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Perspective on 3D printing of separation membranes and comparison to related unconventional fabrication techniques

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ABSTRACT

Additive manufacturing, likewise known as 3-dimensional (3D) printing and rapid prototyping, has the ability to create almost any geometrically complex shape or feature in a range of materials across different scales. It has found its applications in various areas, such as medicine (bioprinting), art, manufacturing and engineering. On the other hand, its use in separation membrane engineering is relatively new. The use of additive manufacturing techniques could provide more control towards the design of separation membrane systems and offers novel membrane preparation techniques that are able to produce membranes of different shapes, types and designs which cannot be made using conventional techniques such as phase inversion or sintering. Here we provide key background information on 3D printing technologies and applications in membrane engineering; a discussion of the potential and limitations of current 3D printing technologies for membrane engineering and future aspects of the technology. Due to the potential benefits of 3D printing in membrane manufacturing, in particular the unprecedented control over membrane architecture the technique could allow, the use of 3D printing in membrane systems should see significant growth in the near future.

1. Introduction

The invention of the first printing press around the 1440s facilitated rapid reproduction of text and images and dissemination of information [1]. Current printed materials are produced using modern offset printing, which involves employing inks made up of light-sensitive chemicals to transfer text and images to printing papers. Over the past few decades, printing technology has advanced from two-dimensional (2D) printing to three-dimensional (3D) printing in which 3D shapes are created by successive deposition of layers of materials [2]. 3D printing, more commonly referred to as additive manufacturing (AM) in the late 20th century, creates end-use products bottom-up, by depositing one layer of material at a time [3]. It has the ability to create almost any geometrically complex shape or feature in a range of materials across different scales [4]. The introduction of AM has revolutionized the prototyping and manufacturing industry, which previously relied on more expensive and time consuming methods such as moulding, forming and machining. Due to its extensive application in making prototypes, the term rapid prototyping (RP), which describes the use of the technology, is also often used to describe the technique. Another term – 3D printing (3DP) was later introduced and was originally referred to the technique that use a inkjet printing head to sequentially deposit 2D material layer-by-layer onto a powder bed to form a 3D structure [5]. While AM may be a more general term suitable to describe the technique, 3DP has gained popularity over time and has now expanded to encompass a wider variety of techniques including, stereolithography (SLA), sintering [6] and extrusion-based processes [7]. All three terms (AM, RP, and 3DP) are still used in the literature, but may or may not refer to the overarching AM technique.

AM begins with a 3D model (or computer-aided design (CAD) drawing), which is sliced into layers and printed layer-by-layer into a 3D build [8]. Materials that can be printed now include conventional thermoplastics, ceramics, metals and graphene-based materials [9]. AM is driving major innovation in many areas including in medical [1,4], art [10], education [11,12], manufacturing and engineering [13,14]. Very recently, the use of AM have been extended to membrane systems, including spacers and membranes [15–17].

The use of AM in separation membrane printing is an exciting new area of research. The past 10 years has seen great advances in AM technology allowing greater control, resolution and precision that is finally allowing separation membranes to be fabricated by this increasingly important and flexible manufacturing technique. AM offers a

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different membrane fabrication method which complements conventional techniques such as the phase inversion method (non-solvent induced and thermally induced), enabling the potential to produce membranes of different shapes, types, and designs which can be more precisely designed, fabricated and controlled than any other fabrication membrane method available currently. Additionally, almost uniquely it allows both the micro- and macro-structure of the membrane to be designed and fabricated in one go, allowing membrane module fabrication to be controlled in a single machine/process from membrane material through to membrane module, giving the unprecedented combined and integrated design possibilities for improving both the membrane separation at both the materials and process architecture levels. However, there exist several limitations of the techniques that still need to be addressed. To help unlock this exciting and vast new area, herein we revisit current available AM techniques and discuss the potential application of various AM technologies to separation membrane engineering. Readers are also referred to a recent review on AM techniques targeted for membrane spacers and membrane modules [18]. The current perspective will differ considerably from this review, as our emphasis will not be on membrane modules and spacers, all of which can in the main be achieved with current and conventional AM technologies. Instead, the emphasis of this perspective will be given to the specification of the techniques and printable materials in order to identify their suitability for separation membrane engineering. To do this we will discuss the limitations of current technologies, methods that could potentially overcome these limitations and future perspective of printing techniques for membrane engineering. This provides a new and future-focussed perspective for membranes and AM, distinct from but complementing other references [18].

2. Techniques and specifications

Various techniques have been developed for AM and can be generally categorized into four types (Fig. 1): (i) photopolymerization, (ii) powder, (iii) material extrusion, and (iv) lamination. A comparison of these techniques, including the advantages, disadvantages, printable materials and specifications, is summarized in Table 1. Among which, photopolymerization is currently the most popular method for membrane fabrication. The other three AM types are also constantly improving, but due to their limited resolution, these systems are currently not quite applicable to membrane fabrication and membrane systems. Below is a short summary of current membrane technologies to provide context to the ensuing discussion. More detailed explanations and reviews of these techniques can be found in [19,20].

2.1. Photopolymerization

The main AM technique that can and will be used in membrane fabrication is based on *photopolymerization* (Fig. 1), which in general refers to the curing of photo-reactive polymers (otherwise known as photopolymers) with a laser, UV or light. Amongst these, photopolymerization based on laser lithography is the most promising one for membrane fabrication. The most common laser-lithography-based technique is known as stereolithography (SLA). An ultraviolet (UV) laser is used to trace and therefore cure the model's cross-section, while the remaining area remains in liquid form. Once the trace is completed, the platform is lowered and the part is coated with a new layer of resin. The process is repeated until the entire part is finished. The final part is then put in an UV oven to complete the curing process. Modern SLA printers have the part raised from the resin during printing (e.g. Formlabs). A similar technique, based on SLA, has also been developed, known as the direct light processing (DLP) printing. In this, instead of using a UV laser, a DLP projector is used to project the entire cross-sectional layer of the 3D structure. Likewise, printing could occur with platform going downwards or upwards, but the latter is the state of the art.

A technological breakthrough in photopolymerization was reported last year, where the print time can be reduced by 25 to 100 times. This technique, known as continuous liquid interface production (CLIP) is based on DLP. Traditional DLP techniques require the cured layer to be mechanically separated from the bottom of the vat containing the resin, followed by resin re-coating before the next layer is exposed [21]. CLIP diminishes the additional mechanical movement by forming an oxygen-containing “dead zone”, a thin uncured liquid layer at the build point which avoids adhesion to the resin vat while keeping the liquid resin in place for the next layer. This approach eliminates the separate and discrete steps required for the traditional SLA printer and radically reduces the build time between layers. The end result is super-fast 3D printing—quicker than any other of the SLA printers—while maintaining feature resolution below 100 micrometers [21]. Two other comparable patent pending techniques (NEXA3D and NewPro3D) could also achieve such printing speed, if not faster but details of their technologies are not yet available.

The highest resolution AM (of about 100 nm) is achieved using two-photon polymerization (TPP) [8,22]. Briefly, the technique is based on the simultaneous absorption of two photons, which induces photochemical or physical transformations within a transparent resin. The inherent optical nonlinearity of two-photon absorption allows localized absorption in regions of high light intensities, i.e. the reaction is restricted to occur within the vicinity of the focal spot of the laser beam, a volume as small as a few attoliters [23].

Material jetting 3D printer (also known as inkjet 3D printer) is based on the principle of customary paper printer, but utilize light-curable resins in place of the usual inks. Two resists are used—build material and support material. The support material is subsequently removed after completion of 3D printing to reveal the printed features.

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2.2. Powder

Powder-based printing systems, as the name suggests, involve the use of powder-type material for printing. General examples include binder jetting, where a chemical binder is jetted onto the spread powder to form the layer; and selective laser sintering (SLS) where a laser is used to sinter the materials such as thermoplastics, metal and ceramics. Binder jetting techniques first create the model layer-by-layer by spreading a layer of powder and printing the binder onto the powder bed with similar methods employed in conventional ink-jet printing [4]. The step is repeated until the 3D structure is obtained. The loose powder that was not hardened acts as a support for subsequent layers.

On the other hand, selective laser sintering (SLS) or direct metal laser sintering (DMLS) involves using a high power laser to sinter small particles of thermoplastic, metal, ceramic or glass powders. The main difference is that SLS uses powder rather than liquid polymer. When the laser beam hits the powder, the intense heat sinters the powders together, while the unsintered materials in each layer act as support structures. Other similar technologies such as selective laser melting (SLM) and electron beam melting (EBM) melt the metal powder instead of sintering the metal powder.

2.3. Material extrusion

In *material extrusion*-based printing systems, fused deposition modelling (FDM, otherwise known as fused filament fabrication, FFF) works by extruding a filament of polymeric material at the appropriate temperature [7]. The nozzle is heated to melt the thermoplastics past their glass transition temperature before depositing them layer-by-layer. The extruded hot material hardens and adheres to the preceding layer.