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Analysis of the adhesion of titanium and carbon-diamond coatings on 3D printed textured surfaces

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Abstract. The importance of coatings in engineering has been predominant throughout the development of the new industrial era. The competitiveness of the field has led to the development of better materials that achieve superior properties. The purpose of this research is evaluating the adhesion to the surfaces coated by magnetron sputtering technique. The adherence quality of the deposited coatings on specimens was evaluated adhesion by scratch and indentation tests guided according to standards, using the Tribolab UMT at constant load. The results obtained allow validating of the additive manufacturing process as possible mechanicals applications.

1. Introduction

The new generations of functional coatings that allow a wide variety of solutions are in great demand today. The current trend for the individualization of products and the increase in their complexity, has meant that new ways of manufacturing the products must be thought of, taking the best of the available technologies. In the case of the individualization of the products, it is important to recognize that in the case of additive manufacturing the costs of making the pieces are practically independent of the number of pieces to be manufactured and that is why it has become so important to use them in the specialized processes. Additive manufacturing processes take information from a computer aided design (CAD) file that is then converted into a stereolithography (STL) file. The precision of this technique needs improvements to replace in some degree the need for a finishing process and therefore until now the use of coatings is the preferred solution in search of superior properties. The rapid creation of prototypes is one of the most striking uses because with this, researchers can build and analyze models of theoretical understanding and advanced studies [1–3].

Most polymeric resins and industrially applied compounds have low surface free energy and lack polar functional groups on their surface, resulting in inherently poor adhesion properties. A strong research drive to understand the adhesion of polymers in the last decade has been motivated by the growing needs of the automotive and aerospace industries for better adhesion of components and surface coatings [4]. Hard coatings have become the solution to problems such as corrosion and wear. The technique physical vapor deposition (PVD) or sputtering is one of the most used processes for obtaining hard coatings, which includes any process of growth of a film in a vacuum environment that involves the deposition of atoms or molecules in a substrate. It consists of evaporating by physical means the material that will form the coating and its subsequent condensation on the substrate, this process has the possibility of being applied simultaneously to assemblies or pieces [5]. In recent years, the efforts made to develop multicomponent coatings as heterostructures in multilayers in order to improve the wear resistance and oxidation of the coated components have been considerable. The improvements are presented in the alternate deposition of two or more chemical and / or mechanically different layers, in such a way that the concentration of tensions and the conditions for the propagation of nano-cracks can be controlled. Therefore, the multilayer structure can act as an inhibitor of nanogrids, as well as increasing the resistance to fracture [6,7].

The scratch test can be used for the characterization of the materials. During the scratch test, a rigid penetrator is pressed on a specimen and a tangential force is applied, which produces a groove on the surface of the analyzed material. The resulting fingerprint is measured to determine the scratch hardness product of a given load [8].

In this work, we investigate the adhesion to the surfaces coated by magnetron sputtering technique following the established by ASTM G171-03 [9], and ASTM E92-17 [10] & E384-17 [11] standard, analyzing the effect of apply force in the specimen surface. We perform experimental tests using Tribolab UMT. The paper is organized as follows: in the next section, we show the methodology, which includes a description of the materials, specimen design and manufacturing, the failure criteria, and the experimental setup. In section 3, we analyze the results generated by the experimental standard tests. The conclusions are given in the final section.

2. Methods and materials

Each of the materials and methods used to evaluate the adhesion of DLC and Ti coatings on 3D printed polymers are described below: first the mechanical properties of each of the resins, followed by the design and manufacture of the textured surfaces to pass to the failure criteria and finally to the experimental assembly of each of the tests performed.

2.1. Materials

Table 1 presents the properties of materials used in the manufacture of the substrates, the commercial photopolymer resins Accura®60 (SLA-3500, 3D Systems) and Clear FLGPCL 02 (Form 1+, Formlabs). The substrates are fabricated layer by layer with a resolution of the layer thickness of 100 microns, in the 3D Systems SLA-3500 and Formlabs Form 1+ printers, which can read the geometric information of the substrates from the CAD files exported in the STL format.

Table 1. Properties of Accura®60 and Clear FLGPCL 02 resins used in the printers 3D Systems SLA-3500 and printer Formlabs Form 1+ respectively.

Parameter	Accura®60 resin	Clear FLGPCL 02 resin
	Value	Value
Density	$1.21\ \mathrm{g/cm^3}$	$1.10\ \mathrm{g/cm^3}$
Tensile strength	$58\ \mathrm{MPa} - 68\ \mathrm{MPa}$	$61.5\ \mathrm{MPa}$
Young modulus	$2.690\ \mathrm{GPa} - 3.1\ \mathrm{GPa}$	$2.7\ \mathrm{GPa}$
Elongation at break	$5\% - 13\%$	5%
Flexural modulus	$2.7\ \mathrm{GPa} - 3.0\ \mathrm{GPa}$	$2.38\ \mathrm{GPa}$
Impact strength	$15\ \mathrm{J/m} - 25\ \mathrm{J/m}$	$29\ \mathrm{J/m}$
Heat deflection temperature (**@66 PSI**)	$53\ ^\circ\mathrm{C} - 55\ ^\circ\mathrm{C}$	$78\ ^\circ\mathrm{C}$

In the SLA method, a laser beam of UV light following the path marked by the STL file scans across the surface in a vat with photosensitive resin that polymerizes to form of each layer of the substrate. This method is fundamental to the history of additive manufacturing and provides one of the best compromises between part size, resolution, and surface quality [12].

2.2. Specimen design and manufacturing

The geometry of the selected substrates in 3D was a circular disk of 21.3 mm in diameter with surface texture of curvilinear cross section of radius of curvature of 1 mm. The substrate was created in the computer aided design (CAD) software, SketchUp Make 2016 version 16.0.19911 (Trimble Navigation Limited), thus allowing the correct realization, modification, analysis and optimization of the model, validating the characteristics, properties and feasibility . design. The substrates were manufactured with commercial resin (photosensitive resin) using the technique of laser stereolithography with a layer thickness of 0.1 mm. The reason for the choice of materials was based on the great potential of use of them, specifically for laboratory applications and in the microfluidic industry, in which canals, grooves, crests and similar textures are found with hundreds of microns or even a few millimeters.

For the coatings a magnetic spray technique was used in order to deposit the Ti and DLC layers. A blank of pure graphite ($400\ mm^2 \times 100\ mm^2$) was used for the deposition of the DLC layer. The magnetron was operated in pulsed DC mode, frequency of 150 kHz, pulse time of 4 microseconds. The working pressure of argon was adjusted to 7×10^{-3} mbar. The substrates are located in a simple and parallel rotation system, at a distance of 8 cm from the target during the deposition. The deposition time was 90 minutes, resulting in a total thickness of the 40 nm DLC layer. In the case of Ti, the deposition was produced with a Ti target of pure rectangular metal ($200\ mm^2 \times 75\ mm^2$) in the argon atmosphere (Ar). The working pressure of Ar and the DC power of magnetry were adjusted to 4×10^{-3} mbar and 200 W, respectively. The deposition time was 7 minutes, resulting in a total thickness of the Ti layer of 200 nm. The thickness measurement of the Ti and DLC film was made with a masked function and a glass slide using a profilometer.

2.3. Failure criteria

The failure criteria allow us to evaluate the final state of the piece under evaluation under comparative parameters. Then the representative variables are presented to consider in each of the tests to be performed.

2.3.1. Scratch test. The scratch test consists of the application of a load on the surface of a certain material. This is achieved by pressing a point of a very hard material on the area of the material to be tested. While the sample is displaced at a certain speed, the resulting stresses in the interface cause marks and abrasions in the coating. The point of fracture initiation is called critical load. From the analysis of the marks left by the indenter and the applied force, it is possible to know properties and characteristics of the tested material such as: the modulus of elasticity, the tension at yield or the coefficient of friction [13]. The main criterion is that in the scratching process a measurable footprint is produced on the surface being analysed, without causing a catastrophic fracture or great damage to the surface of the material. The severe damage on the surface, when the width of the footprint is not clearly measurable or that the edges are cut or twisted, invalidates the use of this method. Therefore, it reflects the permanent deformation resulting from the scratching and not the instantaneous state of the combination of the elastic and plastic deformations of the surface [7].

2.3.2. Indentation test. It is measured by loading an indenter of specified geometry and properties on the material for a specified period of time and measuring the depth of penetration or the dimensions of the resulting indentation or impression. As the material being tested is softer, the depth of penetration or the indentation dimensions become larger. Common types of hardness tests include Rockwell (indentation depth or undeclared indentation), Knoop / Vickers and Brinell (indentation area). Knoop and Vickers tests are more suitable for fine materials, coatings and mounted metallographic components and are therefore the most suitable tests for the study in question [8]. Knoop tests are mainly performed in test forces of 10 g to 1000 g, Knoop tests are known primarily as microhardness or micro-indentation tests and are best used in small test areas or fragile materials, since minimal material deformation occurs in the short diagonal area[14,15].

2.4. Experimental set up

The Bruker's scratch test system is built on the Universal Mechanical Test (UMT TriboLab) platform, which provides precision control of load, speed, and position. The system's modular design ensures the flexibility to cover test capabilities over a wide range of forces and velocities to perform any scratch test. TriboLab utilizes three major drive systems, Carriage, Slider, and Y-stage for Z-, X-, and Y-motion, respectively. Universal mechanical and tribology testing. Figure 1 shows test of specimen photopolymer resins Accura®60 (SLA-3500, 3D Systems) which was tested in CETR-Universal Materials Tester (CETR-UMT). The required data is supplied by the DFH-5.0 sensor.

Figure 1. Universal mechanical and tribology testing. Sensor DFH- 5.0.

2.4.1. Scratch testing. Micro-scratch- tests were performed on four specimens using a diamond stylus with a tip radius of 5 µm. The test was conducted with reference to ASTM G171 [9] modified for thin coatings. The scratch hardness of a material can be determined by producing a scratch on the sample surface with a sharp, hard (diamond) tool 5 mm tip radius with known tip geometry, under a constant, load. For this case, the samples are 4 with the different coating configurations, in this case DLC and Ti, and with the two resins mentioned above. The diamond stylus in a stylus holder was mounted on the force sensor with a spring suspension. The test sample was mounted on a table of the lower linear drive, allowing for automated lateral motion and thereby multiple scratches on a single specimen. A sensor was attached to the stylus holder to monitor the high-frequency signal generated during scratching, which indicates the intensity of material fracture. To begin the test, a normal load of 10 g was applied to the stylus. The scratch was produced by dragging the stylus along the sample surface with the upper lateral slider. The scratch length was 3mm, and dragging speed was 0.02 mm/s. Load was maintained constant throughout the test by controlling the z-carriage motion based on closedloop feedback from the force gauge. The test was repeated three times on each sample to verify the data consistency and repeatability.

2.4.2. Indentation testing. The tests were performed on four samples using a Vickers and Knoop stylus. The test was performed with reference to E92-82 & E384-99 [10,11], modified for thin coatings. The hardness of a material can be determined by producing a fingerprint the surface of the sample with a sharp and hard tool (diamond) with known tip geometry, under a constant load. For this case, the samples are 4 with the different coating configurations, in this case DLC and Ti, and with the two resins mentioned above. The diamond stylus on a stylus holder was mounted on the force sensor with a spring suspension. The test sample was mounted on a table of the lower linear drive, allowing automated lateral movement and, therefore, multiple fingerprints in a single sample. To begin the test, a normal load of 50 g was applied to the pencil for 15 s, the indentation depth h being measured continuously. The load was kept constant throughout the test by controlling the movement of the carriage z based on the closed loop feedback of the force meter. The test was repeated three times in each sample to verify the consistency and repeatability of the data.

3. Results

During the scratch test, the indenter moved slowly on the coating, causing some material removal. A series of runs with progressively increasing normal loads, though constant within each run, was performed. The normal load started from 5 g in the first run and was increased by 10 g each run until coating failure was observed. The critical load characterizing the coating scratch resistance was defined as the minimum load to cut through the coating completely. Constant load scratch testing provides better differentiation of damage levels. However, the constant load scratch test requires more specimen surface and test time. Nevertheless, a constant load test provides a greater statistical confidence in the results.

The relevant in the graphs since it is wanted to evaluate the scratch resistance and not specifically the hardness, stands out in the particular behaviour for each of them. The tendency in the applied force line until it exceeds the maximum force forming a peak amplitude as seen in the Figure 2, Figure 3, Figure 4 and Figure 5, that is more noticeable and abrupt for DLC coatings, which leads us to the hypothesis that the scratch resistance and therefore the adhesion during film formation is more homogeneous and uniform for the coating, in contrast to that obtained by Ti coatings, since the transition does not occur instantaneously, although its penetration is smaller which leads to the conclusion that its film formation is not completely homogenous and may have discontinuities that lead to this behaviour.

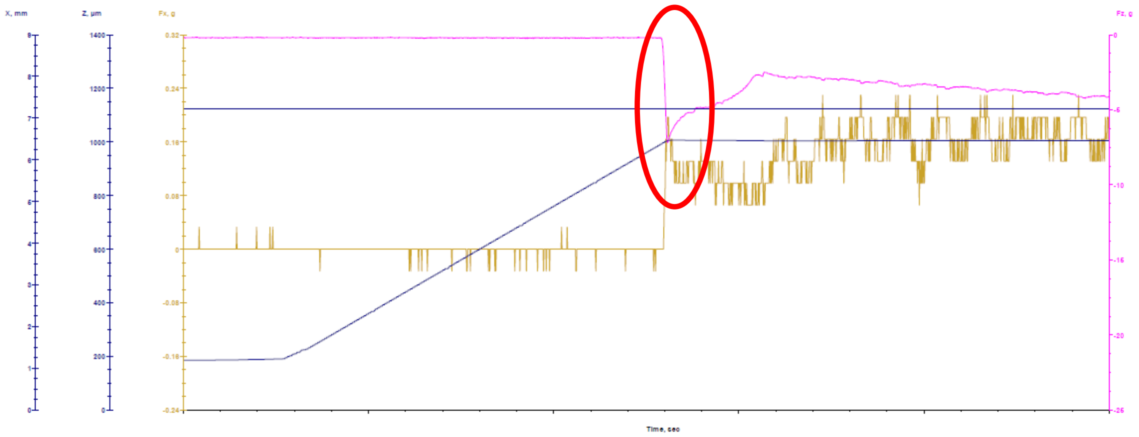

Figure 2. Scratch test, 20 g for photopolymer resins Accura®60 (SLA-3500, 3D Systems), DLC coating.

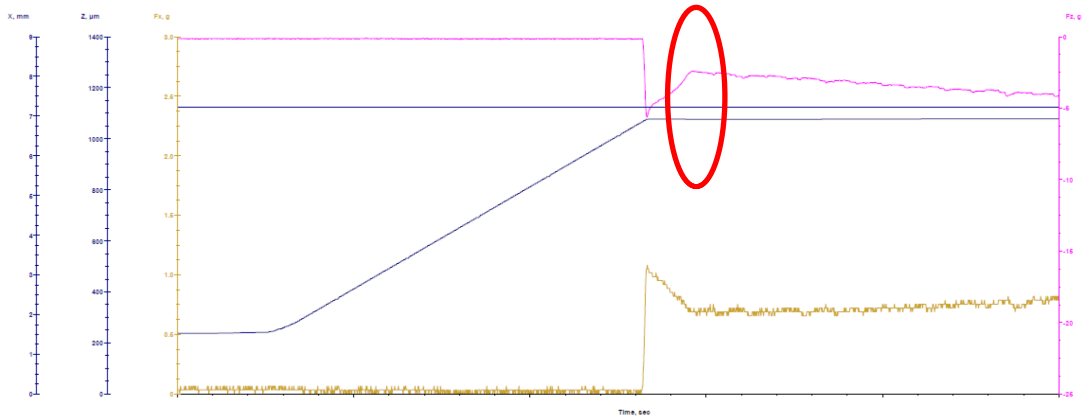

Figure 3. Scratch test, 20 g for photopolymer resins Accura®60 (SLA-3500, 3D Systems), Ti coating.

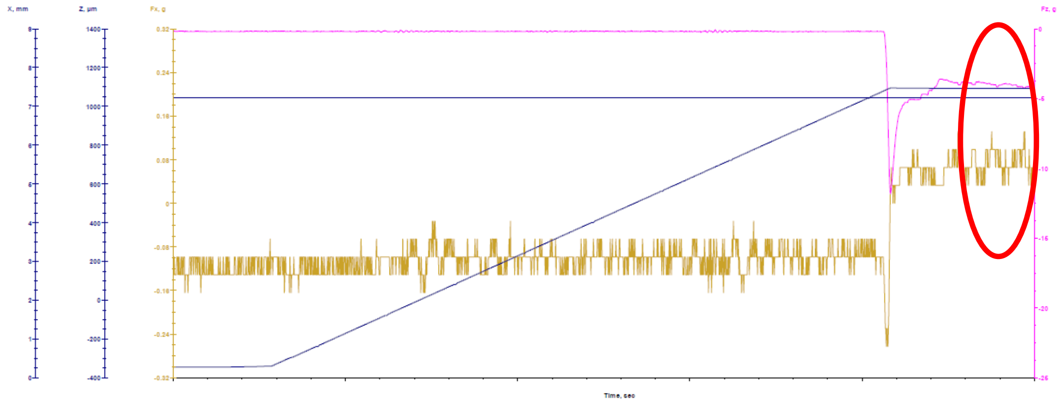

Figure 4. Scratch test, 20 g for Clear FLGPCL 02 (Form 1+, Formlabs), DLC coating.

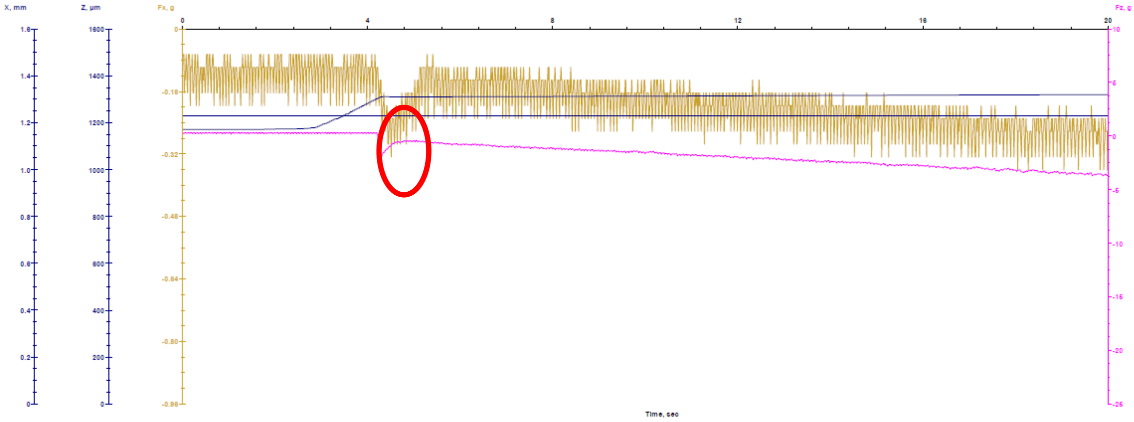

Figure 5. Scratch test, 20 g for Clear FLGPCL 02 (Form 1+, Formlabs), Ti coating.

As for the indentation tests, the same number of tests were carried out, with the parameters mentioned above for the Vickers and Knoop model. For each of them, the results obtained were close to expected but more significant with Knoop Hardness: for the Vickers test the dispersion was much higher and the taking of results was difficult taking into account the measurement of the indenter's footprint. For these tests, you had the geometry of the identator and with the measurement of your diagonals, the equipment allows you to automatically calculate the values (see Table 1 and Table 2).

Table 2. Results scratch test.

Parameter HV micro-hardness	Accura®60 resin DLC	Clear FLGPCL 02 resin DLC	Accura®60 resin Ti	Clear FLGPCL 02 resin Ti
	Value	Value	Value	Value
Test 1	3065.1	2974.1	2585.5	2043.2
Test 2	3622.4	3096.2	2194.7	2196.3
Test 3	3198.3	3155.6	2745.3	2003.7

Table 3. Results indentation test.

Parameter HK micro-hardness	Accura®60 resin DLC	Clear FLGPCL 02 resin DLC	Accura®60 resin Ti	Clear FLGPCL 02 resin Ti
	Value	Value	Value	Value
Test 1	9756.3	9256.1	7423.8	7652.8
Test 2	9845.3	9133.6	7652.3	7155.5
Test 3	9635.2	9035.4	7327.2	6905.1

4. Conclusions

The scratch tests carried out on the different test specimens yielded the results waiting, giving as a conclusion a good adhesion of the film without delamination: the tendency improves for the specimens obtained with the industrial equipment, refer to photopolymer resins Accura®60 (SLA-3500, 3D Systems). Presumably by an improved surface finish and at the same time an adhesion more consistent to the substrate, however for the other samples the results are acceptable. The indentation test gives us results regarding the hardness of the coating. The ranges for tests performed for DCL coatings are 3200 HV and 9100 HK, while for Ti coatings are 2700 HV and 7100 HK. It is also concluded that the Knoop test gave better results than the Vickers test, although in repeated studies the reference is in relation to the last one mentioned.

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