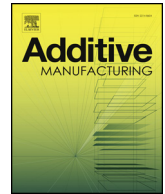




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Environmentally benign metallization of material extrusion technology 3D printed acrylonitrile butadiene styrene parts using physical vapor deposition

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ABSTRACT

Metallization has been widely used to enhance the aesthetics and performance of injection molded plastic parts, but the techniques have not been widely extended to 3D printed parts due to intrinsic differences in surface chemistry and morphology. Here, we investigate direct metallization of acrylonitrile butadiene styrene (ABS) 3D printed thermoplastic parts using low cost environmentally benign surface preparations and physical vapor deposition (PVD) to avoid the use of preparation with toxic chromic acid. Fourier transform infrared (FTIR) spectra are gathered for each surface preparation method prior to metallization. The metallized parts are then characterized for thin film adhesion, electrical resistivity, and optical reflectivity. Additionally, each part is imaged using a scanning electron microscope (SEM) post-metallization. The results show that surface preparation with solvent results in a smooth and aesthetically pleasing surface, but metallic film adhesion is poor. Conversely, when 2000 grit sandpaper is used to mechanically prepare the surfaces, the resulting films have poor electrical conductivity and optical reflectance, but excellent adhesion. Atmospheric plasma treatment of the parts results in the highest overall performance, with superior adhesion strength and optical reflectivity and low electrical resistivity. Electron microscopy and FTIR reveal that the high adhesion resulting from atmospheric plasma is caused by modification surface morphology, but not surface chemical termination. The results indicate that direct metallization of 3D printed ABS is a viable method for creating metallized parts with high performance and an aesthetically pleasing appearance and that the use of chromic acid in surface preparation is not necessary.

1. Introduction

Many objects encountered daily include metal coated plastic parts or pieces. A majority of these parts are fabricated using injection molding and are subsequently metallized using electroless and electroplating methods [1]. However, the practice of electroless plating of non-conductive parts is recognized as a tremendous environmental hazard due to the use of chromic acid in essential surface etching steps [2]. Recently, the use of physical vapor deposition (PVD) metallization of injection molded parts has expanded in industry as an alternative to metallization methods that use chromic acid, which is a known irritant and carcinogen, and other toxic chemical solutions [3–8]. The advent of 3D printing has provided the opportunity to rapidly produce thermoplastic prototypes. Soon, this technology may transition to the mainstream of manufacturing and eventually compete alongside injection molding [9–11]. For 3D printing and additive manufacturing to reach a competitive level with existing methods, 3D printed parts must have the same functional and aesthetic qualities as their conventionally

manufactured counterparts. The utilization of material extrusion technology such as 3D printed ABS parts are among the most commonly created to date due to the low capital cost and relatively high part quality. However, 3D printed ABS parts have inherently different surface morphology from injection molded parts due to many factors such as but not limited to the resolution with which a 3D printer can print, layer thickness, and roughness of the nozzle interior [12,13]. Due to intrinsic porosity, these parts can also absorb significant fluid volume when submerged [14]. Taking this fluid uptake and plating fluid toxicity into account, electroless plating is non-ideal for the metallization of 3D printed ABS [15,16]. PVD offers an alternative to solution based metallization as it has a minimal environmental footprint, which results in lower processing costs at scale, and has no issues of liquid uptake. The combination of the additive methods of material extruded 3D printing and subsequent PVD metallization offers a path to the future of additive manufacturing of functional parts which can compete with their conventionally manufactured counterparts.

Although ABS plastic has a higher surface energy than other

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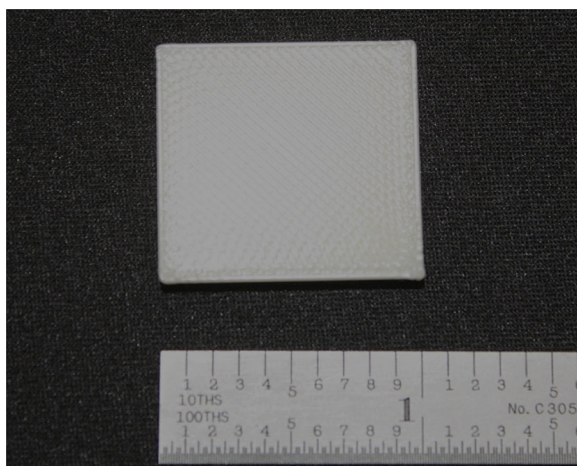


Fig. 1. Testing Coupons. 2.54 cm by 2.54 cm testing samples prior to surface treatment.

plastics, such as polyethylene, it is shown to lack critical surface adhesion strength without prior surface treatment for conventionally manufactured samples [17]. Due to intrinsic differences in surface morphology, it is unclear if the same holds true for 3D printed ABS. Further, it is unknown if the major factor influencing adhesion to ABS parts from the chromic acid etch is the modification to surface chemistry or to surface morphology. Here, using environmentally benign techniques, we also aim to decouple the effects of modification to surface morphology and to surface chemistry and determine if either, both, or neither are necessary for the adhesion of metallic films to 3D printed ABS.

2. Methods

The testing samples consisted of ABS plastic test coupons printed into 2.54 cm by 2.54 cm squares using solid fill and identical 45-degree print orientation and raster, show in Fig. 1 [18]. Samples were printed using a Stratasys Uprint SE desktop 3D printer utilizing ABS-P430™ XL Model (Ivory) material on SR-30™ XL Soluble Support material with a 0.254 mm layer thickness. Ten samples were printed for each type of surface treatment, including the control group.

2.1. Surface treatments

The control group of samples were printed and subsequently vacuum metallized without intermittent handling. The acetone vapor treatment consisted of samples suspended approximately 10 cm above 100 mL of commercial grade acetone (Klean Strip Co.) held within a 1000 mL beaker heated to 90 degrees Celsius for 30 min (Fig. 2). To prevent the acetone vapor from escaping the beaker, it was loosely sealed with aluminum foil. The samples were then dried in suspension for 1 week (168 h) at room-ambient conditions before metallization. The acetone dip was performed by submerging both sides of the test sample in acetone for five seconds before being suspended to dry in room-ambient conditions for 1 week (168 h) prior to metallization. The abraded samples were subjected to 1 min of manual sanding with 2000 grit sandpaper and subsequently rinsed with deionized water to remove any accumulated residue. Samples were subsequently allowed 24 h of drying time in order to allow any deionized water absorbed into the ABS to evaporate. The final group of samples were surface treated via atmospheric plasma generated with a commercial hand-held plasma etcher (Plasma Etch Inc. PW-16-5513). The plasma etcher was swept across each sample for approximately 60 s post print and again for 60 s immediately before metallization providing a clean deposition surface.



Fig. 2. Acetone Vapor Suspension. Acetone vapor surface treatment setup, showing the sample coupons suspended in a 1000 ml beaker with 100 ml of acetone at the base.

2.2. FTIR characterization

Following each surface treatment, FTIR spectra were gathered immediately for a representative sample of each test group using a PerkinElmer Spotlight 400 FTIR Imaging System (product number L1860116), operating a resolution of 1 cm^{-1} and using the accumulation of 32 scans. The spectra were analyzed for any changes in peak intensity and/or location to quantify the effects of the surface preparations on chemical termination [19].

2.3. PVD metallization

All samples were metallized using thermal evaporation PVD [20]. The vacuum chamber used was a stainless-steel tank that is approximately 40-cm tall and 25 cm in diameter. The source material used was, 99.99% Cu and 99.995% Cr (Kurt J. Lesker, Jefferson Hills, PA, USA), and was placed in a tungsten bowl in the thermal evaporation source located at the base of the vacuum chamber. For deposition at 5×10^{-3} Pa, a roughing pump was activated for 5 min to reach a roughing pressure of 1×10^{-1} Pa then the high vacuum stage was reached through using a turbomolecular pump for 30 min. The metallization process was undertaken without breaking the high vacuum stage. A 10 nm Chromium adhesion layer was deposited prior to a 1000 nm layer of Copper, without breaking vacuum between layers. All Samples were metallized at a deposition rate of approximately 10 Å/s, monitored with quartz crystal microbalance [21]. Deposition rates from 1 Å/s to 10 Å/s were tested and the impacts on adhesion strength were deemed statistically insignificant. The resulting metallized samples are shown in Fig. 3.

2.4. Characterization

Following metallization, samples from each test group were imaged using an FEI Quanta 200 scanning electron microscope at varied magnifications. Images were taken using an accelerating voltage of 15 kV, a spot size of 4.0, and a working distance of 10 mm. One additional set of samples were imaged prior to metallization but after surface preparation using 25 nm of Cr as an imaging aid.

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