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Fourier Transform Controlled Stress Parallel Superposition (FT-CSPS): Validation & Application in Processing Printable Functional Materials

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The development of a multifrequency form of Controlled Stress Parallel Superposition rheometry is reported, along with the techniques validation and use on model gelling systems and high value particulate suspensions. The novel technique reported herein, termed Fourier Transform Controlled Stress Parallel Superposition (FT-CSPS), facilitates measurements of the superposition shear moduli and their response to an imposed unidirectional shear stress. FT-CSPS measurements are reported in applications involving (i) the determination of the relaxation properties of incipient gel networks formed in rapidly gelling samples under bulk flow conditions and (ii) measurements of the parallel dynamic moduli of non-gelling samples which experience high rates of solvent loss. By probing the rheological properties of these rapidly evolving materials using a composite waveform comprising multiple harmonic frequencies, sample mutation artefacts (which limit the use of CSPS for such materials) have been minimised. Validation of FT-CSPS has been achieved by (i) showing coincidence of data obtained using CSPS and FT-CSPS for slowly gelling systems and (ii) continuation of the expected relation between gel strength and stress relaxation exponent beyond the range of data accessible to CSPS (limited by sample mutation considerations). The work demonstrates that rapid acquisition of parallel superposition shear moduli is feasible and facilitates the use of CSPS based techniques for tests involving rapidly changing materials (such as those undergoing rapid gelation, or relatively rapid solvent loss).

Keywords: Rheometry, Functional Inks, Superposition Rheometry, Gelation

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I. INTRODUCTION

The use of functional materials, such as those employed in printed electronics applications, relies on the ability to reproducibly formulate materials which display complex rheological properties. These materials must then be processed under complex flow conditions. The use of traditional rheometric techniques to characterise these materials has typically involved the use of either (i) steady shear (viscometry) style experiments or (ii) small amplitude oscillatory shear. However, neither approach is able to adequately probe both the elastic and viscous components of the materials' rheological response *and* the structural modification that may occur in response to the flow field. Additional challenges associated with the characterisation of functional inks concern (i) the use of volatile solvents, where a high rate

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of solvent loss may require that the rheological characterisation be performed rapidly and (ii) the expense of functional particles, which may cause the cost of repeated sampling to become prohibitive. There is a need, therefore, for a technique that facilitates characterisation of the complex rheological nature of functional materials under flow conditions that can be performed rapidly using minimum sample volumes.

Fourier Transform Mechanical Spectroscopy (FTMS) provides a basis for rapid rheological characterisation (under quiescent conditions) by simultaneously probing the viscoelastic properties of a material at multiple harmonic frequencies. The technique involves the application of a small amplitude stress (or strain) waveform which is constructed by summing multiple discrete frequency sinusoidal waveforms. Provided that the linear viscoelastic region is not exceeded, the dynamic response of the material to each component frequency can be probed using Fourier analysis[1,2]. This is in contrast to traditional discrete frequency approaches which require sequential analysis of the material at each frequency within the desired frequency range. Consequently, the use of FTMS offers a significant reduction in the time required to perform a rheological characterisation of a material over a given frequency range. In applications where the material is undergoing rapid microstructural development[2], such as ink curing[3] or the formation of ceramic gels[4], the FTMS technique is far superior. However, FTMS is a Small Amplitude Oscillatory Shear Rheometry technique and its use is hence limited to characterising the linear viscoelastic characteristics of a material (i.e. under essentially quiescent conditions).

In controlled stress parallel superposition (CSPS) an oscillatory stress of amplitude σ_0 and frequency ω are superimposed upon a unidirectional stress σ_s, with both stresses being applied along the same plane (see equation 1). This gives rise to a deformation that is also composed of both unidirectional and oscillatory components.

$$\sigma(t) = \sigma_s + \sigma_0 cos(\omega t) \tag{1}$$

The superposition complex modulus, $G^*_{\|}$, can hence be determined (where the oscillatory deformation does not itself cause structural breakdown in the sample, i.e. represents a linear perturbation on the unidirectional flow) by cross correlating the oscillatory components of the perturbation and response waveforms. The subscript $\|$ is used to differentiate viscoelastic parameters acquired under parallel superposition to those determined in quiescent conditions[5]. The real and imaginary parts of $G^*_{\|}(= G'_{\|} + iG''_{\|})$, can then be extracted and, under certain conditions (such as those under which $\dot{\gamma} \to 0$[6,7]), can be interpreted as per their quiescent counterparts G' and G'' in terms of energy storage and dissipation, respectively. It should be noted that unlike the quiescent complex modulus G^*, the coupling of the oscillatory and unidirectional flow fields in CSPS prevent $G^*_{\|}$ from being interpreted purely in terms energy storage and dissipation[8], however, as shown herein, the parameters do offer useful processibility metrics. An alternative configuration, orthogonal superposition, in which the unidirectional and oscillatory components occur in orthogonal directions, gives rise to the orthogonal superposition modulus $G^*_{\perp}$.

Several authors have noted that parallel and orthogonal superposition moduli are not equal[9] and attribute the difference to coupling of the oscillatory and unidirectional flow regimes in parallel superposition. This coupling has been shown to generate negative values of $G'_{\|}$[10–12] where $\omega_s < \dot{\gamma}_s/2$ and leads to difficulty in interpreting $G'_{\|}$ and $G''_{\|}$[10] . Such problems are avoided in orthogonal superposition since the flow components are decoupled, which clearly makes orthogonal superposition superior to parallel superposition experiments. However, implementing orthogonal superposition experiments requires specific hardware (e.g. TA Instruments Orthogonal Superposition accessory) which may not be available in all research laboratories and is rare in industrial QA/QC facilities. Further, the geometries rely on large quantities of material ($\sim$ 100 ml) being available which, for high value products (such as functional inks or biological samples), may be prohibitive. Contrary to this, the use of parallel superposition can be achieved using commercially available combined motor-transducer rheometer systems and can be implemented using conventional geometries (hence requiring $<$ 1 ml of sample).

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Despite the difficulties associated with interpretation of superposition moduli obtained under parallel superposition conditions, the technique has been used to study the effect of unidirectional shear on, for example, polymer melts[13], biopolymer solutions[12] and flow induced microstructural modification in gelling systems[6,7]. In the present work, parallel superposition is employed in the study of functional inks and gelling materials. For the latter, the evolving rheological properties of the gelling system permit interpretation of the $G'_{\|}$ and $G''_{\|}$ in terms of standard models of gelation following Curtis *et al.*[6] (as discussed in section III) and these systems hence provide an opportunity to validate novel rheometric techniques involving parallel superposition.

Whilst both FTMS and Superposition Rheometry are established techniques, the potential of a combination of the technologies to achieve rapid data acquisition under process relevant conditions has yet to be explored. Herein, a Fourier Transform Controlled Stress Parallel Superposition (FT-CSPS) technique is reported and validated using model viscoelastic materials (Gelatin) before the potential of the technique in formulation optimisation and process control in printed electronics applications is demonstrated. The FT-CSPS perturbation waveform can be expressed mathematically as

$$\sigma(t) = \sigma_s + \sum_{i=1}^{N} \sigma_i cos(\omega_i t) \tag{2}$$

where σ_i and ω_i denote the stress amplitude and frequency of the i-th component of the N frequency waveform, respectively.

II. EXPERIMENTAL

A. Materials

1. Gelatin gels

Aqueous gelatin solutions were prepared with extra-pure grade gelatin powder (Fisher Scientific, G/0150/53). The appropriate mass of Gelatin powder to generate a 10 wt% solution was added to de-ionised water and agitated vigorously for 2 minutes before being placed in a 60 °C water bath for 45 minutes. Samples were removed from the water bath and further agitated every 10 minutes during this 45 minute period.

2. Silicone Dielectric Gels

Silicone dielectric gels (SDG) (ACC Silicones Ltd.) were prepared from a 2 part addition cure system comprised of vinyl-ended silicone polymers, hydride cross-linker, bulking fillers, platinum catalyst, adhesion promoters and a pot life extender. The gelation of the SDG involved cross-linking of vinyl polymers by the hydride cross-linker in the presence of a catalyst with no by-products. Samples were prepared by mixing equal masses of the components of the silicone gel at room temperature. Samples were then placed in a refrigerator at 4°C for at least 30 minutes to allow degassing of the sample (gelation taking approximately 48 hours at this temperature).

3. Functional inks

The model inks comprised of 2 primary components; a resin of poly(vinyl chloride-co-vinyl acetate-co-vinyl alcohol) in a solution of diacetone alcohol and a pigment of silver flake (< 10 μm particle size). All materials were sourced from Sigma-Aldrich (UK).

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Harmonic	Frequency Hz	σ_i Pa
1	0.1	$0.5 \times \sigma_s$
3	0.3	$0.3 \times \sigma_s$
5	0.5	$0.2 \times \sigma_s$
8	0.8	$0.2 \times \sigma_s$
10	1.0	$0.15 \times \sigma_s$
30	3.0	$0.15 \times \sigma_s$
50	5.0	$0.1 \times \sigma_s$
80	8.0	$0.1 \times \sigma_s$
100	10.0	$0.05 \times \sigma_s$

TABLE I. Parameters of the FT-CSPS waveform used in studies of functional inks at a superposed stress σ_s.

The solvent was heated to 60 °C using a hotplate and stirred to produce a vortex using an overhead stirrer fitted with a 4-blade vane. Polymer was then gradually added and allowed to completely dissolve in the solvent before the addition of further polymer. Once the polymer was fully dissolved the resin was allowed to cool and weighed before additional diacetone alcohol was added to replace any lost through evaporation. The pigment of silver flake was then gradually added to the resin in small quantities. For the present study, three sample were prepared with solids contents of 45 wt%, 65 wt% and 75 wt% with the 45 wt% and 65 wt% samples being prepared by dilution of the 75 wt% ink with additional resin.

B. Rheometry

A TA Instruments AR-G2 rheometer fitted with a 60 mm aluminium parallel plate geometry was used to perform all experiments on gelatin and silicone dielectric gels. CSPS measurements on gelatin were performed at 4 frequencies logarithmically spaced between 0.3 Hz and 3.0 Hz (the frequency range being limited by sample mutation[14] and inertia considerations). Experiments were performed at superposed stresses in the range $0Pa \leq \sigma_s \leq 10Pa$ with $\sigma_o = \sigma_s$. The oscillatory component of the FT-CSPS waveform consisted of a fundamental frequency of 0.2 Hz with 3rd, 6th and 10th harmonic components. The stress amplitude of the fundamental frequency was set to $0.5 \times \sigma_s$, with the harmonic amplitudes being $0.2 \times \sigma_s$ for the 3rd harmonic, $0.15 \times \sigma_s$ for the 6th harmonic and $0.15 \times \sigma_s$ for the 10th harmonic.

The waveform employed in the study of SDG samples consisted of a fundamental frequency of 2 Hz with 3rd, 5th, 7th and 10th harmonic components, and superposed stresses of 10 Pa, 20 Pa and 30 Pa. The stress amplitude of the fundamental frequency was set to $0.2 \times \sigma_s$ for each experiment, with the harmonic amplitudes being $0.5 \times \sigma_s$ for the 3rd harmonic, $0.5 \times \sigma_s$ for the 5th harmonic, $0.5 \times \sigma_s$ for the 7th harmonic and $0.5 \times \sigma_s$ for the 10th harmonic.

For functional inks, CSPS frequency sweeps ($0.1Hz \leq f \leq 10Hz$) with 11 logarithmically spaced frequencies were performed with $0.1Pa \leq \sigma_s \leq 10Pa$ and $\sigma_o \simeq 0.5 \times \sigma_s$. The FT-CSPS waveform consisted of a fundamental frequency of 0.1 Hz with 3rd, 5th, 8th, 10th, 30th, 50th, 80th and 100th harmonic components with component stress amplitudes as shown in table I. Preliminary experiments with functional inks indicated that wall slip occurred for these samples, hence a roughened 60 mm Stainless Steel parallel plate geometry (TA Instruments) was used for studies involving these materials, no evidence of slip was observed using this geometry.

An initial assessment of the Linear Viscoelastic Range (LVR) for the materials studied herein was undertaken using stress amplitude sweeps. For the case of gelling systems the stress amplitude sweeps were performed in both the pre- and post-GP regimes. For gelling

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systems, a more rigorous assessment of linearity at the Gel Point (GP, which occurs at the sol-gel transition of a material undergoing gelation[15]) is challenging due to the transient nature of the critical gel, however, the deformation waveforms recorded under CSPS were subject to Fourier analysis. A ratio of the deformation amplitude associated with the third harmonic and fundamental frequencies θ_3/θ_0 was used to characterise the deviation from linearity (a ratio in excess of 0.001 being considered to indicate the onset of non-linearity[14]). The absence of mutation artefacts was ensured by excluding data associated with rapid gelation where the mutation number (N_{mu}) exceeded 0.15[14,16].

III. VALIDATION OF FT-CSPS

Accurate characterisation of the GP requires valid rheological measurements to be performed in both viscoelastic liquid and viscoelastic solid states. Hence the ability of a novel rheometric technique to accurately determine the GP provides a critical evaluation of the validity of the technique[6,17].

At the GP, a gelling material will display power law stress relaxation (following the Winter and Chambon gel equation[15]):

$$G(t) = St^{-\alpha} \tag{3}$$

where

$$S = \frac{2\Gamma(\alpha) sin(\frac{\alpha\pi}{2}) G'_c}{\pi} \tag{4}$$

and

$$G'_c = \frac{G'(\omega)}{\omega^\alpha} \tag{5}$$

In equations 3-5, $G(t)$ denotes the stress relaxation modulus, S the gel strength parameter (a pseudo property with units of $Pa.s^\alpha$) and α the stress relaxation exponent. Scanlan & Winter[18] considered S to consist of a short time constant λ_0 and a modulus G_0 that are representative properties of the prepolymer, where

$$S = G_0\lambda_0^\alpha \tag{6}$$

These authors observed the expected exponential relationship between S and α in several divinyl-terminated poly(dimethylsiloxane) prepolymers crosslinked with tetrakis(dimethylsiloxy)-silane where the critical gel microstructure (quantified as α) was altered by manipulating sample stoichiometry. This observation was taken to confirm the validity of equation 6 and the interpretation of G_0 and λ_0 as properties of the prepolymer. Since the study of Scanlan & Winter in 1991 the exponential relationship between S and α has been noted by many authors in systems such as laponite[19], triblock copolymer hydrogels[20] and silicone dielectric gels[6] as well as biopolymer systems such as gelatin and fibrin gels[6].

It follows that for samples in which the critical gel network is formed from the same gelation precursor but which display dissimilar microstructures (and hence differing stress relaxation properties), valid rheological measurements yield $S(\alpha)$ data which conform to equation 6. In the present work this critera was used as a foundation for the validation of estimates of α derived from FT-CSPS measurements where the GP has been defined based on attainment of frequency independent $\tan(\delta_{\|})$ following Curtis *et al.*[6]. Identification of frequency independent $\tan(\delta_{\|})$ was performed using a MATLAB[21] routine which identified the roots of the $\tan(\delta_{\|})$ data[22]; a root being defined as the point at which the $\tan(\delta_{\|})$ data for two distinct frequencies intersect. The average of the roots was taken as GP and the standard deviation of all roots was taken as a measurement of gel point accuracy. A model GP would have all roots at the same value of $\tan(\delta_{\|})$.

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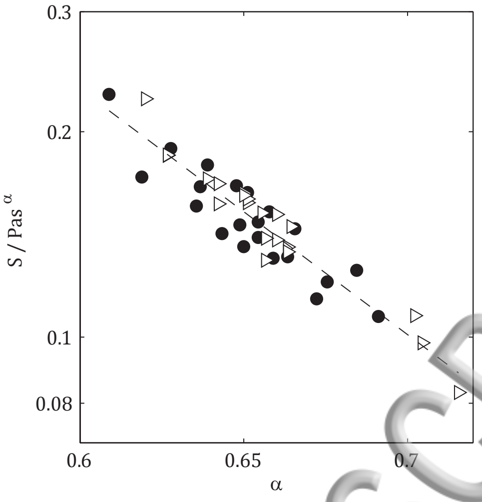

FIG. 1. Gel strength (S) as a function of stress relaxation exponent for gels formed under CSPS (●) and FT-CSPS (▷) conditions obtained at 26°C, both data sets show excellent agreement (with $G_0 = 33.49Pa$ and $\lambda_0 = 0.3ms$) indicating that FT-CSPS generates valid GP data

Figure 1 shows the expected exponential relationship between S and α for gelatin gels formed under CSPS conditions, at 26°C, probed using CSPS and FT-CSPS. The time required for the sample to reach the GP (i.e. 'the gel time', t_g) at 26 °C was sufficiently long to allow both FT-CSPS and CSPS data to be acquired over a range of σ_s whilst avoiding sample mutation artefacts (as discussed in more detail in section IV A). The data clearly indicate that measurements performed under CSPS and FT-CSPS conditions follow an identical exponential relationship (with $G_0 = 33.49Pa$ and $\lambda_0 = 0.3ms$) thus confirming the validity of the FT-CSPS experimental procedure.

IV. APPLICATIONS OF FT-CSPS

Having shown that measurements performed under FT-CSPS conditions are valid, we now demonstrate the application of the technique in three materials relevant to the printing/coating industry.

A. Gelatin

Gelatin, sold commercially as a natural polymer for 3D printing, has applications in cell culture scaffold fabrication[23]. However, the effect of shear on the material during processing appears to be broadly unexplored. Figures 2 and 3 show phase angle at the gel point ($\delta_{\|GP}$) as a function of σ_s for gelatin gels probed using CSPS and FT-CSPS at 25°C. Both datasets have values of $\delta_{\|GP}$ that appear to decrease with increasing unidirectional shear stress (where $\sigma_s > 3Pa$). However, figure 4, which shows corresponding mutation numbers for the data shown in figure 2, indicates that where $\sigma_s > 3Pa$ the CSPS data is invalid since the N_{mu} exceeds the critical mutation number of 0.15[2,16]. Hence the data shown for CSPS in figure 2 cannot be used to confirm microstructural modification of gelatin when the gelation process occurs under a constant unidirectional stress. By contrast, the FT-CSPS data shows both significantly reduced error bars (figure 2) and $N_{mu} < 0.15$ across the entire range of σ_s" studied thus confirming modification of the incipient microstructure of gelatin gels in response superposed flow. With CSPS data in isolation, it could be suggested that the

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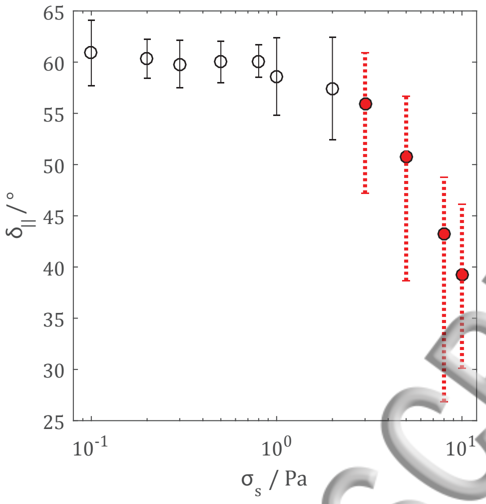

FIG. 2. Gel point phase angle as a function of unidirectional stress for 10 wt% gelatin obtained using CSPS at 25°C, data shown in red has $N_{mu} > 0.15$

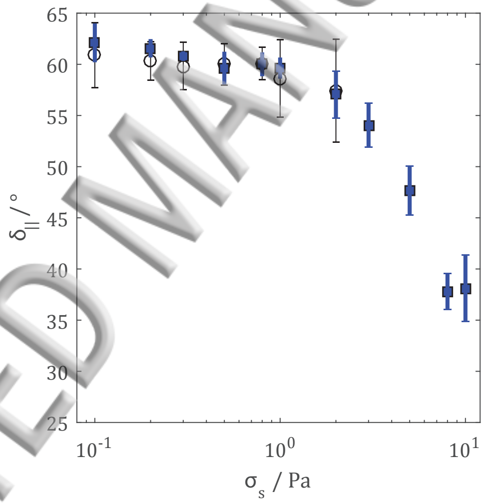

FIG. 3. Gel point phase angle as a function of unidirectional stress for 10 wt% gelatin obtained using FT-CSPS at 25°C (blue squares), open circles show corresponding CSPS data where $N_{mu} < 0.15$

apparent decrease in ($\delta_{||GP}$) with increasing σ_s may be an experimental artefact caused by the increasing rapidity of the gelation process (the term 'rapidity' is used herein to refer the rate of change of $\delta_{||}$ in the vicinity of the GP rather than the length of time required for the gelation process to reach the GP, the latter increasing as σ_s is increased as shown in figure 5).

B. Silicone Dielectric Gels

Silicone dielectric gels are commonly used as coating materials for electronic components and it is possible to manipulate both the microstruture and critical gel strength of these materials by varying the gelation temperature[6]. However, it has also been shown that

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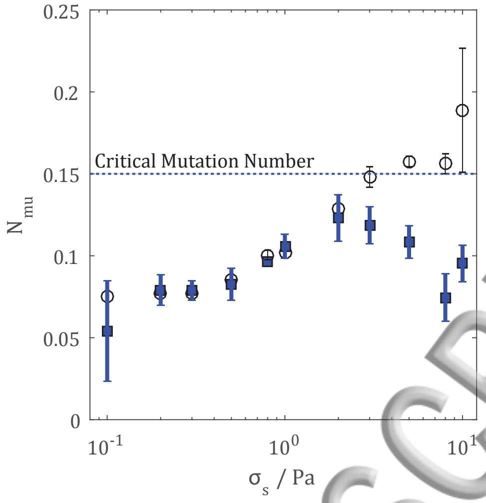

FIG. 4. Sample mutation number (N_{mu}) as function of unidirectional stress for 10 wt% gelatin obtained using CSPS (open) and FT-CSPS (closed) for corresponding data in figure 2.

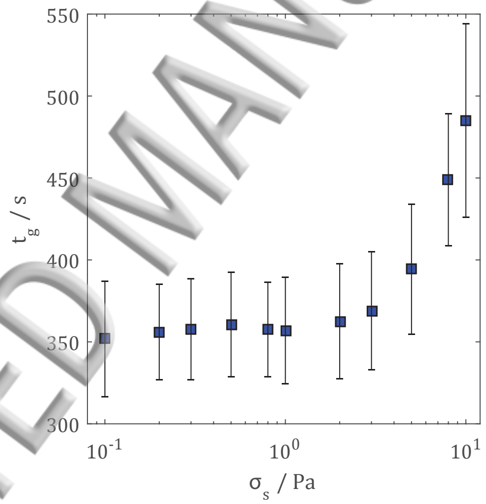

FIG. 5. t_g as a function of σ_s for 10wt% gelatin

identical control of microstructure and gel strength can be achieved by manipulating the fluid mechanical environment (in terms of the applied shear stress) during the print process[6]. Herein, FT-CSPS has been used to extend the scope of this relationship and show that a significant enhancement in critical gel strength can be achieved by further increasing σ_s above the range used in previous studies; such data being unobtainable using CSPS due to the rapidity of the gelation process.

Figure 6 shows the expected exponential relationship between S and α for silicone dielectric gels, where microstructural control has been achieved through manipulation of (a) temperature under quiescent conditions (b) σ_s at constant temperature and probed using CSPS and (c) σ_s at constant temperature probed using FT-CSPS (data sets (a) and (b) have been previously published[6]). The data clearly fit the exponential relationship predicted by equation 6 with the FT-CSPS data (•) significantly enhancing the range of microstructures (and corresponding critical gel strengths) over which the relationship (equation 6) is known

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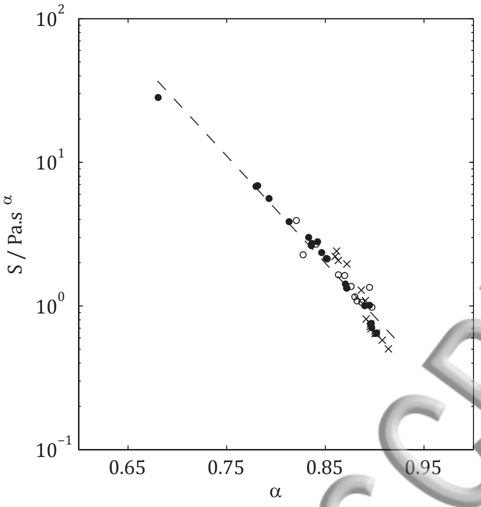

FIG. 6. Gel strength (S) as a function of α for silicone dielectric gels (a) formed under quiescent conditions and in which microstructural modification is achieved by manipulating temperature (×)[6] (b) formed under flow conditions and characterised using CSPS (○)[6] and (c) formed under flow conditions and characterised using FT-CSPS (●). Dashed line shows the a fit to the FT-CSPS data to equation 6.

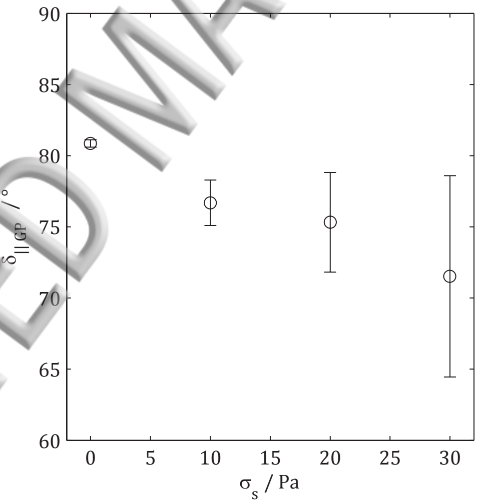

FIG. 7. $\delta_{\parallel GP}$ as a function of σ_s for silicone dielectric gels formed under CSPS conditions and probed using FT-CSPS.

to apply ($0Pa \leq \sigma_s \leq 30Pa$). ($\sigma_s \leq 20Pa$). Figure 7 shows $\delta_{\parallel}$ at the GP as a function of σ_s for SDGs in which increasing σ_s is seen to cause a decrease in $\delta_{\parallel}$ up to $\sigma_s = 30$ Pa, in previous work mutation artefacts limited the study of these gels to $\sigma_s \leq 20$ Pa[6]. Hence, the use of FT-CSPS has demonstrated that fluid mechanical control of critical gel strength is possible over a wider range of operating conditions than previously demonstrated. The large error bars at high levels of σ_s which appear in figure 7 are symptomatic of the sensitivity of the SDG system to experimental variations in gel composition when measured under CSPS conditions.

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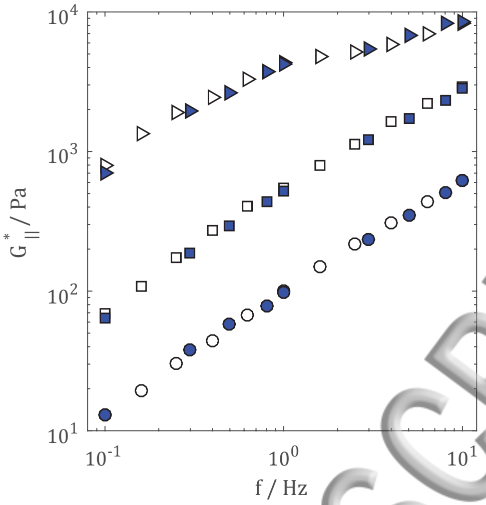

FIG. 8. Comparison of $G^*_{\|}$ of a silver based functional ink measured using CSPS (open) and FT-CSPS (closed) at 45wt% (o), 65wt% (□)and 75wt%(▷). Excellent agreement is observed between the data sets.

C. Functional Inks

The FT-CSPS approach offers the ability to obtain $G^*(f)$ over a wide frequency range in a fraction of the time that would be required to perform the same frequency sweep using an CSPS experiment. Hence, the potential exists for the FT-CSPS technique to be used in routine QA/QC applications where time constraints and the cost of functional particles may preclude the use of CSPS characterisation. One such issue arises in the print industry where variations in print quality (often arising from minor differences in ink formulation) can result in significant economic losses. Figure 8 shows a direct comparison of $G^*(f)$ obtained using CSPS and FT-CSPS for a silver based functional ink systems. The data show excellent agreement across the entire experimental frequency range for the three inks with increasing silver solids content.

V. CONCLUSIONS

It has been demonstrated herein that a superposition rheometry implementation of FTMS allows rapid acquisition of the parallel superposition moduli $G'_{\|}$ and $G''_{\|}$). The FT-CSPS technique has been implemented in a study of flow induced microstructural changes in the incipinet gelatin network which appears at the gel point (as $\dot{\gamma_s} \rightarrow 0$) and provides identical 'processibility metrics' ($G'_{\|}$ and $G''_{\|}$ where $\dot{\gamma_s} \neq 0$) to the slower CSPS technique for samples of relevance to the printed electronics sector. This is an important milestone towards an improved understanding of how products respond to imposed flows, how changes in formulation affects manufacturability and the deployment of advanced rheometric techniques in process control applications.

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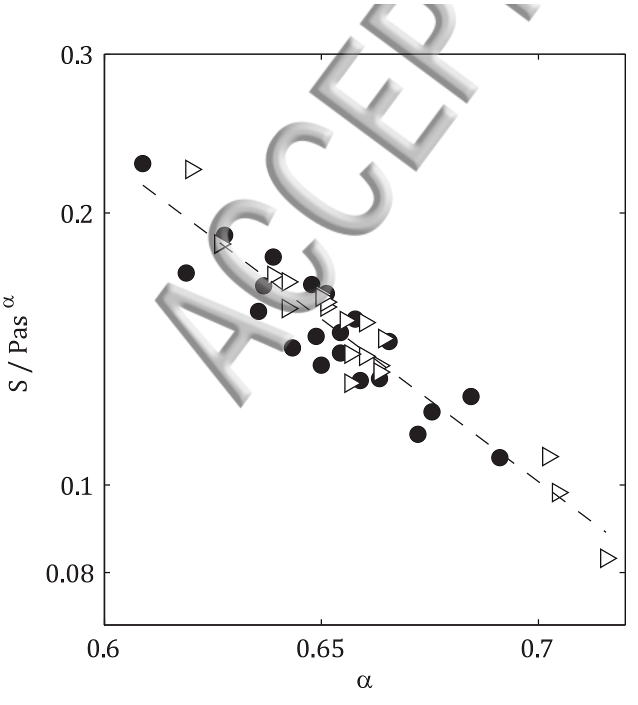

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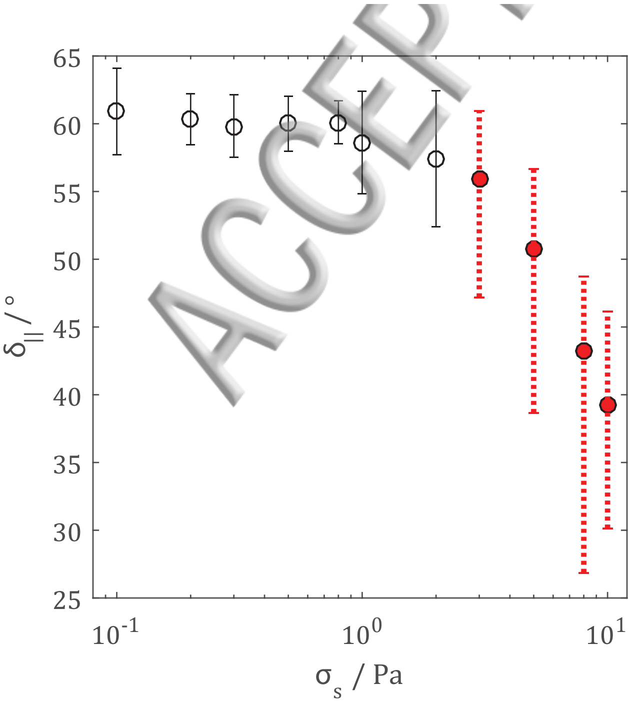

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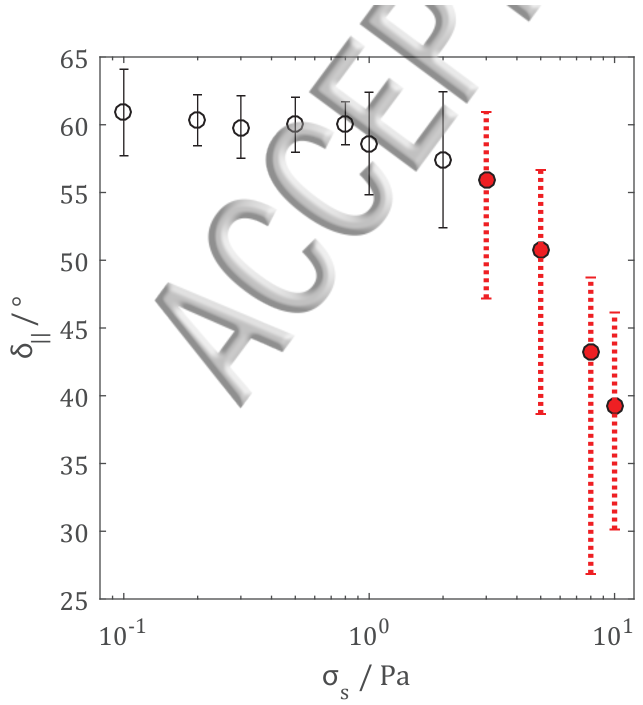

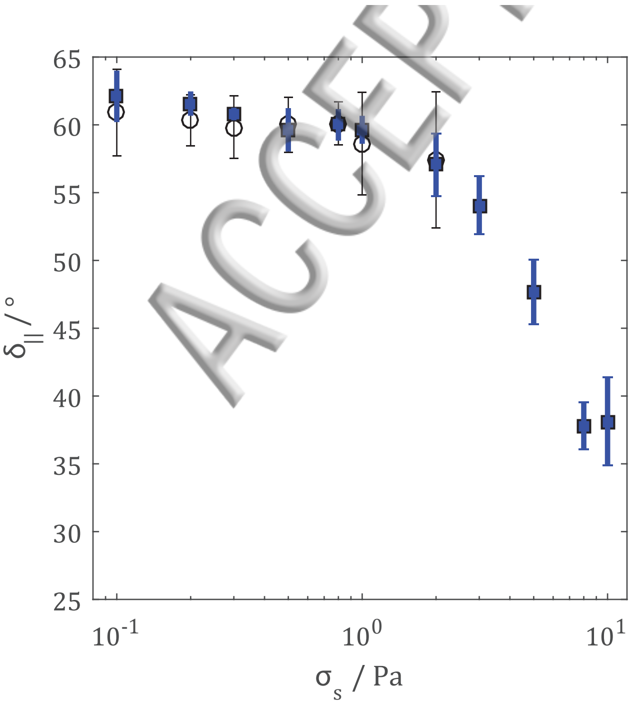

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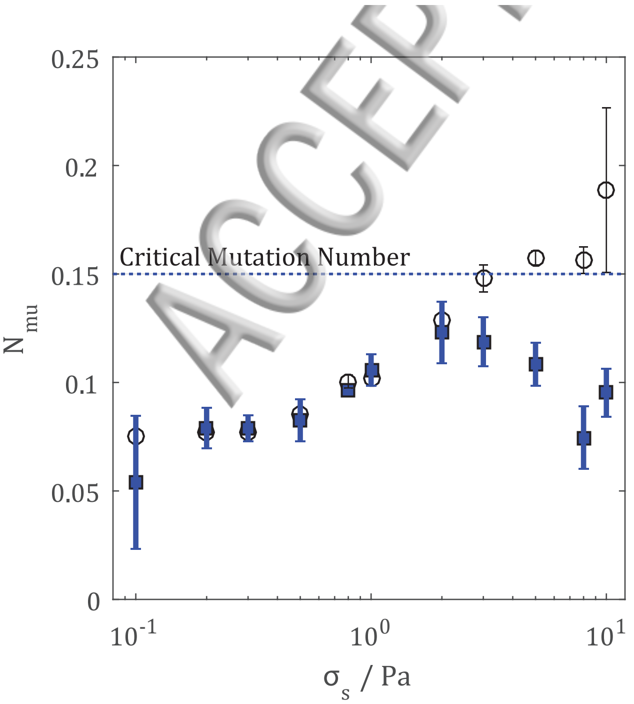
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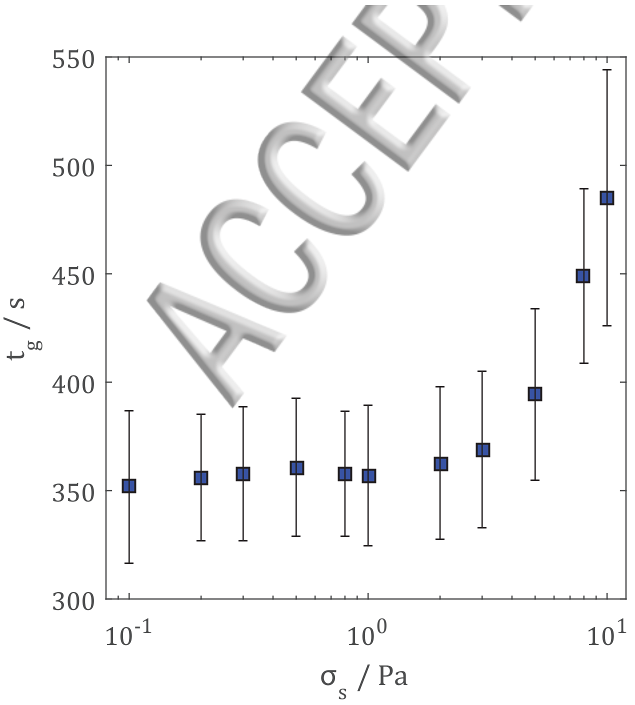

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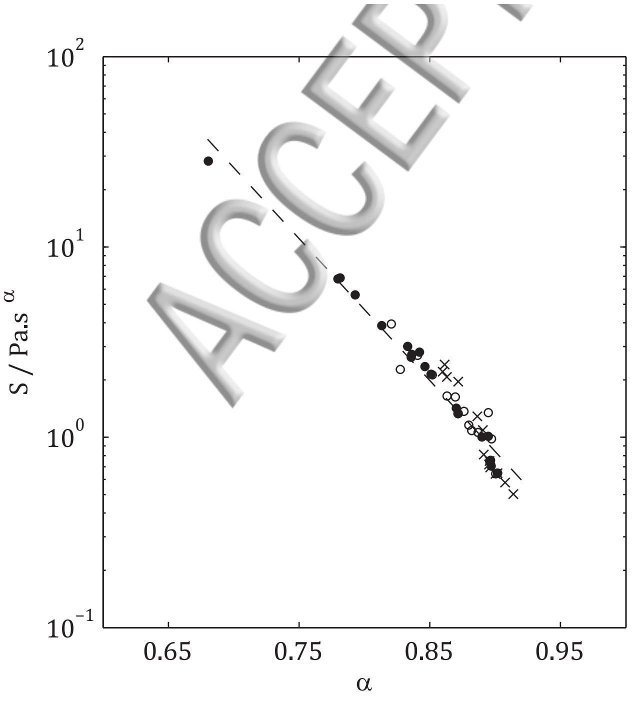

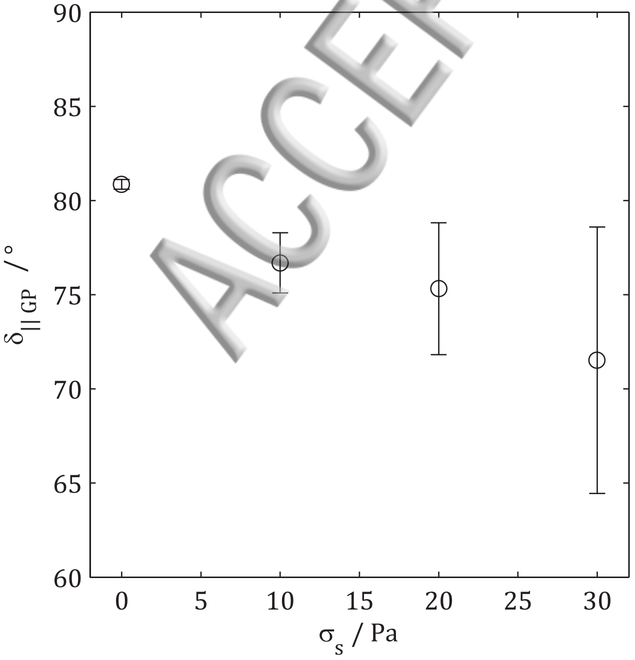

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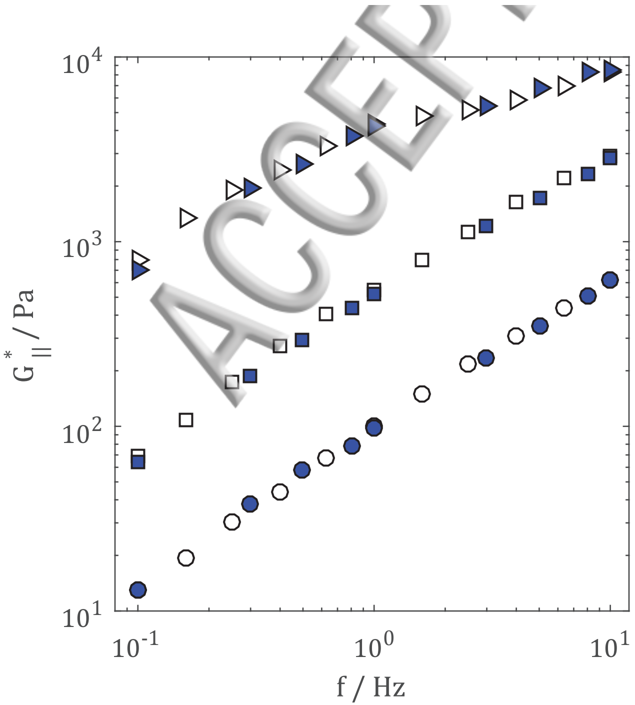

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