Additive manufacturing has become a useful technique in a wide variety of applications, including do-it-yourself 3D printing (1, 2), tissue engineering (3–5), materials for energy (6, 7), chemistry reactionware (8), molecular visualization (9, 10), microfluidics (11), and low-density, high-strength materials (12–15). Current additive manufacturing methods such as fused deposition modeling, selective laser sintering, and stereolithography (2, 16) are inordinately slow because they rely on layer-by-layer printing processes. A macroscopic object several centimeters in height can take hours to construct. For additive manufacturing to be viable in mass production, print speeds must increase by at least an order of magnitude while maintaining excellent part accuracy. Although oxygen inhibition of free radical polymerization is a widely encountered obstacle to photopolymerizing UV-curable resins in air, we show how controlled oxygen inhibition can be used to enable simpler and faster stereolithography.

Typically, oxygen inhibition leads to incomplete cure and surface tackiness when photopolymerization is conducted in air (17, 18). Oxygen can either quench the photoexcited photoinitiator or create peroxides by combining with the free radical from the photoexcited photoinitiator (fig. S1). If these oxygen inhibition pathways can be avoided, efficient initiation and propagation of polymer chains will result. When stereolithography is conducted above an oxygen-permeable build window, continuous liquid interface production (CLIP) is enabled by creating an oxygen-containing “dead zone,” a thin uncured 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 describe the dead zone thickness and resin curing process, and, in turn, result in a straightforward relationship between print speed and part resolution. We demonstrate that CLIP can be applied to a range of part sizes from undercut micropaddles with stem diameters of 50 μm to complex handheld objects greater than 25 cm in size.

Figure 1A illustrates the simple architecture and operation of a 3D printer that takes advantage of an oxygen-inhibited dead zone. CLIP proceeds via projecting a continuous sequence of UV images (generated by a digital light-processing imaging unit) through an oxygen-permeable, UV-transparent window below a liquid resin bath. The dead zone created above the window maintains a liquid interface below the advancing part. Above the dead zone, the curing part is continuously drawn out of the resin bath, thereby creating suction forces that constantly renew reactive liquid resin. This nonstop process is fundamentally different from traditional bottom-up stereolithography printers, where UV exposure, resin renewal, and part movement must be conducted in separate and discrete steps (fig. S2). Even for inverted top-down approaches in which photopolymerization occurs at an air-resin interface (i.e., the part is successively lowered into a resin bath during printing (16, 19)), these steps must be conducted sequentially for the formation of each layer. Because each step takes several seconds to implement for each layer, and because each layer of a part has a typical thickness of 50 to 100 μm, vertical print speeds are restricted to a few millimeters per hour (16). By contrast, the print speed for CLIP is limited by resin cure rates and viscosity (discussed below), not by stepwise layer formation. For example, the gyroid and angle structures shown in Fig. 1B were printed at 500 mm/hour, reaching a height of ~5 cm in less than 10 min (movies S1 and S2). An additional benefit of a continual process is that the choice of 3D model slicing thickness, which affects part resolution, does not influence print speed, as shown in the ramp test patterns in Fig. 1C. Because CLIP is continuous, the refresh rate of projected images can be increased without altering print speed, ultimately allowing for smooth 3D objects with no model slicing artifacts.

Establishing an oxygen-inhibited dead zone is fundamental to the CLIP process. CLIP uses an amorphous fluoropolymer window (Teflon AF 2400) with excellent oxygen permeability (1000 barrers; 1 barrer = 10^-10 cm^3(STP) cm^-2 s^-1 cmHg^-1) (20), UV transparency, and chemical inertness. Dead zone thickness measurements using a differential thickness technique (fig. S3) demonstrate the importance of both oxygen supply and oxygen permeability of the window in establishing the dead zone. Figure 2 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 (see below). 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. Without a suitable dead zone, continuous part production is not possible.

For the case of ambient air below the window, Fig. 3A shows the dependence of dead zone thickness on incident photon flux (Φ0), photoinitiator...
absorption coefficient ($\alpha_{\text{反应}}$), and resin curing dosage ($D_\text{c0}$). These three control parameters are related to dead zone thickness according to

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

where $\Phi_0$ is the number of incident photons at the image plane per area per time, $\alpha_{\text{反应}}$ is the product of photoinitiator concentration and the wavelength-dependent absorptivity, $D_\text{c0}$ quantifies the resin reactivity of a monomer-photoinitiator combination (fig. S4), and $C$ is a proportionality constant. This relationship is similar to the one that describes photopolymerizable particle formation in microfluidic devices that use oxygen-permeable channel walls (21, 22). The dead zone thickness behaves as follows: Increasing either $\Phi_0$ or $\alpha_{\text{反应}}$ increases the concentration of free radicals in the resin (fig. S1) and decreases the initial oxygen concentration by reaction. Additional oxygen diffuses through the window and into the resin but decays with distance from the window, so that free radicals will overpower inhibiting oxygen at some distance from the window. At the threshold distance where all oxygen is consumed and free radicals still exist, polymerization will begin. Increasing the reactivity of the resin (i.e., decreasing $D_\text{c0}$) causes the polymerization threshold distance from the window to also shrink, thus making the dead zone thinner. The proportionality constant $C$ in Eq. 1 has a value of ~30 for our case of 100-μm-thick Teflon AF 2400 with air below the window, and has units of the square root of diffusivity. The flux of oxygen through the window is also important in maintaining a stable dead zone over time, which is commonly described in terms of the ratio of film permeability to film thickness (23). Using these relationships enables careful control of the dead zone, which provides a critical resin renewal layer between the window and the advancing part.

Above the dead zone, photopolymerization occurs to a certain cured thickness that depends on $\Phi_0 \alpha_{\text{反应}}/D_\text{c0}$ along with exposure time ($t$) and the resin absorption coefficient ($\alpha$) according to the relationship

$$\text{Cured thickness} = \frac{1}{\alpha} \ln \left( \frac{\Phi_0 \alpha_{\text{反应}} t}{D_\text{c0}} \right)$$  \hspace{1cm} (2)

Figure 3B shows cured thickness for three different resins with varying $\alpha$ (holding $\alpha_{\text{反应}}$ constant) where thicknesses were measured for different UV photon dosages (products of $\Phi_0$ and $t$) (fig. S3). These curves are akin to the so-called “working curves” used in stereolithography resin characterization (16, 19). For these resins, $\alpha$ is varied by adjusting the concentration of an absorbing dye or pigment that passively absorbs light (i.e., does not produce radicals) but contributes to overall resin absorption via $\alpha = \alpha_\text{res} + \alpha_{\text{dye}}$. Note that $\alpha$ is the inverse of the characteristic optical absorption height ($h_\alpha$) of the resin:

$$h_\alpha = \frac{1}{\alpha}$$  \hspace{1cm} (3)

The value of $h_\alpha$ in conjunction with the model slicing thickness (fig. 1C), projected pixel size, and image quality, determines the part resolution. The projected pixel size (typically between 10 and 100 μm) and image quality are functions of the imaging setup and determine lateral part resolution. As with slicing thickness, $h_\alpha$ affects vertical resolution but is a property of the resin. If $h_\alpha$ is high, then previously cured 2D patterns will continue to be exposed, causing unintentional overcuring and “print-through,” which in turn results in defects for undercut and overhang geometries.

From the expressions for dead zone thickness and cured thickness, a simple relationship among print speed, $h_\alpha$ (i.e., resolution), and $\Phi_0 \alpha_{\text{反应}}/D_\text{c0}$ is derived:

$$\text{Speed} \propto \frac{\Phi_0 \alpha_{\text{反应}}}{D_\text{c0}}$$  \hspace{1cm} (4)

(see supplementary materials). Figure 3C shows a contour plot of speed as a function of $h_\alpha$ and the ratio $\Phi_0 \alpha_{\text{反应}}/D_\text{c0}$; the dead zone thickness (Eq. 1) is indicated. For a given $h_\alpha$, speed can be increased by increasing $\Phi_0$ or $\alpha_{\text{反应}}$ or by using a resin with lower $D_\text{c0}$. However, as speed increases, dead zone thickness decreases and will eventually become too thin for the process to remain stable. For CLIP, the empirically determined minimum dead zone thickness is ~20 to 30 μm. Part production with a dead zone thickness below this minimum is possible but can lead to window adhesion–related defects. Once the minimum dead zone thickness is reached, the print speed can only be increased by relaxing the resolution (i.e., using a resin with higher $h_\alpha$).
This analysis shows that for a dead zone thickness of 20 μm, speeds in excess of 300 mm/hour with $h_A = 100$ μm are accessible. By increasing $h_A$ to 300 μm and sacrificing resolution, speeds greater than 1000 mm/hour are readily achieved. The trade off between speed and resolution is demonstrated in Fig. 3D with resolution test patterns using resins with different $h_A$ controlled with dye loading. (C) CLIP print speed contours as functions of $h_A$ and $\Phi_0 t / D c_0$. (D) Photographs of resolution test patterns using resins with different $h_A$ from (B). Colored triangles correspond to process conditions in (C). The dye-free test pattern produced at highest print speed (blue triangle) is semitransparent.

Fig. 4. A variety of parts can be fabricated using CLIP. (A) Micropaddles with stems 50 μm in diameter. (B) Eiffel Tower model, 10 cm tall. (C) A shoe cleat >20 cm in length. Even in large parts, fine detail is achieved, as shown in the inset of (B) where features <1 mm in size are obtained. The micropaddles were printed at 25 mm/hour; the Eiffel Tower model and shoe cleat were printed at 100 mm/hour.

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Using this process control framework, Fig. 4 shows an array of expediently produced parts ranging in size from undercut micropaddles with stem diameters of 50 μm (Fig. 4A) to full-size shoe cleats 25 cm in length (Fig. 4C). The Eiffel Tower model in Fig. 4B illustrates that fine detail is achieved even in macroscopic parts: The horizontal railing posts (diameter <500 μm) are resolved on this 10-cm-tall model. This ratio of scales (1:200) confirms that the CLIP process enables rapid production of arbitrary microscopic features over parts having macroscopic dimensions. For these parts, the speed-limiting process is resin curing (Eq. 4); however, for other part geometries, the speed-limiting process is resin flow into the build area. For such geometries with comparatively wide solid cross sections, parameters that affect
resin flow (e.g., resin viscosity, suction pressure gradient) become important to optimize.

Preliminary studies show that the CLIP process is compatible with producing parts from soft elastic materials (24, 25), ceramics (26), and biological materials (27, 28). CLIP has the potential to extend the utility of additive manufacturing to many areas of science and technology, and to lower the manufacturing costs of complex polymer-based objects.

REFERENCES AND NOTES

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SUPPLEMENTARY MATERIALS
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PALEOANTHROPOLOGY

Early Homo at 2.8 Ma from Ledi-Geraru, Afar, Ethiopia

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Our understanding of the origin of the genus Homo has been hampered by a limited fossil record in eastern Africa between 2.0 and 3.0 million years ago (Ma). Here we report the discovery of a partial hominin mandible with teeth from the Ledi-Geraru research area, Afar Regional State, Ethiopia, that establishes the presence of Homo at 2.80 to 2.75 Ma. This specimen combines primitive traits seen in early Australopithecus with derived morphology observed in later Homo, confirming that dentognathic departures from the australopithecine pattern occurred earlier in the Homo lineage. The Ledi-Geraru discovery has implications for hypotheses about the timing and place of origin of the genus Homo.

Fifty years after the recognition of the species Homo habilis as the earliest known representative of our genus (1), the origin of Homo remains clouded. This uncertainty stems in large part from a limited fossil record between 2.0 and 3.0 million years ago (Ma), especially in eastern Africa. Some taxa from this time period, such as Australopithecus africanus (~2.8 to 2.3 Ma) and the less well known A. garhi (~2.5 Ma) and A. aethiopicus (~2.7 to 2.3 Ma), appear too specialized cranially and/or dentally to represent the probable proximate ancestral conditions for Homo species known in ~2.0 Ma (H. habilis and H. rudolfensis). This leaves a thin scatter of isolated, variably informative specimens dated to 2.4 to 2.3 Ma as the only credible fossil evidence bearing on the earliest known populations of the genus Homo (2, 3).

Here we describe a recently recovered partial mandibular hominid, LD 300-1, from the Ledi-Geraru research area, Afar Regional State, Ethiopia, that extends the fossil record of Homo back in time a further 0.4 million years. The specimen, securely dated to 2.80 to 2.75 Ma, combines derived morphology observed in later Homo with primitive traits seen in early Australopithecus. The discovery has implications for hypotheses concerning the timing and place of Homo origins.

The LD 350 locality resides in the Lee Adoya region of the Ledi-Geraru research area (Fig. 1). Geologic research at Lee Adoya (4) identified fault-bounded sedimentary packages dated 2.84 to 2.58 Ma. The LD 350-1 mandible was recovered on the surface of finely bedded fossiliferous silts 10 m conformably above the Guermahma Tuff (Fig. 1). The matrix adherent to the specimen is consistent with it having eroded from these silts [for details on stratigraphy and depositional environment, see (4)]. The Guermahma Tuff is radiometrically dated to 2.822 ± 0.006 Ma (4), a date that is consistent with the normal magnetic polarity of the Guermahma section, presumably the Gauss Chron. An upper bounding age for LD 350-1 is provided by an adjacent downfaulted younger block that contains the 2.669 ± 0.011 Ma Lee Adoya Tuff. A magnetostratigraphic reversal of 2.58 Ma conformably above the Lee Adoya Tuff is inferred to be the Gauss/Matuyama boundary at 2.58 Ma (4). Because no significant erosional events intervene between the Guermahma Tuff and the fossiliferous horizon, the age of LD 350-1 can be further constrained by stratigraphic scaling. Applying a sedimentation rate of either 14 cm per thousand years (kyr) from the Lee Adoya fault block or 30 cm/kmyr from the Hadar Formation (5) provides age estimates of 2.77 and 2.80 million years (Myr), respectively, for LD 350-1. Based on the current chronostratigraphic framework for Ledi-Geraru, we consider the age of LD 350-1 to be 2.80 to 2.75 Myr. The hominin specimen, found by Chalachew Seyoum on 29 January 2013, comprises the left side of an adult mandibular corpus that preserves the partial or complete crowns and roots of the canine, both premolars, and all three molars. The corpus is well preserved from the symphysis to the root of the ascending ramus and retromolar platform. Surface detail is very good to excellent, and there is no evidence of significant transport. The inferior margin of the corpus and the lingual alveolar margin are intact, but the buccal alveolar margin is chipped between P4 and M2. The P4, M2, and M3 crowns are complete and well preserved, but the C, P3, and M1 crowns are incomplete (Fig. 2 and text S2). The anterior dentition is represented by the broken root of the lateral incisor and the alveolus of the central incisor.

Given its location and age, it is natural to ask whether the LD 350-1 mandible represents a late-surviving population of A. aferiensis, whose...
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