Printability of elastomer latex for additive manufacturing or 3D printing

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ABSTRACT: Additive manufacturing, sometimes referred to as 3D printing is a new, rapidly developing technology which has the potential to revolutionize fabrication of certain high value, complex products. Until now conventional elastomers have not been widely used in the additive manufacturing process. The goal of our work was to determine the feasibility of additive manufacturing using ink jet printing of elastomeric latex materials. Particle size, viscosity, and surface tension were measured for five different latex materials—poly(2-chloro-1,3-butadiene), carboxylated styrene-butadiene rubber, carboxylated butadiene-acrylonitrile copolymer, natural rubber, and prevulcanized natural rubber. The XSBR latex was predicted as the one most likely to be printable. Printing trials carried out with the XSBR as the ink proved it to be printable, although technical problems of agglomeration and print head clogging need to be addressed and both the material and process need to be optimized for consistent printing to be achieved. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42931.

INTRODUCTION

Additive manufacturing is defined as the fabrication of an object by progressive addition of layers of material. Within each layer the material is either laid down or solidified in lines or strips, in much the same way that a 2D image is printed. Hence, additive manufacturing machines include a means of depositing or solidifying material and a means of scanning in *X*, *Y*, and *Z* directions to control the positioning of the material. There are many different additive manufacturing technologies available, usually classified according to the means by which the material is deposited or solidified.

Since its advent in the 1980s, rapid prototyping has developed into a broader and more capable technology referred to as additive manufacturing. Technology development is currently expanding rapidly, as its potential to produce highly complex and custom-made products is recognized. However, the main disadvantages of additive manufacturing are the limited range of materials that can be processed in this way and the fact that the material properties are often inferior to those used in more conventional fabrication methods. Rubbers or elastomers are one of

the classes of materials particularly underprovided for in the additive manufacturing industry. A brief review of the current additive manufacturing technologies relevant to rubber-like materials is given below.

Elastomers can be divided into two groups: firstly the conventional crosslinked or thermoset elastomers, and secondly the thermoplastic elastomers (TPEs). For the TPEs, the techniques that are available for use with thermoplastics can be applied. One of the earlier methods to be developed is selective laser sintering (SLS). In SLS, the object is built up within a bed of powdered material by selectively sintering or melting the thermoplastic powder with a laser. For each layer the bed is moved down a step and a layer of fresh powder is spread over the whole bed, including the partly formed object. The laser is then used to melt the next layer onto the object, fusing it to the already completed object. Published work in this area shows that there are very few TPEs commercially available for SLS and those that are available generally have inferior mechanical properties to those materials available for conventional processing, such as injection molding and extrusion.[1–5] Another technology which can be applied to TPEs is fused filament deposition

modeling. In recent years this technology has been taken up by many machinery manufacturers and it has become the cheapest form of 3D printer, even affordable to have in schools and at home. The material is supplied as a filament and is fed into a heated extruder head from which it is deposited, solidifying on cooling. There are commercially available TPEs in filament form but very little published research in this area.[6] There is clear scope for further research into TPEs, however, the development of thermoset elastomers for additive manufacturing is even more challenging.

There are currently two main types of thermoset elastomeric materials suitable for additive manufacturing (3D printing), one is liquid silicone rubber and the other is a set of UV curable materials, including polyurethane and acrylic-based polymers. The liquid silicone elastomers can be processed using an extrusion process, sometimes referred to as direct writing. The material is deposited from a micro-dispensing device or syringe. The high viscosity of the material is largely relied upon to maintain the shape of the product, while most of the crosslinking reaction can be carried out as a separate process after forming. This technique has been used to make a product with a controlled porosity and indicates it may have a niche application for silicone elastomer materials.[7] However, this form of direct extrusion is not suitable for the vast majority of elastomers which can be classified as soft solids and have much too high a viscosity to be extruded in this way. There are two types of additive manufacturing process that can be applied to UV curable elastomers. The first is stereolithography, in which the object is built up in a batch of liquid polymer which is selectively cured, as the object is lowered step-wise into the bath as each layer is cured. In the second method, the liquid polymer is printed by an inkjet process and is cured after deposition by a UV light attached to the print head.[8–11] This combination of UV curable polymer and inkjet printing technology is potentially very powerful, allowing a range of materials to be printed at the same time to a high level of precision. However, although rubber-like materials with a range of hardness are commercially available, their mechanical properties fall well below those of most conventional rubber compounds.

In summary, it is clear that additive manufacturing of elastomers is currently extremely limited from a material point of view because only three classes of rubbery materials (TPE, liquid rubbers, photo-curable polymers) are suitable for the technology. The types of elastomer with the required performance for most automotive, aerospace, construction, and engineering applications cannot be used in additive manufacturing processes at the moment.

This article reports an investigation into an alternative approach to additive manufacturing with elastomeric materials; inkjet printing of latex, a suspension of nanoscale elastomer particles in water. Taking this approach, a range of conventional elastomers becomes available, with a winning combination of high-molecular weight and low viscosity. The high-molecular weight leads to good mechanical properties, while the low viscosity means the latex is potentially inkjet printable.

If it proves possible to print with latex, there follows an opportunity to create elastomeric composites with a controlled distribution of filler, leading to novel properties being developed that would be unobtainable by any other means. An application where this may be particularly useful is components which also incorporate electromagnetic interference (EMI) and radio frequency interference (RFI) shielding. However, there are many interesting mechanical performance characteristics that could also be obtained be controlling the distribution of filler and hence local stiffness and strength of a product.

To determine whether elastomer latex is potentially inkjet printable it is necessary to consider the inkjet process and the required properties of the ink. In most inkjet printing techniques, an electric field applied to a piezoelectric print head causes the piezoelectric plates within to oscillate and eject the ink. There are many properties of the ink that affect the printing process, such as the viscosity, density, pH, particle sizes, and surface tension. The ideal viscosity for jetting ink is 20 cp with an ideal surface tension of ~40 mN m^{-1}.[12] These properties have been brought together by Fromm into a dimensionless number, Z, which predicts printability of the ink if the value of Z is larger than 2.[13] Fromm's equation, which also provides the Ohnesorge number, is given in eq. (1) below.

$$Z = \frac{(d\rho\gamma)^{\frac{1}{2}}}{\eta} = Oh^{-1} \tag{1}$$

where η—viscosity,

ρ—density

γ—surface tension of the liquid

d—diameter of the nozzle aperture

Oh—Ohnesorge number

The formula was used in the research reported in this article to determine the potential printability of five elastomer latex materials, using viscosity, density, and surface tension of the liquid latexes. Particle sizes of the latexes were also measured because it is necessary that they should be small enough to pass through the print head without blocking. In 3D printing, the printed material forms the base for the following layer and so its properties as a substrate are important, for example, its wetting behavior with the ink. For this reason, the surface energy of the dried latex material was also measured. Printing trials were carried out using latex as the ink.

EXPERIMENTAL

Materials
The five liquid latex materials were supplied by Synthomer (Synthomer Deutschland GmbH, Werrastraße 10, 45768 Marl, Germany). The elastomer type, abbreviation, and trade names are given in Table I.

Viscosity
To determine the viscosities of the liquid latex, a Brookfield viscometer was used with Spindle 2 and a speed of 50 rpm. A Malvern Kinexus Pro rheometer was also used to determine the shear viscosity of the latex at a range of strain rates. The viscosities were measured at strain rates from 10 s^{-1} to 500 s^{-1} at a temperature of 24.5°C.

Table I. Liquid Latex Materials Provided by Synthomer

Material	Abbreviation	Trade name	Description
Poly(2-chloro-1,3-butadiene)	CR	Lipren T®	A colloidal dispersion of a poly(2-chloro-1,3-butadiene).
Carboxylated styrene-butadiene rubber	XSBR	Litex T 71S20®	A colloidal dispersion of carboxylated styrene-butadiene rubber
Carboxylated butadieneacrylonitrile copolymer	XNBR	Synthomer X426C®	A colloidal dispersion of a carboxylated butadiene-acrylonitrile copolymer with a medium acrylonitrile level
Natural rubber natural cis-polyisoprene	NR	Revultex VRB884® NR	A natural rubber latex stabilized and preserved with ammonia
Natural rubber natural cis-polyisoprene	PVNR	Revertex HCE68® PV NR	High solids content pre-vulcanized natural rubber concentrate stabilized with ammonia and potassium hydroxide.

Surface Tension of the Liquid Latex

The surface tension measurements were carried out using a Kruss KSB Instruments Contact Angle Goniometer. Using the pendant drop method on the contact angle equipment it was possible to measure the surface tension of each latex material by ejecting small quantities of latex through a needle and measuring the drop dimensions with the aid of a camera and image analysis software.

Particle Size

A Malvern Mastersizer 2000 was used to determine particle size of the liquid latex materials by laser light scattering. A few drops of liquid latex were dispersed in de-ionized water and sonicated at 3000 Hz for 60 s to disperse any particles that may have agglomerated. The equipment provided average particle sizes and particle size distributions.

Latex Sheet Preparation

Cast latex sheets were prepared so that their properties and behavior as a printing substrate could be determined. For each latex sample, approximately 4 g of latex was poured into a 5 cm diameter petri dish. A lab oven with fan was used to dry the latex materials at 70°C. The samples were placed onto a metal tray to ensure that the samples were leveled in order to obtain a uniform thickness of the latex once dried. At 15 min intervals, the samples were removed from the oven and weighed until

constant weight had been achieved. The maximum total drying time was 1 h 45 min for each sample measured. The final result provided 2 mm thick sample materials that were used to determine surface energy.

Surface Energy of the Latex Sheets

The sessile drop contact angle method was used to measure the surface energy of the latex sheets using a Kruss KSB Instruments Contact Angle Goniometer. Deionized water and diiodemethane were used for the measurements. Once the drop touched the surface an image was captured and with the aid of the software on the Dataphysics equipment the contact angle was calculated.

Printing Trials

A Dimatix Materials Printer DMP-2800 was used for the printing trials. A diluted sample of XSBR containing 35% solids content combined with 1% concentration by weight of Triton surfactant was passed through a 5-micron filter, to prevent any particle agglomerates from blocking the nozzles, prior to filling a 2-mL cartridge. The settings for printing were a maximum jetting frequency of 20 kHz and jetting voltage of 26 V calibrated for each nozzle. A silicone coated paper was used as the substrate for the latex. The area for printing was selected on the computer using the camera attached to the printer and the dimensions of a 2 cm × 2 cm square were set to print.

Table II. Some Properties of the Latex Materials

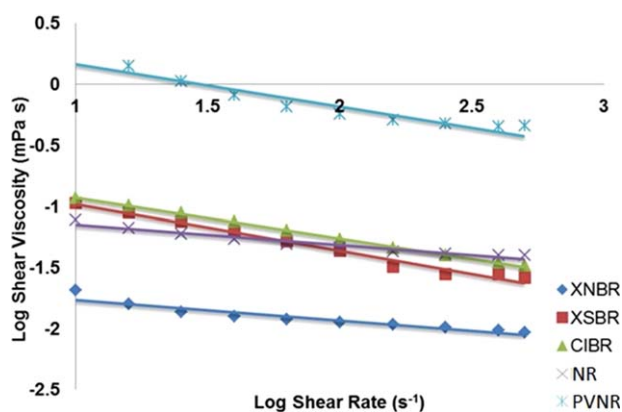| Material	Surface energy of the cast latex (mN m^{-1})	Liquid latex		
		Solids content (wt %)	Ammonia content (wt %)	Brookfield viscosity (mPa s)
XNBR	71.09	39	n/a	4
XSBR	35.13	52	n/a	12
CR	71.06	56	n/a	12
NR	39.2	60.25	0.7	120
PVNR	38.72	68.5	0.62	140

Figure 1. Log shear rate vs. log shear viscosity for the liquid latex materials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Cleaning cycles were set during the printing process for every ten passes the printer made over the substrate, to prevent any latex ink that may have leaked out from drying and blocking the nozzles on the printer head. It was not essential to wait for the latex ink to dry before printing on additional layers.

Thickness and Morphology of Printed Layers

Samples of latex from the printing trials were examined using scanning electron microscopy (SEM) to observe their morphology. All the samples were sputter coated with silver. A Carl Zeiss (Leo) high resolution field emission gun scanning electron microscope (FEGSEM) model 1530VP was used with 10–12 mm working distance, EHT (extra high tension) of 5 kV and a standard aperture size of 30 μm.

An InfiniteFocus Alicona benchtop optical 3D surface measurement and characterization system was used to measure the thickness of the printed XSBR latex. The Alicona uses a small depth of focus optical system with vertical scanning to provide an area analysis. A 10 nm vertical resolution and 2.5 mm s^{-1} scan speed was used to determine sample thickness.

RESULTS AND DISCUSSION

Viscosities of the Liquid Latex

Viscosities for all latex samples found using the Brookfield viscometer are shown in Table II. The viscosities measured over a range of strain rates are displayed in Figure 1 on a logarithmic scale, the negative slope showing shear thinning behavior.

Numerical values for viscosity at strain rates of 10 and 500 s^{-1} are presented in Table III. Inks with viscosities less than 20 mN m^{-1} are best suited for inkjetting as they will not block the print head nozzles.[12] Therefore, the latex samples with the viscosities best suited for inkjetting are the XNBR, XSBR, and CR. However, there is also the possibility of diluting the natural rubber latexes to obtain a lower viscosity.

Surface Tension of the Liquid Latexes

Surface tension values of the latexes are shown in Table III. The values for surface tension that are most favorable are those of XNBR, CR, NR, and PVNR latexes as they are lower than 40 mN m^{-1}. A surface tension higher than 40 mN m^{-1} can prevent the ink from jetting properly, and a surface tension that is too low could result in the ink leaking out of the print head.

Surface Energy of the Cast Latex Sheets

The surface energy values of the cast latex samples are displayed in Table II. The surface energies of the cast sheets of XNBR and CR are significantly higher than the XSBR and NR materials. A high surface energy of a material means that it is more receptive to surface wettability. This characteristic could be detrimental when printing other liquid substances that have high water content onto these materials as the droplets will not retain their shape and will want to merge with other droplets, resulting in compromised control of the entire printing process and a low resolution of the printed material.

Particle Size

To prevent clogging of the print head nozzle and enable consistent ejection of the ink, it is generally considered that the particle size for materials in ink should be less than 10% of the nozzle diameter, 5 μm in this case. The particle size results for all five liquid latex materials are presented in Table III.

Figure 2 shows the particle size distributions for XSBR latex before and after sonication. Before sonication there is a bimodal distribution of particle sizes, the larger particle size peak indicating that agglomeration of the particles has occurred. After sonication a single peak is observed at sub-micrometer size, indicating that the XSBR latex is compatible with inkjet printing, at least with respect to particle size and after sonication.

These results show that sonication can be a pragmatic solution to agglomeration. If the samples that are to be used for printing are exposed to medium intensity bursts of ultrasound with a sonication probe for a period between 60 and 120 s, then the

Table III. Properties of the Liquid Latex Related to Printability

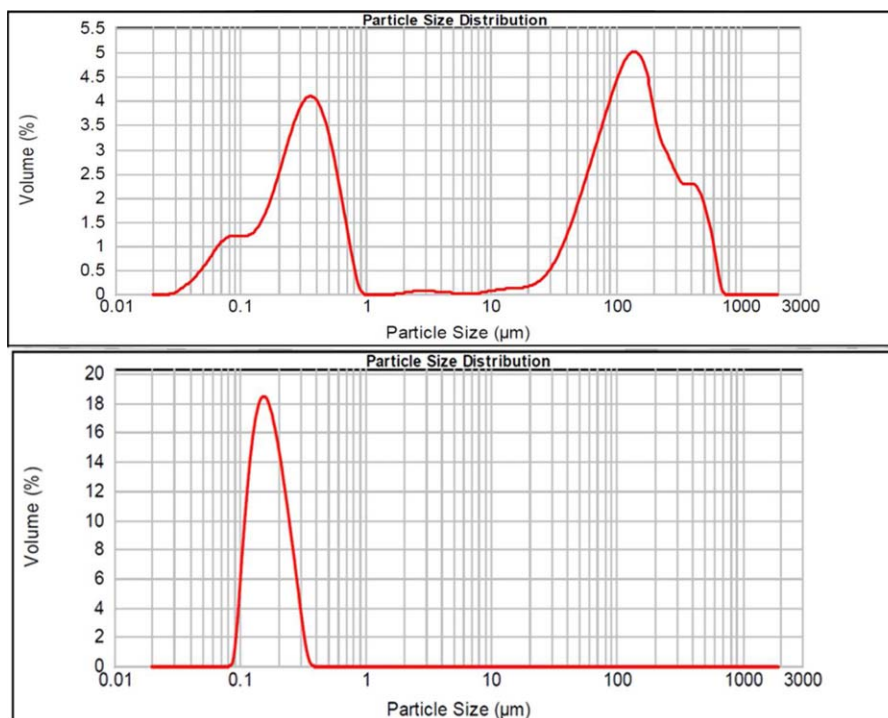| Materials	Upper decile particle diameter (μm)		Surface tension (mN m^{-1})	Viscosity Pa s		Z	
	Before sonication	After sonication		at strain rates of			
				10 s^{-1}	500 s^{-1}	10 s^{-1}	500 s^{-1}
XNBR	279	272	29	20	9	1.9	4.2
XSBR	303	0.25	49	106	26	0.5	1.9
CR	138	73	33	117	33	0.4	1.2
NR	1.6	1.6	38	169	45	0.3	1.0
PVNR	134	124	39	77	40	0.6	1.1

Figure 2. Particle size distribution for XSBR latex before sonication (above) and after sonication (below). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

agglomerated particles can be separated and the material will be ready to be inserted into the ink cartridge.

Latex Sheet Preparation

The behavior of the drying latex was a factor that depended purely on the temperature to which the materials were exposed. For the drying behavior of the liquid materials, there were two types of tests that were carried out: one was to create a relatively thick cast latex sheet ($\sim$1–3 mm thick) in one go, and the second was to build up a sheet from very thin layers to determine how the material structure will be affected overall as well as to determine whether the drying durations change.

The most effective drying temperature for the latex materials was found to be 70°C. Higher temperatures between 80°C and

Figure 3. An SEM image showing the top surface of the printed rubber at the edge of the square.

90°C resulted in the formation of cavities within the dried cast latex due to the formation of bubbles as the aqueous solutions in the material were close to boiling temperatures. These high temperatures also resulted in cracks forming on the surface of the latex, which created materials that have a grainy surface texture for the CR, and a leathery surface texture for the XNBR. However, temperatures below 70°C resulted in the liquid materials drying at a significantly slower rate.

It was observed during the drying process of the thicker sheets of latex that the material would form a thin film on the top surface. The liquid on the bottom did not have the opportunity to dry at the same rate as the liquid near the surface due to the relative permeability of the dried latex film on the surface. It also caused voids to form around the edges of the materials as the gas from the evaporating liquids would become trapped under the surface film. The material that exhibited these drying properties the most was the XNBR. In some tests, which ran over a period of 6 h, the bottom surface of the XNBR was still not entirely dry and some residual liquid material was still present.

Overall, the materials that showed the best drying behavior were the CR and the XSBR.

Printing with Liquid Latex as the Ink

Measured surface tension and viscosity values are shown in Table III, together with the values for printability, Z, calculated from eq. (1). Density of all the latexes was assumed to be 1000 kg m^{-3}. The latexes showed some shear thinning behavior so two values of Z were calculated, one using the viscosity measured at a low strain rate (10 s^{-1}) and the other using the viscosity measured at a high strain rate (500 s^{-1}).
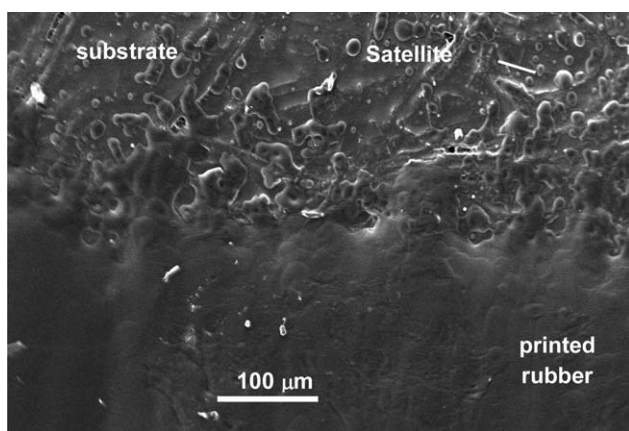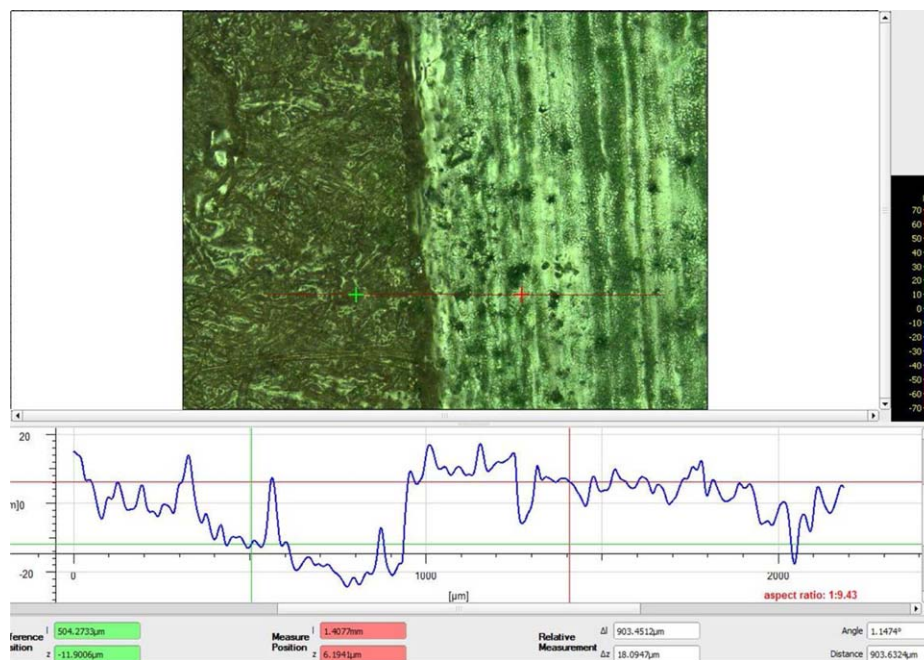
Figure 4. Captured image from InfiniteFocus Alicona equipment showing a thickness for the printed latex of 18 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Only XNBR had a Z value above 1 for both low and high strain rates, but at the higher strain rate, the values of Z are greater than 1 for all the latexes. The printability will therefore depend on the strain rate experienced by the latex during printing. XNBR and XSBR latex samples having the higher Z values would appear to be potentially the best latexes for printing. The XNBR cannot be used because of the large particle sizes and so the XSBR latex was selected to carry out printing trials.

The first printing trial was unsuccessful because although the latex was ejected from the head, the nozzle became blocked. Considering that the solids content of about 50% for the XSBR was rather high for printing, most inks having solids contents of the order of 10%, a trial was carried out diluting the latex to a solids content of 35%. It was thought that the reduction in solids content would also reduce the viscosity of the ink, increasing the Z value to a potentially more favorable level. In addition, Triton X-100, a non-ionic surfactant, was added at 1%

to reduce the risk of agglomeration. In the trial with the diluted latex, a 2 cm square was printed onto a silicone-treated paper substrate. A SEM image of the surface of the printed latex is displayed in Figure 3. The lower half of the image shows the printed rubber, while the upper half shows the substrate. The edge of the printed rubber layer, perpendicular to the printing direction, is not perfectly straight, varying by ~±50 μm. There are also some satellite drops visible on the substrate, where some of the drops have broken up during printing. Although this may not indicate a high resolution in terms of conventional printing, for a first attempt, the results look promising. With optimization of the latex material and the printing process itself it is expected that a good control of dimensions in a manufactured product could be achieved. Ten layers were printed successfully, although there was a slight problem with latex leaking from the printer head which meant that frequent cleaning cycles
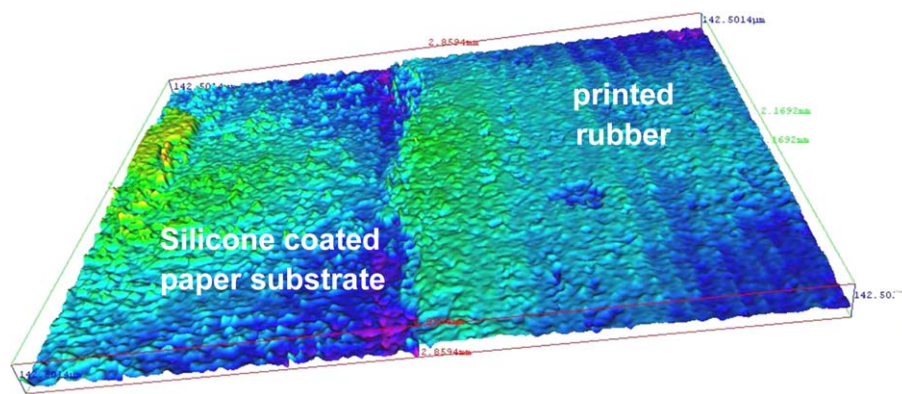

Figure 5. A 3D of a section of printed latex and substrate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were required during printing. A thickness measurement taken . on the InfiniteFocus Alicona equipment is displayed in Figures 4 and 5. Figure 4 shows the substrate on the left and the printed rubber on the right. The profile below shows a substrate sloping down from left to right and an average thickness of the rubber layer of roughly 18 μm. Figure 5 shows a thickness map of the area, with the printed rubber on the right. In both Figures 4 and 5, a peak and trough topography is shown corresponding to the lines of printing. Although ideally the surface would be smooth, the fact that the lines are visible does indicate that uncontrolled pooling of the printed latex has not occurred and suggests that with optimization, a sufficiently good surface topography could be obtained.

The successful printing trial shows the potential for printing with latex, but it is clear that the process needs to be optimized and problems addressed before it can be considered as a viable process for additive manufacturing.

CONCLUSION

This study has shown that there is a great potential for using liquid latex materials as inks in 3D printing with inkjet technology. Measurement of surface tension and viscosity of the liquid latex, followed by application of the printability equation helped to screen the latex materials for inkjetting. Measurement of particle size by laser scattering was useful in identifying where agglomeration had occurred and when it had been eliminated by ultrasonic treatment. However, the printing trials showed that the latex ink composition may still need to be adapted for printing to be successful, for example by dilution of the latex and addition of surfactants. The results reported it this article show the great potential for 3D printing of elastomeric materials by inkjet printing but many more printing trials need to be carried out in order to establish the real capability of this technique.

ACKNOWLEDGMENTS

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