3D Printed Superhydrophobic Structures for Sustainable Manufacturing Benefits: An Overview

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Abstract

Superhydrophobic properties have been present in nature for many millennia before human beings discovered their true capabilities and utilized them to revolutionize modern societies. The most familiar form of hydrophobicity found in nature is that of the lotus leaf, where its ultra-low water adhesion and self-cleaning properties make it one of the best hydrophobic elements formed naturally. Since its discovery, artificially created superhydrophobic elements have been used in many industries—maritime, automobile, and medical—due to their self-cleaning, antibacterial, and corrosion-prevention properties. However, for a surface to become superhydrophobic, it must possess a greater roughness. To achieve this, microscopic- or nanoscopic-level modifications must be made to the surface through various experimentations. For a surface to be considered superhydrophobic, it must have a water contact angle greater than 150°. One cost-effective method of manufacturing superhydrophobic materials is three-dimensional (3D) printing (additive manufacturing), which has been gaining popularity in the recent past. A 3D printing design is initially created using computer-aided design (CAD) software. Then, the design information is transferred to a 3D printer through digital slicing of the CAD design. 3D printing allows the printing of objects with various functionalities at pre-designed locations in the object, so it is important to investigate these phenomena. This paper provides an overview of several studies that were conducted to achieve superhydrophobicity through the 3D printing process. The following section of the manuscript includes an introduction, literature review, methods of increasing surface roughness for superhydrophobicity, market-available 3D printing materials, and their applications, discussion on 3D printing technologies and concluding remarks.

Keywords: Superhydrophobicity, surface structure, additive manufacturing, topography

1. Introduction

Superhydrophobicity has been gaining recognition during the past few years, especially since the Corona Virus pandemic of late 2019. From the beginning of the pandemic, researchers and companies across the world have been working relentlessly to develop new remedies and materials that could save thousands of lives from the grips of the virus. Superhydrophobicity is one such phenomenon that could be implemented in the creation of microbe-resistant materials. The best instance of naturally occurring superhydrophobicity can be found in the lotus leaf. For a surface to be classified as superhydrophobic, it

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must possess a water contact angle greater than 150° (Uddin et al., 2021). To achieve this state, alterations must be made on a surface at a microscopic/nanoscopic scale through various techniques that lead to greater surface roughness which in turn increases the hydrophobicity. Superhydrophobic materials are sought after in many industries—automobile, naval, aerospace, and biomedical—due to their many desirable properties. These properties include antibacterial, corrosion-resistant, de-icing, drag reduction, and self-cleaning, and they mainly arise due to the water-repelling characteristics of superhydrophobic materials (Ijaola et al., 2020).

Consequently, superhydrophobic materials can be an asset in the medical field. For instance, equipment such as surgical masks, surgical gloves, and other surgical tools could be manufactured using superhydrophobic material, thereby preventing the buildup of dirt and microbes on their surfaces, which is of paramount importance to patients and health care workers (Subeshan et al., 2021). Also, parts of ships created using superhydrophobic materials could help reduce or prevent corrosion, which is crucial in salty environments. Moreover, superhydrophobic coatings can reduce a ship's drag forces, which occur as the result of friction generated between a moving ship and water, thereby slowing its speed. Superhydrophobic materials are also extensively used in the aerospace industry (Subeshan et al., 2022). Composites comprised of aluminum and superhydrophobic coatings are employed to manufacture planes since they assist in the prevention of ice buildup in airplane parts, such as wings, which can have catastrophic consequences during mid-air flight maneuvering (Baddam et al., 2021). In addition, superhydrophobic coatings are used in such automobile parts as windscreens and mirrors to protect against water droplet buildup during extreme weather. One low-cost and efficient method to produce superhydrophobic materials is through three-dimensional (3D) printing (additive manufacturing).

2. Literature Review

Yang et al. (2020) devised an experiment to enhance the hydrophobicity of polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS). They managed to form hydrophobic coatings on parts of PLA and ABS through the fused deposition modeling (FDM) of 3D printing. Later, the hydrophobicity and surface roughness of the samples created, along with the effects of the 3D printing parameters on the samples, were measured. Based on the results, they concluded that the surface roughness of the 3D-printed samples was notably affected by the filling method and layer thickness. They also found that surface roughness was not affected by the printing speed. Additionally, the wettability of the samples was determined through an orthogonal experiment analysis technique, and the maximum observable water contact angle was 104.6° at a maximum sample layer thickness of 0.25 mm (Yang et al., 2020).

Lee et al. (2019) succeeded in creating superhydrophobic surfaces through the 3D printing technique. In this experiment, samples containing surface structures of various patterns were produced through an FDM 3D printer using a polylactic acid (PLA) filament. Later, the samples were dip-coated in methyl ethyl ketone and hydrophobic silica nanoparticles to form hydrophobic coatings that possessed nanoscale structures. The wettability of the samples was then determined, and a maximum water contact angle greater than 150° was observed.

Kaur et al. (2020) achieved superhydrophobicity through the digital light processing (DLP) method. They initially created a unique ink composed of photocurable acrylates and dispersed silica nanoparticles to produce objects with specific microstructures. The sample surfaces consisted of several micron pillars immersed in submicron hydrophobic particles. During experimentation, it was discovered that superhydrophobicity was achievable for certain dimensions within the structure, and the greatest superhydrophobicity was attained at pillar side lengths less than 100 µm, interpillar spacings ranging from 200–300 µm, and a height four times the side length. A floating test was conducted to further confirm superhydrophobicity. This was carried out by submerging superhydrophobic and non-superhydrophobic samples in water. Here, the superhydrophobic sample floated to the top, while the non-superhydrophobic sample remained submerged at the bottom, thus proving superhydrophobicity. Finally, wettability testing revealed a water contact angle of 155° at a side length of 70 µm and an interpillar spacing of 300 µm.

Yang et al. (2018) managed to obtain superhydrophobicity through the immersion surface accumulation process (ISAP). Initially, superhydrophobic, microscopic, artificial hairs consisting of eggbeater-shaped heads were formed via the ISAP process. Multi-walled carbon nanotubes were then added to improve the surface roughness and mechanical strength of the resin. During testing, it was discovered that hydrophilic surfaces could mimic hydrophobic surfaces under the correct microstructural features. Wettability tests were then conducted, and a water contact angle of 170° was achieved.

Kang et al. (2019) fabricated superhydrophobic surfaces through the FDM process. A PLA mold was initially created using several printing angles ranging from 0° to 90° and a low printing resolution of 400 µm. The mold was then utilized in the surface casting of polydimethylsiloxane (PDMS) polymers with waveform patterns. Finally, water contact angle testing revealed a water contact angle of 160° at a printing angle of 70°, which was a 52.3% percent increase in the water contact angle when compared to a flat-surfaced PDMS polymer.

Zhang et al. (2020) created 3D polytetrafluorethylene (PTFE) microstructures and tested them for superhydrophobicity. Initially, PTFE nanoparticles were mixed in a photocurable solution of polyethylene glycol diacrylate, and the mixture was used to create a predefined microstructure through 3D microprinting. The microstructure was fabricated one layer at a time through exposure to ultraviolet (UV) lithography. The samples were then sintered to remove any impurities and obtain pure PTFE. Finally, wettability testing revealed a water contact angle of 151.8°, thereby confirming superhydrophobicity.

He et al. (2017) constructed superhydrophobic surfaces with the aid of a homemade 3D printer. Here, a polydimethylsiloxane ink was used to etch various geometric patterns onto a glass substrate. During experimentation, it was discovered that by adjusting the 3D printing parameters such as filament spacing and printing speed, it was possible to achieve superhydrophobic structures. Later the printed structures were peeled off the substrate, and their water contact angles were tested. Results indicated that a water contact angle of 154.9 °was achievable at a filament spacing of 0.80 mm and a printing speed lower than 1.0 mm/s.

Yuan et al. (2017) were able to achieve superhydrophobicity through a combination of techniques such as 3D printing, solution immersion, and heat treatment. Initially, polysulfone (PSU) membranes were formed via 3D printing. These PSU membranes were then immersed in a solution containing candle soot (obtained by scraping a burned metal plate) and hexane, and then mixed in a sonicator. These membranes were placed in an oven for 10 min at 60°C to remove any hexane on the surface. Later, they were rinsed again in hexane to remove any excess soot particles and further dried. Finally, the water contact angle was measured, revealing 161°.

Laser-induced breakdown spectroscopy (LIBS) is a kind of atomic emission spectroscopy that utilizes an intense laser pulse as the excitation source. Patole (2021) used LIBS to verify biofouling's elemental composition via examining the sample's spectral emission. Here, a 1 MHz femtosecond laser from Clark MXR was used. The biofilm samples were gathered by suspending Stainless Steel grade 316 plates with a depth of 1m in the field of Pascagoula Bay intended for 5, 10, 15, and 20 days. As a result, the significant elements visible in the LIBS spectra are Mg, Al, Ca, Si, Ba, Br, Fe, N, S, Na, and so. Additionally, this study will benefit in understanding the elemental composition of biofouling and work within the detailing of novel antifouling coatings (Patole 2021).

Figure 1 shows various methods to enhance surface hydrophobicity. Table 1 provides a summary of the literature review.

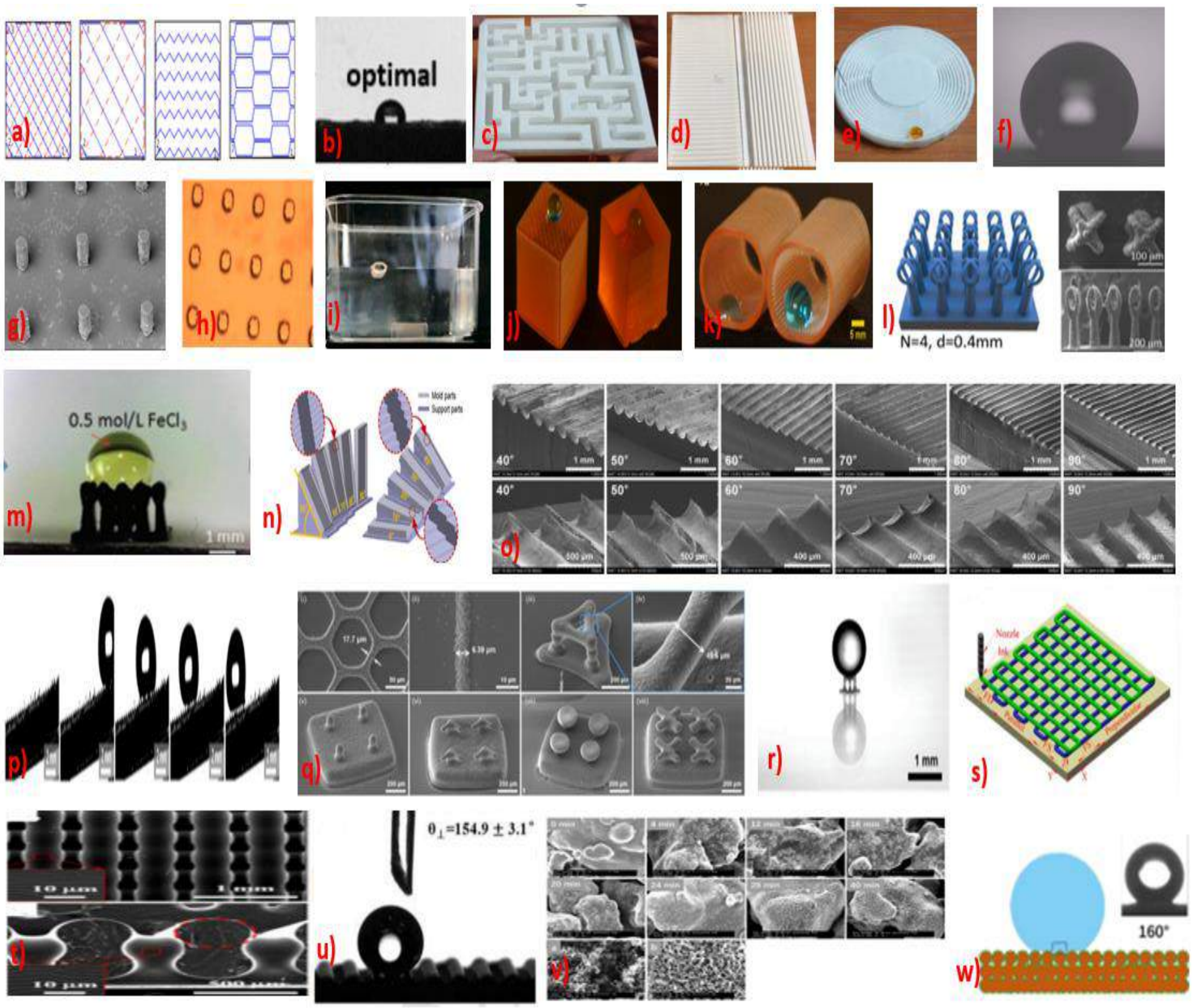

Figure 1: Various images revealing surface hydrophobicity: (a) various patterns of the filling method (left to right): rectilinear pattern, grid pattern, wiggle pattern, fast honeycomb pattern (Yang et al., 2020); (b) image of maximum water contact angle of 104.6° (Yang et al., 2020); (c,d,e) images of final product at various stages of experimentation (Lee et al., 2019); (f) maximum water contact angle of 161.5° (Lee et al., 2019); (g) scanning electron microscopy (SEM) image of micron pillars (Kaur et al., 2020); (h) optical microscope image of micron pillars (Kaur et al., 2020); (i) submersion test (Kaur et al., 2020); (j) cube-shaped superhydrophobic objects (left) and non-superhydrophobic objects (right) (Kaur et al., 2020); (k) cylindrical-shaped superhydrophobic objects (right) and non-superhydrophobic objects (left) (Kaur et al., 2020); (l) eggbeater-shaped structures (Yang et al., 2018); (m) maximum water contact angle of 170° (Yang et al., 2018); (n) CAD model of mold with various printing angles in experiment 5 (Kang et al., 2019); (o) SEM images of surfaces (waveform pattern) of PDMS polymers cast using PLA mold (Kang et al., 2019); (p) images of roll-off test conducted on PDMS polymer surface at printing angle of 70° (Kang et al., 2019); (q) SEM images of PTFE microstructures created via 3D printing (Zhang et al., 2020); (r) maximum water contact angle of 151.8° (Zhang et al., 2020); (s): 3D printing process (He et al., 2017); (t): SEM images at filament spacing of 0.60 mm (He et al., 2017); (u) maximum water contact angle of 154.9° [He et al., 2017); (v) SEM images of candle soot-coated PSU membranes (Yuan et al., 2017;) (w) maximum water contact angle of 160° (Yuan et al., 2017).

Table 1: Summary of Literature Review

References	Materials	Method(s)	Results WCA (°)	Bibliography
He et al., 2017	PDMS ink and glass substrate	3D printing	154.9	Fabrication of polydimethylsiloxane films with special surface wettability by 3D printing
Yuan et al., 2017	Polysulfone (PSU), hexane, and candle soot	3D printing, solution immersion, and heat treatment	161	Super-hydrophobic 3D-printed polysulfone membranes with switchable wettability by self-assembled candle soot for efficient gravity-driven oil/water separation
Yang et al., 2018	Resin and multi-walled carbon nanotubes	Immersion surface accumulation process (ISAP)	170	3D-printed biomimetic super-hydrophobic structure for microdroplet manipulation and oil/water separation
Kang et al., 2019	PLA and PDMS polymers	Fused deposition modeling (FDM)	160	Realization of superhydrophobic surfaces based on three-dimensional printing technology
Lee et al., 2019	PLA, silica, and methyl ethyl ketone	3D printing and dip coating	>150	Fabrication of superhydrophobic surface using FDM 3D printer with poly lactic acid (PLA) filament and dip coating with silica nanoparticles
Kaur et al., 2020	Photocurable acrylates, resin and silica nanoparticles	Digital light processing (DLP)	155	Fabrication of superhydrophobic 3D objects by digital light processing.
Yang et al., 2020	PLA and ABS	FDM and 3D printing	104.6	Preparation of hydrophobic surface on PLA and ABS by fused deposition modeling

References	Materials	Method(s)	Results WCA (°)	Bibliography
Zhang et al., 2020	PTFE and Polyethylene glycol diacrylate	3D-micro printing and sintering	151.8	3D µ-printing of polytetrafluoroethylene microstructures: route to superhydrophobic surfaces and devices
Dong, et al., 2021	Butyl acrylate (BA), lauryl acrylate (LA), and hexafluorobutyl acrylate/butyl acrylate (HFBA-BA) mixture	Digital light processing	152	3D printing of superhydrophobic objects with bulk nanostructure

3. Methods of Increasing Surface Roughness for Superhydrophobicity

3.1 Chemical Etching

The chemical etching process, shown in Figure 2, utilizes a strong chemical solution (etchant) to remove undesirable material from an object's surface via controlled dissolution, thereby creating a permanent-etched metal image. Through this process, surface roughness can be increased, thus giving rise to superhydrophobicity (Çakır et al., 2005)

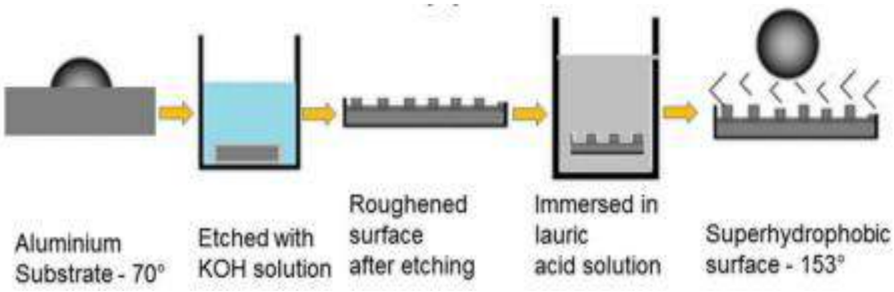

Figure 2: Chemical Etching Process (Varshney et al., 2016)

3.2 Solution Immersion

During solution immersion, as shown in Figure 3, a sample is immersed in a solution at room temperature for a certain time and dried. As a result, the surface roughness of the sample increases, creating superhydrophobicity (Wang et al., 2006).

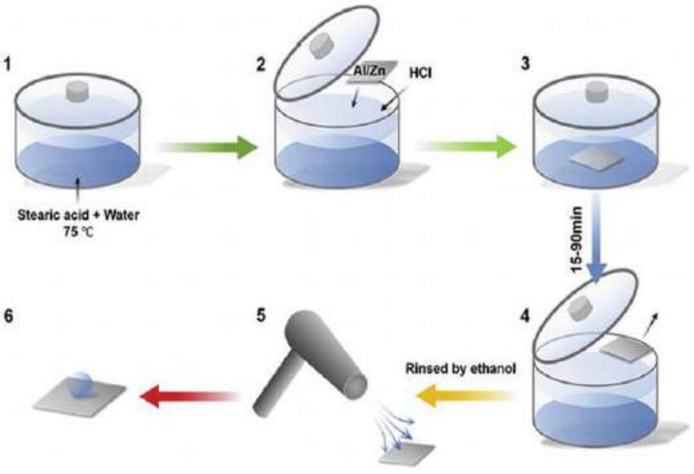

Figure 3: Solution Immersion Process (Ali et al., 2018).

3.3 Electrodeposition

The electrodeposition process, shown in Figure 4, creates a metallic coating through an electric current. The current is applied to a conductive material that is immersed in metallic salt, thus creating increased surface roughness and leading to superhydrophobicity (Liu et al., 2014).

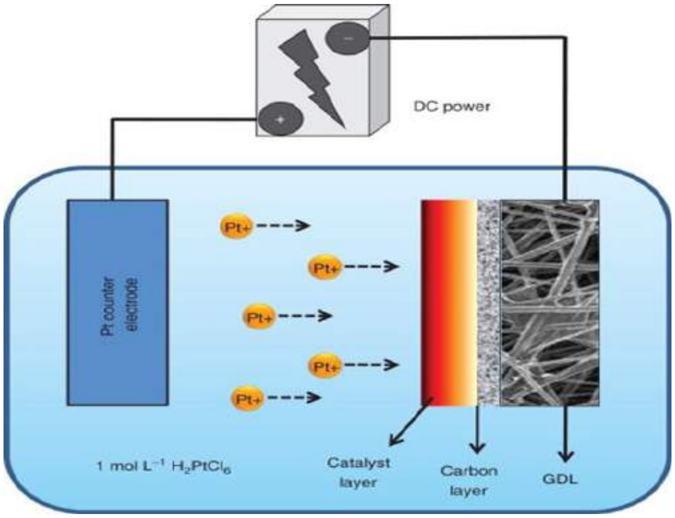

Figure 4: Electrodeposition Process (Liu et al., 2014).

3.4 Spray Coating

During spray coating, as shown in Figure 5, a stream of high-velocity particles in a molten or semi-molten state are deposited onto a substrate. This process has the ability to increase the surface roughness, thereby causing superhydrophobicity (Polizos, et al., 2018).

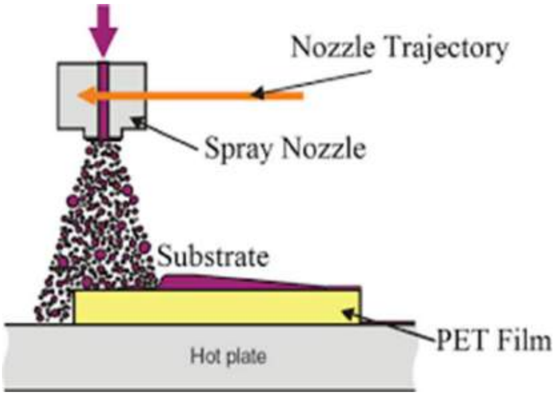

Figure 5: Spray Coating Process (Kooy et al., 2014)

The various methods of increasing surface roughness, discussed above, are commonly multi-stepped processes that require considerable time and resources. On the other hand, 3D printing (additive manufacturing) is a one-step process offering a faster and cheaper method of creating superhydrophobic surfaces with large surface roughness.

3.5 Digital Light Processing

DLP (Digital Light Processing) is a 3D printing innovation used to quickly create photopolymer parts. It's basically the same as SLA with one tremendous contrast where SLA machines utilize a laser that follows a layer, a DLP machine utilizes an extended light source to fix the whole layer on the double. The part is shaped layer by layer. DLP printing can be utilized to print very complex resin objects like jewelry and dental molds, toys and different things with fine subtleties. Since it restores the whole layer at once, it's a lot quicker than SLA (Mouzakis, 2018).

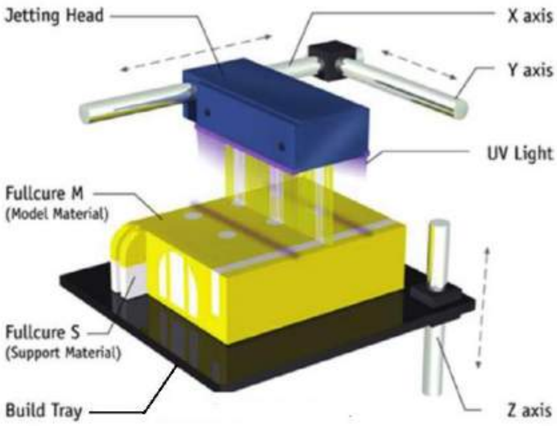

Figure 6: Digital Light Processing (Mouzakis, 2018)

4. Market-Available 3D Printing Materials and Their Applications

The 3D printing/additive manufacturing procedure uses a variety of techniques and materials that are currently available in the market to create a plethora of objects. One such technique is known as fused deposition modeling where materials such as thermoplastic filaments and continuous fiber-reinforced polymers are utilized in forming objects with a layer thickness of 20–100 µm, such as advanced composite parts and rapid prototyping toys (Ngo et al., 2018). Another method used to develop objects via 3D printing is the digital light processing method. Here, a light source is projected into a resin tank using a digital micromirror device to form a patterned layer on the bottom of it. This method cures the entire platform simultaneously, forming an object with a layer thickness of 140–150 µm, using resins rather than filaments in printing objects (Kaur et al., 2020). The DLP method could be further modified to achieve objects possessing augmented nanostructures with virtually unrestricted freedoms of geometry (Dong et al., 2021). During this technique, an ink comprising porogen solvents and monomers of hydrophobic (meth) acrylate experiences a phase separation through the photopolymerization stage of the DLP process, which leads to the production of superhydrophobic and nanoporous structures.

Additionally, the immersion surface accumulation process uses resins in creating objects and employes a similar process as that in the DLP method. This method is used to etch 3D-microscale patterns of a high resolution onto macroscale surfaces at a thickness of 140–150µm (Yang et al., 2018; Subeshan 2018).

5. Discussion on 3D Printing Technologies

Additive manufacturing (AM) offers great opportunities compared to other traditional manufacturing methods. With AM, the production of any part can be started immediately, saving time and money (Ford and Despeisse, 2016). It also allows for more complex components and almost total design freedom. This design freedom also reduces assemblies by producing complex parts without assembly steps, compared to traditional manufacturing methods, and obviously reduces material losses (Lynn et al., 2018). Although AM is a breakout technology that can change production in various industries, the introduction of this technology is still in its infancy, and there are several challenges to applying AM in a way that allows for its significant and rapid development (Tofail et al., 2018). Numerous studies have shown the many obstacles to faster adoption, the largest of which is the cost of both material and systems, as shown in Figure 7. AM polymers and metals are still five times more expensive than their counterparts (Jiménez, et al., 2019). In most cases, the selection of a part's material, in combination with the specific process to be used, determines the geometric limits of the part design.

Another challenge is the lack of design knowledge related to AM. After using almost the same injection molding or extrusion method for more than 60 years, it is essential to change the manufacturing thought processes and start to design for additive manufacturing (DFAM) (Lee et al., 2017).

Another major challenge AM faces is the limited technical knowledge of the designers. Since AM technology is relatively new to most designers, a general understanding of its design is lacking, which creates considerable confusion when using AM processes (Jiménez, et al., 2019).

3D printers can only produce objects that are smaller than the size of the printer casing, which limits the size of items that can be manufactured. In addition, although there are larger printers, they must be housed in a large enough space to accommodate their size (Jiménez, et al., 2019). Consequently, in most cases, components manufactured with AM require secondary operations to create corresponding surfaces, which increases the cost.

Compared to traditional mass production, AM mass production is relatively slow. There is no changeover time between AM production lines and production output trails compared to conventional mass production run times. If printer production time cannot be improved when large quantities are required, traditional production is the preferred production mechanism. AM technologies are most often used to adapt mass production because they offer the possibility of creating highly customized products with a limited inventory (Jiménez, et al., 2019).

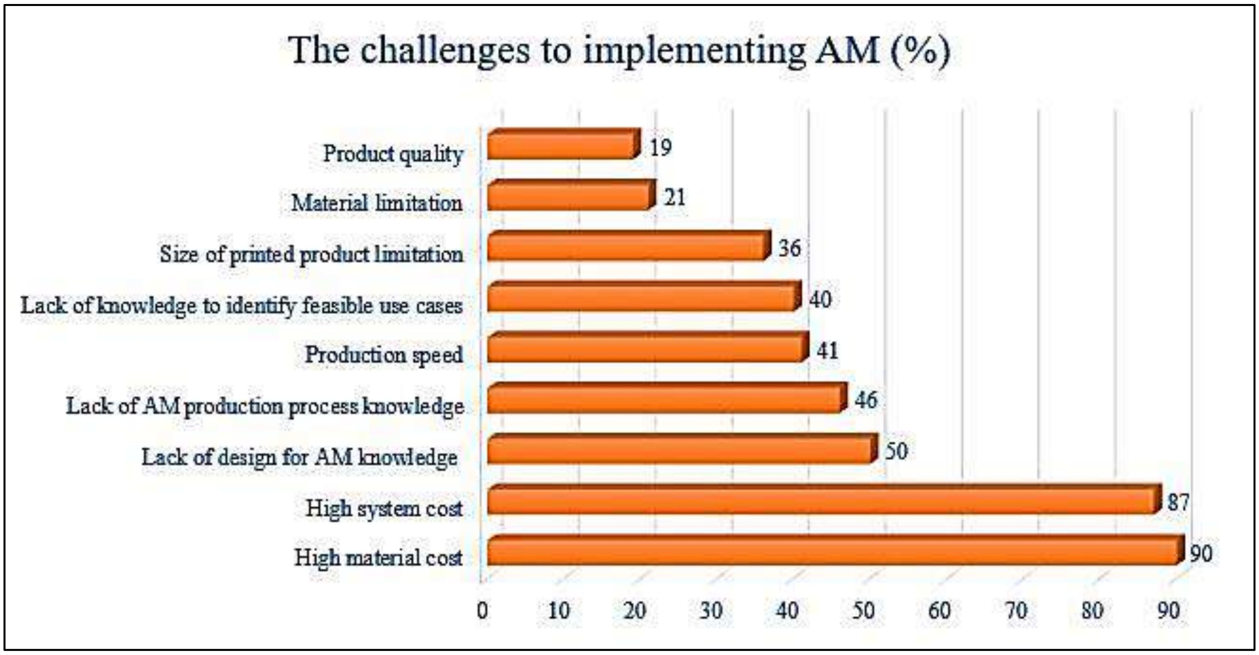

Figure 7: Most-recognized challenges to implementing AM.

5. Conclusions

This paper discusses several studies that were conducted to achieve superhydrophobicity via 3D printing. According to the research, it was evident that the digital light processing method is the best technique to produce superhydrophobic surfaces. The DLP method is much faster than the fused deposition modeling process since a single layer is cured instantly, unlike the FDM process which creates a single layer at a slow pace. The DLP method also produces objects with a greater resolution, which is not achievable via the FDM process, where accuracy is restricted due to nozzle size. Furthermore, the DLP method offers a smoother finish when compared to FDM. In subsequent testing utilizing 3D printing, eco-friendly chemicals and products could be used instead of the current chemicals and products, which are harmful to both human beings and the environment. Also, 3D printing could be used in the biomedical industry to create superhydrophobic surgical tools with favorable anti-bacterial and self-cleaning properties.

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