO_2 20-40µm powder mixed 1hour as Atrittor (c), polymer 1hour as Cryoatrittor (d).*

In Figure 11 we can see that both cases, the polymer and the polymer with TiO_2, have a size smaller in milling by Cryoatrittor. This means that as expected, use a temperature under the ductile-brittle point are more likely to break than to deform the particles. It can also be observed, especially in Figure 5 (d), compared with the results of the PSD, that there are some particles between 1 to 5µm. These correspond to the titanium oxide particles that had not been anchoring

with the polymer. The shape of the particles is also tending to be spherical, although quite irregular, like the 63-80µm particles seen before.

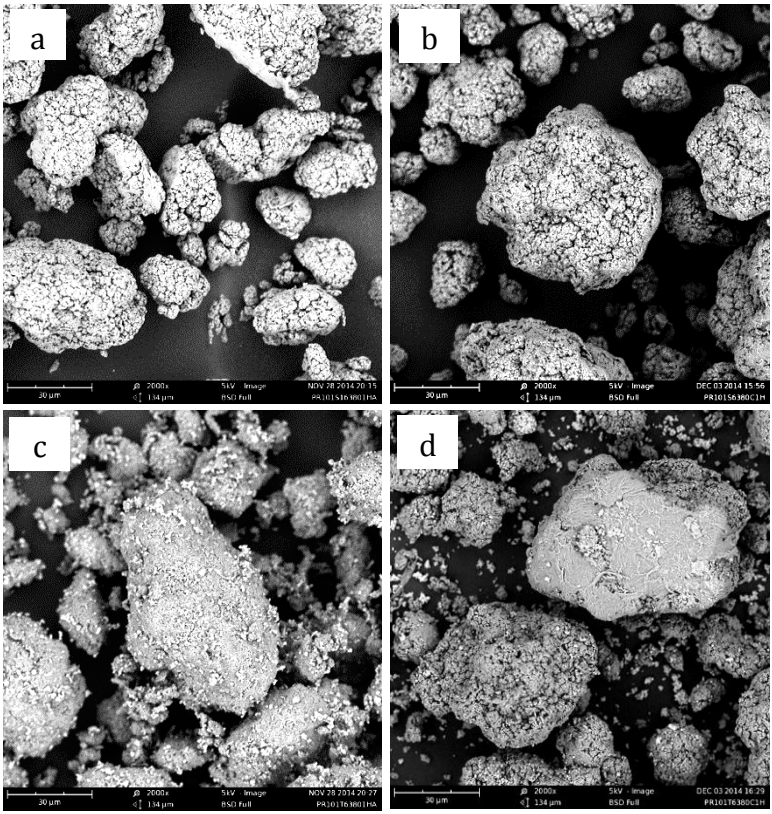

Figure 12. *Morphologies of ECTFE 63-80µm powder mixed 1hour as Atrittor (a), 1hour as Cryoatrittor (b); and ECTFE with TiO_2 63-80µm powder mixed 1hour as Atrittor (c), 1hour as Cryoatrittor (d).*

Figure 12 shows the same as Figure 9, but at higher magnifications. This allows us to see that in the case of the mixture, titanium oxide particles were uniformly attached to the polymer. So, the Atrittor mill (Figure 12 (c)) would be a good milling technique to mix different materials and other factors would also be appropriate (number and size of balls, speed ...). In addition, the particle size obtained is also a part of the optimal range for the projection technique with cold gas spray.

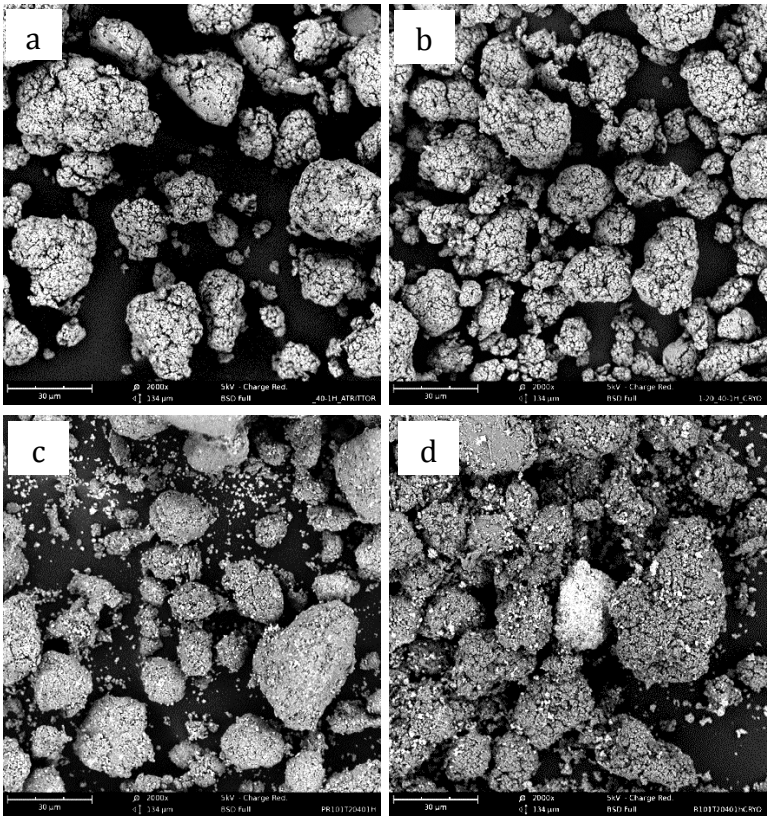

Figure 13. *Morphologies of ECTFE 20-40μm powder mixed 1hour as Atrittor (a), 1hour as Cryoatrittor (b); and ECTFE with TiO_2 20-40μm powder mixed 1hour as Atrittor (c), 1hour as Cryoatrittor (d).*

Figure 13 shows Figure 11 increased. It can be seen therefore as the results by Atrittor and Cryoatrittor are different. It can be observed that Cryoatrittor will not mix properly, as there are several particles of TiO_2 alone have not been anchored. This has been because the Cryoatrittor works to a temperature below the ductile-brittle point, the surface of the particles has been hard and more brittle. This makes the particles of titanium oxide are not properly anchored. Instead, the Atrittor, the surface of particles is more ductile and can be more deformed. In the Figure 12(d) and Figure 13(d) you can see how the surface is rougher. This allows a more optimal mixture. However, the size of the particles would be feasible for a projection technique with cold gas spray, but it would not be optimal because the particles would be too small and would not

contain so much titanium oxide than the 63-80μm ones. In addition, these tests were performed with Cryoatrittor that uses a liquid N_2 atmosphere. This is important because it will allow knowing what temperature the mixture can be projected using nitrogen. The projection, as mentioned above, is the next stage after completing the mixtures. If you want to project with air, it would be verified how it can affect temperatures.

The 20-40μm (Figure 13) particles that have a smaller size, the energy transferred by the balls and the crashes are lower, and this causes them much less adding TiO_2. This means that when 20-40μm particles are compared with those 63-80 (Figure 14), the smaller particles have the worst TiO_2 mixed.

Finally, the mixture 63-80 microns with titanium oxide mixed 1hour by Atrittor was embedded inside an epoxy resin, grinded and polished to be able to observe particles cross sections.

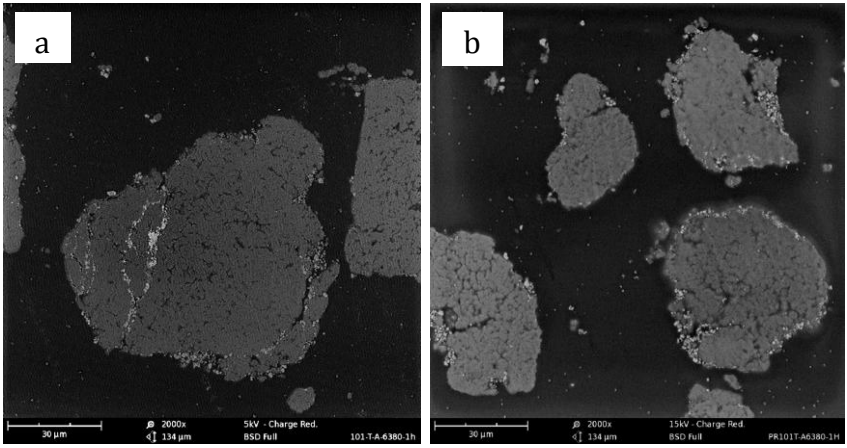

Figure 14. *Morphologies of ECTFE 63-80μm powder mixed 1hour as Atrittor and cold stuffed embedded*

In the Figure 14 (a), there are particles that after they had already anchored with titanium oxide, they joined together again. This can be seen in the particle of Figure 14, it can be observed titanium oxide in the middle of it. That means that two particles are united. On the

other side, the image (b) of Figure 14 shows, as in most of particles, titanium oxide is only on the surface of the polymer particles.

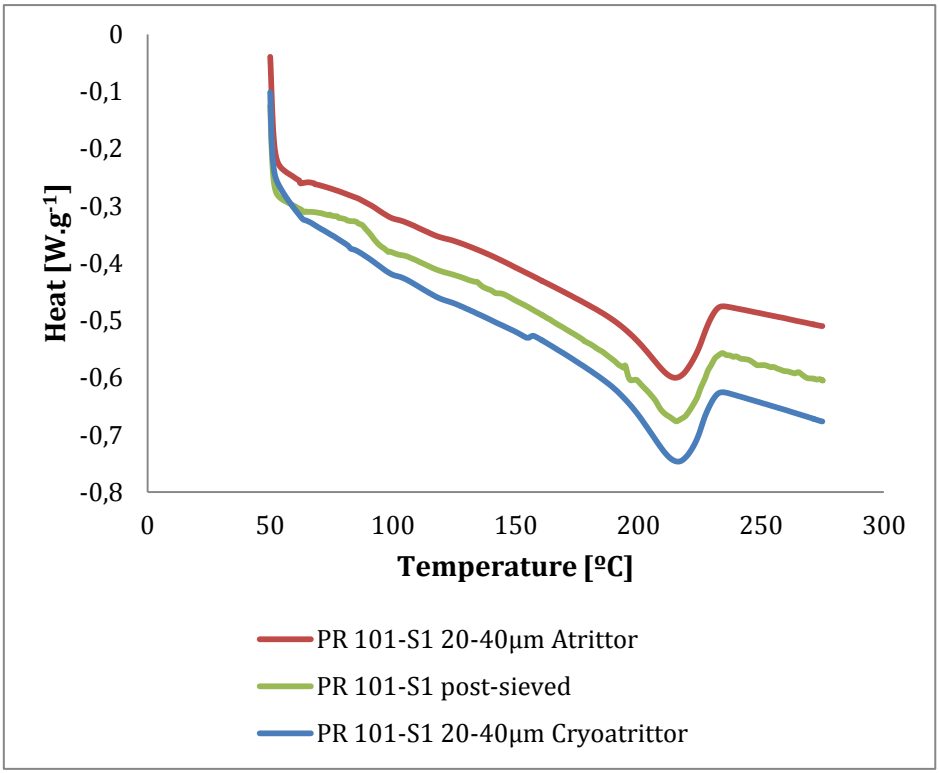

Figure 15. Differential Scanning Calorimetry of different mixtures

Figure 15 shows that the melting point of ECTFE is almost the same in the case of polymer that has only been sieved (PR101-S1 post-sieved) -that is of 215,17ºC- with the ECTFE that has been 1 hour in the Atrittor (PR101-S1 20-40µm) -that is 216,17ºC- and for the one that has been 1 hour is Cryoatrittor(PR101-S1 20-40µm) -that is of 215,33ºC-.

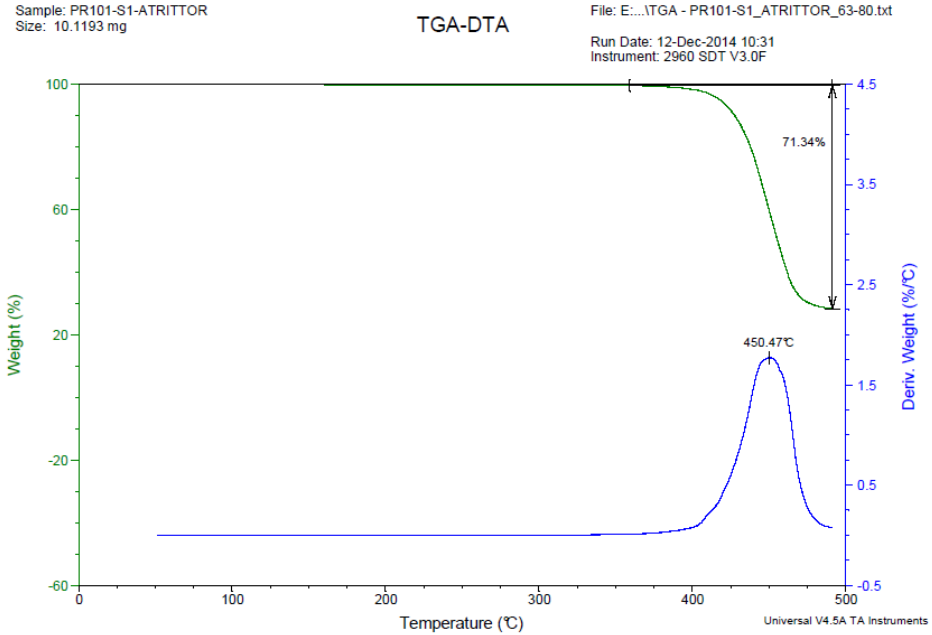

Figure 16. *Thermogravimetric analysis of ECTFE mixed 1hour in Atrittor mill*

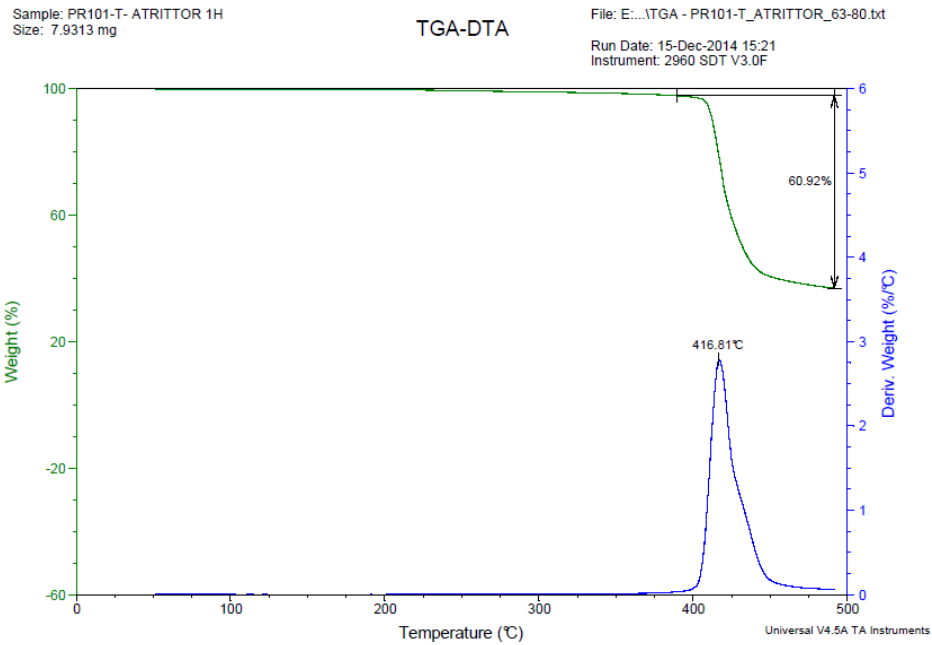

Figure 17. *Thermogravimetric analysis of ECTFE with TiO_2 mixed 1hour in Atrittor mill*

Figure 16 and 17 shows the Thermogravimetric Analysis (TGA) of ECTFE and the polymer with TiO_2, respectively. Both experiments are with 1 hour by Atrittor. The complete degradation temperature is higher in the case of ECTFE without titanium oxide; this temperature is about 34ºC more. The percentage of disintegrated melted polymer is also higher in the case of just polymer, being 10% higher. This is because the mixture of titanium oxide contains a smaller amount of polymer, so it has a lower temperature and a lower percentage as well. However, this percentage value is correct, since it corresponds to the amount of titanium oxide that has been added to the mixtures. In addition, the titanium oxide is a strong catalyst, and this causes a more quickly weight loss in the case of mixtures than the ECTFE. Titanium oxide increases the speed of degradation of the polymer chains and this can be seen in Figure 17, which weight loss occurs at a lower temperature, 416ºC,than the mix (Figure 16) which weight loss occurs at 450ºC. Appendix 4 shows more TGA figure, which ones have the same tendency.

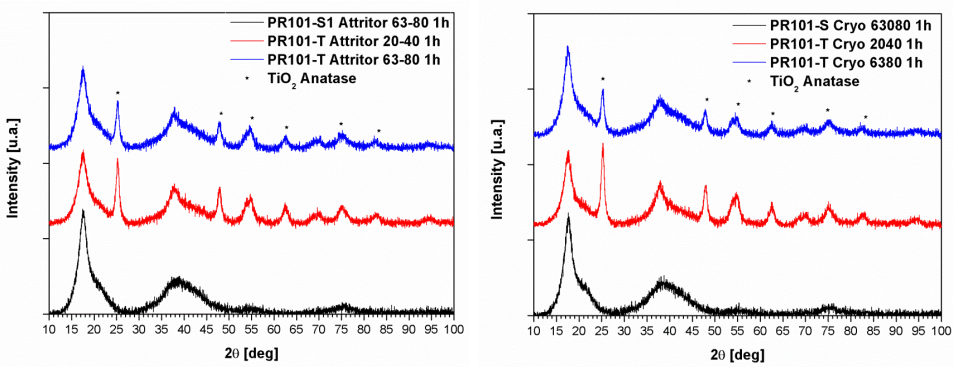

Figure 18. *X-Ray Diffraction of ECTFE with TiO_2 mixed 1hour*

Figure 18 shows the X-Ray Diffraction of 1 hour experiments done with Atrittor and cryoatrittor. As mentioned above, it is important to keep TiO2 as anatase and do not become to rutile. However, the grinding process has been carried out with low energy conditions, which do not allow reach high temperatures in the crystalline phase change, which one would form rutile. XRD shows that in the case of TiO_2 preserved 2θ = 25,3º and 48º peaks, while if it had formed rutile would find 2θ = 27,4º and 54,5º peaks, which represent the phase of rutile. Therefore, we

can ensure that we continue with anatase, which is especially important for its photocatalytic properties which we want to preserve.

7. CONCLUSIONS

This project has been carried out to obtain a ceramic - polymer composite using ECTFE as polymer and titanium oxide as nano-structured ceramic. Obtaining this compound has the objective of been projected by cold gas spray technique for producing coatings taking advantage of the photocatalytic properties of titanium oxide. This compound has been prepared by milling process with low energy conditions, in order to obtain a well-bonded compound for the cold gas spray projection, but not a milled compound.

Although the polymer joins the ceramic not through a proper chemical bond, their interaction is closely linked and their union can be considered a mechanical anchoring. At the same time, it is important to preserve the TiO_2 anatase phase, which must be preserved throughout the process, so it must not lose his properties. The results obtained by Atrittor and Cryoatrittor are significantly different mainly due to the temperature effect because the second one works below the ductile-brittle point.

The results have established that the best compound obtained is the one whose particles were previously sieved in a range between 63-80μm and then milled in Atrittor for 1 hour. The times employed have been 30 minutes, 1 hour and 4 hours. The 30 minutes length was too short and it not allows to anchoring effectively all the TiO_2 particles with the polymer, while the 4 hours was too long, and the number of particles fractured were too much. Therefore, due to the low Cryoatrittor's temperature, cooled with liquid N_2, the surface of the particles of the polymer becomes harder. This makes it more fragile and the TiO_2 particles not adhere to the surface. In Atrittor's case, the polymer is more ductile and therefore mechanical anchoring is better than the other mill. Due to the size of balls, the energy that was transferred to the powder is more effective for bigger particles than the smaller ones. So, 63-80μm particles receive more energy from the balls, for the same diameter balls. Smaller sizes (20-40μm) cannot receive the same amount of energy and the TiO_2 particles that anchored are less. This is also another reason to want a greater size of the polymer particles. Some of the particles joined between themselves mechanically, after they had been joined with TiO_2 during the milling process. Finally, the titanium oxide had not lost its anatase phase, which is improbable to lose due to the process

was done with low energy milling, which do not reach to the required temperature for the phase change. Particles that were obtained also have a good dispersion of TiO_2 on the surface, in addition to the necessary amount of titanium oxide. Although some particles were anchored together, they have not formed any mass, which it is an important factor for projecting. The fluidity of the compound is not really good, but it is not a serious problem because it will be projected with pressure. However, it has improved the polymer fluidity.

In conclusion, in order to cover the compounds more effectively, it will be used the optimal mixture. The optimal mix was made with the Atrittor, using 63-80μm particles for one hour. The characteristics the mill are 1:1 ratio of materials:polymer, steel container and steel blades, 75rpm and 10%vol of TiO_2. In addition, this mixture keeps the best properties of both, of the ECTFE and the of titanium oxide ones.

11. REFERENCES AND NOTES

1. W. Mekprasart, W. Jarenboon, W. Pecharapa. TiO_2/CuPc hybrid nanocomposites prepared by low-energy ball milling for dye-sensitized solar cell application. Materials Science and Engineering B 172 (2010) 231-236.
2. G. Zhang, A.K. Scharb, S. Tria, O. Elkedim. Tensile and tribological behaviors of PEEK/nano-SiO_2 composites compounded using a ball milling technique. Composites Science and Technology 68 (2008) 3073-3080.
3. Roger Amade, Paul Heitjans, Sylvio Indris, Mina Finger, Andreas Haeger, Diethard Hesse. Defect formation during high-energy ball milling in TiO_2 and its relation to the photocatalytic activity. Journal of Photobiology A: Chemestry 207 (2009) 231-235.
4. Y.G.Zhu, Z.Q. Li, D. Zhang, T. Tanimoto. PET/SiO2 Nanocomposites Prepared by Cryomilling. Journal of Polymer Science: Part B: Polymer Physics, Vol. 44, 1161-1167 (2006)
5. C. Suryanarayana. Mechanical alloying and milling. Progress in Materials Science 46 (2001) 1-184.
6. M. Fabián, G. Tyuliev, A. Feldhoff, N. Kostova, P. Kollár, S. Suzuki, F. Saito, V. Šepelák. One-step synthesis of nanocrystalline ZnO via cryomilling. Powder Technology 235 (2013) 395-399.
7. Sajjad Amirkhanlou, Mostafa Ketabchi, Nader Parvin. Nanocrystalline/nanoparticle ZnO synthesized by high energy ball milling process. Materials Letters 86 (2012) 122-124.
8. Rabab Khalid Sendi, Sharom Mahmud. Quantum size effect on ZnO nanoparticle-based discs synthesized by mechanical milling. Applied Surface 258 (2012) 8026-8031.
9. Dania Olmos, Eugenio Rodríguez-Gutiérrez, Javier González-Benito. Polymer Structure and Morphology of Low Density Polyethylene Filled With Silica Nanoparticles. Wiley Online Library (2012)
10. D. Olmos, C. Domínguez, P.D. Castrillo, J. Gonzalez-Benito. Crystallization and final morphology of HDPE: Effect of the high energy ball milling and the presence of TiO_2 nanoparticles. Polymer 50 (2009) 1732-1742.
11. O. Korostynska, A. Arshak, K. Arshak, D. Morris. Investigation into real-time pressure sensing properties of SnO_2, TiO_2, and TiO_2/ZnO thick films with interdigitated electrodes. Materials Science and Engineering B 176 (2011) 1297-1300
12. E. Leivo, T. Wilenius, T. Kinos, P. Vuoristo, T. Mäntylä. Propierties of thermally sprayed fluoropolymer PVDF, ECTFE, PFA and FEP coatings. Progress in Organic Coatings 49 (2004) 69-73.
13. Y.W. Lao, S.T. Kuo, W.H. Tuan. Influence of ball milling on the sintering behaviour of ZnO powder. Ceramics International 35 (2009) 1317-1320.
14. Mamoru Senna, Vladimir Šepelák, Jianmin Shi, Benjamin Bauer, Armin Feldhoff, Vincent Laporte, Klaus-Dieter Becker. Introduction of oxygen vacancies and fluorine into TiO2 nanoparticles by co-milling with PTFE. Journal of Solid State Chemistry 187 (2012) 51-57.
15. Dongling MA, Yvone A. Akpalu, Ying Li, Richard W. Siegel, Linda S. Schadler. Effect of Titania Nanoparticles on the Morphology of Low Density Polyethylene. Journal of polymer science: Part B: Polymer Physics, Vol. 43, 488-497 (2005).
16. W.Y. Li, G. Zhang, O. Elkedim, H. Liao and C. Coddet. Effect of ball milling of feedstock powder on microstructure and properties of TiN particle-reinforced Al alloy-based composites fabricated by cold spraying. Journal of thermal spray technology Volume 17(3) September 2008-317.
17. Paul J. Hubert, Krishna Kathiresan, Katsuyuki Wakabayashi. Filler exfoliation and dispersion in polypropylene/as-received graphite nanocomposites via cryogenic milling. Polymer and science (2011) 2275.

18. Emilio Napolitano, Gabriele Mulas, Stefano Enzo, Francesco Delogu. Kinetics of mechanically induced anatase-to-rutile phase transformations under inelastic impact conditions. Acta Materialia 58 (2010) 3798-3804.

12. ACRONYMS

PTFE	Polytetrafluoroethylene
PET	Polyethylene terephthalate
PFA	Perfluoroether
ECTFE	Ethylene ChloroTriFluoroEthylene
PSD	Particle-size distribution
SEM	Scanning electron microscopy
ºC	Celsius degrees
XRD	X-Ray Diffraction
FI	Flow Index
DSC	Differential Scanning Calorimeter
TGA	Thermogravimetric analysis
LS	Laser Scattering
μm	Micrometer
UV	Ultraviolet
vol%	Volume percent
rpm	Revolutions per minute
ml	Milliliters
θ	Theta angle
W	Watts
g	Gram
º	Degree
u.a.	Arbitrary units

APPENDICES

APPENDIX 1: PROCESS VARIABLES

	Cryoatrittor	Atrittor
Revolutions for minute	75	75
Number of balls	120	120
Balls:Material Ratio	1:1	1:1
Shaft Material	Steel	Steel
Tank Material	Steel	Steel
Grinding medium	N_2	Air
Temperature of milling	< -76ºC	20ºC
Balls diameter	10 mm	10 mm
Balls Material	Al_2O_3	Al_2O_3

Table 1. Process variables

APPENDIX 2: REFERENCES OF EQUIPMENT AND MATERIALS USED

Equipment or Material	Equipment or Material Reference
Atrittor mill	Model O1HD, Union Process Inc.
Cryogenic mill	Atrittor O1HD modified by CPT, Union Process Inc.
Optical Microscope (OM)	Leica DMI 5000M
Scanning Electron Microscope (SEM)	JEOL JSM-5310 and Phenom ProX
Particle Size Distribution Analyzer (PSD)	LS 13 320, Universal Liquid Module
Diffractometer (RDX)	PANalytical X'Pert PRO MPD Alpha1 powder diffractometer in Bragg-Brentano q/2q geometry of 240 millimetres of radius
Differential Scanning Calorimeter (DSC)	Mettler-Toledo DSC-1
Thermogravimetric Analyzer (TGA)	TA Instruments
Resin for cold stuff embedding process	EpoFix (Struers) and ExpoxiCure (Buehler)

Table 2. References of equipment and materials used

APPENDIX 3: SEM IMAGES

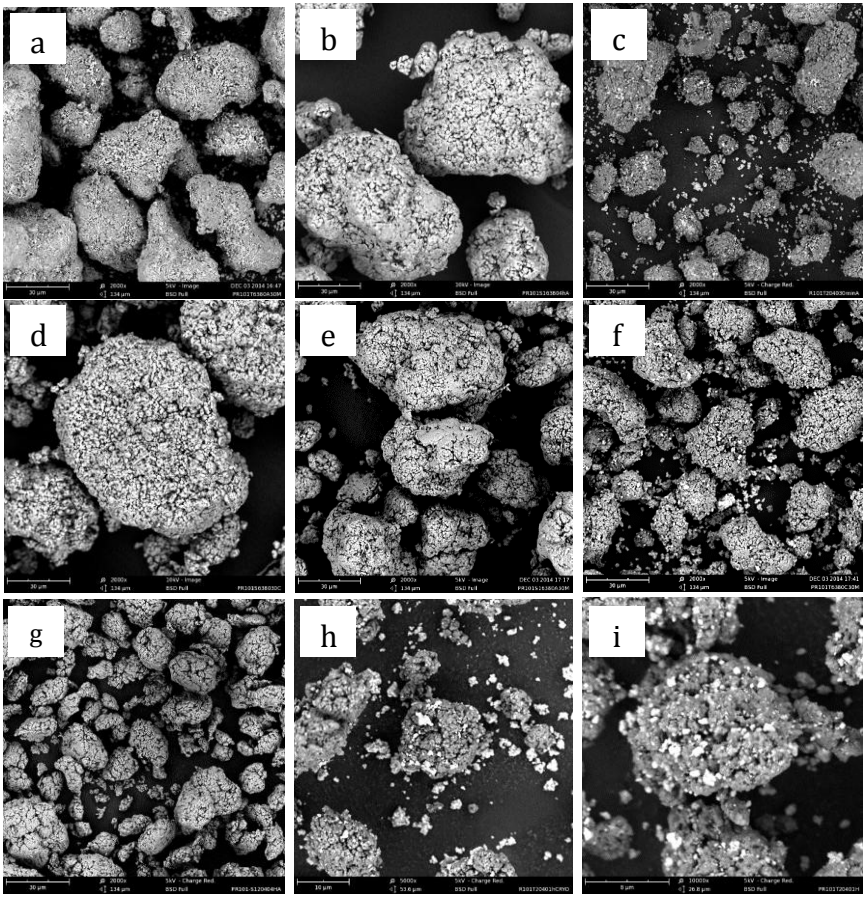

Figure 19. *More SEM images: ECTFE+TiO_2 Cryoatrittor 63-80μm 30 minutes (a), ECTFE Atrittor 63-80μm 4 hours (b), ECTFE + TiO_2 Atrittor 20-40μm 30 minutes (c), ECTFE Cryoatrittor 63-80μm 30 minutes (d), ECTFE Atrittor 63-80μm 30 minutes (e), ECTFE + TiO_2 Cryoatrittor 63-80μm 30 minutes (f), ECTFE Atrittor 20-40μm 4 hours (g), ECTFE + TiO_2 Cryoatrittor 20-40μm 1 hour (h) and ECTFE + TiO_2 20-40μm 1 hour (i).*

APPENDIX 4: TGA

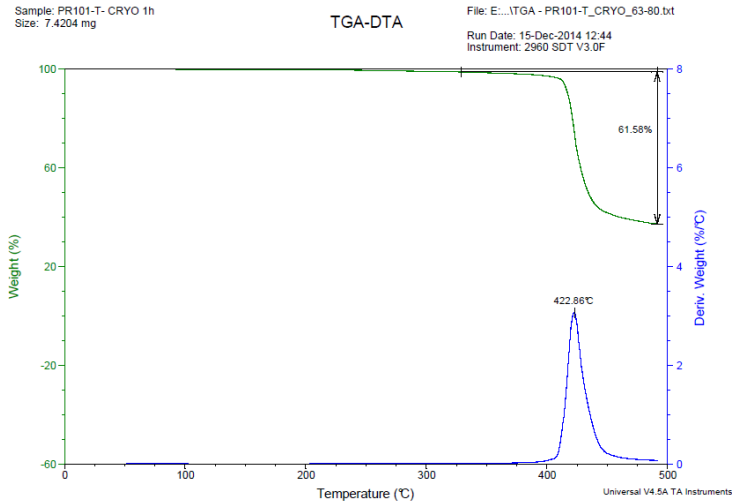

Figure 20. *Thermogravimetric analysis of ECTFE with TiO_2 mixed 1hour in Cryoatrittor mill (63-80 µm)*

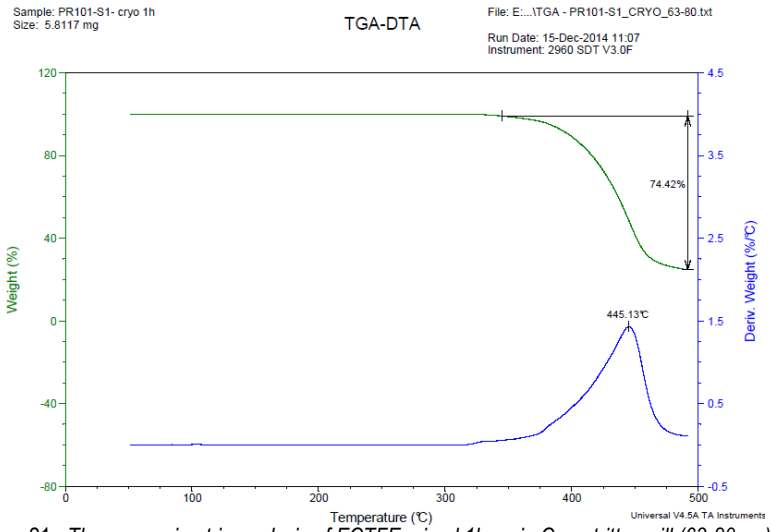

Figure 21. *Thermogravimetric analysis of ECTFE mixed 1hour in Cryoatrittor mill (63-80µm)*

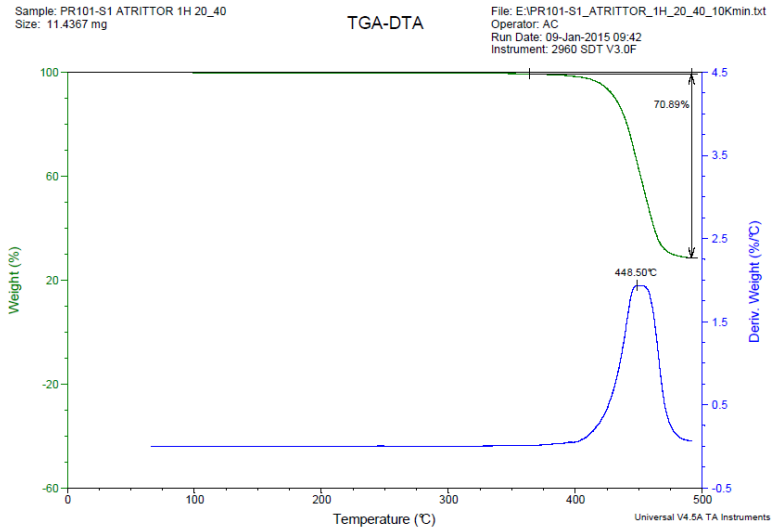

Figure 22. *Thermogravimetric analysis of ECTFE mixed 1hour in Atrittor mill (20-40μm)*

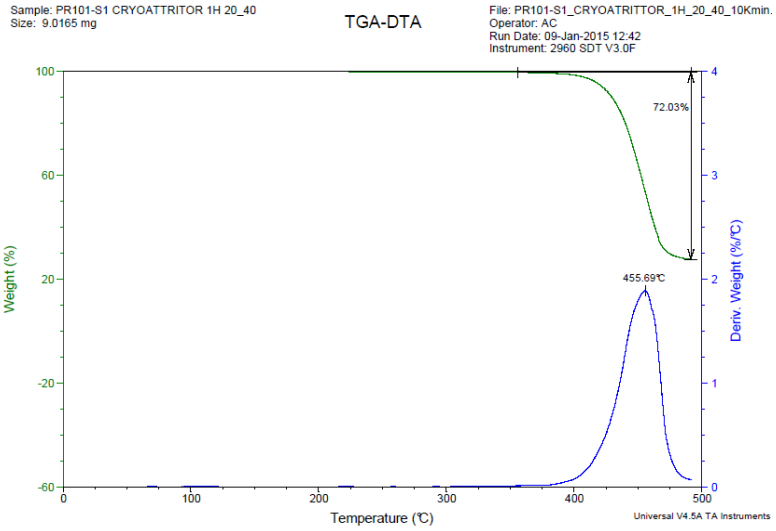

Figure 23. *Thermogravimetric analysis of ECTFE mixed 1hour in Cryoatrittor mill (20-40μm)*

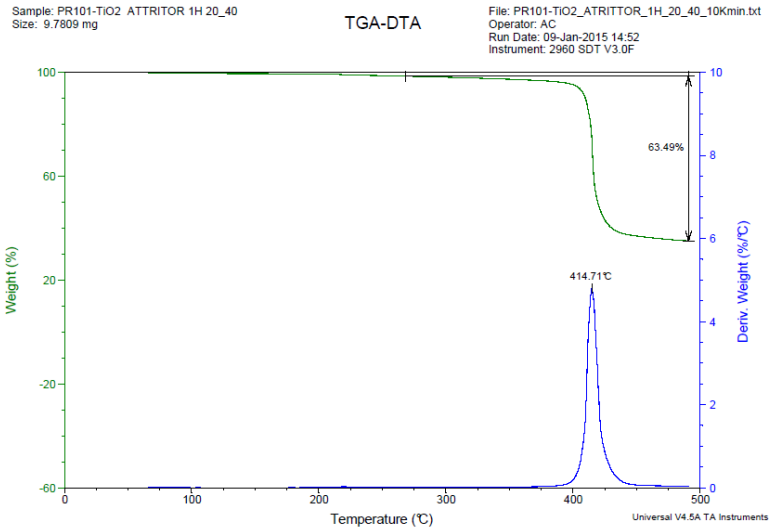

Figure 24. *Thermogravimetric analysis of ECTFE with TiO_2 mixed 1hour in Atrittor mill (20-40µm)*

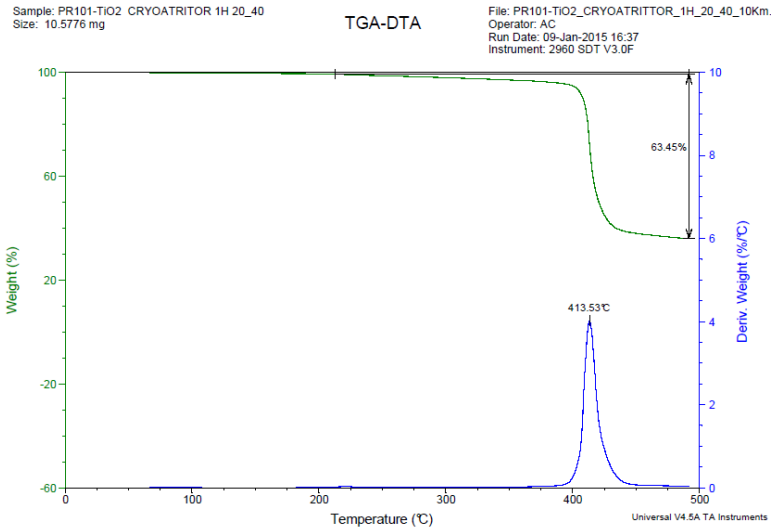

Figure 25. *Thermogravimetric analysis of ECTFE with TiO_2 mixed 1hour in Cryoatrittor mill (20-40µm)*