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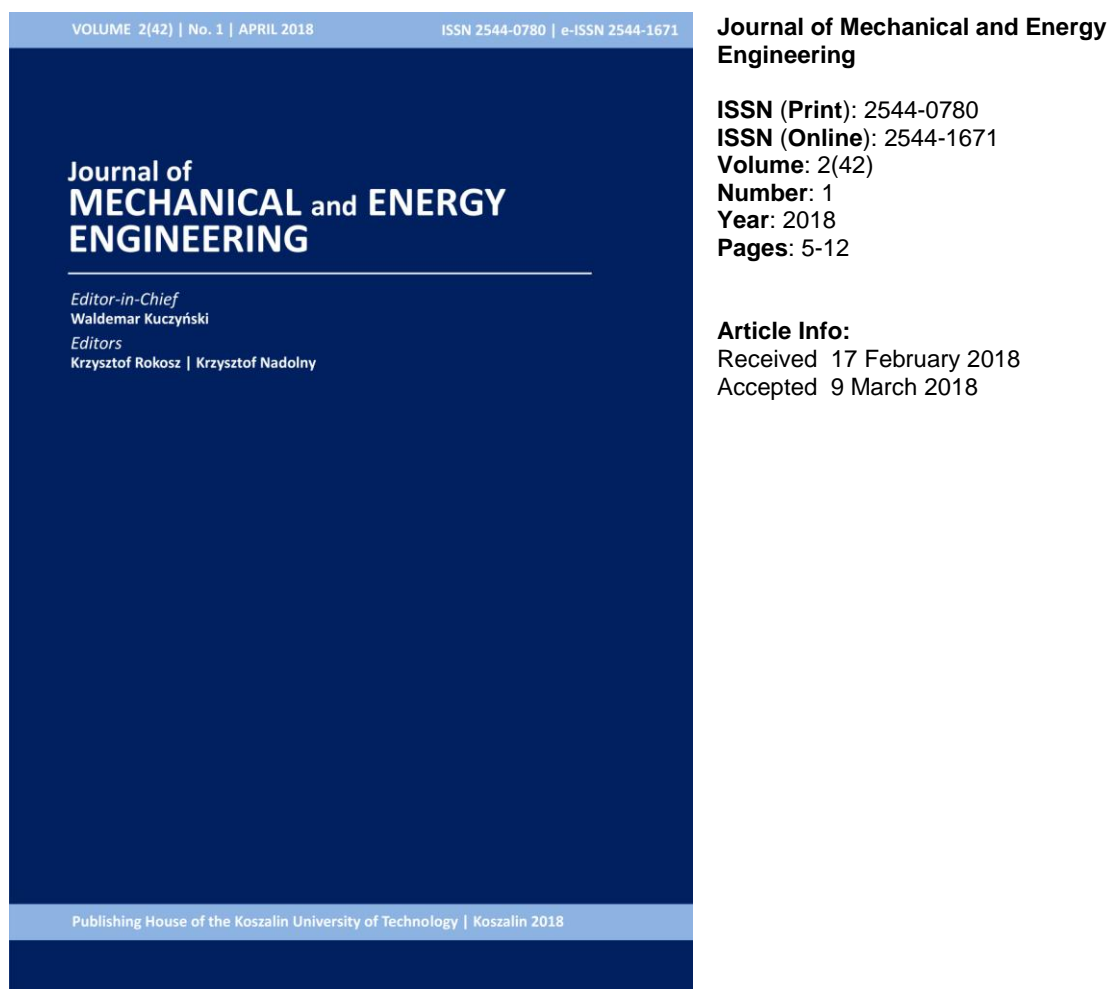
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CONTINUOUS LIQUID INTERFACE PRODUCTION (CLIP) METHOD FOR RAPID PROTOTYPING

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Abstract: Additive Manufacturing (AM) processes such as three-dimensional (3D) printing are one of the most important technologies of our century. Additive manufacturing is a manufacturing process in which 3D solid objects are created. It enables the creation of physical 3D models of objects using a series of an additive or layered development framework, where layers are laid down in succession to create a complete 3D object. Additive manufacturing is also known as 3D printing. The strongest reasons for the use of rapid prototypes in manufacturing are the production of parts with a small quantity or a complex shape, the obtaining of lighter parts, the prevention of waste of raw materials, a wider availability of testing and design and further personalization. Continuous liquid interface production (CLIP) is an alternative approach to AM by exploiting the basic principle of oxygen-impaired photopolymerization to create a continuous fluid interface of uncured resin between the growing section and the exposure window.

Keywords: rapid prototyping, additive manufacturing, continuous liquid, 3D printing, continuous liquid interface production (CLIP)

1. INTRODUCTION

Additive manufacturing is a rapid prototyping and formalization of terms commonly referred to as 3D printing. Rapid prototyping (RP) is used in various industries to describe an operation that is used to rapidly create a system or component representation before a final release or commercialization. In other words, this is an emphasis on a prototype or a basic model in order to create something quick and the outputs will be derived from more advanced models and ultimately the final product. Management consultants and software engineers also use the term of rapid prototyping to define a process that develops business and software solutions to allow customers and other stakeholders to test their ideas and to provide feedback throughout the development process. In short, the basic principle of this technology is called Additive Manufacturing (AM), which means that a model initially created using a three-dimensional Computer Aided Design (3D CAD) system can be manufactured without direct process planning. AM

technology significantly simplifies the production process from CAD data directly to complex 3D objects [2]. Additive manufacturing or 3D printing, is a growing field with selective layering of material to build a part with distinct advantages when compared to increased production. The benefits of additive on subtractive manufacturing are numerous and include an unlimited design area, the freedom of complex geometries and a reduction of waste by-products. An important development for AM in the 1980s was the development of a stereolithography (SL) device, a platform that uses an exposure of a rastering UV laser to selectively solidify a resin top-down manner during a photopolymerization process. [1]. The current additive manufacturing methods, such as fused deposition modeling, selective laser sintering and stereolithography, are extremely slow because they are based on layer-by-layer printing processes. In order for the additive production to be suitable for mass production, print speeds must be increased at least one level while maintaining excellent part accuracy. Although an inhibition of oxygen for free radical polymerization is a diffuse obstacle to photopoly-

merization of UV-curable resins in air, it shows how controlled oxygen inhibition can be used to provide easier and faster stereolithography [3].

2. CHARACTERISTIC OF RAPID PROTOTYPING METHODS

Three-dimensional printers based on the Fused Deposition Modeling (FDM) and Stereolithography (SL) technologies are the most widely used commercial 3D desktop printers. 3D printers allow researchers to quickly produce concept models and parts at a low cost and they allow multiple designs to rapid prototype in the comfort of their desk [4]. The method has since been modified to solidify in a process from the bottom-up using a digital light projection (DLP) chip that eliminates the rastering laser. The bottom up SL process begins with a computer-aided design (CAD) file, which is then transformed into a series of 2D rendering using a “slicing” method (Fig. 1a). Then, the original object is reconstructed in a layer-by-layer such that reproducing these 2D renderings a slice at a time. The SL file can then be interpreted and converted into a G-code (numerical control programming language) file containing information about the 2D horizontal cross-sections to print 3D copies of the 3D CAD model entered with the printer slicer software in a layer-by-layer fashion. The resolution of 3D printed objects can be changed by controlling the number of

triangulated sections [1, 4]. Whereby this process is repeated by selectively exposing a photo-active resin to UV light through a transparent substrate providing a selective photopolymerization corresponding to a particular slice shape. After an exposure of the slice, a series of mechanical step separation, recoating, and repositioning follow (Fig. 1b) to allow subsequent exposure [1].

Different types of multi-material 3D printers are available in the form of Fused Deposition Modeling (FDM), Stereolithography (SLA), Selective Laser Sintering (SLS) and syringe-based extrusion 3D printers. The types of commonly used 3D printing technologies are covered under the following four general headings: Material Extrusion, Photopolymerization, Powder Bed Fusion and Construction Printing [4]. Photopolymerization is an additive manufacturing process in which a liquid polymer is selectively cured by a polymerization process that is activated by a light source (most commonly a UV light source). Stereolithography forms 3D objects using UV curable photopolymer liquid resins. Similar to FDM printers, SLA printers (Fig. 2) create 3D objects in a layer-by-layer format. While a focused source of UV light cures the liquid resin in a layer-by-layer format, the construction platform of the printer slowly pulls the printed 3D object into the liquid resin bath by a distance equal to one layer thickness (ranging between 50 and 150 μm).

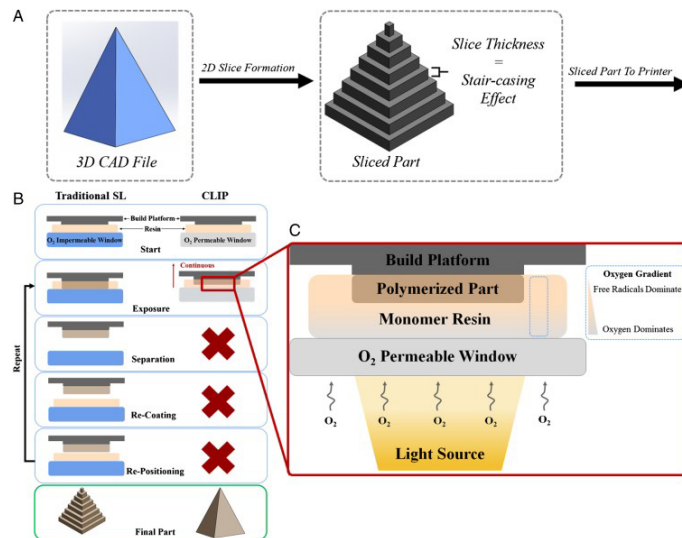


Fig. 1. Basic step comparison of SL to CLIP: a) producing and slicing a 3D CAD file are necessary steps for SL and CLIP platforms; b) traditional SL requires five fundamental steps to print a part: build elevator placement on resin (i), UV exposure to selectively cure resin (ii), separation of cured resin from the O₂-impermeable window (iii), mechanical recoating of resin (iv), and, finally, repositioning of the build elevator (v) to repeat the process until the part is fully printed – CLIP uses a constant liquid interface activated by the O₂-permeable window, which eliminates the need for steps (ii, iii and iv); c) schematic of the dead zone (DZ) produced in the presence of oxygen and the formation of free radicals when exposed to UV rays – inside of the DZ there exists a concentration gradient of O₂ whereas within the bulk there exist gradient light intensity and, to some degree, conversion before vitrification [1]

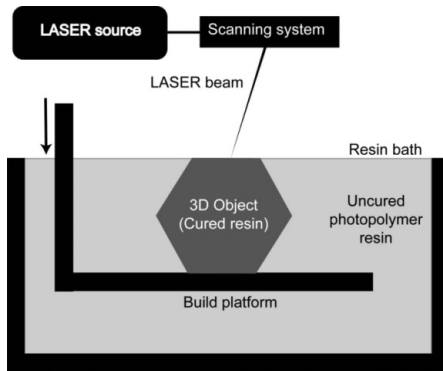


Fig. 2. Schematic representation of a typical SLA 3D printer that cures a liquid photopolymer resin by scanning a laser beam to build a 3D object [4]

The UV laser cures one entire 2D cross-section (of the final 3D object) based on the input 3D CAD model by scanning the laser along the 2D cross-section. After curing of a layer, a blade loaded with resin levels the surface of the resin to supply a uniform layer of liquid before the curing of next layer [4].

A relatively new derivation of SL technology is the Digital Light Processing (DLP) 3D printing, which uses a DLP projector light instead of a scanned laser for the photopolymerization of liquid resins. The biggest difference between SL and DLP 3D printing technologies is that in DLP printing the DLP projector cures one entire 2D cross-section in a single shot, and the laser needs to be scanned across the entire 2D cross-section in SL printing. Owing to this big difference, the speed of DLP 3D printers is much higher compared to the SL 3D printers. Similar to DLP-based 3D printing, Continuous Liquid Interface Production (CLIP) is a continuous 3D printing technology but makes use of a photochemical process that allows rapid printing of 3D objects, such as injection-molded objects with excellent mechanical properties, feature resolution below 100 μm , and surface finishing. UV Light is sent to the reservoir of the vulcanized resin with a liquid interface (known as the dead zone) containing 20-30 μm oxygen in the window through a window into a UV-curable resin reservoir through an oxygen permeable window, the resin hardening above the dead zone. As the 3D printing advances by pulling out the printed 3D part out of the resin bath, the resin flows underneath the curing resin, and maintaining a continuous liquid interface. The dead zone is formed due to the oxygen inhibition of the photopolymerization; allowing layer-less printing via simultaneous UV curing, resin renewal, and drawing out of printed object. CLIP 3D printing technology could draw 3D objects out of the resin at hundreds of millimeters per hour, so that objects could be fabricated in a matter of minutes

instead of a few hours [4]. Recently, continuous liquid interface production (CLIP) was introduced to overcome these inherent obstacles and to increase the adoption of AM. CLIP is based on the inhibition of free radical photopolymerization in the presence of atmospheric oxygen. Oxygen can quench either the excited-state photoinitiator or form a peroxide upon interaction with a free radical of a propagating chain. Thus, performing SL on an oxygen permeable build window results in the formation of a dead zone, or a region of an uncured liquid resin. Polymerization and solidification occurs once the O_2 has been depleted such that the kinetics of propagation ($k_p[\text{monomer}]$) are in a competitive balance with the kinetics of radical generation and subsequent O_2 inhibition ($k_i[\text{O}_2]$). The dead zone in the production process represents the uncured liquid layer between the growing part and the window and is the distinguishing difference between CLIP and traditional SL (Fig. 1b). As shown in Figure 1c, the presence of the dead zone allows, opposite to the separate steps of SL, part production, resin renewal and elevator movement at the same time. This mechanism eliminates the traditional resolution and speed of production trade-off because of the continuity of the manufacturing process. At the molecular level, the kinetic competition between oxygen inhibition and free radical generation, once reached, is maintained throughout the fabrication of the part. In traditional SL, all reactions are limited to the solidification of a single layer, which occurs over and over throughout the printing. Here, we show that the CLIP method of manufacturing parts provides monolithic production resulting in isotropic mechanical properties, and it enables a reduction of the staircasing effect without affecting the overall build time (Fig. 3) [1, 6].

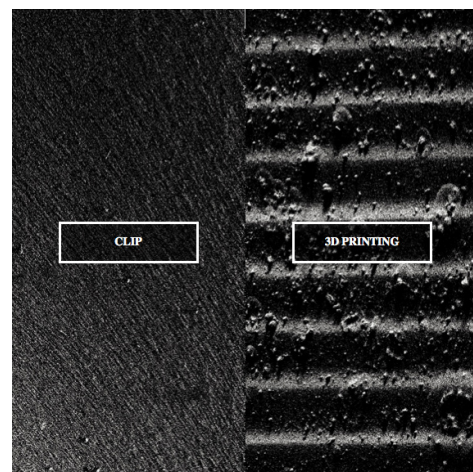


Fig. 3. Surface comparison with CLIP process and 3D printing [6]

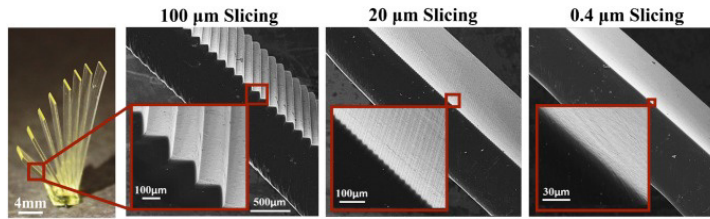


Fig. 4. Open book benchmark fabricated with changing slicing conditions – the ESEM micrographs obtained by imaging the 20° page of the open book benchmark under the three slice thicknesses [1]

Typically, oxygen inhibition leads to incomplete cure and surface stickiness when photopolymerization is conducted in air. Oxygen can either decompose the photoexcited photoinitiator or create peroxides by combining with the free radical from the photocleaved photoinitiator. If these oxygen inhibition routes are prevented, efficient initiation and propagation of polymer chains will be ensured. When stereolithography is performed on an oxygen permeable building window, continuous liquid interface production (CLIP) is achieved by creating a “dead zone” containing oxygen with a thin irregular liquid layer between the window and the cured part surface. We show that dead zone thicknesses on the order of tens of micrometers are maintained by judicious selection of control parameters (e.g., photon flux and resin optical and curing properties). Simple relationships define the dead zone thickness and the resin curing process and thereafter result in a direct relationship between the print speed and the part resolution [3].

3. THE MOST IMPORTANT FEATURES OF THE CLIP METHOD

The advantages of continuous production include especially the manufacture of layerless parts. These advantages allow manufacturing of large protrusions without the use of supports, a reduction of the staircasing effect without sacrificing manufacturing time, and isotropic mechanical properties. In combination, these advantages result in multiple indications of layerless and monolithic manufacture using CLIP technology.

The AM field has incorporated various benchmark structures to evaluate the performance of different platforms that vary depending on the aspect of the platform being probed. The open book benchmark was designed to assess a platform’s ability to print large overhangs at different angles with or without supports, alluding to the mechanical integrity of the final part. The open book benchmark was adapted for the CLIP platform and manufactured with a changing input slice thickness to isolate and minimize the observed staircasing effect. Due to the continuous nature of the resin renewal mechanism for CLIP, parts with different slice thicknesses (100, 20 and 0.4 μm) were manufactured with the same construction speed of 40

mm/hand and gave the same build time. By reducing the slice thickness, the smooth slope property of the open book can be better approximated, thus allowing to reduce the staircasing effect shown in Figure 4, independent of the traditional trade-off with build time. As the formation of the dead zone is kinetically driven, parameter optimization of light intensity, build speed, and weight percent UV absorber was required. In short, the cure thickness of the resin was calculated under static conditions using methods outlined in Tumbleston et al. to yield initial fabrication parameters.

Therefore, the resulting surface topology is imparted solely by the treatment of the CAD file, rather than the fabrication process itself. Moreover, the sloped “pages” of the open book are freely extending in space and are manufactured without supports, partly aided by the bottom-up build approach. Conventional AM approaches either lack chemical bonding between the layers or give mechanical strain to the part during the separation phase, thus preventing the fabrication of large protrusions without additional adjuncts in the form of supports. The continuity of the manufacturing provided by CLIP allows the staircasing effect to be reduced without affecting the build time, and becomes part of mechanical integrity to support large overhangs. Two “pages” of the open book were evaluated using optical laser scanning (OLS) noncontact profilometer imaging, shown in Figure 5, to quantify the change in surface topology with respect to changing slicing parameters. As a function of the slice thickness, a scanning laser was used to obtain the density profiles of the 20° page of the open book. The laser intensity corresponds to the part height where the darker regions are lower than the lighter regions. The total scanned length was kept constant [1].

Two parameters of surface roughness were used: arithmetical mean deviation (Ra) and mean length (RSm). The orientation of the slicing direction relative to the analysis direction indicates that the RSm parameter yields a frequency of length measurement and thus the distance between steps, whereas the Ra parameter specifies a mean depth of the steps. The illustrations of the two parameters applied to the 20° open book page are shown in Figure 6a.

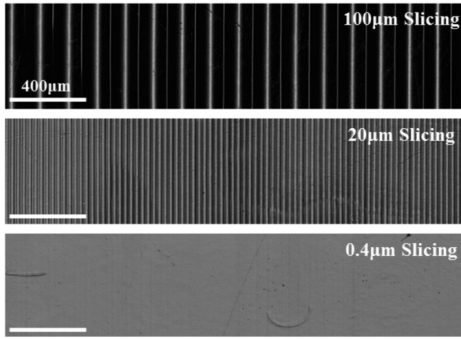


Fig. 5. OLS density images of open book criteria obtained by noncontact profilometry [1]

The R_a parameter was measured on both 90° and 20° pages to determine the effect of the slice thickness on the surface topology. For the monolithic nature of the part, the R_a of the 90° page surface should be independent of slicing when considering that the exposure frame has not changed during the manufacturing illustrated in Figure 6b. For both approaches, 20° should theoretically give similar surface effects. For this reason, the 90° page is the decisive feature between layered and layerless production due to dependence and independence on the input slice thickness [1].

Another one shows that tens of micrometers are guarded by careful selection of control parameters (eg. photon flux and resin optical and curing properties) of dead zone thicknesses. Simple relationships define the dead zone thickness and the resin curing process and thereafter result in a direct relationship between print speed and part resolution. We show that CLIP can be applied to various part sizes ranging from lower cut micro paddles with a root diameter of 50 mm to complex handheld larger than 25 cm [3].

The creation of an oxygen-inhibited dead zone forms the basis of the CLIP process. CLIP uses an amorphous fluoropolymer window (Teflon AF 2400) with excellent oxygen permeability (1000 barrers, 1 barrer = 10^{-10} cm³ (STP) cm cm⁻²s⁻¹ cmHg⁻¹), UV transparency and chemical inertness. Measurements of dead zone thickness using a differential thickness technique demonstrate the importance of both oxygen supply and oxygen permeability of the window in establishing the dead zone. Figure 7 shows that the dead zone thickness when pure oxygen is used below the window is about twice the thickness when air is used, with the dead zone becoming thinner as the incident photon flux increases. When nitrogen is used below the window, the dead zone vanishes. A dead zone also does not form when Teflon AF 2400 is replaced by a material with very poor oxygen permeability, such as glass or polyethylene, even if oxygen

is present below the window. Continuous parts production is not possible without a suitable dead zone.

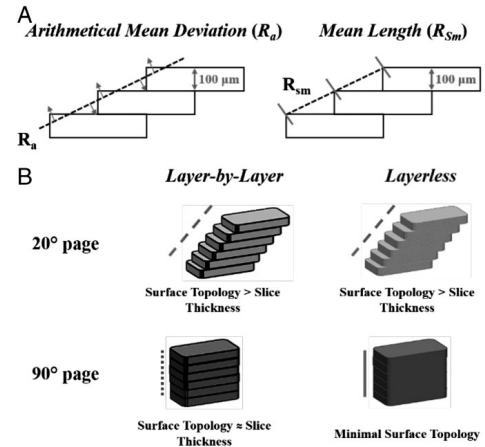


Fig. 6. Illustrations of the theoretical differences in the surface topology induced by the AM technique: a) an illustration of two surface roughness parameters used in topological analysis; b) theoretical surface topological effects given by a layer-by-layer (SL) and layerless (CLIP) manufacturing approaches [1]

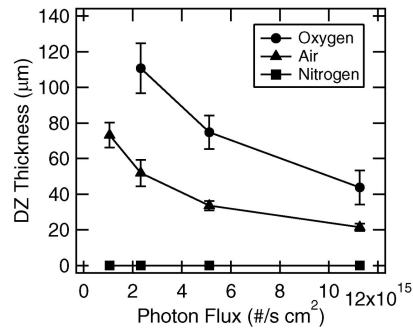


Fig. 7. The dead zone is created by oxygen permeation through the window [3]

For ambient air below the window, Figure 8a shows the dependence of dead zone thickness, photon flux (Φ_0), photo-initiator absorption coefficient (α_{pi}) and resin curing dosage (D_{c0}). These three control parameters depend on the dead zone thickness:

$$\text{Dead zone thickness} = C \left(\frac{\Phi_0 \alpha_{pi}}{D_{c0}} \right)^{-0.5} \quad (1)$$

where Φ_0 is the number of event photons per image area per time per field, α_{pi} is the product of photo-initiator concentration and wavelength dependent absorptivity, D_{c0} quantifies the resin reactivity of a monomer-photoinitiator combination, and C is a proportionality constant.

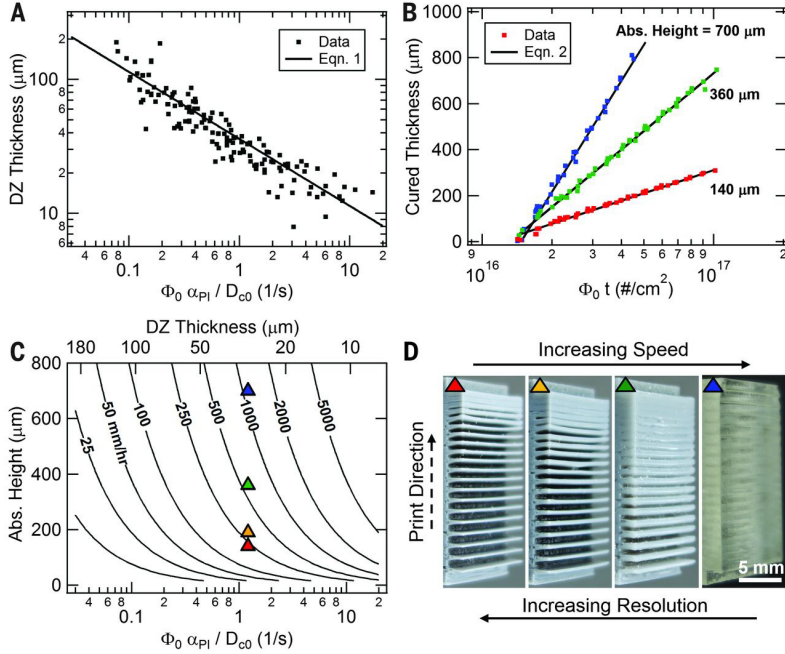


Fig. 8. A trade off exists between print speed and part resolution: a) liquid interface dead zone (DZ) thickness as a function of $\Phi_0 \alpha_{pl} / D_{c0}$; b) cured thickness as a function of UV photon dosage ($\Phi_0 t$) for three resins with different h_A controlled with dye loading; c) CLIP print speed contours as functions of h_A and $\Phi_0 \alpha_{pl} / D_{c0}$; d) photographs of resolution test patterns using resins with different h_A from Fig. 8b (colored triangles correspond to process conditions in Fig. 8c; the dye-free test pattern produced at highest print speed – blue triangle – is semitransparent) [3]

Above the dead zone, photopolymerisation takes place at a certain cured thickness, which depends on $\Phi_0 \alpha_{pl} / D_{c0}$ together with the exposure time (t) and the resin absorption coefficient (α) with respect to the bond:

$$\text{Cured thickness} = \frac{1}{\alpha} \ln \left(\frac{\Phi_0 \alpha_{pl} t}{D_{c0}} \right). \quad (2)$$

Figure 8b shows cured thickness for three different resins with varying α (holding α_{pl} constant) where the thicknesses were measured for different UV photon dosages (products of Φ_0 and t). These curves are similar to what is called “working curves” used in stereolithography resin characterization. For these resins, α is modified by adjusting the concentration of an absorber dye or a pigment that absorbs light passively (i.e. it does not produce radicals), but contributes to overall resin absorption via $\alpha = \alpha_{pl} + \alpha$ a dye. Note that α is the inverse of the characteristic optical absorption height (h_A) of the resin:

$$h_A = \frac{1}{\alpha}. \quad (3)$$

The model determines the slice thickness, projected pixel size and image quality as well as the h_A component value. The estimated pixel size (typically between 10 and 100 μm) and image quality indicate the functions of the display and the resolution of the

lateral part. As with the slicing thickness, h_A affects the vertical resolution, but the resin has a feature. If the h_A is high, the previously improved 2D patterns continue to be exposed, resulting in unintentional over-curing and “print-through”, which causes defects for the undercut and overhang geometries. From the dead zone thickness and hardened thickness expressions, a simple relationship between print speed, h_A (i.e., resolution) and $\Phi_0 \alpha_{pl} / D_{c0}$ is derived:

$$\frac{\text{Speed}}{h_A} \propto \frac{\Phi_0 \alpha_{pl} t}{D_{c0}}. \quad (4)$$

Figure 8c shows a contour plot of speed as a function of h_A and the ratio $\Phi_0 \alpha_{pl} / D_{c0}$; dead zone thickness is shown. For a given h_A , the speed can be increased by increasing the Φ_0 or the α_{pl} or by using a resin with a lower D_{c0} . However, as the speed increases, the dead zone thickness decreases and it will eventually become too thin for the process to remain stable. For CLIP, the empirically determined minimum dead zone thickness is ~ 20 to $30 \mu\text{m}$. Part production with a dead zone thickness below this minimum is possible but can lead to window adhesion-related defects. When the minimum dead zone thickness is reached, the print speed can be increased only by alleviating the resolution (i.e., using a resin with higher h_A).

4. CONCLUSIONS

In summary, CLIP uses oxygen inhibition to enable continuous fabrication that yields truly layerless parts. These parts have improved surface finish without sacrificing build time as well as isotropic mechanical properties enabling fabrication of large overhangs, as in the case of the open book benchmark. The ability to additively manufacture parts that are layerless and monolithic using CLIP is a key step for AM to move out of the realm of rapid prototyping and into manufacturing. The most important reasons for the use of rapid prototypes in the manufacturing field are the production of parts with a small quantity or a complex shape, the obtaining of lighter parts, the prevention of waste of raw materials, a wider availability of testing and design, and further personalization. 3D printing technologies offer exciting opportunities for rapid prototyping of complex and customized models at a low cost. CLIP has a potential to expand the benefits of additive manufacturing to many areas of science and technology, and to lower the manufacturing costs of complex polymer-based objects.

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Biographical notes



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Krzysztof Nadolny received his M.Sc. degree in Mechanics and Machine Design and next Ph.D (with honors) as well as D.Sc. degree in Machinery Construction and Operation from the Koszalin University of Technology, in 2001, 2006 and 2013, respectively. Since 2006, he has been a researcher in the Department of Production Engineering at the Koszalin University of Technology, where currently he works as an associated professor and the head of a research-didactic team for production planning and control. His scientific interests focus on problems concerning machining processes and tools, efficiency, monitoring and diagnostics of machining processes as well as tribology. He has participated in 2 international and 3 national research projects, presenting results of his work at 10 international and 21 national conferences, published more than 180 scientific papers in international and national journals, book chapters, as well as conference proceedings. He is also the author of 4 monographs and 9 national patents.

