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# Innovative Manufacturing Process of Functionalized PA2200 for Reduced Adhesion Properties

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**Abstract:** This work proposes an approach to fabricate micro patterned surfaces on PA2200 polyamide in order to improve its performance in terms of wettability and adhesion. In more detail, the present work aims to change the wettability of the surface and decrease their bacteria adhesion tendency. The experimental procedure consists of imprinting a set of different micro patterned structures over the polymer in order to verify the effectiveness of the methodology to change the contact angle of the surface, and in turn, reduce the occurrence of bacteria adhesion. Four different surface patterning were produced by laser ablation of a commercially pure titanium alloy, and then imprinted over the polyamide by surface stamping. The resulting surfaces were analyzed by topographical characterization and scanning electron microscopy. The wettability was probed by contact angle measurements while the bacteria adhesion was analyzed by adhesion test. The experimental results demonstrate the effectiveness of the method to modify the surface characteristics and to obtain a reliable patterned surface without using chemical hazardous material; opening to the possibility to replicate more complex structures and to obtain graded engineering surfaces.

**Keywords:** textures; surfaces; laser; titanium; adhesion; wettability; PA2200

## 1. Introduction

A great number of applications are based on engineering surfaces, and many are their industrial applications.

Methods based on the lotus effect have been proposed to produce paints, roof tiles, fabrics and other surfaces that can be made dry and clean [1–3]. The ability of these surfaces to make water bead off completely and thereby wash off contamination very effectively has been termed the lotus effect, although it is observed not only on the leaves of the lotus plant but also on many other plants such as strawberry, raspberry, etc. [4]. Water repellents are very important in many industrial and biological processes [5], such as the prevention of the adhesion of snow and fog to antennas, raindrops, self-cleaning windows and traffic indicators, low-friction surfaces, and cells mobility [6]. Most leaves that exhibit strong hydrophobicity have hierarchical surface roughness with micro and nanostructures made of unwettable wax crystals. The roughness enhances the hydrophobic behavior, so that the water droplets on top tend to become nearly spherical [7]. As a result, the leaves also have a self-cleaning property: the rain-drops roll away, removing the contamination particles from the surface, due to the small adhesion energy and the small contact area between the contaminant and the rough leaf. The hydrophobicity of solid surfaces is determined by both the chemical composition and the geometrical micro or nanostructure of the surface. Renewed interest in this problem has been generated by the discoveries of surfaces with small scale corrugations that exhibit very large contact angles for water and other liquids, in some cases, the contact angle is close to 180° [8,9]. Such surfaces are referred to as super-hydrophobic and they also exhibit low adhesion properties.

This effect can be obtained through physical and chemical treatments or by texturing surfaces [10,11]. The term surface texture includes a series of characteristics which make the surface "functionalized" to exhibit superior performance, such as different size and shape of features, their distribution, arrangement, and orientation, enabling the multi functionality of a surface [12–14]. Thus, scientific interest in surface modification for changing chemical, mechanical and physical properties is growing. Concerning the physical properties, surface energy plays a fundamental role in the applications of engineered surfaces, wetting first and foremost [15]. The phenomenon is governed by the minimization of energy of the interfaces theory and it depends on intermolecular interactions, referring to the contact between a solid surface and a liquid.

In addition, structured surfaces play a key role in optics such as in the manufacturing of metrology surfaces [16] or voice coil fast tool servo [17]. Thus, micromachining of such surfaces has been demonstrated to be effective in producing precision devices to be employed in different fields [18]. Micromachining has attracted great attention for its capability to produce microcomponents such as microdisplays, microsensors, microbatteries, etc. These materials are usually made of multimaterials (may include hard-to-machine materials) and possess complex shaped microstructures requiring sub-micron machining accuracy. Thus, a number of micromachining processes have been developed as reported by [19].

Bioengineering as well, puts a lot of interest in structured surfaces manufacturing by investing a lot of resources for the research in nanotechnologies, microengineering and bioengineering. The research allows for the development of a large number of devices for biomedical applications like tissues and organs regeneration, bone reconstruction, ceramic scaffolding etc. but also for the medical diagnostic field like microfluidic applications such as micro TAS (total analysis systems) and LOC (laboratory on chip) and biochips [20,21]. The capability to fabricate passive antibacterial surfaces on industrial components has profound implications for human health and there is the stringent need to develop an appropriate scalable technology able to generate the self-cleaning surfaces in a fast, environment-friendly and economic way.

Photolithography is the most used technology to modify surfaces because of its high production rate, but on the other hand, notwithstanding that it is possible to fabricate various geometries, it is difficult to obtain complex features such as those required for micro- and nano-devices [14,22]. Furthermore, the technology involves a high initial startup cost. Resolution dependence on the numerical aperture (NA) of the lens, and the wavelengths of the light source are also other leaks leading to difficulties in scaling down the features. Photolithography can also be risky for the environment and human health, because it involves the use of chemical hazardous products. Other methods to modify polymeric materials include plasma treatments or expensive processes such as low energy ion beam. The technology described in the paper aims to produce engineering surfaces avoiding problems occurring with conventional technologies such as those encountered during photolithography methodologies or plasma treatments.

## 2. Materials and Methods

The material under investigation is the PA2200 which is a bio compatible polymer. Thus, the experimental campaign aimed to develop a customized methodology to manufacture structured surfaces on PA2200 for possible biomedical applications. The PA2200 is a thermoplastic biocompatible material with potential use in the biomedical field for prostheses manufacturing. However, it is necessary to treat the surface in order to reduce the chance of bacteria adhesion.

The process proposed in this paper is used to produce structured surfaces at the micro scale range in an environmentally sound way. It involves the creation of the structured surfaces in two steps:

1. Laser treatment for surface texturing on titanium alloy as shown in Figure 1a;
2. Replica of the structured surfaces on PA22000 by surface stamping as shown in Figure 1b.

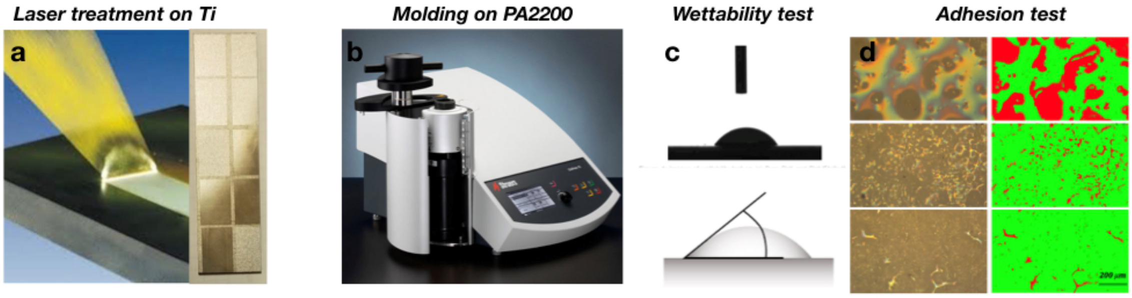


**Figure 1.** Process set up for microstructure modification on (**a**) Titanium by laser texturing, (**b**) stamping process on PA2200, (**c**) wettability tests on Titanium and PA2200, (**d**) adhesion test on PA2200.

The microstructures are obtained as follows:

The laser treatment is performed on a 1.5 mm thick commercially pure Titanium sheet metal using an ytterbium doped fiber laser with a laser spot diameter of 25 µm, a maximum power of 50 W and a wavelength of 1064 nm (CL50 Clean-Lasersysteme, Dresden, Germany). The scanning speed ($v$, mm/s) dictates the production rate of the whole process, and the pulse frequency ($f$, kHz), and consequently the pulse fluence ($F$, J/cm$^2$), were varied to manufacture the needed surfaces. As suggested in previous related work [23,24], laser power was kept constant to 5 W, while the line spacing (i.e., pitch) was set equal to 25 µm. Thus, F and v were varied over five levels as described in Table 1, resulting into 25 laser processing combinations.

**Table 1.** Laser parameters for Titanium modification.

| Pulse Fluence, $F$ (J/cm$^2$) | Laser Scanning Speed, $v$ (mm/s) | Test Number |
|---|---|---|
| 10 -20- 30- 40- 50 | 50 | Ti 1- Ti 2- Ti 3- Ti 4- Ti 5 |
| 10 -20- 30- 40- 50 | 350 | Ti 6- Ti 7- Ti 8- Ti 9- Ti 10 |
| 10 -20- 30- 40- 50 | 650 | Ti 11- Ti 12- Ti 13- Ti 14- Ti 15 |
| 10 -20- 30- 40- 50 | 950 | Ti 16- Ti 17- Ti 18- Ti 19- Ti 20 |
| 10 -20- 30- 40- 50 | 1250 | Ti 21- Ti 22- Ti 23- Ti 24- Ti 25 |

It is worth noting that laser was selected as the method for surface texturing since it has been demonstrated to be one of the best suitable processes for producing micropatterns because of its high accuracy, repeatability, and machining rate over the advanced machining processes [25].

Prior to laser ablation, samples were cleaned by means of ultrasonic bath in ethanol (99%) for 10 min at room temperature. After the treatment, the contact angle was measured to verify the changes in adhesion of the titanium samples providing information on the effectiveness of the laser treatment.

SEM analyses were then performed to allow assessing the evolution of surface topography as a function of laser processing conditions. The images were acquired at an acceleration voltage of 15 kV with variable resolutions (DSM 982 Gemini, Zeiss, Germany).

After the surface laser treatment, the surfaces were stamped over the PA22000. The stamping process was necessary to reproduce the negative surface of the Titanium alloy over the polymer since it is not feasible to texture it using the laser ablation directly. Thus, the Titanium samples were used as male dies to imprint the desired surface over the polymer. Many kinds of structured surfaces have been created by embossing, molding or casting (replication methods for example) since they are considered technologies for economic production. Precision machined masters may be used directly, although masters are commonly electroformed to produce working molds. Hot roller embossing is used to reproduce nominally planar surface relief microstructures in polymer films such as polyvinylchloride and polycarbonate. Production costs are low, but difficulties are encountered with deep microstructures. The customized stamping process was performed using an electro-hydraulic, heated programmable single cylinder mounting press (Cito press-15 Struers). In fact, the titanium textured sample is placed into the press cylinder in contact with the polymer sample. A temperature of around 180 °C and a force of about 250 bar is applied during the embedding of the specimen. Water cooling is used to obtain the shortest possible mounting time. Different combinations of pressure and temperature were tested in order to obtain the desired surface over the PA22000, thus, the process temperature of 180 °C at a pressure of 250 bar for 1 min and a cooling time of 1 min were selected.

Then, the contact angle of the obtained surfaces was also measured in order to verify the changes in surface wettability. The measurements were completed by a contact angle measurement device (OCA-20 Data Physics, Germany) equipped with a charged coupled device (CCD) camera with a resolution of (768 × 576) pixels. The sessile drop technique was applied by delivering a 3 μL drop of liquid on the samples surface. SEM images of the obtained PA22000 samples were also acquired. Finally, the bacteria adhesion tests were performed to verify the effectiveness of the methodology to develop micro structured surfaces for reduced bacteria adhesion.

The experiments were performed using a liquid composed of distilled water and 0.2% LG21 which is *Lactobacillus gasseri* OLL 2716 strain. Although the experiments could be performed with a lot of different liquids, LG21 was chosen for its characteristic as a useful probiotic in the treatment and prevention of Helicobacter pylori infection [23]. Probiotics are now accepted as being useful in the prevention and treatment of certain pathological conditions, mainly (but by no means exclusively) infections of the small and large intestine.

The drop containing 3 mL of the LG21 liquid was placed over the sample and then the sample was tilted at 90° at room temperature in order to completely dry off. The procedure was repeated for the as-received polymeric samples and the textured ones, then a comparison of the overall amount of bacteria still attached over the surface was completed.

Figure 1 reports a schematic of the overall process set up and performed tests.

## 3. Results and Discussion

Figure 2 shows the surface topography changes on Titanium samples as a function of fluence and scanning speed. In particular, the lowest fluence does not lead to a significant variation of surface topography. On the contrary, values of $F > 10$ J/cm$^2$ laser irradiation had a severe effect and induced extended surface melting leading to visible changes in surface topography. For a given speed, a further increase in pulse fluence does not lead to substantial modifications of surface topography, while the increasing speed at a given fluence value results in a reduction of the melted area giving rise to more defined surface structures.

It is worth noting that the SEM analysis on surface modifications of Titanium highlighted the mark of the laser scanning direction when 50, 350 and 650 mm/s scanning speeds were used. Thus, the surface response to liquid flow can easily exhibit a directional behavior. In fact, it is clearly visible from the SEM (i.e., $F = 40$ J/cm$^2$ and speed = 350 mm/s) that the laser passes generate horizontal channels (i.e., in the direction of laser scanning) which can easily lead to deviating the liquid in the same direction. On the contrary, this effect vanishes when higher speeds are used (950 and 1250 mm/s) evidencing also a more defined pattern, especially when higher pulse fluence was used. In particular, SEM images showed a distinct pattern when the higher scanning speed was used. However, in order to verify the effectiveness of the surface modifications, the surface contact angle was also measured. The results are reported in Figure 3 for the Titanium material.

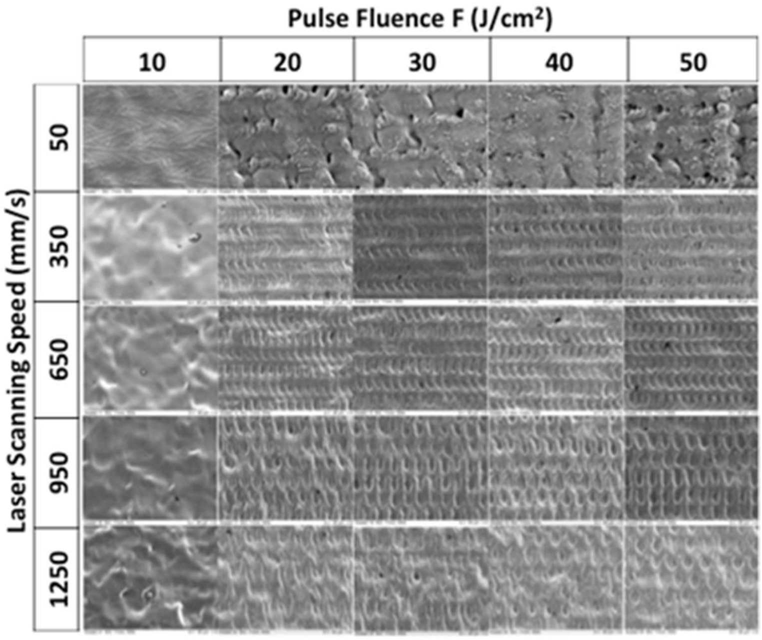


**Figure 2.** Surface topography of Titanium after laser ablation at varying pulse fluence and laser scanning speed.

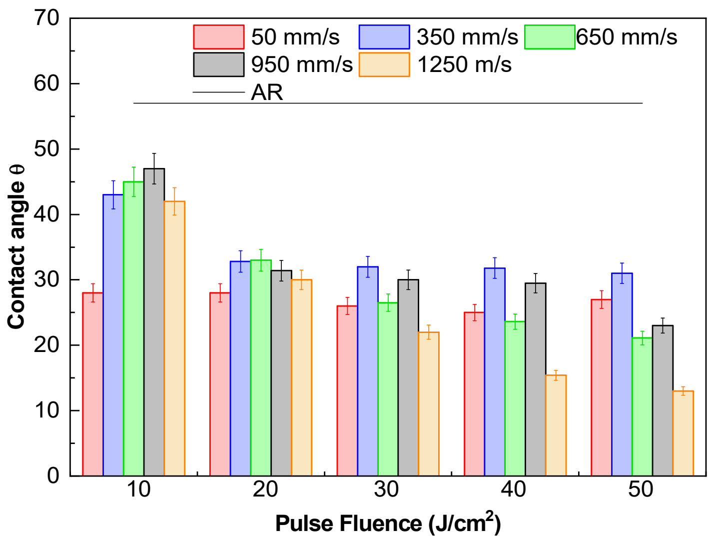


**Figure 3.** Contact angle of Titanium at varying pulse fluence and laser speed.

As shown in Figure 3, the as received surface had a contact angle of about 58°. The results show that a pulse fluence greater than 10 J/cm$^2$ had little or no effect on surface wetting while $\theta$ consistently decreased by reducing the scanning speed. This is a combined effect induced by modifications of surface topography and chemistry. Considering that the received surface had a mean surface roughness *Ra* of about 2 µm, it resulted strongly modified by laser irradiation. In particular, *Ra* increased for increasing pulse fluence and decreasing scanning speed [24]. Thus, as an overall assessment, it is possible to conclude that increasing the pulse fluence and decreasing the scanning speed may lead to increased wettability due to a synergic contribution of the surface topographical changes. The drastic change between the as-received contact angle and that which measured for the treated surface highlights the effectiveness of the treatment.

In order to verify a possible correlation between the contact angle of the Titanium samples and that of the PA2200 after stamping, the replica process was performed for all the treated specimens and the resulting contact angles were probed.

Figure 4 reports a SEM image of the polymer prior stamping. It is worth noting that such material was obtained by additive manufacturing, and thus it was rough and porous as a result of the manufacturing process.

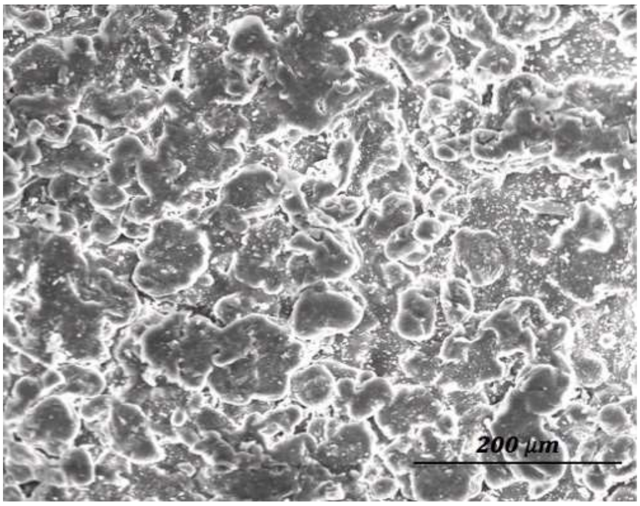


**Figure 4.** SEM of as received (AR) PA2200.

Thus, when such material needs to be employed for biomedical applications, a series of post processing is needed in order to make the surface suitable for the use in the human body environment [26]. Figure 5 reports the measured contact angle of the molded PA2200. It is worth noting that the stamping process itself led to a modification of the contact angle from the titanium to the polymer substrate. Also, since the latter surface is the negative of the original titanium one, the contact angle resulted in being different to that measured for any titanium sample.

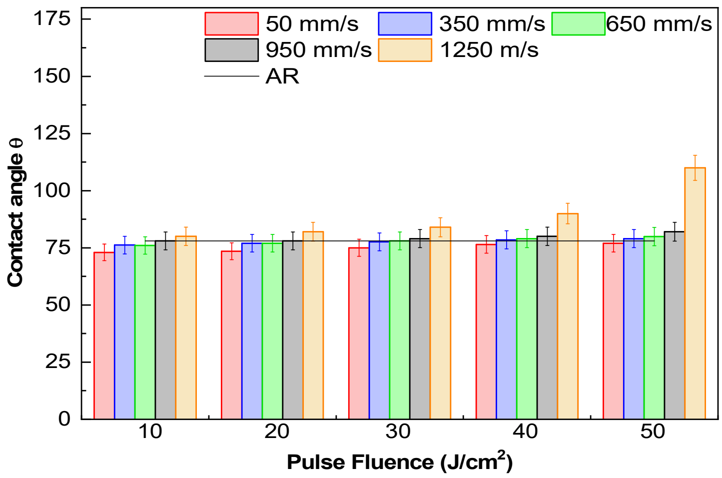


**Figure 5.** Measured contact angle of PA2200 obtained by stamping of Titanium samples.

However, the contact angle of the stamped polymer indicates a relationship with the contact angle of the original Titanium samples. In particular, the lower contact angles obtained by a sufficiently deep surface on Titanium samples generated the textured surface on PA2200 with the higher contact angle.

In particular, for low fluence and speed, the surface was not sufficiently modified to lead to a significant change in the contact angle. On the contrary, at higher pulse fluence and speed, it was possible to fabricate an efficient die leading to an important change in the PA2200 surface contact angle.

Thus, the surfaces with repeatable structures (e.g., homogeneous periodic textures) and deeper surface modifications (lower contact angle) were selected. The higher scanning speed was preferred since it led to higher production rate while the fluence level was selected to be 40 and 50 J/cm$^2$.

Figure 6 reports the obtained surfaces on PA2200 named Texture 1 and Texture 2, by the selected Titanium masters (Ti-24 and Ti-25, respectively).

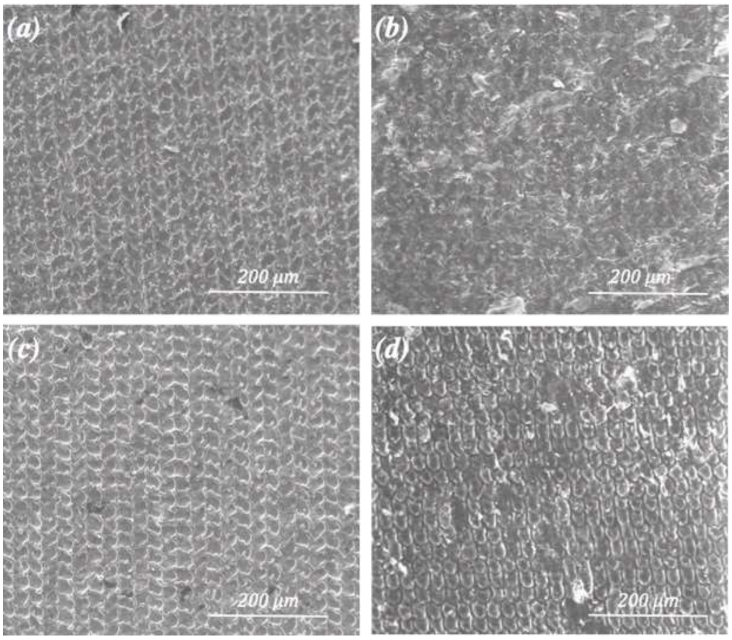


**Figure 6.** Surface topography of Titanium at (**a**) 1250 mm/s and 40 J/cm$^2$ and (**c**) 1250 mm/s and 50 J/cm$^2$ used for the replica on PA22000 (**b**,**d**), respectively.

In particular, the surfaces with the deeper holes were selected as dies and the resulting contact angle over the nylon samples was recorded to be 78° for the AR, 90° and 110° for Texture 1 and Texture 2, respectively. It is worth noting that the surface obtained by the replica of Titanium alloy processed at 40 J/cm$^2$ and 1250 mm/s (Ti-24) resulted in a nonperiodic pattern over the PA2200. This result is due to the small depth of the hole imprinted over the Titanium. In fact, the surface of Texture 2 led to better results in terms of surface texture and pillars height. The contact angle of the latter surface drastically increased reaching values of a hydrophobic surface.

The last test performed over the PA2200 samples was the bacteria adhesion test. In medical areas where intrusive nonbiological surfaces are present, the adhesion of blood cells or bacteria can cause serious problems. Examples of such solid surfaces include joint prostheses, heart valves, vascular catheters, contact lenses and dentures. Figure 7 shows the adhesion results proving the reduced amount of bacteria left for the textured surfaces as a consequence of the increased hydrophobicity of the material.

The overall bacteria adherent to the AR was measured to be about the 50% of the total surface area, while it considerably decreased by up to 15% for Texture 1 and 2% for Texture 3. These results highlight the possibility of using the proposed methodology in an industrial context. In fact, the proposed process is easily integrable in a manufacturing line. Also, the process is safe and fast leading to a significant reduction in production time.

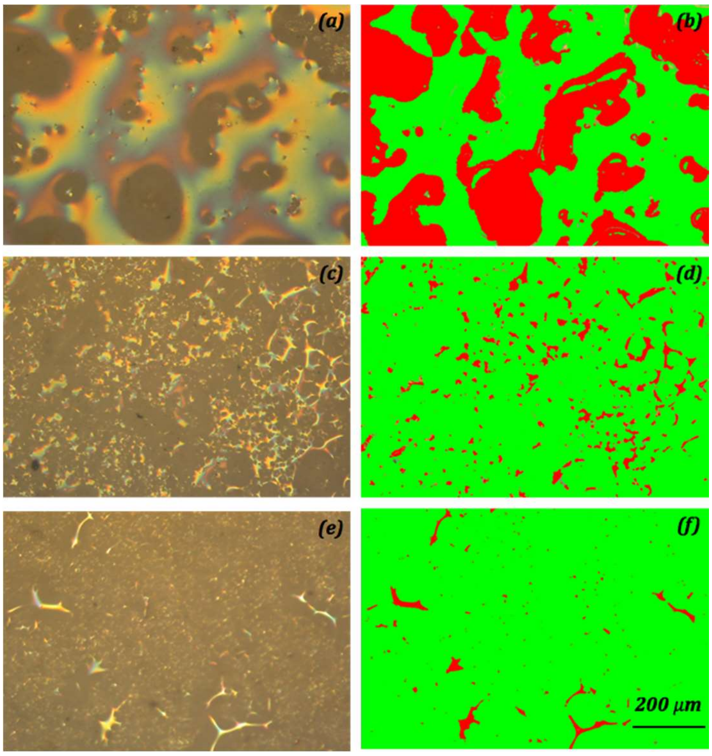


**Figure 7.** Optical microscopy and processed images for adhesion counting for (**a**,**b**) AR, (**c**,**d**) Texture 1 and (**e**,**f**) Texture 2 surfaces.

## 4. Conclusions

This paper presents an easy, rapid and economic way to manufacture microscale surface patterning over polymeric materials for modified wettability and adhesion. The experimental results demonstrate the effectiveness of the developed methodology to properly texture PA2200 for increased hydrophobicity and bacteria adhesion. In particular, a two-step methodology was employed. The desired texture was obtained by laser ablation of Titanium samples and then replicated over the PA2200 by an in-house hot stamping procedure involving the selection of a proper pressure and temperature. The overall process led to high production rate without involving the use of environmental or health hazards. The overall results show a drastic reduction of bacteria adhesion corresponding to an increased hydrophobicity of the surface. In particular, different texture of the metal led to a different polymer performance. Future works will involve the creation of sub-micro and nano-scale modifications and more complex patterns (such as hierarchic structures) able to generate high performance surfaces with different physical properties.

**Author Contributions:** Conceptualization, G.R. and A.D.P.; methodology, G.R. and M.M.; software, G.R.; validation, D.U. and M.M.; formal analysis, G.R., M.M. A.D.P., D.U.; investigation, G.R.; resources, D.U. and M.M.; data curation, G.R., D.U., M.M., A.D.P.; writing—original draft preparation, G.R.; writing—review and editing, G.R., D.U., M.M., A.D.P; visualization, G.R., D.U., M.M., A.D.P.; supervision, D.U. and M.M. All authors have read and agreed to the published version of the manuscript.

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