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PRELIMINARY STUDY ON NANO PARTICLE/PHOTOPOLYMER HYBRID FOR 3D INKJET PRINTING

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ABSTRACT: 3D inkjet printing is one of the new generation Additive Manufacturing technologies for the production of multi-material and multifunctional 3D products. Due to the critical condition for ink deposition and the stringent requirements for ink solidification, only limited ranges of materials are suitable for 3D inkjet printing. These include low viscosity photo curable polymers, and low melting temperature materials like wax. In this study, a hybrid printing ink prepared by mixing nano silica particles into photopolymer resin was developed for 3D printing, and the influence of silica particle concentrations on the viscosity, surface tension, printability and mechanical properties of cured polymer was studied. Results show that untreated nano silica particles would influence the rheological properties which is critical to the printability, but did not improve the mechanical properties due to the aggregation of nanoparticles during photo curing.

INTRODUCTION

3D Printing (3DP), also known as additive manufacturing, has great potential as a manufacturing tool for creation of complex shaped products. A number different 3DP technologies have been developed over the past 20 years, which includes stereolithography (SLA) (Zhou et al. 2013), selective laser sintering and melting (Goodridge et al. 2012 and Khan 2010), extrusion fabrication like multi-material Fused Deposition Modeling (FDM) (Espalin et al. 2012) and direct writing (DW) (Nam-Soo & Kenneth 2010). A recent development in 3DP is to explore the possibilities of using ink jet based printers for the production of 3D objects (Singh et al. 2010), and in particular, for multi-material, multi-functional fabrications.

Drop-On-Demand (DOD) piezoelectric inkjet printing is the most common jet based printing technique, which can in principle deposit different materials to a given location with high precision and zero material waste (Singh et al. 2010). Despite such advantages, the technique has the limitation that the rheological properties of the material as printing ink must fall within some given narrow ranges. A common solution to this problem has been to dilute or thicken the ink liquid

using additives and solvents, to match the rheological properties requirements. However, this has the consequence that after printing, the solvent needs to be removed using separate procedures, as the solvent remained on the product will likely induce detrimental effects on mechanical and chemical properties of the final products.

An alternative solution to the situation is to divide the procedure into two steps of printing and deposition: first printing some easy flowing ink material directly without using additives solvents, and then using other procedures to solidify the ink jet to produce the final product. Photo curable materials with high curing speed are ideal candidate for such purposes in 3D inkjet printing. In this method, a photo polymerization system (e.g., using ultraviolet radiation) is combined with the printing system to cure the droplets jetted on substrate to form the final solidified polymer product. This approach has been implemented in some commercial class 3D inkjet printers like Polyjet 3D printer of Stratasys.

So far only a small number of materials have been successfully printed with the above two steps technique; these includes photo curable polymers and several low melting temperature materials like wax. These materials have the deficiency of low mechanical strengths and thermal properties, and thus can only be used for applications of product prototyping. To expand the technique for more practical manufacturing applications it is an urgent task to develop new materials that are suitable for the two step 3D inkjet printing.

Organic-inorganic hybrid materials have shown good material properties, including good transparency, high strength and hardness, anti-abrasion/scratch, anti-erosion to solvent and thermal stability. Such materials are often prepared by dispersion of inorganic nanoparticles, such as nano silica (Bauer & Mehnert 2005), carbon nanotube etc, into a polymer matrix. To investigate the feasibility of 3D inkjet printing with nanocomposite, in this study a hybrid printing ink prepared by mixing nano silica particles into the photopolymer resin is developed. The influence of nano silica particle concentrations on the printability and mechanical properties of the cured polymer is then studied.

METHODS

Preparation of hybrid inks

Hybrid printing ink samples with three different silica particle concentrations were prepared, by mixing nano silica particles (fumed silica, Sigma-Aldrich) with a 3D inkjet printing material (Objet Fullcure720), in which silica particles have 0.5%, 1.0% and 1.5% of weight proportions in the hybrid ink.

Fluidic characterization

Viscosity of each sample was measured using rotational rheometer (Physica MCR 301, Anton Paar, UK) configured with a 50mm plate. The viscosities of the samples were measured under different temperatures and different shear rate conditions. Surface tension of each sample was measured on an OCA40 Automatic Contact Angle Meter (Dataphysics, Germany) using the pendant drop method.

Mechanical properties

Thin films (about 200 μ m) of samples were prepared on glass by coating and curing with UV Flood light curing system (Techno Digm, Singapore). The surface profile of the samples was observed with an Olympus Metallurgical MX51 Upright Microscope, and the surface roughness was

measured with a Stylus Profilometer (Form Talysurf Series 2, Taylor-Hobson). The surface hardness of the cured films was measured using a Nano-indenter (Micro Materials NanoTest 550, UK). Films were then removed from substrates and cut into strips of 35mm for length and 5mm for width for tensile testing. The tensile test was carried on a Tensile Micro Tester (Model 5548 MicroTester, Instron, USA) equipped with a 2kN load cell. A set of five samples were tested for each material.

RESULTS AND DISCUSSION

Printability assessment

DOD inkjet printing has been commonly used for not only daily document printing but also for modern industrial applications. Functional inks can be deposited with precise quantities on a surface through a nozzle of 20-50 μ m diameter. When a voltage is applied, the piezoelectric inkjet print head generates a short pressure pulse. The pressure pulse is applied on the fluid filling the pathway behind an orifice, where the fluid meniscus is maintained by surface tension. Under suitable electrical conditions, the ejected fluid develops into a single droplet for quality ink-jetting.

Besides the operational parameters like voltage, printing frequency and waveform, the printing fluid properties including viscosity, surface tension and density are also critical to the achievement of a good jetting quality. A non-dimensional character Z (the inverse of Ohnesorge number, Oh), has been introduced to evaluate the printability of different printing fluids. Z is only related to ink viscosity, density, surface tension and the orifice diameter. Oh is the ratio of the square root of the non-dimensional number We (Weber number) to another non-dimensional number Re (Reynold's number). Equations 1 to 4 show the calculation of Z , where ρ is density, V is drop velocity, r is the nozzle diameter, γ is surface tension, and μ is viscosity.

$$We = \frac{\rho V^2 r}{\gamma} \quad (1)$$

$$Re = \frac{\rho V r}{\mu} \quad (2)$$

$$Oh = \frac{\sqrt{We}}{Re} = \frac{\mu}{\sqrt{\gamma \rho r}} \quad (3)$$

$$Z = \frac{1}{Oh} = \frac{\sqrt{\gamma \rho r}}{\mu} \quad (4)$$

Fromm (1984) first predicted that stable drop formation in DOD system happens only when $Z > 2$. Reis and Derby (2005) later suggested that a printable fluid should have a Z value of between 1 and 10 based on computational fluid dynamics and experimental studies. When Z is too big, satellite forms instead of single droplet. When Z is too small, the separation of the droplet is difficult. In those cases the position accuracy is difficult to control.

Table 1 Properties of photo curing resin with different silica content

Silica content %	Surface tension (mN/m)	Density (Kg/m ³)	Viscosity Range(mPas)	
			$r=10.5\mu\text{m}$	$r=25\mu\text{m}$
0%	31.3±0.81	1092	2-19	3-29
0.5%	31.76±0.57	1095	2-19	3-29
1.0%	32.71±0.53	1099	2-19	3-30
1.5%	29.35±0.86	1102	2-18	3-28

Table 1 lists the surface tension and density of the photo curing resin with different silica content. Base on Derby's suggestion that Z should be less than 10 and greater than 1, the ranges of the viscosity for printing are estimated, corresponding to different sizes of nozzles (21 μm and 50 μm). The results show that the surface tension did not show an obvious change when the silica content is lower than 1%, but has a slight reduction when the silica content is increased to above 1.5%. The viscosity of inks is generally the same for all the four composites using same size nozzle. To achieve a better printing result, the viscosity should be less than 19mPas when the nozzle diameter is 21 μm and less than 30mPas when the nozzle diameter is 50 μm .

Figure 1 Effect of temperature to the viscosities of nano silica/photo curing resin hybrids: viscosities reduced with the increase of temperature, shear rate 100s^{-1} (a); Effect of the content of silica to the viscosities of hybrids: Rheological property of nano silica/photo curing resin hybrids with 0.5% silica hybrid (b), 1.0% silica hybrid (c), 1.5% silica hybrid (d), temperature 75°C .

The pure photo curable resin Fullcure720 is a near Newton fluidic resin. When mixed with nano silica particles, the material showed increasing level of shear-thinning property with the increase of silica particle concentration. This is because that the extremely high surface area and high surface energy of the nano particle silica help to form a 3 dimensional structure with the polymer chain through hydrogen bonding, and the 3D structure can be destroyed by strong enough mechanical force.

Figure 1 (a) shows the viscosity change when the temperature is increasing from 25 to 75°C, while the shear rate is maintained at 100s⁻¹. Even at 75 °C and under a shear rate of 100s⁻¹, the viscosity of the hybrid material with 1.5% silica concentration is still above 100mPas. Under higher shear rate (over 3000 s⁻¹) and higher temperature (above 75°C), the viscosity of all the three ink samples are reduced to around 20mPas (Figure 1 (b), (c) and (d)). During inkjet printing, the shear rate working on the printing materials is normally higher than 3000 s⁻¹, so it is possible to print those hybrid materials. However the printing performance of non-Newtonian fluid is still far from being understood, the influence of non-Newtonian fluid on the printing quality will be investigated later.

Mechanical properties of photocured film

After being mixed with nano particles, there is no particle visibly observed in the ink mixture, and the samples are still highly transparent. However, after cured with UV light, the surface of the samples became rough and particle aggregations are observed. Figure 2 shows the surface profile in the samples after they are fully cured. The nano particles were aggregated and separated from the cured polymer matrix.

Figure 2. Images of the surface profile of cured materials: pure photopolymer (a); photopolymer with 0.5% nano silica (b); photopolymer with 1.0% nano silica (c); and photopolymer with 1.5% nano silica (d) .

Table 2 shows the results of the surface roughness, hardness and tensile test results. Overall the mechanical properties of the cured hybrids have not been improved by adding nano silica particles. The tensile module of the product is reducing with the increasing of nano particle concentrations. The main reason for this is that the aggregation of the particles during curing reduced the enforcement of the nanoparticles.

Table 2 Mechanical properties of cured nano silica/photopolymer hybrids

Silica content %	Surface roughness	Surface hardness	Tensile test	
			Tensile stress(MPa)	Modulus(MPa)
0%	0.0146 μ m	38MPa	76.74 $\pm$ 10.36	3351 $\pm$ 21.35
0.5%	0.0979 μ m	34MPa	60.1 $\pm$ 8.04	2494 $\pm$ 344.5
1.0%	0.3356 μ m	28MPa	46.99 $\pm$ 2.75	2485.21 $\pm$ 472
1.5%	0.6144 μ m	31MPa	43.47 $\pm$ 3.08	1969 $\pm$ 508

CONCLUSION

Preliminary study on photopolymer/nano silica hybrid ink showed that untreated nano silica particles would influence the rheological properties of the ink, which is critical for inkjet printing. Future work will focus on reducing the particle aggregation and increasing the silica content in the ink hybrid, and using functional modified silica particles to solve the above problem.

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