SIEM measurements of ultimate tensile strength and tensile modulus of jetted, UV-cured epoxy resin microsamples

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Abstract
Resin jetting with piezo print-heads is in increasing use, and in the rapid prototyping industry, the merging quality between adjacent droplets will determine the mechanical properties and reliability of the products. Therefore, it is essential to find an experimental technique to ensure seamless inter-droplet merging. Speckle interferometry with electron microscopy (SIEM) is a micro-mechanics measurement technique that has a spatial resolution approaching a few nanometers. In this paper, SIEM is successfully applied to measure the ultimate tensile stress and tensile modulus of jetted, UV-cured cationic resin microsamples. Results show that the microsamples exhibit similar properties to the bulk material properties and that jetting two layers on top of each other is not detrimental to the material properties.

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Introduction
Piezo Print-head Systems have been emerging in recent years to enable digital deposition of picoliter-size droplets of a wide range of materials, e.g. inks, biological solutions, conductive metals and polymers (Hayes et al., 1998; Waldvogel et al., 1998). This paper pertains to the digital deposition of reactive resins, which is useful for a variety of applications in the traditional two-dimensional printing markets, such as UV-curable acrylic resins for bespoke wall and floor coverings, vinyl/latex format printing, textiles, direct and high speed magazine printing, as well as future specialist outlets into SMART textiles, batteries and fuel cells, auto windscreen heaters, aerials, antennas, etc. (Springford, 2003). More recent areas are in three-dimensional printing by layer-wise deposition such as "Objet Geometries" Quadra™ and Eden™ PolyJet™ Systems (Objet, 2003).

In many of these applications, seamless inter droplet merging between adjacent droplets is essential to achieve useful stable images: deficiencies in the merging of adjacent droplets can result in low strength jetted material, as well as lead to sources for future defects, for instance, cracks in long-term use. A technique to investigate the extent of defect free droplet merging at the microscale is therefore, highly desirable.

Another issue concerns the investigation of the mechanical properties of the microsamples that can be printed with Piezo Print-head Systems such as the one used in this study. The typical size of a solidified splat, on the order of 100 µm, allows the manufacturing of structures whose mechanical properties cannot be investigated with devices designed for larger samples. Furthermore, the faster processing and solidification time associated with microsamples might induce different material properties than the ones in the bulk material. This shows the need for a technique to characterize the mechanical properties of a microsample. In order to reveal fully the micro-mechanical behavior of a material one needs a strain measurement technique that has a gauge length of at least one order of magnitude smaller than the characteristic length of the material structure. Furthermore, to reveal strain concentration, the technique should be a full field method whereby two-dimensional deformation distribution can be obtained. Thus, the preferred experimental technique should be able to measure strains directly on the specimen and perform full-field testing. The recently developed technique speckle interferometry with
electron microscopy (SIEM) (Chiang et al., 1997) is a similar technique.

In this paper, SIEM was applied to evaluate the properties of jetted, UV-cured cationic resin microsamples at microscale and compare the properties of bulk and micro material properties.

**SIEM technique**

The SIEM method is a technique of quantitative non-destructive evaluation (QNDE). A random intensity distribution of any sort can be considered as a speckle pattern, and it may be naturally present or artificially created. The development of the speckle technique evolves from the laser optical speckle technique (Chiang, 1989) to the white light speckle technique (Asundi and Chiang, 1982), and then to the digital speckle technique (Chen et al., 1993). The digital speckle technique maintains all the advantages of conventional speckle photography, but eliminates the tedious tasks of photograph development and fringe pattern analysis. In this study, we use computer aided speckle interferometry (CASI), a digital speckle technique (Asundi and Chiang, 1982). The essence of CASI is schematically shown in Figure 1.

A distinctive random speckle pattern is first created on the specimen surface. The typical size of a speckle is on the order of 10 μm. Two speckle patterns, one before and one after deformation of the specimen are recorded using a digital CCD camera. They are first segmented into small sub-images and the displacement of all points in a sub-image is assumed to be constant. The size of the sub-image is chosen by the user based on considerations of speckle size, speckle distribution, and the magnitude and gradient of the strain field. The corresponding sub-images are "compared" via a two-step fast Fourier transform (FFT) process to find the displacement vector collectively represented by the speckles. Let \( h_1(x,y) \) and \( h_2(x,y) \) be the complex amplitudes of the light disturbance of generic speckle sub-images, before and after deformation, respectively:

\[
h_2(x,y) = h_1[x - u(x,y), y - v(x,y)]
\]

where \( u \) and \( v \) are the displacement components along the \( x \) and \( y \) directions, respectively. First, a FFT is applied to both \( h_1 \) and \( h_2 \). Then, a numerical "interference" between the two speckle patterns is performed on the spectral domain, i.e.:

\[
F(f_x, f_y) = \frac{H_1(f_x, f_y)H_2^*(f_x, f_y)}{|H_1(f_x, f_y)H_2(f_x, f_y)|} \exp\{j[\phi_1(f_x, f_y) - \phi_2(f_x, f_y)]\}
\]

where \( \phi_1(f_x, f_y) \) and \( \phi_2(f_x, f_y) \) are the phases of \( H_1(f_x, f_y) \) and \( H_2(f_x, f_y) \), respectively. Finally, a halo function is obtained by the second FFT, i.e.

\[
G(\xi, \eta) = \mathcal{F}\{F(f_x, f_y)\} = \mathcal{G}(\xi - u, \eta - v)
\]

which is an expanded impulse function located at \( (u, v) \). Thus, by detecting the crest of this impulse function, the displacement vector represented by the cluster of speckles within the sub-image is

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**Figure 1** Schematic diagram of CASI for calculating displacement vectors

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uniquely determined. Strains are then determined using appropriate displacement/strain relationships.

The displacement resolution of the speckle method is determined by the size of the speckles. Using light in the visible spectrum implies that the smallest observable speckle is about 0.5 \( \mu \text{m} \) in diameter. To increase the sensitivity of the technique, it is necessary to resort to radiation sources with shorter wavelength. SIEM is a technique involving measurements at the microscopic level. SIEM technique involves three successive procedures: the creation of micro/nano-speckles that are used as gauging devices on the surface of the specimen to map the full field deformation, the recording and digitizing of speckle patterns using a scanning electron microscope, and the analysis of speckle images by CASI.

Creating minute speckle patterns is a challenging task. The difficulty is not only to make speckles extremely small but also to make it in a controlled manner to satisfy the requirements of a specific measurement. In the laboratory at Stony Brook University, the micro/nano speckle patterns are mainly created by the process of physical vacuum vapor deposition.

CASI usually can resolve at least 0.5 pixel displacement. Therefore, the displacement resolution of SIEM depends on the magnification and the number of pixels of each image. In the case where the magnification of the image is 400x and the image consists of 2,048 \( \times \) 2,048 pixels, the resolution of displacement is about 0.07 \( \mu \text{m} \) in \( x \) and 0.06 \( \mu \text{m} \) in \( y \) directions, respectively. If a larger magnification or an image of more pixels is used, the resolution is then enhanced accordingly. Thus, by using an electron microscope, the sensitivity of the speckle technique is increased by several orders of magnitude as compared to using light within the visible spectrum.

Material

The material was developed, and samples therefrom were jetted at Huntsman Advanced Materials UK Ltd’s Debruyne Research & Development Building in Duxford, Cambridge. A UV curable resin mixture (LMD2397 available from Huntsman Group Vantico Ltd) was used for the evaluation of micro-properties using the SIEM technique and comparison to bulk properties from standard mechanical measurements. LMD2397 is a jettable resin mixture of polymerisable epoxy resins that are used to achieve strength, flexibility and toughness.

Viscosity of LMD2397 was measured using a Brookfield HBTD Viscometer (0.8° cone spindle) at both 25 and 70°C.

Table I records the viscosity, which is too high at 25°C for stable jetting using current piezo-based jetting devices. At 70°C, the composition has requisite low viscosity, and is stable for long-term use in a jetting device held at 70°C. Once jetted and cured, this resin provides high mechanical strength as desired for durable cured materials. The surface tension of LMD2397 is 42 dynes/cm, measured using a Du Nouy Tensiometer, (Cambridge Instrument Co. Ltd).

Analysis of bulk properties

Test bars for uniaxial bulk tensile testing were prepared, using a mould method, with the dimensions shown in Figure 2, according to ASTM D638.

Mould method

The resin LMD2397 was poured into a silicone mould (2 mm thick) and cured using a UV exposure device, housing a UV source (Fusion Systems F450 lamp, 120 W/cm²). The mould sample was placed on a conveyor belt and passed under the exposure device at a speed of 10 m/min. Three passes were made for top surface cure. The cured test bars were removed from the moulds, turned upside-down, and cured for further three passes.

Tensile properties were measured using a Stable Micro Systems TA-Hdi Texture Analyser. Testing speed was 0.08 mm/s and the gauge length was 55 mm.

The resultant bulk mechanical properties are:
- tensile stress: \(-75 \text{ MPa} \ (\pm 4 \text{ MPa})\),
- tensile modulus: \(-2,490 \text{ MPa} \ (\pm 100 \text{ MPa})\), and
- elongation at break: \(-4.5 \text{ per cent} \ (\pm 0.3 \text{ per cent})\).

Preparation of jetted samples

LMD2397 was jetted using a 50 \( \mu \text{m} \) single nozzle jet device MJ-SF-01-50 mounted in a Jetlab™ (Microfab Technologies Inc., Plano, Texas), with the reservoir held at 70°C. Peak voltage and rise, dwell and fall times were adjusted until stable jetting, without satellites, was obtained (Table I). The mass of each droplet was measured by weighing the amount of fluid dispensed in a known time, and the droplet size was deducted from the mass measurement. The size of a single droplet deposited on a glass slide
Table 1 Optimum conditions for jetting LMD2397

<table>
<thead>
<tr>
<th>Viscosity/ cps @25°C</th>
<th>Viscosity/ cps @70°C</th>
<th>Rise and fall (µs)</th>
<th>Dwell (µs)</th>
<th>Dwell (V)</th>
<th>Temperature (°C)</th>
<th>Frequency (Hz)</th>
<th>Droplet mass (ng)</th>
<th>Deposited droplet diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>69</td>
<td>8</td>
<td>5</td>
<td>30</td>
<td>45</td>
<td>70</td>
<td>4,000</td>
<td>138</td>
<td>130</td>
</tr>
</tbody>
</table>

Figure 2 Specimen for bulk properties testing

![Figure 2 Specimen for bulk properties testing](image)

was measured using a calibrated graticule in a microscope.

With LMD2397, once the conditions for stable jetting were obtained at 70°C, reproducible jetting could be commenced readily for long duration.

**Production of samples for SIEM testing**

LMD2397 was deposited on a polyethylene film (110 µm, PE Firma-Goglio), using the single piezoelectric jet printer head MJ-SF-01-50 from Microfab Technologies Inc., Plano, Texas, USA. Polyethylene was chosen because LMD2397 could be successfully jetted onto this substrate with good quality, allowing the cured film to be easily removed for the SIEM analysis. Ready optimization could be done of inter droplet merging to form the samples required for SIEM studies:

- length: ~ 10-15 mm,
- width: ~ 300 ± 50 µm, and
- thickness: ~ 50 µm or more

The printhead was heated to 70°C and jetting was done using the following parameters:

- printhead scan rate: ~ 20 mm/s, and
- drop density: ~ 150 droplets/mm with a line space of 0.25 mm.

Two overlapping lines (1 cm) of droplets were deposited with a line space of 0.25 mm.

The jetted line was UV-cured under a 4 W UVA lamp, as described above for the bulk properties, with a curing energy of 120 mJ/cm². For the two-layer deposit, a second layer was deposited on to the cured first layer and then the deposit was cured under the same conditions.

**SIEM examination**

Two specimens of about 20 mm in length were cut from two depositions, one from the one-layer deposition and the other from two-layer deposition. Speckles were vacuum-deposited on the bottom (flat surface) of the two specimens. Each specimen was then bonded at its ends to a loading stage, which is located inside a scanning electron microscope (SEM) for uniaxial tension testing. Figure 3 shows the experimental set-up.

**Two-layer specimen**

Figure 4 shows the flat surface of the two-layer specimen with speckles on it at 400X magnification. The y displacement field at a vertical load of 50 g is shown in Figure 5.

In Figure 5, the observed area is approximately 200 x 250 µm. The lines in the displacement field are displacement contour lines with a unit of mm. The interval between contour lines is 0.2 µm. The line labeled ”3.8E-19” corresponds to a negligible displacement and is therefore, the reference line. All lines above the reference line show a positive number (moving upward). All lines below show a negative number (moving downward). One should expect the lines to be horizontal since the load is applied in the Y-direction. However, there is a very small rigid body rotation of the sample (θ = atan(1/250 µm) = 0.23°). This angle is so small that the effect of the rigid body rotation on the strain calculation can be neglected. It must be noted that this angle is much smaller than the angle observed in Figure 5 between the lines of same displacement and the horizontal line. The relative displacement is calculated over the observed area. The strain is then calculated by the average of the differentiation of the vertical displacement field over the area. The stress is calculated from the load and the measured cross-section area (with the NIH software) of the specimen. The stress-strain curve is shown in Figure 6.

Young’s modulus E is calculated by a linear regression of the first five points of the stress strain curve. The E obtained is 2.73 GPa. The specimen

Figure 3 The uniaxial tensile loading device

![Figure 3 The uniaxial tensile loading device](image)
Figure 4 SEM picture of the two-layer specimen with speckles (white spots) before (left) and after (right) loading.

![SEM picture of the two-layer specimen with speckles](image)

Figure 5 V displacement field at a vertical load of 50 g.

![V displacement field](image)

Figure 6 Stress-strain curve of the two-layer specimen.

![Stress-strain curve](image)

showed some plastic deformation and broke at a stress of approximately 70 MPa. It must be noted that this stress value might be lower than the ultimate tensile strength of the material since stress concentration at irregularities along the specimen surface weakens the specimen. The breaking point cannot be shown on the stress-strain curve because the image at the moment of the specimen broken cannot be captured. This is an important difference between the SIEM measurements and conventional mechanical properties measurements, which show the breaking point on the stress-strain curve. However, the error induced can be kept reasonably small by minimizing the mass differences between the loads used successively in the load cell.

**One-layer specimen**

Figure 7 shows the flat surface of the one-layer specimen with speckles on it at 800 × magnification. The v displacement field at a vertical load of 22 g is shown in Figure 8.

In Figure 8, the observed area is approximately 90 × 110 µm. The interval between the contour lines is 0.1 µm. The relative displacement is calculated over the observed area. The stress-strain curve is shown in Figure 9.

Young’s modulus \( E \) is calculated by a linear regression of the first four points of the stress-strain curve. The \( E \) obtained is 2.4 GPa. The specimen broke at a lower load than the two-layer specimen (so we have less points) probably because of more severe stress concentration. The ultimate stress of this specimen is 40 MPa. The specimen did not show plastic deformation at the measured area due to the low broken load.

The results of the SIEM stress-strain analysis for both specimens are provided in Table II.
The uncertainties come primarily from the measurements of the cross-sections of the specimens.

**SEM microstructure examination**

The microstructures of the specimens were examined under the SEM and the resulting images are shown in Figure 4 for the two-layer specimen and in Figure 7 for the one-layer specimen. The relics of each individual droplet deposit would be expected to be on the order of 130 μm and accordingly should be visible in the SEM pictures unless the droplets merge together to form a uniform deposit. The microstructures of both samples are homogeneous with neither grain nor patterns being visible at magnifications between 250X and 800X, as can be seen in Figures 4 and 7. The microstructure is homogeneous even when under load. No sign of an imperfect contact between the two layers has been found in the two-layer specimen. The lack of identifiable droplet relics indicates that each droplet stitches together with the adjacent droplets to form a cohesive uniform deposit. This is believed to be due to the careful choice of the resins in the composition, which keeps the reacting resin solvated and mobile while it is being cured. Surface tension of each resin component was adjusted for seamless droplet merging. The resins can therefore, diffuse between deposited droplets, thereby giving the uniform appearance shown in Figures 4 and 7.
Conclusions

SIEM has been successfully applied to the study of the mechanical properties of jetted resin microsamples. Electron microscopy has shown that the microstructure of the micro-samples from Huntsman Advanced Materials UK Ltd's LMD2397 remains homogeneous (up to a magnification of 800x), even when loaded. SIEM experimental results showed that jetted resin microsamples have similar mechanical properties as bulk material, in terms of ultimate tensile strength and Young's modulus. This strongly indicates that SIEM examination is valid for microsamples, and that the rapid prototyping method described in this paper is able to produce microsamples with mechanical properties similar or superior to the bulk material properties. The two-layer specimen has shown a substantially higher ultimate tensile strength than the single layer specimen, probably because the stress concentration responsible for crack initiation has less effect on two bonded layers than on a single layer. However, this is a remarkable sign that a layer-by-layer jetting process conserves the mechanical properties of the bulk material and might actually enhance these properties. Further studies are needed to better quantify this fact and SIEM appears to be a very valuable tool to investigate the mechanical properties of micro-samples. This investigation tool is particularly useful at present that there is a growing interest to deposit various materials (de Guns and Schubert, 2003).

References

Objet (2003), available at: www.2objet.com