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Original Research Paper

Attrition and Cryogenic milling powder production for Low Pressure Cold Gas Spray and composite coatings characterization

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ABSTRACT

Inside the wide field of thermal spray, the possibility to spray ceramic nano-particles by Low Pressure Cold Gas Spray (LP-CGS) represents an interesting and innovative trend. In this work, titanium dioxide TiO_2 nanoparticles were mixed with a polymer in order to obtain a tailor-made nanocomposite powder and afterwards cold-sprayed coatings were produced, which might be attractive for their photocatalytic activity. Firstly, two different routes were used to incorporate the ceramic nanoparticles within the polymeric matrix: Attrition Milling (AM) and Cryogenic Milling (CM). Samples composition was not varied, while milling time was changed. The main objective was to investigate the mechanical physical union of TiO_2 nanoparticles around polymeric microparticles. The effect of ceramic particles on the structure and morphology of the polymer, as well as the influence of the temperature of the different combining processes were studied. The fundamental properties of the nanocomposite mixture were investigated by Scanning Electron Microscopy (SEM), Laser Scattering (LS Beckman Coulter) and X-ray Diffraction (XRD). Secondly, the best mechanically combined mixture was selected in order to be sprayed by LP-CGS technology. Adequate spraying parameters were chosen in order to develop different composite coatings. Thickness, roughness and porosity of manufactured products were measured.

1. Introduction

Nanocomposites materials are nowadays in the spotlight of both industry and research groups. The increasing interest in this type of composites arises from the possibility of preparing tailor-made materials that combine the advantages of ceramic nanoparticles, for instance electrical conductivity and photocatalysis [1,2], with the ones of polymers, e.g. ductility, deformability and plasticity. Nanostructured ceramics are conventionally defined as inorganic materials composed of structural units with a size scale of less than 100 nm in any dimension. Nanoceramics are classified as zero-dimensional nanocrystals, one-dimensional nanowires and nanotubes, two-dimensional nanofilms and nanowalls, and three-dimensional bulk materials with at least one nanocrystalline phase. These materials permit to obtain superior and unique properties in conventional ceramics with coarser structured units. As a large fraction of interfacial areas is created between a nanofiller and a polymeric matrix due to the high surface to volume ratio of nanoparticles, it is expected that the interphase formed in nanocomposites will have more importance for the final properties than that in conventional polymer composites. However, this only should occur with uniform dispersion of nanoparticles [3,4], which most of the times is a really difficult challenge. For this reason, characterization of interphases in nanocomposites with uniform dispersion is a key factor to understand their final properties and performance. Up to this moment, several strategies [5,6] have been followed to achieve uniform nanoparticle dispersions within polymer matrices; however, most of them required the use of solvents, chemical modification of the matrix and/or the filler, long processing times, and even sometimes high processing temperatures. Nevertheless, they do not seem to ensure uniform dispersion in terms of isolated nanoparticles when sizes of particles are less than 50 nm and filler loads are greater than 5% by weight (wt). Recently, with solid-state methods, such as Attrition milling (AM) [7,8], mechanical mixture of nanoparticles that remain well-bonded around the polymer has been achieved. Usually, AM provides good results with small chemical modifications, if any, of the polymer or the nanoparticles, avoiding, at the same time, the use of solvents and high processing temperatures [9]. A second mixing method, Cryoattrition Milling CM, commonly used for amorphous alloys and intermetallic materials, is also taken into account as new potential alternative for composite powder blending at low energy conditions. The main theory of the dispersing mechanism of

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particles on polymer proposed in this paper is the so-called mechanical anchoring [3,10]. This phenomenon takes into account the deformation of the polymer, especially on the surface, and the consequently mechanical adhesion of ceramic particles onto it. This approach has been studied in recent years and considerable effort has been devoted to the development of methods for the preparation of composite particles consisting of polymer cores covered with shells of different chemical composition. Several of these composites have been used as catalysts, coatings, raw materials recovery, drug delivery and anticorrosion protection [1,11,12]. In this case, ceramic–polymeric nanocomposites will be manufactured and developed for coating production through the Low Pressure Cold Gas Spray technology [22,23,26]. Polymeric particles with shells of nanoceramics do not lose their flowability and this is a significant aim inside the spraying process [24]. Therefore, the present work is twofold: (i) polymer nanocomposite obtainment by Attrition milling and Cryogenic milling of a polymer with oxide nanoparticles and (ii) coating build up by LP-CGS with the optimized powders.

2. Experimental materials and methods

In this work, titanium dioxide TiO_2 nanoparticles were room temperature and cryogenically milled with a copolymer as ductile matrix. The polymeric material is a commercial one: Halar® 6014 from Solvay. Laser Scattering (LS 13 320, Universal Liquid Module) was carried out in order to determine the particle size distribution of the raw materials. Two different mixing systems were used to produce composite powder materials: Attrition Mill (Model 01HD, Union Process Inc.) and Cryogenic Mill (Attritor 01HD, Union Process Inc.). Top surface of starting powders and milled composite mixtures as well as cross sections of final coatings were observed by SEM scanning electron microscope (Pro-X, Phenom). Diffraction data were studied by X'Pert PRO MPD diffractometer (PANalytical). Composite coatings were obtained by means of Low Pressure Cold Gas Spray system (Dymet 423). Produced coatings were mounted in an epoxy resin (EpoFix, Struers) and subsequently metallographic preparation was carried out.

2.1. Polymer

The polymeric matrix is a semi-crystalline, melt processable resin copolymer. The polymeric chain consists in a sequence of ethylene and chlorotrifluoroethylene monomers. Good chemical resistance, excellent thermal properties, optimal permeation resistance, anti-corrosion behaviour and outstanding flame resistance are just part of its interesting characteristics. Since the aim of this manuscript was to study the behaviour of polymeric and ceramic nanoparticles inside both AM and CM systems, it was necessary to study a narrow range of particle size distribution in order to comprehend well the mixing mechanisms. For this reason, the polymer was sieved in two different ranges: 20–40 μm (PR101-S1 in Fig. 2a) and 60–80 μm (PR101-S2 Fig. 2b). Though this way, it is possible to work with more homogeneous starting materials, so that it is easier to understand what happens to finest particles and to biggest ones during the mixing processes: also, the particle size of the final composite powder will be important regarding cold spray application. Not only the deformation of polymeric particles is important, but also the crystallinity of the material; in Fig. 3 the XRD pattern is shown and it is possible to notice a crystalline diffraction peak at 17.4° and a second broader peak at around 40° which represents the amorphous part of the polymeric matrix.

2.2. Titanium dioxide

LS curves showed in Fig. 4a confirm the fact that the titania powder possesses a medium particle size distribution of 1.88 μm. Two peaks can be observed: a first peak consists in sub-micrometric particles from 0.05 μm to 0.3 μm, while the second peak represents the majority of material volume. In this second case d_{90} corresponds to 4.4 μm. In the SEM top surface micrograph on Fig. 4b it is possible to notice both small particles and groups of agglomerated ones. This phenomenon is mainly due to electrostatic agglomeration because of the small dimensions of titania. Nevertheless, powders with these grain sizes could not be easily sprayed by Low Pressure Cold Gas Spray technique [28] due to their bad flowability. Diffraction peaks of TiO_2 shown in Fig. 5 correspond to the anatase phase and possess a wide width due to the nanometric size of the powder. This broadening is an intrinsic characteristic of the material, i.e. the large width is due to the nano sized crystals of the material. Titania nano dimensions were specifically selected in order to achieve the best mechanical union with micrometric polymeric particles. The new composite material has a polymeric matrix surrounded by TiO_2 nanoparticles and this way it is possible to have a correct flowability inside the LP-CGS nozzle and also be able to spray ceramic nanomaterials [18,21,25].

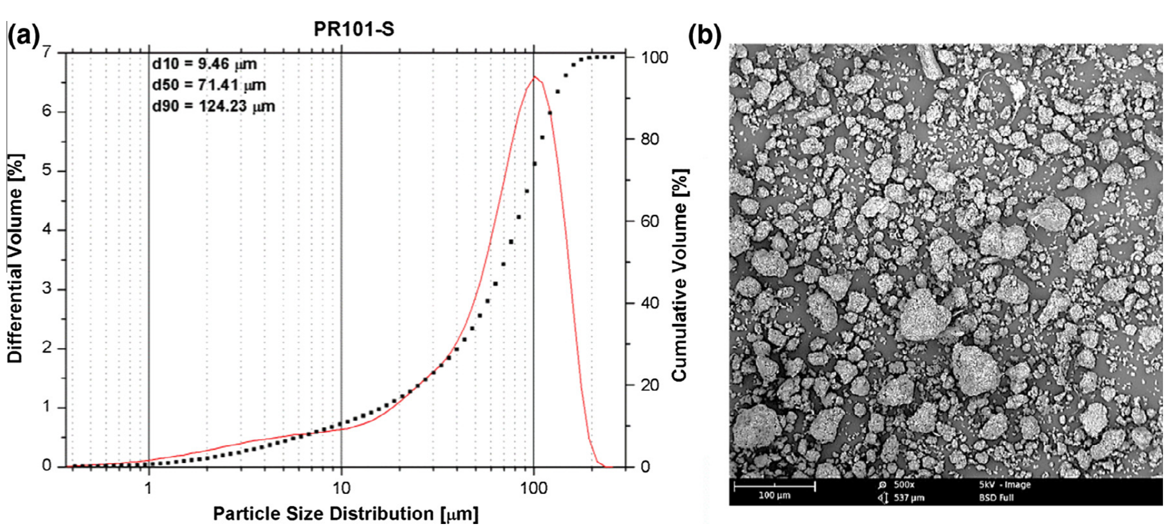

Fig. 1. Wide particle size distribution (a) and SEM (secondary electrons) top surface (b) of polymer.