

Journal of Materials Chemistry C

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3D printing of porous structures by UV-curable O/W emulsion for fabrication of conductive objects

Cite this: DOI: 10.1039/x0xx00000x

I. Cooperstein,^a M. Layani^a and S. Magdassi^a

Received 00th January 2014,
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

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The growing interest in the field of three-dimensional printing has led to great demand for new materials. In this paper we should like to present a new ink for printing porous structures that can be used for embedding various functional materials. The ink is composed of a UV polymerizable Oil-in-Water emulsion which converts into a solid object upon UV irradiation, and upon evaporation of the aqueous phase, forms a porous structure. The 3D objects with their various porosities, were printed by a Digital Light Processing (DLP) printer. The total surface area of the object can be controlled by changing the emulsion's droplets size and the dispersed phase fraction. The printed 3D porous structures can be used in a variety of applications, and here we show a composite conductive object, made of silver and cross-linked polymer. After the porous object is formed, the pores are filled by vacuum, dipping in a dispersion of silver nanoparticles, followed by chemical sintering at room temperature, which results in conductive percolation paths within the 3D structure. Application of this structure is demonstrated for use as a 3D connector of an electrical circuit.

Introduction

The field of three-dimensional (3D) printing has developed significantly in recent years¹, consequently increasing the need for new materials for the fabrication of functional 3D structures.^{2, 3} An additive manufacturing process is currently being used for a variety of applications such as modelling and medical structures.⁴⁻⁷ All current methods are based on layer-by-layer fabrication of a structure, each layer being built by one of the following methods: (1) Fuse Deposition Modelling (FDM) based on melting a polymer that enables patterning with the liquid filament, (2) Selective Laser Sintering (SLS) based on obtaining 3D structures by starting with powder, or (3), Color Jet Printing (CJP) obtaining 3D structures by jetting a binder onto the powder. Another technique is stereo lithography which is based on selective curing of polymerizable monomers. A common method for this technique is Digital Light Processing (DLP) which is based on selective polymerization of individual pixels within a thin layer. This is done by using a digital micro mirror device (DMD) that results in small dots (dozen of micrometers).⁸ The DLP method is currently used mainly for the production of 3D structures, using different types of monomers and additives to affect the mechanical properties and colour of the final printed structure. In this research we aim at obtaining a porous structure for further embedding of functional particles, mainly metal nano-particles (NPs), in order to achieve electrical conductivity. Makitie et al⁹ printed photo-curable polycaprolactone to fabricate 3D structures with voids by the DLP method, obtaining voids in the size range of 500-1000 μm .

3D printing of curable, high internal phase emulsion (HIPE) was reported for porous structures. For example, Wenliang et al¹⁰ used a water-in-oil (W/O) HIPE in which the oil phase (10% by volume) was an organometallic material which, after its polymerization, could be used as a photo-catalyst. It was found that the obtained structure had voids with a pore size of $\sim 10 \mu\text{m}$, and were formed due to evaporation of the dispersed water droplets (90% by volume). Sušec et al¹¹ combined the

printing and HIPE to form a hierarchically porous material, by preparing a W/O emulsion with 80 wt% droplet phase and photocurable continuous phase. The W/O emulsion was printed by the DLP technique, which resulted in a monolithic porous structure with an average cavity size of 2-4 μm . To the best of our knowledge, there are no reports on printing non-HIPE emulsions or oil-in-water (O/W) emulsions, in which the dispersed oil droplets are polymerized to fabricate monolithic porous structures. The advantage of using the non-HIPE emulsion is its greater stability that is crucial for the printing of large monolithic structures. Furthermore, due to the high volume fraction in HIPE, typically high viscosity inks are obtained, thus limiting their possible use in various printing methods, for example, inkjet printing. In order to obtain functionality of a porous structure by entrapment of nano particles along the structure, continuous voids in the size scale of the nanoparticles should be present within the structure. Here we present a new approach for obtaining 3D porous structures by polymerizing UV curable oil droplets in an O/W emulsion using the DLP technique. The result will be a porous structure with interconnected voids, which will enable penetration of the nanoparticles such as silver throughout the printed 3D object. Currently, there have been reports on the use of several methods for the fabrication of 3D conductive structures. Leigh et al¹² printed polycaprolactone (PCL) filament containing carbon black by a Fused Deposition Modelling printer (FDM), and achieved a 3D structure with high resistivity. Ahn et al¹³ fabricated 3D structures with hundreds of micron heights by depositing high-viscosity silver NPs ink from a nozzle, followed by rapid evaporation of the volatile solvent within the ink. The resulting structures were heated to 250°C, yielding a structure with low resistivity. We recently reported¹⁴ on achieving 3D conductive structures by using an inkjet ink composed of metal NPs, dispersed in a curable oil-in-water emulsion. Upon UV radiation, the printed monomers polymerize and a composite material with embedded silver NPs

is obtained. The structure is not conductive and requires further sintering.

Here we use an oil-in-water emulsion to print a 3D porous structure, followed by the embedment of silver NPs within the pores. This new approach enables a new strategy for the production of conductive 3D large structures, which upon sintering at room temperature¹⁵, yields a composite metal-polymer conductive object.

Result and discussion

For the preparation of the O/W emulsions, we performed preliminary screening of surfactants. We found that the combination of the surfactant with high hydrophilic-lipophilic balance (HLB), Tween 20, with a lipophilic surfactant, Span 20 yielded an HLB of 15.5, which was optimal in terms of emulsion stability. This is favorable, since for fabricating a 3D object with this type of ink, the polymerized droplets should form a continuous matrix, and for this reason the droplets must be in close contact during printing. Therefore, the emulsions were prepared with 50 wt% to 75 wt% monomer as the oil phase.

Controlling the surface area of the resulting porous printed object can be achieved by changing the emulsion droplet size and the phase fraction. Therefore, we prepared the emulsions by using various equipments at a constant composition of the emulsion. It was observed that the size of the oil droplets in the emulsion decreased when using higher energy mixing techniques. Fig. S1 shows the different sizes that can be obtained, using various techniques of homogenizing the two phases, ranging from about 0.5 μm to 5.5 μm . Another approach to decreasing the size of the droplets is by increasing the amount of surfactants, as shown in Fig. S2. These two parameters enabled us to control the porosity of the 3D objects.

1. Printing 3D porous structures

The emulsions were irradiated at 395nm in a DLP printer. The polymerized object made of emulsion containing 60% monomer was measured by FTIR (Fig S3) in order to evaluate the conversion degree during the polymerization occurring upon printing. The conversion degree was 55%, meaning that there is still free monomer. As presented in Fig. 1A, the printed emulsion yielded a white solid object due to light reflection caused by the spherical cured droplets. Fig. 1B and 1C is an HRSEM image of surface and cross section of this structure, showing that the printed structure is composed of polymeric spherical particles in close contact.

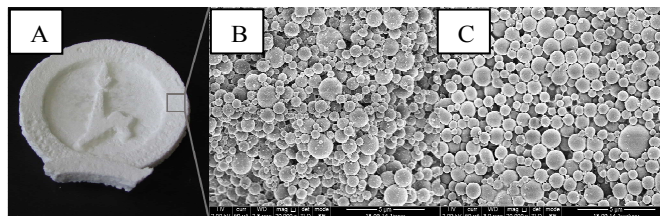


Fig. 1: Images of printed emulsion with 60 wt% droplets phase (DPGDA) with average diameter of $1.5 \pm 0.03 \mu\text{m}$ (A) Image of HUJI symbol (B) UHR-SEM image of a cross section (C) UHR-SEM image of the upper surface of the structure.

A quantitative analysis of the porosity of printed objects was performed by measuring their surface area by the Brunauer–Emmett–Teller (BET) method. The measurement was performed on printed objects formed by emulsions having different average droplet sizes (Fig. 2A), or different dispersed phase fractions (Fig. 2B). In general, the surface area of the printed object was in the range of 2-10 m^2/gr . As expected, decreasing the emulsion's droplets size and increasing the dispersed phase fraction led to an increase of the specific surface area of the structures, thereby enabling a simple approach to controlling the porosity. Fig. 2A shows also the theoretical values of the expected surface area (calculated from the emulsion's droplets size as described in the experimental section) compared to the measured surface area of the printed objects. As can be seen, the general trend for surface area reduction is similar for both the theoretical and measured points, indicating that the 3D structure is composed of polymerized particles with only few contact points (as observed in Fig. 1B). It should be noted that the theoretical values, shown as squares, are slightly smaller than the measured values, as may be attributed to shrinkage of the monomer droplets during polymerization. It should be noted that at this stage, due to the light scattering of the emulsions, the printing of the emulsion by the DLP method can only be performed with a setup of layer thickness below 30 μm and droplet sizes above 500 nm. Furthermore, it should be noted that the resulting 3D structures have are brittle, and further mechanical improvement may be performed in the future, according to specific intended applications.

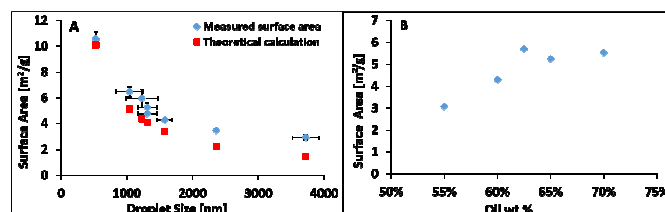


Fig. 2: (A) Surface area vs. droplet diameter of emulsions with 60 wt % oil weight percentage. The squares are calculated surface area according to emulsion droplet size. (B) Surface area vs. oil phase fraction with emulsions droplets size of $1.7 \pm 0.5 \mu\text{m}$.

2. Conductive objects

The above porous structures were utilized to form conductive objects by embedding silver NPs within the pores. The printed objects were immersed in dispersion of silver NPs and, by applying vacuum, the liquid and the particles were expected to penetrate into the pores¹⁶. In general, we found that the ink with the silver NPs indeed penetrated into the pores of the printed structure, accompanied by change of colour, from white to greyish.

In order to obtain a conductive percolation path between the silver NPs, sintering must be performed. Usually sintering is done by heating at elevated temperatures, such as 200-300°C. However, since at such temperatures the organic matrix might deform, we performed the sintering at a low temperature. This process is based on ligand exchange mechanism and is achieved by exposing the silver NPs to chloride ions.¹⁵ Therefore, after the insertion of the NPs, the structure is exposed to HCl vapours. Fig. 3 shows the inner structure of a printed object with sintered silver NPs. As seen, the silver is present in the voids, in between the spherical polymeric particles, which are the polymerized oil droplets of the starting emulsion. It should be noted, that while all the voids are filled with silver NPs (Fig. 3A), the densest silver layer is at the outer 5 μm of the structure (Fig. 3B). This may result from the porous structure of the object which functions like a depth filter, in which most of the material is present in the outer layers. This issue can be resolved by proper control of the insertion parameters (vacuum and time of immersion) and properties of the ink (surface tension, viscosity and particle size). Cubic structures of 60% oil phase emulsion were printed and the average resistance was measured to be $1 \pm 0.2 \Omega$ from both sides of the cube.

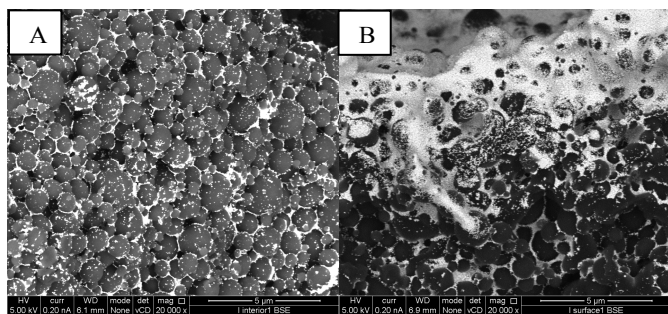


Fig. 3: UHR-SEM cross section image of printed 70 wt% oil phase emulsion, with $1.1 \pm 0.2 \mu\text{m}$ droplets size, in 25 μm layers thickness printing, after insertion and sintering of Ag NPs of (A) object's surface (B) object's inner bulk.

For evaluation of the 3D object as a conductor, we simplified the oil phase of the emulsion to contain only one bi-functional monomer, dipropylenglycol diacrylate, and one photoinitiator, Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide.

To demonstrate one possible application we printed an electric circuit using such an emulsion to obtain a porous 3D structure

(Fig. 4A), followed by impregnation with silver NPs and sintering (Fig. 4B). This electric circuit was connected to a 3V power source at one end, and a light emitting diode (LED) at the other. While applying the voltage, the electric current passed through the conductive 3D printed structure, resulting in light emitting from the diode.

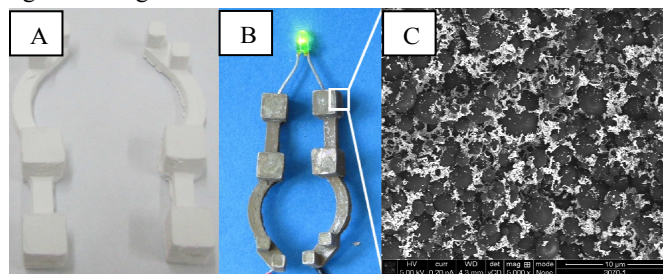


Fig. 4: Images of electric circuit printed from emulsion of 70 wt% DPGDA as oil phase (A) Image of the clean porous 3D structure (B) Image of the porous structure after inserting Ag in DB dispersion, sintering and connecting to 1.5V and LED, (C) UHR-SEM cross-section image of the printed structure with embedded Ag NPs.

Experimental

1. UV reactive phase

The dispersed phase of the emulsion (reactive phase) was composed of the following components: (1) monomers: dipentaerythritol hexaacrylate (DPHA), trimethylolpropane-triacrylate (TMPTA) and dipropylenglycol diacrylate (DPGDA) (Sartomer), at a 1:1:1 weight ratio, and (2) a mixture of photoinitiators: 32% ethyl-4-dimethylaminobenzoate (EDMAB), 13% 2-isopropylthioxanthone (ITX, Sigma Aldrich), 12% benzyl-2 dimethylamoni-1-4-morpholinophenyl-butanone-1 (Irgacure 369, BASF), 28% dimethyl-1,2-diphenyllehan-1-one (Irgacure 651, BASF), and 15% benzophenone (Sigma-Aldrich). The concentration of the photoinitiators in the monomers was 16.9 wt%. The obtained mixture was a yellowish clear solution.

2. O/W emulsion

The emulsions were prepared with 50-70 wt% dispersed phase, and surfactant concentration of 4-8 wt%. The surfactants were a mixture of Tween 20 and Span 20 (Sigma-Aldrich) at a 17:3 weight ratio. The Tween 20 was dissolved in triple-distilled water and the Span 20 in the UV reactive phase. A coarse emulsion was made by adding the UV reactive phase with the surfactant, to the water with the surfactant, while stirring by a magnetic stirrer for 30 minutes. To achieve different droplet sizes, the coarse emulsions were further homogenized by one of the four kinds of the following: (1) Dispermat CV (VMA, Germany) at 8000 rpm for 10 min, (2) Ultra-Turax Homogenizer T25 (IKA, USA) at 15,000 rpm for 8 min, (3) Probe Sonicator VCX 750W (Sonics & Materials, INC, USA) for 30 sec, at 10/5 sec pulses, 100% intensity, (4) High pressure

homogenizer (HPH) model M-110L (Microfluidics, USA) at 60PSI for 10 cycles.

3. Printing procedure

The printing was performed by Freeform Pico Plus39 Digital Light Process printer (ASIGA, Australia). The printing was performed at 10-30 μ m layer thickness with 2 sec irradiation at $\lambda=395$ nm. After printing, the object was immersed overnight in isopropyl alcohol, under stirring and at room temperature, in order to extract the unreacted monomers, the initiators and the water. The wet objects were dried under vacuum at room temperature for 30 minutes.

4. Silver embedding

The consequent porous objects were immersed in a silver dispersion containing 40 wt% silver NPs with an average diameter of 10 nm (Xjet-Solar, Israel). The process was performed inside a vacuum chamber in which, after the air was evacuated for 2 minutes, insertion of the dispersion into the pores occurred upon releasing the vacuum¹⁶. After the insertion, the object was dried in a vacuum oven at 70°C for 2 hours in order to evaporate the solvent.

To achieve conductivity, the porous object, filled with Ag NPs, was exposed to HCl vapours for 10 seconds.

5. Characterization

The resistance was measured by using Milliohm Meter (220VAC) (Extech instrument, USA) and placing each probe at the opposite faces of the printed objects. The resistance measurement was performed on cubes (5X5X5 mm) composed of 60% monomer as $1.3 \pm 0.03 \mu\text{m}$ average droplets diameter. For the calculation of the theoretical surface area, we used the equation: Surface Area / weight = $3V_{\text{oil}} / R \times \text{weight}$. Where V_{oil} is the value of the monomer fraction and R is the radius of the emulsion droplets as measured in the DLS device. The weight was calculated from the density of the monomer phase which is 1.11 gr/ml. Conversion degree of the C=C bond was determined according to Tasic et al¹⁷ using the C-H band of the vinyl group at 809 cm^{-1} by ATR-FTIR measurements (IRAffinity-1S, Shimadzu, Japan), while comparing to the band which remains constant, at 2980 cm^{-1} .

Droplets size was measured for emulsions diluted in water by Dynamic Light Scattering method using a NanoZS Zetasizer (Malvern, UK). The surface area measurements for the printed porous objects were performed by the Brunauer–Emmett–Teller (BET) method using the NOVA 1200e (Quantachrome, USA) for the experiments of droplets vs. surface area, and using the ASAP 2020 (Micromeritics, USA) for the experiments of phase fraction vs. surface area. Ultra high resolution scanning electron microscopy (UHR-SEM) observations were performed by Magellan XHR SEM (Field Emission Instruments (FEI, USA)).

Conclusions

We have presented a new ink for printing 3D porous structures. The ink is composed of UV polymerizable Oil-in-Water emulsions, which converts into a solid object upon UV irradiation. The 3D objects were printed by using a Digital Light

Processing (DLP) printer, but the same can be achieved with other printers which are based on photo-polymerization. The pore sizes can be controlled by changing the droplets size and phase fraction of the dispersed phase. These pores can be filled with various functional materials. In the present study we filled the voids with silver NPs, which upon sintering, yielded a 3D conductive object, due to the percolation paths. The porous structure presented in this work can be utilized in functional 3D printing, such as printing embedded conductors or electrical bridges in electrical circuits. Obviously, the properties of the resulting structures should meet the requirements of the intended application, such as mechanical properties, electrical conductivity and thermal stability.

Acknowledgements

This research was partially supported by the Singapore National Research Foundation under the CREATE program: Nanomaterials for Energy and Water Management, and by the Israel National Nanotechnology Initiative FTA project on functional coatings and printing.

^a Casali Center, Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem, Israel 91904.

E-mail: Magdassi@mail.huji.ac.il

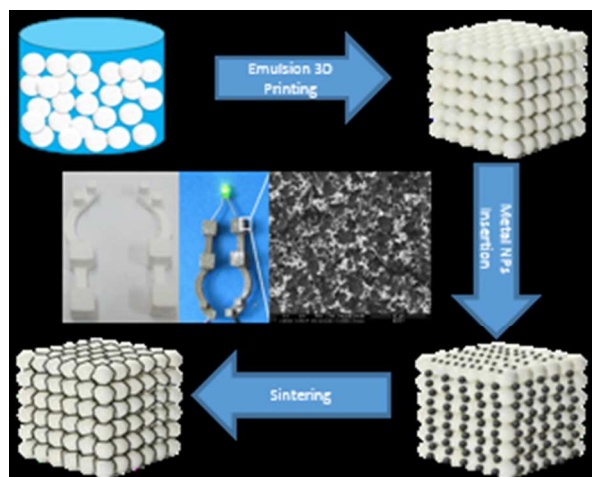
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We present a new approach for fabrication of a porous structure with controllable pore size for later embedment with nano particle. We showed how this method can be applied for fabrication of a 3D conductive circuit.
49x39mm (150 x 150 DPI)