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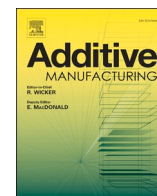
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## Review

## 3D inkjet-printing of photo-crosslinkable resins for microlens fabrication

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## ABSTRACT

The demand for optical components such as microlenses has been growing at a rapid rate in recent years. While conventional methods for manufacturing these components are well known, they are often time-consuming, detrimental for the environment and unable to keep up with the increasing demand. To overcome these issues, the technique of three-dimensional (3D) inkjet printing has attracted much attention. The aim of this review was to investigate the 3D inkjet printing process as a technique for the fabrication of microlenses and identify the key components and methodologies which can be used to control the properties of the resultant microlenses. 3D Inkjet printing was identified as a viable alternative for the production of microlenses owing to its high flexibility, scalability and efficiency as well as its ability to produce good quality products. Substrate modification was shown as a key method by which the geometric and optical properties of microlenses can be controlled. Organic materials such as acrylates and epoxies, and hybrid materials such as siloxanes were shown to be the most common base materials in photo-crosslinkable inkjet formulations and the effects of incorporation of organic compounds and inorganic nanoparticles on the material refractive index were studied.

## 1. Introduction

The last two decades have seen considerable growth in the development of optical, micro-optical and optoelectronic devices. These devices range from sensors, photodetectors and optical cables to cameras, lasers and light emitting diodes (LED's) [1–4]. Key components of these devices are microlenses and microlens arrays, which are primarily used in optical products owing to their ability to collect light efficiently [5]. Microlenses are small lenses with sizes ranging from the millimeter to the nanometer range [6]. Depending on the method of fabrication, microlenses with varying sizes can be achieved and when prepared via inkjet printing, microlenses with diameters around 50–100  $\mu\text{m}$  can be achieved [7]. As the demand for these components continues to grow, there is a need to identify methods by which these components can be fabricated in increased quantities, while simultaneously maintaining their desirable properties and reducing the environmental footprint of their manufacturing processes.

Amongst the numerous techniques under consideration for the future mass production of microlenses is three-dimensional (3D) inkjet printing

of photo-crosslinkable resins. Inkjet printing of photo-crosslinkable resins allows for the production of microlenses at an extremely fast rate, while maintaining flexibility and low costs [8,9]. However, the properties of the resins used for the preparation of microlenses have to be very well controlled in order to achieve a high-quality product [10]. Furthermore, the control of certain properties of the lenses, such as its refractive index, often necessitates the modification of the resins employed [11]. Therefore, there is a need to better understand the different types of materials that can be employed for the production of microlenses as well as identify the alterations needed to produce components with the desired properties.

This article aims to investigate the components and properties of photo-crosslinkable materials that can be employed for the fabrication of microlenses via 3D inkjet printing. The effect of different component characteristics on the resultant microlenses will also be investigated and a special emphasis will be placed on identifying ways by which the refractive index of the produced microlenses can be controlled. Furthermore, the different techniques that can be employed for the fabrication of microlenses will be compared.

**Abbreviations:** 3D, three-dimensional; BMA, benzyl methacrylate; CAD, computer aided design; CCVD, combustion chemical vapor deposition; CLJ, continuous inkjet; CVD, chemical vapor deposition; DMPA, 2,2-dimethoxy-2-phenylacetophenone; dpi, dots per inch; DOD, drop-on-demand; FOTS, trichloro(1H,1H,2H,2H-perfluorooctyl) silane; GBL, gamma-butyrolactone; GRIN, gradient refractive index; LED's, light emitting diodes; MW, molecular weight; PDMS, polydimethylsiloxane; SAM, self-assembled monolayer; THC, hexacoordinated titanium complexes; UV, ultraviolet; VOC's, volatile organic compounds.

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## 2. Manufacturing techniques for microlenses

Several modern-day techniques are available for the fabrication of microlenses [12]. Some of the most common fabrication techniques include thermal reflow, hot embossing, inkjet printing, wet etching, soft lithography, two photon polymerization and Digital Light Processing (DLP) based vat photopolymerization [7,12–17].

The thermal reflow technique first involves the fabrication of photoresist cylinders, which are in turn prepared by photolithography, by utilizing a mask with circular patterns. The cylindrical photoresist material is then heated until it melts and takes up a spherical shape due to the influence of surface tension [13]. The main advantages of this technique include its relative simplicity, low cost and low surface roughness of the produced microlens. However, the melting of the photoresist requires high temperatures and it can often be difficult to obtain lenses with large numerical apertures [18–20].

The process of hot embossing first involves the fabrication of a mold with circular openings. Then, the mold is brought into contact with the polymeric material which is itself placed between two heating plates. Heat and pressure are then applied and subsequently removed to produce the microlens [21]. This technique is a low cost process and allows for high repeatability, however, it suffers from the need for higher temperatures during fabrication [22–24].

The process of wet etching utilizes chemical reactions to obtain microlenses. This involves the usage of mask layers on the substrate. The substrate is then etched to produce the spherical shape followed by the removal of the mask itself [25]. The need for a mask makes processing difficult and drives up equipment costs, however maskless wet etching has also been developed, which allows for good surface properties of the lenses and a high repeatability [26,27].

Soft lithography requires the use of a master mold onto which polydimethylsiloxane (PDMS) is cast. This is then followed by curing and peeling off of the PDMS mold. This PDMS mold then acts as the base layer onto which the photo-crosslinkable material is cast and cured and in the end, this mold is removed to attain the microlenses [28]. The main advantage of this technique is that it can produce microlenses over large areas; however, the need to fabricate a master mold in advance leads to increased costs [29–31].

The technique of two photon polymerization involves the application of femtosecond laser energy onto a photosensitive material. The nonlinear, multiphoton absorption of this energy leads to the polymerization of the material at the focal spot of the laser [6,16]. This technique allows for the fabrication of highly accurate, high resolution microlenses. However, femtosecond lasers tend to be expensive and lead to high processing costs [6,7].

Digital Light Processing based vat photopolymerization is an additive manufacturing technique in which ultraviolet (UV) light is projected onto a photopolymer resin placed inside a vat. The application of UV light leads to the curing and hardening of an entire layer of the resin at once and the build platform is then moved to accommodate subsequent layers [17]. The main advantages of this technique for the fabrication of microlenses are low cost, high processing speeds and ability to generate microlenses with different curvatures. The surface roughness of microlenses produced using this technique is however greater than those produced using other methods [17,32].

While the use of these techniques produces high quality microlenses, these methods also suffer from numerous disadvantages such as poor cost-efficiency, low rates of production, material wastage and high complexity [8,11,33].

In comparison to these techniques and conventional methods, the direct method of inkjet printing offers several advantages. The printed parts are built up in the form of layers, where only the amount of raw material required for the manufacturing of the part is used. In addition, many post manufacturing processes such as shaping and grinding can be eliminated, which prevents wastage of valuable raw materials and leads to a more cost effective, efficient and sustainable process [34,35].

Moreover, inkjet printing allows for the precise control of the droplets of ink or resin onto the substrate. This control over the droplet positioning allows for the accurate tailoring of properties of the printed part and provides a good quality optical product. Additionally, since the part can be printed directly from Computer Aided Design (CAD) data, it eliminates the need for tooling [34,35]. It is also a non-contact method, which allows for the use of a variety of substrates of different sizes and materials [36]. In addition, the substrates themselves can be modified as required. For example, to produce microlenses with a higher numerical aperture, the surfaces of substrates can be chemically modified to achieve larger contact angles, leading to a higher numerical aperture of the final component [37,38].

Finally, inkjet printing is also a scalable process. If a larger number of parts need to be printed, multiple printheads with several nozzles can be utilized to fabricate more parts. This makes it an ideal method for the mass production of components. All these factors make inkjet printing an attractive method to produce microlenses [35,37,39]. The major advantages and disadvantages of different manufacturing techniques for microlenses are summarized in Table 1.

## 3. 3D inkjet printing

### 3.1. Fundamentals of 3D inkjet printing

The process of 3D inkjet printing involves the generation of droplets of material, which are deposited onto a substrate under digital control and subsequently solidified to produce the final product. Different classes of materials have been used to produce components via inkjet printing, including metals, ceramics and polymers. There are numerous ways to solidify the deposited droplets such as solvent evaporation, cooling of low molecular weight (MW) polymers and ultraviolet curing, which are illustrated in Fig. 1 [40,41].

The first inkjet printing process utilizing a UV lamp for the solidification of deposited droplets was the PolyJet process [42]. The first step of this process involved the generation of a software data file containing a virtual representation of the desired part. This data file was then altered into a set of different data files until the required virtual representation was produced. This data file was then used to build up the actual part in a layer by layer manner with the printer generating droplets which were deposited onto a platform and cured using light from a UV lamp [42,43]. A schematic diagram of the process is presented in Fig. 2. Modern day inkjet printers are based on the same principles; however, modifications and enhancements to the technique have allowed for the development of products with a higher resolution.

### 3.2. Drop formation

The fabrication stage of the inkjet printing process begins with the generation of droplets, which ultimately solidify to form the final component. Continuous Inkjet (CIJ) and Drop-on-Demand (DOD) are two major methods by which drops can be generated in inkjet printing [44].

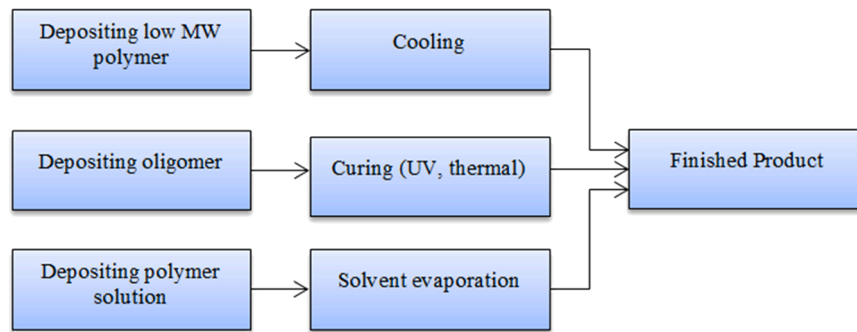
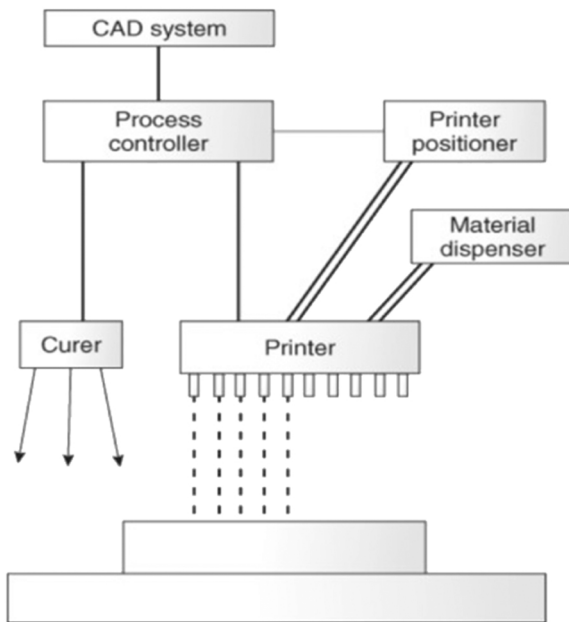
In the CIJ method, a continuous stream of the ink or resin is ejected from the nozzle. As the stream leaves the nozzle and travels downwards, it breaks and separates into a series of drops. The spacing between the individual droplets as well as their volume is modified as required by controlling different parameters of the printer such as the nozzle diameter [40]. The print quality of this process, however, is not sufficiently high to be used for the fabrication of microlenses and is generally used to generate codes on packaged products.

DOD inkjet printers only generate droplets as and when required. In addition, DOD inkjet printers do not contain the system of electrodes present in CIJ printers to control droplet positioning, and their absence means the nozzles can be placed closer to the substrate itself and smaller drop sizes can be obtained. The most common DOD inkjet printers are the thermal and piezoelectric type printers [35,45–47].

**Table 1**

A summary of the major advantages and disadvantages of different techniques used for the manufacturing of microlenses.

Technique	Advantages	Disadvantages	References
Thermal reflow	Relatively simple, low cost, low surface roughness	High temperature requirements, large aperture values are hard to obtain	[18–20]
Hot embossing	Low cost, high repeatability	High temperature requirements	[22–24]
3D Inkjet	Highly flexible, accurate tailoring of optical properties, option of substrate modification, suitable for mass production, minimal post-processing, negligible material wastage, noncontact method	Uncertain printing parameters, limited knowledge of ink formulations, difficult geometry control for unmodified substrates	[6–8,10–12,33–41,52,57,72,87,88,90–95,98,112,114,117,118]
Wet etching	Good surface properties, high repeatability in the maskless process	High equipment costs and difficulty in processing due to the need for a mask	[23,24]
Soft lithography	Produces microlenses over large areas	High cost due to need for master mold	[29–31]
Two photon polymerization	High accuracy and resolution	High cost due to expensive femtosecond laser	[6,7]
DLP based vat photo-polymerization	Low cost, fast fabrication, ability to prepare different microlenses	High surface roughness	[17,32]

**Fig. 1.** Methods to solidify polymer droplets in 3D inkjet printing.**Fig. 2.** A schematic diagram of the PolyJet process [42].

Thermal DOD inkjet printers generate droplets by imparting a pressure pulse onto the ink via a heating element. The ink to be printed is brought into contact with a heating element, resulting in the development and collapse of a vapor bubble which forces the ink through the nozzle [34,35]. These printers are generally not employed for 3D fabrication owing to its larger droplet sizes and the need for inks to withstand high temperatures.

Piezoelectric DOD inkjet printers employ a piezoelectric element to

generate a pressure pulse which ultimately leads to drop formation [41, 45]. A voltage or electric impulse is applied onto the piezoelectric element. This generates a pressure pulse which forces the ejection of a droplet from the nozzle. The removal of the voltage then allows the ink to be refilled as the piezoelectric element returns to its original shape. Piezoelectric DOD inkjet printers are generally preferred over other DOD printers for 3D fabrication. A schematic of this technique is illustrated in Fig. 3.

Each parameter in the inkjet printing process can affect other parameters and eventually influence the final properties of the fabricated component. The properties of the ejected droplets depend on several factors such as surface tension, density and viscosity of the inks used as well as the waveform characteristics used for piezoelectric excitation [35,48]. The influence of the interfacial, viscous and inertial forces can be represented by the Ohnesorge number, which is the ratio of the square root of the Weber number to the Reynolds number. The inverse of the Ohnesorge number is known as the Z parameter and it is the Z number which identifies the printability of an ink. The limits for the Z parameter of an ink which lead to stable drop formation are between 10 and 1 [49].

The piezoelectric excitation process itself is dependent on a number of variables such as the waveform, driving voltage and pulse width. Researchers have attempted to design several waveforms to control droplet behavior. These range from single square waveforms, double square waveforms, bipolar waveforms and W and M shaped waveforms [48,50]. Liu et al. [48] investigated the effect of employing different waveforms on the process of droplet formation for fluids with varying viscosities. They showed that for droplets of low viscosity fluids generated under the same conditions, the single waveform led to the formation of satellite drops while the double waveform generated a single droplet. They also showed that the use of a bipolar waveform for high viscosity fluids led to better drop generation than the single waveform. Gan et al. [50] studied the effect of different waveforms on droplet volumes. They showed that using an M shaped waveform produced

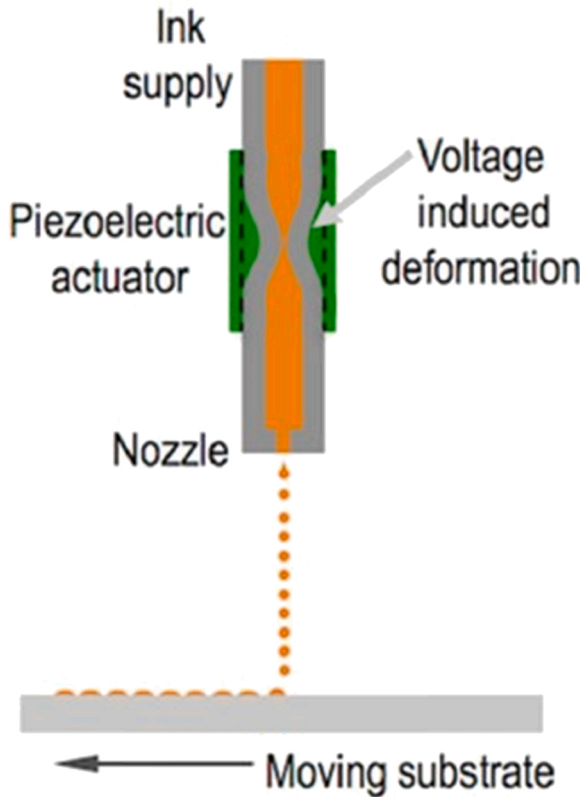


Fig. 3. A schematic of the piezoelectric DOD process [35].

droplets with lower volumes for both high and low viscosity fluids as compared to a unipolar waveform. A bipolar waveform was then introduced which showed a further reduction in droplet volumes only for low viscosity fluids, while further volume reduction for high viscosity fluids was then achieved by using a W shaped waveform.

The size of the formed droplet can also be altered by varying the voltage applied to the piezoelectric element [35,51,52]. Droplets with smaller volumes can be obtained by the application of lower voltages while larger droplets are formed by applying higher voltages, with the two showcasing a linear relationship. Similarly, low voltages generally produce droplets with low velocities while increasing the applied voltage also increases drop velocities. The drop velocity itself can influence the final properties of the deposited droplets, with large velocities generating droplets with higher diameters.

The pulse width shows a complex relationship with drop velocity, with an increase in pulse width also leading to increasing drop velocity until a point of maximum velocity is attained, beyond which increasing pulse width reduces drop velocity. This maximum velocity remains the same on increasing voltage and is instead influenced by the properties of the fluid used for the printing process [53,54]. The viscosity of the ink droplets is largely controlled by the presence of reactive diluents and monomers but heating the nozzle to higher temperatures can also control ink viscosities. Voigt et al. [33] achieved stable droplet formation by heating the nozzle to temperatures ranging from room temperature up to 70 °C, thereby altering the viscosity of different inks. It is therefore important to understand the interplay between these different parameters and the influence they have over the final product properties.

### 3.3. Drop deposition and ink fixation

In order to fabricate an inkjet-printed component with a high resolution as well as good quality, it is necessary to precisely position the generated droplets onto a substrate. The successful deposition of a droplet onto a substrate and its subsequent phase change from the liquid

to the solid state is a multi-stage process governed by a number of factors. Precise control over each of these factors allows for the fabrication of a component with the desired properties [40,55].

One factor which can negatively interfere with the positioning of the droplets is atmospheric drag, which is largely dependent on the distance between the nozzle and the substrate [35,56]. Every droplet ejected from a nozzle contains a certain amount of kinetic energy; however, as the droplet travels through the air before contacting the substrate, it loses a part of that energy. In order to reduce this loss and precisely control droplet positioning, the distance between the nozzle and the substrate must be below 2 mm.

After impacting the substrate, the droplet spreads due to inertial forces and takes a spherical cap shape. The droplet then spreads further as its kinetic energy is converted into surface energy. A maximum point of spreading is then obtained, following which the droplet retracts and releases energy due to viscous forces and finally takes a stationary shape [35,40]. The final size of the stationary droplet can be represented by Eq. (1)-

$$d_{eq} = d_0 \left( \frac{8}{\tan^2 \frac{\theta_{eq}}{2} \left( 3 + \left( \tan^2 \frac{\theta_{eq}}{2} \right)^2 \right)} \right)^{\frac{1}{3}} \quad (1)$$

Where  $d_{eq}$  is the base equilibrium diameter,  $d_0$  is the diameter of the initial droplet and  $\theta_{eq}$  is the equilibrium contact angle.

From Eq. 1, it can be seen that the diameter of the droplet present on the substrate after ejection is dependent on the diameter of the ejected droplet, controlled via the nozzle, and the equilibrium contact angle of the ink with the substrate, which are represented in Fig. 4.

The resolution in inkjet printing can be improved by reducing the size of the generated droplets, which in turn can be achieved by printing with nozzles of small diameters or applying a low excitation voltage onto the piezoelectric element. However, smaller droplet sizes can lead to difficulties in controlling their positioning on the substrate and lead to the clogging of the nozzle. Generally, droplet diameters below 10  $\mu\text{m}$  are not generated [51,57]. Today, several commercial DOD inkjet print-heads with high resolutions of up to 1200 dpi (dots per inch) are available, such as the Xaar 5601, Kyocera KJ4B-1200 and the HP PageWide Web Press T250 HD [58].

### 4. Inks for inkjet printing and their properties

One of the most crucial aspects of a 3D inkjet printing setup is the ink used to fabricate the required components or products. The selection or formulation of a 3D inkjet printing ink is done based on the desired properties and applications of the fabricated part. However, for an ink to be compatible with the inkjet printing process, it must fulfill certain basic requirements in addition to providing the right blend of properties to the final product. An inkjet printing ink should consist of components which are compatible with the material of construction of the printer, the viscosity of the ink must lie within the limitations of the inkjet

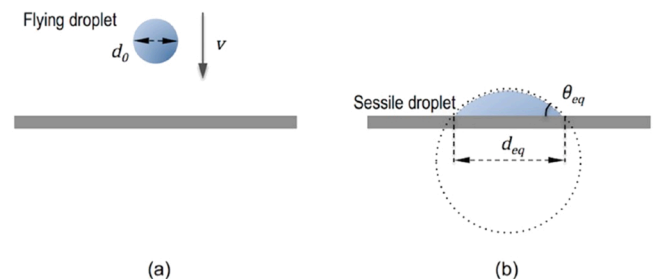


Fig. 4. The diameter and contact angle of a) a flying and b) stationary droplet at equilibrium [35].



printer employed and the ink must form a stable meniscus at the nozzle of the print head to enable good droplet formation [40].

Based on the nature of the solvent, inkjet inks can be of many types. These include aqueous inks, oil-based inks, solvent-based inks and UV curable inks or resins [40]. While all these inks are regularly employed in additive manufacturing, the usage of UV curable inks has grown significantly in recent years [59]. This increase in the use of UV curable inks can be attributed to its many advantages, which include the presence of little to no volatile organic chemicals (VOC's), instantaneous cross-linking, good quality products due to the absence of solvent evaporation, good adhesion with a number of substrates and low energy requirements [59–61]. All of these factors make UV curable inks highly suitable for digital fabrication.

#### 4.1. Components of UV cured inks

The components of a UV curable ink can in general be divided into three categories. These are – monomers/oligomers, photoinitiators and additives. The monomers or oligomers are the base raw material present in the largest quantities in all UV resin formulations. These materials undergo polymerization and subsequent cross-linking, which converts deposited droplets from the liquid state to the solid state. Photoinitiators are substances, which bring about polymerization of the monomers or oligomers upon contact with UV radiation. Additives are a class of materials that are added into a formulation to impart certain desired properties to the resin. Different types of substances can be used as additives. These include substances which enhance the performance, adhesion, and durability of the ink. For the fabrication of microlenses via inkjet printing, resin formulations often contain additives that reduce the viscosity of the resin as well as substances which can modify or influence the refractive index of the material [59,62].

##### 4.1.1. Monomers and oligomers in UV curable inks

Suitable monomers and/or oligomers act as the base raw material for every UV curable ink. There are two types of UV curable inks depending on their technique and mechanism of solidification. These are free radical polymerization-based inks and cationic polymerization-based inks. While both types of inks rely on UV radiation to bring about solidification, the raw materials and polymerization mechanisms of both inks are different [63].

Free radical polymerization-based inks are seen more predominantly in the field of additive manufacturing. These inks provide a good blend of final properties. In addition to this, a wider range of raw materials are available for use as components in free radical inks as compared to cationic-based inks. The curing process is also faster for free radical inks. However, the curing of these inks is inhibited by the presence of oxygen [62,63]. This can be prevented by curing in a nitrogen rich atmosphere [64].

Cationic polymerization-based inks have no oxygen sensitivity and provide high adhesion with a range of substrates. They also demonstrate lower shrinkage. These inks also require a lower energy density as cross-linking continues even after the removal of the UV radiation source. However, the raw materials for these inks tend to be expensive and are very moisture sensitive [63,65]. Some features of both types of UV curable inks are compared in Table 2.

The most commonly used monomers in UV ink formulations are monofunctional and multifunctional acrylates, which cross-link via free radical chain-growth polymerization [34]. Their main advantages include high reactivity, good resistance to hydrolysis, photo stability, excellent optical performance and transparency. They also provide good mechanical and thermal stability to the final product. Acrylate monomers also help in lowering the viscosity of the overall ink composition, allowing for the printing of parts via the inkjet technique. Acrylates are also highly versatile and can accommodate a wide range of functionalities. The different functionalities all provide their own set of properties to the monomer, allowing for a wide range of properties to be achieved

**Table 2**

A comparison of the major differences between free radical and cationic-based UV curable inks [65].

Feature	Free Radical Inks	Cationic Inks
Cure Speed	High	Moderate to high
Initiation	Light	Light or heat
Oxygen sensitivity	Yes	No
Shrinkage	Large	Negligible
Adhesion	Moderate to good	Excellent
Post Cure	Limited effect	Strong effect
Chemical resistance	Good	Moderate to good
Humidity resistance	No	Yes
Acid/base sensitivity	No	Yes

as required [34,66]. Table 3 shows the influence of varying acrylate functionalities on the properties of the ink.

As can be seen in Table 3, an increase in acrylate functionality of the monomer increases the curing response, hardness and solvent resistance and reduces the flexibility and adhesion of the ink, which is due to increasing cross-linking density [34]. In addition, increasing the functionality of acrylates also increases the viscosity of the ink, which must be regulated for inkjet printing. Acrylate monomers generally provide good adhesion with polar plastics; however, their adhesion to non-polar plastics is generally lower. In addition to acrylate monomers, oligomers are also used in UV ink formulations [62,67]. Oligomers are the components which are largely responsible for imparting the basic properties to the printed part. They are highly viscous, and as a result, they are generally used in conjunction with acrylate monomers in UV ink formulations. Commonly used acrylate oligomers include polyester acrylates, urethane acrylates and epoxy acrylates. Of these, the polyester acrylates generally have the lowest viscosity, which makes them more suitable for inkjet printing. However, they tend to have inferior properties as compared to the others. Urethane acrylates are highly versatile and can provide a wide range of different properties; however, their high viscosities limit their use in inkjet applications [68].

While acrylate-based monomers and oligomers remain the material of choice for many inkjet printing applications, there are also other classes of materials that have been employed to produce microlenses via inkjet printing. The biggest among these are epoxy-based resins. These provide good mechanical properties, relatively high thermal as well as chemical resistance and good optical properties [69]. Fig. 5 shows microlens arrays produced by employing epoxy resins. Vinyl ethers are another class of materials which have received significant interest from researchers in recent years owing to their fast curing rates. Both materials cross link via cationic polymerization [70].

In addition to purely organic monomers and oligomers, the use of hybrid organic-inorganic resins as raw materials in UV inkjet formulations is receiving increased attention. Hybrid organic-inorganic resins provide several advantages such as straightforward preparation, good mechanical and chemical properties, relatively simple modification, and good optical quality [71]. However, the viscosities of these resins are generally too large to be printed directly using 3D inkjet printing, which necessitates the use of solvents to reduce their viscosity and make them suitable for inkjet printing [72].

Siloxane-based polymers and resins are the most commonly used class of materials for the manufacturing of microlenses within the field

**Table 3**

The effect of different acrylate functionalities on the final properties of the ink [34].

Property	Monoacrylate	Diacrylate	Triacrylate	Tetraacrylate
Cure response	Slow	Moderate	Fast	Fastest
Flexibility	Very flexible	Flexible	Rigid	Brittle
Hardness	Softest	Moderate	Hard	Hardest
Solvent resistance	Low	Moderate	Good	Best
Adhesion	Good	Good	Moderate	Poor

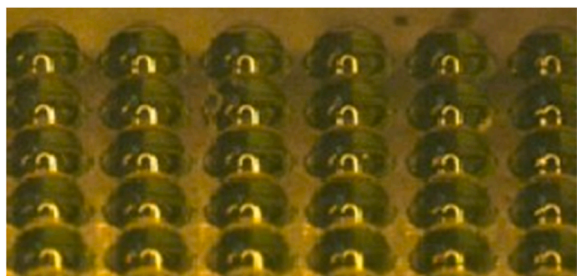


Fig. 5. Epoxy microlens arrays at a magnification of 50x [36].

of hybrid materials. In addition to providing good mechanical properties, they also demonstrate high optical transparency and show little to no yellowing [73]. In addition, siloxane-based materials generally exhibit good solubility in organic solvents which makes them suitable for use in the low viscosity inkjet printing process. The properties of siloxane materials can be effectively modified by changing the identity of the neighboring organic groups [34,74]. The attachment of certain organic groups such as vinyl ethers, which are UV curable, to the structures of siloxane-based materials allows these materials to be used in processes such as 3D inkjet printing. Another advantage of these materials is the possibility of modifying their refractive index, which is generally between 1.4 and 1.54 [73,74]. Fig. 6 shows microlenses produced using siloxane-based materials.

#### 4.1.2. Photoinitiators

Photoinitiators are key components of every UV ink formulation. These are substances that absorb UV radiation and generate reactive species, which in turn initiate the cross-linking reaction of the base monomer and/or oligomer present in the ink [68]. The cross-linking process transforms the UV ink from the liquid to the solid state and allows for the fabrication of the desired components in a layer-by-layer manner.

Depending on the mechanism of polymerization and the identity of the monomers or oligomers used in a UV ink, photoinitiators can be divided into two major classes – free radical photoinitiators and cationic photoinitiators [65]. Free radical based photoinitiators are used extensively in UV ink formulations, owing to the large variety of compatible monomeric systems.

Benzoin derivatives such as benzoin ethers were amongst the first materials to be employed as photoinitiators and provided good results with silicon-based monomers [62,68,76]. However, the use of this photoinitiator results in yellowing post cure, which makes them unsuitable for use in microlenses. Furthermore, benzoin ethers show inferior initiation properties with acrylate-based monomers as compared to silicon-based ones. As acrylates are the most common class of base monomers in UV ink formulations, the use of benzoin derivatives as the photoinitiator of choice is limited. Benzyl ketones such as 2,

2-dimethoxy-2-phenylacetophenone (DMPA) are a popular choice of photoinitiator as they show good compatibility with acrylate-based monomers. The initiation process of acrylates is significantly faster for benzyl ketones as compared to benzoin ethers. However, they are still susceptible to yellowing over time.  $\alpha$ -hydroxyalkylphenones improve upon the properties of DMPA by providing better initiation properties with acrylates as well as being non-yellowing.

The second class of photoinitiators used in UV ink formulations are cationic photoinitiators. When UV radiation is directed onto these photoinitiators, they generate Lewis or Bronsted acids. These acids then act as initiators bringing about cationic polymerization of the vinyl monomers present in the UV ink [65]. The most common cationic photoinitiators are onium salts such as diazonium and triphenylsulfonium salts owing to their efficient initiation and the stability of their generated Lewis acids. However, the use of cationic photoinitiators in modern day inkjet-based UV ink formulations is relatively small owing to the low availability of compatible monomers [34,76,77].

The selection of a photoinitiator for a monomer/oligomer system is a process often decided by trial and error [34]. While most ink formulations use a single photoinitiator, it is often necessary to use a combination of different photoinitiators to obtain efficient and effective generation of radicals.

#### 4.1.3. Additives

Additives are materials that are added to inkjet printing formulations to enhance or alter the properties of the final material. Given the availability of different types of inkjet inks, there also exist several different types of additives. These include colorants [61], surfactants [45], adhesion promoters [78] and various nanoparticles [79]. Amongst these, only nanoparticles are primarily employed in the development of UV inkjet microlens formulations for developing microlenses.

Nanoparticles are often added to inkjet formulations in order to control certain properties. Their incorporation provides several advantages such as reduced organic content, better mechanical properties and improved temperature resistance of the final products [28]. These nanoparticles have found a plethora of applications, such as  $\text{TiO}_2$ , ZnO and platinum for catalysis applications [80] silver for conductive inks [81] and  $\text{Al}_2\text{O}_3$  for improved mechanical properties [82]. For microlens development, nanoparticles are used to modify the refractive index of the fabricated component. The generally higher indices of refraction of the nanoparticles allows for the use of microlenses in a larger variety of applications such as for sensors and encapsulation materials [83].

Additionally, certain additives are also added to commercial inkjet formulations to improve their stability [34]. These can include materials such as inhibitors that prevent early polymerization of inkjet formulations and UV light absorbers that protect the ink from UV damage. Ink formulations can also contain photosensitizers that aid the photopolymerization of monomers or oligomers present in the ink.

## 5. Parameters affecting the printing process

### 5.1. Cross-linking

The cross-linking of UV inkjet inks is a process that is controlled by a number of key factors and plays a major role in the successful fabrication of an inkjet-printed part. The base polymer as well as the monomers/diluents for viscosity control have a major influence on this process. Ni et al. [84] stated that a greater proportion of the base polymer brings about a faster cross-linking reaction. The speed of cross-linking was also shown to be higher when the monomer/diluent contained more functional groups.

The UV dosage is another factor that controls the cross-linking process. Simon and Langenscheidt [85] studied the cross-linking behavior of a UV cured inkjet ink containing both acrylic and vinyl bonds at different UV dosages. They showed that acrylic  $\text{C}=\text{C}$  bonds showed a percentage conversion of 98.8 at a UV dosage of  $691 \text{ mJ/cm}^2$ , with the

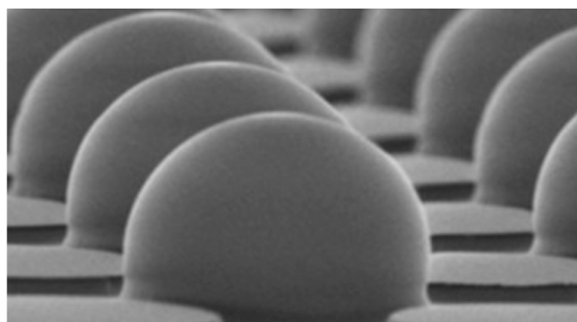


Fig. 6. Micrographs of microlens arrays with a diameter of  $100 \mu\text{m}$  produced by employing a hybrid organic-inorganic siloxane-based material [75].

percentage conversion already reaching 90 at  $237 \text{ mJ/cm}^2$ . However, the vinyl C=C bonds showed a much lower conversion of 45.7 at the UV dosage of  $691 \text{ mJ/cm}^2$  and even at a dosage of  $1254 \text{ mJ/cm}^2$ , the conversion remained below 50. Higher intensities also provide greater conversion of the monomer as well as an increased polymerization rate [86].

The time of irradiation and photoinitiator concentration also influence the cross-linking process of UV inkjet formulations, with higher photoinitiator concentrations providing faster cross-linking [86]. Biehl et al. [72] studied the effect of time of irradiation on a hybrid inkjet formulation, with the photoinitiator concentration varying from 1 to 10 wt%. They observed that for the samples containing 10 wt% photoinitiator, polymerization was completed after 200 s while samples containing lower photoinitiator concentrations required a longer time of irradiation to achieve polymerization.

## 5.2. Viscosity control

The success of an inkjet printing operation is highly dependent on the viscosity of the ink. The optimal viscosity of an inkjet printing formulation lies between 2 and 20 mPa.s, although formulations with viscosities between 20 and 50 mPa.s have also been printed successfully [40]. However, most oligomers used for inkjet printing have higher viscosities at room temperature, which can lead to the clogging of the nozzles. This necessitates the incorporation of solvents, reactive diluents or low viscosity monomers into inkjet formulations. Various materials have therefore been employed to reduce the viscosities of inkjet formulations. Voigt et al. [33] employed two aliphatic epoxy based reactive diluents to control the viscosities of their inkjet formulations, with the respective dynamic viscosities of the diluents being 469 and 2.3 mPa.s respectively. Using a combination of reactive diluents and a solvent allowed for overall viscosities in the printable range of 20–30 mPa.s. Danzebrink and Aegerter [87] utilized water in concentrations between 30 and 50 wt% to achieve ideal viscosity for their sol-gel polymer formulation. Biehl et al. [72] employed ethanol (> 30 wt%) as solvent for their hybrid organic-inorganic polymer formulation. This allowed for an overall kinematic viscosity of  $3 \text{ mm}^2/\text{s}$ , which is suitable for inkjet printing at room temperature. It was also noted that ethanol in amounts less than 30 wt% led to clogging of the nozzles due to a higher viscosity of  $5 \text{ mm}^2/\text{s}$ . Gleissner and Hanemann [88] used benzyl methacrylate (BMA) to control the viscosity of an epoxy acrylate formulation. They demonstrated that increasing BMA concentration in the formulation from 0% to 100% reduced the overall viscosity from 48 Pa.s to 3.5 mPa.s, thus making it suitable for inkjet printing. Additionally, increasing temperatures also allowed for reduced viscosities.

## 6. Lens properties

### 6.1. Substrate modification

One of the key factors that influences the geometry and optical properties of inkjet-printed microlenses is the interaction between the ink and the substrate. A major advantage of inkjet printing is the ability to print parts on a variety of substrates. The large number of substrates provides inkjet printing with the potential to produce components with different characteristics and properties by modifying the substrate itself [89].

However, given the low surface tension of inkjet-printable polymers, it can be difficult to control the geometry of the lens. This leads to droplets with low contact angles and lenses with low numerical apertures [7]. Therefore, in order to achieve higher contact angles, the wettability of the substrates is modified by pre-patterning. Vilmi et al. [90] pre-patterned their substrate via photolithography. This was achieved by spin coating SU-8 photoresist on the substrate. This resulted in the formation of spherical reservoirs. Ink deposition generated uniform lenses with a smooth surface whose focus could be modified by changing

droplet volume. Blattmann et al. [91] also used photolithography to pattern their substrate and produce convex microlenses. A Pyrex substrate was coated with a hydrophobic polymer and its subsequent photolithography led to the development of circular areas with low wettability's surrounded by a hydrophobic surface, thus limiting the contact angle. Chen et al. [92] coated a photoresist onto a substrate and patterned it into spherical shapes. This was followed by a hydrophobic Teflon coating and the removal of the photoresist, leading to the formation of hydrophilic circular regions surrounded by a hydrophobic surface. The microlenses deposited on these modified circular regions showed a contact angle of  $51^\circ$  as opposed to  $20^\circ$  for the unmodified substrate.

The wettability of a substrate can also be altered by the deposition of coatings. Alamán et al. [37] achieved substrate modification by combustion chemical vapor deposition (CCVD) and chemical vapor deposition (CVD). A silane layer was first coated onto a glass substrate by CCVD followed by a fluorosilane layer coating by CVD, forming a nano roughness on the substrate, which in turn allowed for an increase in the contact angles between the ink and the substrate, giving large numerical apertures. Unmodified glass substrates showed water contact angles of  $110^\circ$  while modified substrates showed water contact angles between  $164^\circ$  and  $170^\circ$ . Caparros [52] produced microlenses on an unmodified silicon wafer substrate as well as a silanized silicon wafer. The microlenses produced by using 10  $\mu\text{L}$  cartridges showed an average diameter of  $100 \pm 2 \mu\text{m}$  on the untreated substrate and  $20 \pm 2 \mu\text{m}$  on the treated substrate and more spherical microlenses were obtained by printing on the treated substrate. Kim et al. [38] used molecular vapor deposition (MVD) to treat the glass substrate with trichloro(1H,1H,2H,2H-perfluorooctyl) silane (FOTS) in order to provide a high contact angle and resolution of the microlenses. Kim et al. [93] used the same technique to deposit FOTS on glass substrates and observed that the contact angle of a 40% photoresist was increased from  $18^\circ$  for untreated glass to  $91^\circ$  for FOTS treated glass. Ishii et al. [94] produced microlenses on three substrates - glass, glass with a silica surface treatment and glass treated with a fluorinated polymer. This allowed for the development of microlenses ranging from large numerical aperture to small numerical aperture values. Similarly, Fakhfouri et al. [95] fabricated microlenses on differently treated substrates. Due to their different wettability, each substrate produced lenses with different radii, focal lengths and heights. The untreated glass substrate showed the largest radii and lowest height while the self-assembled monolayer (SAM) coated silicon showed the lowest radii and highest height, while other substrates showed intermediate values.

It can therefore be observed that by modifying the substrate, microlenses with very different geometries and optical properties can be produced.

### 6.2. Light transmittance

The transmittance of light through the microlens material represents an important characteristic for the development of microlenses. In order to fully realize the benefits of using microlenses for different optical applications, the material composition must be transparent in the desired wavelengths. Generally, microlenses prepared by 3D inkjet printing have a wavelength application range in the visible and near IR range [35].

Xie et al. [36] investigated the suitability of employing a UV curable epoxy material for the fabrication of microlenses by measuring its optical performance. They prepared a sheet of material with a thickness of  $300 \mu\text{m}$  and measured its transmittance for wavelengths between 400 and 900 nm. The prepared sheet showed a transmittance of up to 90% for visible and near IR wavelengths, indicating a high suitability of the material for the preparation of microlenses. Danzebrink and Aegerter [87] measured the optical transparency of a silane-based hybrid organic-inorganic precursor ink as well as a  $6 \mu\text{m}$  thick polymerized product. Both the precursor ink and the polymerized product showed a



transparency of over 92% in the wavelength range between 300 and 2700 nm, indicating good suitability of the ink for the development of microlenses. Biehl et al. [72] measured the optical performance of another hybrid organic-inorganic ink and determined that the polymerized product was highly transparent in the wavelength range between 375 and 2700 nm, making it suitable for microlens preparation.

Voigt et al. [33] determined the optical properties of different inks used for the preparation of microlenses. They identified that the use of low viscosity, highly volatile reactive diluents for viscosity control led to a reduction in the transparency of the overall material when compared with a similar material containing a higher viscosity reactive diluent. Additionally, Kim et al. [38] showed that microlenses prepared from hybrid organic-inorganic inks provided a higher degree of transparency as compared to purely organic inks in the wavelength range from 400 to 1600 nm.

### 6.3. Surface roughness

Surface roughness is a vital characteristic for the functionality of a microlens. High surface roughness can lead to undesirable side effects such as light scattering and poor light collection. A sufficiently smooth surface is characterized by a roughness which is significantly lower than the wavelength of light at which the microlens must operate [96]. Given this requirement, present-day microlenses must have a surface roughness of less than 10 nm [32]. Microlenses produced via inkjet printing have regularly been shown to meet this criteria [33,36,87].

### 6.4. Refractive index modification

The control over the refractive index of an inkjet resin formulation, and in turn the refractive index of the product fabricated from that formulation, represents an important parameter in the inkjet printing process concerning the development of microlenses. However, since the literature about refractive index modification for 3D printed microlenses through inkjet printing is limited, in this section, the papers which reported methods for improving the refractive index of inks in inkjet printing or optical devices were discussed. Materials such as epoxies and silicones, which are commonly used in inkjet printing, have refractive index values between 1.45 and 1.55 [97]. However, for a number of applications, such as the microlenses needed for CMOS image sensors, refractive indices of over 1.70 are required [83]. As a result, conventional inkjet polymers by themselves cannot be used to achieve high refractive index values.

Several methods have been developed in order to alter the refractive index values of resin formulations, with the most common method amongst these being the incorporation of organic groups and functionalities into the ink [83]. Gleissner and Hanemann [98] increased the refractive index of an epoxy acrylate polymer by adding phenanthrene in amounts from 0 to 15 wt%. The refractive index of the 100 wt% cross-linked resin was determined to be 1.548, however, the addition of phenanthrene into the formulation allowed for a maximum attainable refractive index of 1.561 for the same resin. Increasing the concentration of phenanthrene led to an increased refractive index for both the liquid and the cross-linked samples. Gleissner and Hanemann [88] then improved upon their previous study by adding two components; phenanthrene and benzyl methacrylate (BMA). While BMA was primarily used for viscosity control, it was observed that increasing BMA concentration led to a reduced viscosity as well as an increase in overall refractive index by about 0.02 without the addition of phenanthrene. By adding increasing amounts of phenanthrene, the refractive index of the formulation with 60 wt% BMA increased from 1.560 to 1.578. The change in the refractive index of a polymeric formulation due to the addition of organic groups and other functionalities is dependent on the molar refraction and molar volume of those organic groups and atoms [99]. Using organic groups or atoms with high molar refractions and low molar volumes increases the refractive index of the formulation.

Examples of these groups include aromatic groups, sulfur atoms and halogen and phosphorus-based groups [83,100].

In the case of siloxanes, the presence of different substituents on the Si-O-Si backbone allows for the modification of its refractive index. The presence of methyl substituents provides a different set of refractive indices as compared to the presence of phenyl substituents, and by changing the ratio of methyl to phenyl groups in a siloxane, the refractive index of the material can be varied from a value of 1.40–1.55 [73].

Another technique for the alteration of the refractive index of polymeric inkjet formulations is the addition of inorganic nanoparticles into the inks, which are used to achieve higher refractive indices [83]. A number of different materials have been used to achieve this. Zhang et al. [101] utilized silicon nanoparticles to achieve a high index of refraction. These were combined with a siloxane-based polymer in concentrations varying from 0 to 15 wt% and it was observed that increasing the amount of silicon nanoparticles increased the overall refractive index, with the pure polymer having a refractive index of 1.563 while the 15 wt% nanoparticle sample showed a refractive index of 1.727. Ereemeeva et al. [102] used hexacoordinated titanium complexes (THC) to achieve a high index of refraction. The THC was combined with a dimethacrylate with dimethacrylate to THC ratios ranging from 1:1–1:8. Films prepared from this material showed high transparency in the visible region and it was observed that increasing the amount of THC in the material led to a uniform increase in the refractive index until a ratio of 1:6, following which the refractive index remained relatively constant. For the films containing a 1:1 ratio of acrylate to THC, the refractive index was measured at 1.42 while the samples with a ratio of 1:6 showed a refractive index of 1.83. Guschl et al. [103] prepared high refractive index materials by using zirconium dioxide nanocrystals. This was combined with an acrylate and it was noted that 1-micron thick films with up to 90 wt% zirconium dioxide nanocrystals have shown a refractive index of 1.78 at 450 nm as well as transmittance values greater than 95%.

While the addition of nanoparticles increases the refractive index of the materials into which they are embedded, they can also adversely impact the transmittance of light through the matrix material and lead to undesirable light scattering [104,105]. This is caused by the difference in the refractive index of the nanoparticles and the matrix. To avoid this, the size of the nanoparticles must be sufficiently small, and they must be well dispersed in the system into which they are embedded. This dispersion is achieved by functionalizing the nanoparticles with ligands, which form covalent bonds at both ends with the matrix material and the nanoparticle respectively [106]. Treat and Patel [107] employed silanes for this purpose. The resulting samples, with a nanoparticle concentration ranging from 0.001% to 25%, provided highly transparent results, thus successfully preventing light scattering.

### 6.5. Gradient refractive index materials

Traditionally, the materials used to fabricate lenses for use in different optical applications have a uniform refractive index throughout their composition, i.e., they can be considered to be homogeneous. Gradient Refractive Index (GRIN) materials, on the other hand, are a class of materials whose refractive index changes along either its optical axis or radial axes [108]. Given this difference, GRIN lenses provide several advantages over conventional homogeneous lenses. These include a reduction in the overall weight and size of the optical system, the ability to replace a convoluted lens system with a single lens, improved optical performance as well as significantly reduced monochromatic and spherical aberrations owing to their generally flatter shape [64,108]. These advantages have led to the use of GRIN lenses in applications such as fiber collimators and optical data storage systems [64,109].

The manufacture of GRIN lenses can be carried out by several different methods. One method of producing GRIN lenses involves the

manufacturing of different films, with each having a different refractive index [110]. The separate films are then forced together in a mold to obtain the GRIN lens. Another method for producing these lenses involves the incorporation of ions into the lens material, with lead being amongst the most commonly used ions [111]. However, both of these techniques are expensive, and the resulting lenses suffer from large amounts of chromatic aberrations [109].

The emergence of inkjet printing has provided a new avenue for the fabrication of GRIN lenses and other related optical components. As the inkjet printing process involves the generation and deposition of droplets followed by their curing, droplets with different refractive indices can be deposited one after the other and cured immediately upon deposition, resulting in the formation of a material with differing refractive index values [112]. However, developing materials which produce good quality GRIN components while also being suitable for inkjet printing remains a challenging task with scope for further development [106].

The key requirements an inkjet formulation must satisfy in order to produce GRIN components include the use of a base material which shows a shrinkage of less than 20% upon curing, transmittance values of over 90% for both the monomer and the nanoparticles, a composition of nanoparticles that is at least 2% by volume, sufficiently small nanoparticles that do not lead to large scale light scattering and a viscosity lower than 20 cPoise [106]. Also, a larger difference between the refractive indices of the polymer and the nanoparticle eases the fabrication of GRIN lenses with shorter focal lengths [113].

However, despite the potential of inkjet printing to fabricate GRIN lenses, developing materials which produce good quality GRIN components while also being suitable for inkjet printing remains a challenging task with scope for further development [106]. As a result, most research into inkjet printing of GRIN lenses/components is currently focussing on optimizing and characterizing the inks and the polymer networks obtained after printing [106,112,114]. The consensus between the reported inks is the incorporation of nanoparticles into the formulation to eventually be able to inkjet print GRIN lenses. Schut et al. [106] prepared GRIN films by combining diamond nanoparticles with the base polymer. These nanoparticles show a refractive index of 2.42. To prevent agglomeration of these nanoparticles and provide good dispersion in the matrix material, they are surface treated with ligands such as carboxylates and amines, with the other end of the ligand being similar in structure to the matrix polymer. The concentration of the nanoparticles was between 20 and 25 wt%. McMorro et al. [112] used silicon carbide nanoparticles to prepare GRIN films as well. They were combined with an acrylate monomer and in order to aid their dispersion in the base monomer, the nanoparticles were treated with a silane. The GRIN product was then formed by depositing different formulations of the ink in layers, with the concentration gradient of the nanoparticles in the polymer varying from 0 to 4.5 wt%. All the individual layers were first partially cured with a UV exposure of 0.50 W/cm<sup>2</sup> and then completely cured with a UV dose of 1.5 W/cm<sup>2</sup>. The obtained final film showed a smooth surface, and the nanoparticles present within the film were well dispersed. In addition, it was impossible to identify the interface between the different layers, indicating they had combined well. While the pure acrylate films were transparent in the visible region, films containing 4.5 wt% silicon carbide nanoparticles showed significant absorption in the visible range, with this value only decreasing to lower levels in the infrared range. Check et al. [114] prepared nano-composites suitable for use as GRIN lenses by adding ZrO<sub>2</sub> nanoparticles to a diacrylate monomer, with the nanoparticle concentration ranging from 10 to 30 wt%. The samples were prepared in a layer-by-layer manner with each layer being partially polymerized. It was observed that the presence of ZrO<sub>2</sub> nanoparticles increased the conversion of the monomer and that in order to achieve a good interface; the degree of cure must be limited to 60–80% by varying the UV dosage. The findings of these studies demonstrate the potential of inks for the inkjet printing of GRIN lenses.

## 7. Applications of microlenses

Microlenses and microlens arrays act as key components for several optoelectronic systems and find applications in a wide range of devices. Microlenses can be used for imaging applications such as in photocopiers, cameras and microscopes. They also find use in several sensing applications such as in astronomical telescopes owing to their ability to increase the photosensitivity of these devices. They also find use in numerous devices requiring collimation and focusing such as organic light emitting diodes and optical interconnects [6,7,115,116].

One of the key advantages of inkjet printing is the possibility to print directly onto optical substrates such as quartz glass and polymer plates [36]. Given this advantage, the ability to print microlenses directly onto optoelectronic components such as diode lasers and optical fibers remains an attractive option and an area of significant research.

Cox and Guan [117] used inkjet printing to directly fabricate collimating microlenses onto the ends of optical fibers. The fibers were held in place by means of a collet, which essentially forms a collar around the fiber. Photo-crosslinkable ink was then allowed to collect in the gap between the top of the collet and the fiber, which was subsequently cured via UV radiation, leading to the formation of a microlens. A de-wetting solution was also applied at the surface opening, allowing for the development of microlenses with a small radius of curvature. The application of this coating was not shown to have any clear impact on the functioning of the fabricated microlenses. Tien et al. [118] directly printed decoupling microlens patterns over the back of a light guiding plate used for display backlighting applications. The plate itself was made from polymethyl methacrylate and subjected to various surface treatments in order to control the wettability of the ink. The fabricated patterns showed high extraction efficiencies and reduced development time.

Hayes and Chen [119] printed microlenses onto pedestals fabricated on top of a diode laser wafer. This resulted in lenses with heights ranging from 25 to 38 µm, depending on the number of drops, and improved the coupling efficiency from the diode laser to multi-mode fibers.

Zhao et al. [120] fabricated a diode laser-based sensor system incorporating microlenses. A pedestal was first prepared on a diode laser chip using direct UV laser writing. Microlenses were then printed on top of the pedestals via inkjet printing, as shown in Fig. 7. The diode lasers integrated with microlenses showed a much lower laser beam divergence when compared to laser-less diodes.

Ishii et al. [94] fabricated a microlens directly onto a laser diode, as shown in Fig. 8. The surface of the diode was coated with a fluorinated polymer to control the wettability of the lens. The fabricated microlens had a diameter of 45 µm, showed a strong focusing effect and as compared to a diode without a microlens, it showed significantly higher

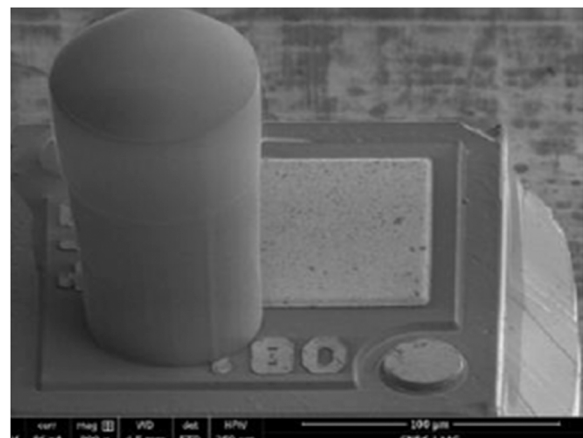


Fig. 7. Scanning electron microscope images of a microlens fabricated on a pedestal on the surface of a diode laser chip [120].

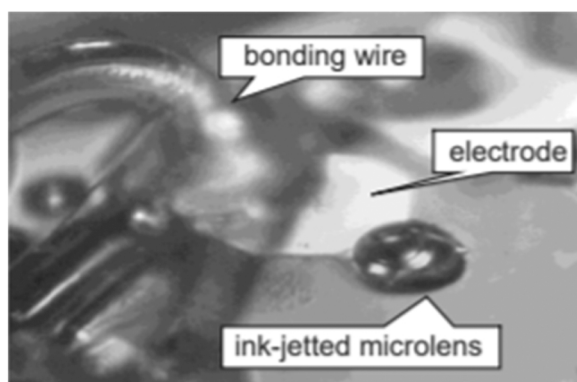


Fig. 8. Optical microscope photograph of a diode laser integrated with an inkjet-printed microlens [94]. (Copyright (2000) The Japan Society of Applied Physics.)

coupling efficiency.

## 8. Conclusions and outlook

3D Inkjet printing is demonstrated as a viable technique for the fabrication of microlenses, possessing several advantages such as high flexibility, scalability, low costs, low material wastage and no post-processing requirements. A key advantage of this technique is the ability to print on different modified substrates, allowing for the development of microlenses with a wide range of optical properties and geometries from the same material. This, however, comes at the cost of increased process complexity. Within 3D inkjet printing, the DOD droplet generation method is seen as the preferred option for digital fabrication. Acrylates and epoxies are identified as the most common monomers in microlens inkjet formulations, while the use of hybrid organic-inorganic materials has rapidly increased in recent years owing to their superior mechanical and optical properties. These monomers also allow for the tailoring of microlens properties by the incorporation of different functionalities. Furthermore, the ability of these monomers to incorporate organic compounds and inorganic nanoparticles enables the generation of high refractive index materials and GRIN films via inkjet printing, with organic compounds enabling a small increase in the refractive index while inorganic nanoparticles can produce much higher refractive index materials. The dispersion of these compounds within the formulations represents the key characteristic controlling microlens optical properties. Preventing the formation of an interface between the combined droplets containing different formulations and reduced transparency due to nanoparticle aggregation remain key challenges in the development of GRIN materials. To aid dispersion and prevent nanoparticle aggregation, materials such as silanes, carboxylates and thiol groups have been used.

While 3D inkjet printing provides several advantages for the production of microlenses, there are still a number of key challenges that must be addressed before this method achieves widespread commercial use. Chief amongst these challenges is the need for extensive trial and error in order to determine the ideal printing parameters. Additionally, UV curable inkjet inks are also well covered in terms of intellectual property, which makes identification of suitable formulations a difficult task. It can also be challenging to obtain a smooth surface profile for the lenses. This is especially the case for inks containing volatile components which are released during curing and leave behind an uneven surface. In order to compete with conventional manufacturing techniques, 3D inkjet printing must be able to produce parts at a rapid pace. This requires increasing the number of nozzles for printing; however, this can lead to reliability issues and increased machine costs. Finally, without the use of modified substrates, microlens geometries can be difficult to repeat and control.

Despite these challenges, the field of inkjet-printable photo-cross-linkable resins has seen immense research and development in recent years. Several companies now produce formulations which provide reliable and repeatable results for the development of microlenses. A few examples also exist in industry where inkjet printing is being used to produce microlenses. With a better understanding of the properties of complex formulations and their desirable printing parameters as well as the optimization of the printing process to enable higher volume and low-cost production, 3D inkjet printing can play a major role in meeting the ever-increasing demands of the future in a more sustainable and economical manner.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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