Paper:
Holder, A., Claypole, J., Claypole, T., Cooper, P., Williams, P. & Curtis, D. (2018). Fourier Transform Controlled Stress Parallel Superposition (FT-CSPS): Validation and application in processing printable functional materials. Physics of Fluids, 30(7), 077105
http://dx.doi.org/10.1063/1.5029819

Distributed under the terms of a Creative Commons CC-BY 4.0 Licence.

This item is brought to you by Swansea University. Any person downloading material is agreeing to abide by the terms of the repository licence. Copies of full text items may be used or reproduced in any format or medium, without prior permission for personal research or study, educational or non-commercial purposes only. The copyright for any work remains with the original author unless otherwise specified. The full-text must not be sold in any format or medium without the formal permission of the copyright holder.

Permission for multiple reproductions should be obtained from the original author.

Authors are personally responsible for adhering to copyright and publisher restrictions when uploading content to the repository.

http://www.swansea.ac.uk/library/researchsupport/ris-support/
Fourier Transform Controlled Stress Parallel Superposition (FT-CSPS): Validation and application in processing printable functional materials

A. J. Holder, J. Claypole, T. Claypole, P. G. Cooper, P. R. Williams, and D. J. Curtis

Citation: Physics of Fluids 30, 077105 (2018); doi: 10.1063/1.5029819

View online: https://doi.org/10.1063/1.5029819

View Table of Contents: http://aip.scitation.org/toc/phf/30/7

Published by the American Institute of Physics

Articles you may be interested in

Hydrodynamic dispersion in thin channels with micro-structured porous walls
Physics of Fluids 30, 076601 (2018); 10.1063/1.5031776

Supercritical fluid flow dynamics and mixing in gas-centered liquid-swirl coaxial injectors
Physics of Fluids 30, 075106 (2018); 10.1063/1.5026786

Channel flow of viscoplastic fluids with pressure-dependent rheological parameters
Physics of Fluids 30, 073102 (2018); 10.1063/1.5042330

Comment on L. M. Hocking, “On contact angles in evaporating liquids” [Phys. Fluids 7, 2950–2955 (1995)]
Physics of Fluids 30, 079101 (2018); 10.1063/1.5041445

Stability of plane Couette flow of Carreau fluids past a deformable solid at arbitrary Reynolds numbers
Physics of Fluids 30, 074103 (2018); 10.1063/1.5041771

Oscillatory instability in a weakly non-Boussinesq fluid layer with a deformable surface
Physics of Fluids 30, 074102 (2018); 10.1063/1.5024979
Fourier Transform Controlled Stress Parallel Superposition (FT-CSPS): Validation and application in processing printable functional materials

A. J. Holder,1 A. J. Holder, T. Claypole, 1,2 T. Claypole,2 P. G. Cooper, 3 P. R. Williams,1 and D. J. Curtis1,a)
1Complex Fluids Research Group, College of Engineering, Swansea University, Swansea, United Kingdom
2Welsh Centre for Printing and Coating, College of Engineering, Swansea University, Swansea, United Kingdom
3EPSRC Centre for Innovative Manufacturing in Large Area Electronics, University of Cambridge, Cambridge, United Kingdom

(Received 15 March 2018; accepted 17 June 2018; published online 26 July 2018)

In this paper, the development of a multifrequency form of controlled stress parallel superposition rheometry is reported, along with the technique’s validation and use in 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 that 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). This work demonstrates that the 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). © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5029819

I. INTRODUCTION

The use of functional materials, such as those employed in printed electronics applications, relies on the ability to reproducibly formulate materials that 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 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 can facilitate the 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 that 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 that 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 curing1 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 σ0 and frequency ω is superimposed upon a unidirectional stress σz, with both stresses being...
applied along the same plane [see Eq. (1)] such that,

\[
\sigma(t) = \sigma_s + \sigma_0 \cos(\omega t).
\]  

(1)

This gives rise to a deformation that is also composed of both unidirectional and oscillatory components. 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 \( \parallel \) is used to differentiate viscoelastic parameters acquired under parallel superposition to those determined in quiescent conditions.\(^5\) The real and imaginary parts of \( G^\parallel(= G_\parallel + i G_\parallel^\prime) \) can then be extracted and, under certain conditions (such as those under which \( \dot{\gamma} \to 0 \)), can be interpreted as per their quiescent counterparts \( G^\parallel \) and \( G_\parallel^\prime \) in terms of energy storage and dissipation, respectively. It should be noted that unlike the quiescent complex modulus \( G^\parallel \), the coupling of the oscillatory and unidirectional flow fields in CSPS prevents the components of \( G^\parallel \) from being interpreted purely in terms of energy storage and dissipation;\(^6\) 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 \( G^* \).

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 \( G_\parallel^\prime \)\(^10\)\(^-12\) where \( \omega_i < \dot{\gamma}_i/2 \) and leads to difficulty in interpreting \( G_\parallel^\prime \) and \( G_\parallel^\prime \).\(^9\) 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 (~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).

Despite the difficulties associated with the 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 the interpretation of \( G_\parallel^\prime \) and \( G_\parallel^\prime \) in terms of standard models of gelation following Curtis et al.\(^6\) (as discussed in Sec. III), and these systems hence provide an opportunity to validate novel rheometric techniques involving parallel superposition.

While 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 is 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

\[
\sigma(t) = \sigma_s + \sum_{i=1}^{N} \sigma_i \cos(\omega_i t),
\]

(2)

where \( \sigma_i \) and \( \omega_i \) 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 min before being placed in a 60 °C water bath for 45 min. Samples were removed from the water bath and further agitated every 10 min during this 45-min period.

2. Silicone dielectric gels

Silicone dielectric gels (SDGs) (ACC Silicones Ltd.) were prepared from a 2 part addition cure system composed 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 min to allow degassing of the sample (gelation taking approximately 48 h at this temperature).

3. Functional inks

The model inks were composed 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 the silver flake (<10 μm particle size). All materials were sourced from Sigma-Aldrich (UK).

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. The 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 loss through...
evaporation. The pigment of the silver flake was then gradually added to the resin in small quantities. For the present study, three samples were prepared with solid 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 aluminum 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 and inertia considerations). Experiments were performed at superposed stresses in the range of 0 Pa \( \leq \sigma_s \leq 10 \) Pa with \( \sigma_o = \sigma_s \). The oscillatory component of the FT-CSPS waveform consisted of a fundamental frequency of 0.2 Hz with the 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 0.1 \( \times \sigma_s \).

For functional inks, CSPS frequency sweeps (0.1 Hz \( \leq f \leq 10 \) Hz) with 11 logarithmically spaced frequencies were performed with 0.1 Pa \( \leq \sigma_s \leq 10 \) Pa and \( \sigma_o = \sigma_s \). The FT-CSPS waveform consisted of a fundamental frequency of 0.1 Hz with the 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 systems, a more rigorous assessment of linearity at the gel point (GP, which occurs at the solgel transition of a material undergoing gelation) 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 \( \theta_3/\theta_0 \) was used to characterise the deviation from linearity (a ratio in excess of 0.001 being considered to indicate the onset of non-linearity). The absence of mutation artefacts was ensured by excluding data associated with rapid gelation where the mutation number \( (N_{mu}) \) exceeded 0.15.

III. VALIDATION OF FT-CS PS

An 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.

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

\[
G(t) = St^{-\alpha},
\]

where

\[
S = \frac{2\Gamma(\alpha)\sin(\alpha\pi/2)G'_c}{\pi}
\]

and

\[
G'_c = \frac{G'(\omega)}{\omega^\alpha}.
\]

In Eqs. (3)–(5), \( G(t) \) denotes the stress relaxation modulus, \( S \) denotes the gel strength parameter (a pseudo-property with units of Pa \( \times \alpha \)), and \( \alpha \) denotes the stress relaxation exponent. Scanlan and Winter considered \( S \) to consist of a short time constant \( \lambda_0 \) and a modulus \( G_0 \) that are representative properties of the prepolymer, where

\[
S = G_0\lambda_0^\alpha.
\]

These authors observed the expected exponential relationship between \( S \) and \( \alpha \) in several divinyl-terminated poly(dimethylsiloxane) prepolymer cross-linked with tetrakis (dimethylsiloxy)-silane, where the critical gel microstructure (quantified as \( \alpha \)) was altered by manipulating sample stoichiometry. This observation was taken to confirm the validity of Eq. (6) and the interpretation of \( G_0 \) and \( \lambda_0 \) as properties of the prepolymer. Since the study of Scanlan and Winter in 1991, the exponential relationship between \( S \) and \( \alpha \) has been noted by many authors in systems such as laponite, triblock copolymer hydrogels, and silicone dielectric gels as well as in biopolymer systems such as gelatin and fibrin gels.

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 that conform to Eq. (6). In the present work, this
criterion was used as a foundation for the validation of estimates of $\alpha$ derived from FT-CSPS measurements where the GP has been defined based on the attainment of frequency-independent $\tan(\delta_{||})$ following Curtis et al. The identification of frequency-independent $\tan(\delta_{||})$ was performed using a MATLAB routine that identified the roots of the $\tan(\delta_{||})$ data: 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 the GP and the standard deviation of all roots was taken as a measurement of GP accuracy. A model GP would have all roots at the same value of $\tan(\delta_{||})$.

Figure 1 shows the expected exponential relationship between $S$ and $\alpha$ 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 $\sigma_s$ while avoiding sample mutation artefacts (as discussed in more detail in Sec. IV A). The data clearly indicate that measurements performed under CSPS and FT-CSPS conditions follow an identical exponential relationship (with $G_0 = 33.49$ Pa and $\lambda_0 = 0.3$ ms), 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. However, the effect of shear on the material during processing appears to be broadly unexplored. Figures 2 and 3 show the phase angle at the gel point ($\delta_{||GP}$) as a function of $\sigma_s$ for gelatin gels probed using CSPS and FT-CSPS at 25 °C. Both data sets have values of $\delta_{||GP}$ that appear to decrease with increasing unidirectional shear stress (where $\sigma_s > 3$ Pa). However, Fig. 4, which shows corresponding mutation numbers for the data shown in Fig. 2, indicates that where $\sigma_s > 3$ Pa, the CSPS data are invalid since the $N_{mu}$ exceeds the critical mutation number of 0.15. Hence, the data shown for CSPS in Fig. 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 show both significantly reduced error bars (Fig. 3) and $N_{mu} < 0.15$ across the entire range of $\sigma_s$ studied, thus confirming modification of the incipient microstructure of gelatin gels in response to
superposed flow. With CSPS data in isolation, it could be suggested that the apparent decrease in \( \delta_{\parallel GP} \) with increasing \( \sigma_s \) 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 \( \delta_{\parallel} \) 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 \( \sigma_s \) is increased, as shown in Fig. 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 microstructure and the critical gel strength of these materials by varying the gelation temperature.\(^6\) However, it has also been shown that 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 \( \sigma_s \) 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 \( \alpha \) for silicone dielectric gels, where microstructural control has been achieved through manipulation of (a) temperature under quiescent conditions \( (\times) \) and constant temperature and probed using CSPS, and (c) \( \sigma_s \) at constant temperature probed using FT-CSPS \( (\bullet) \) \([\text{data sets (a) and (b) have been previously published}^5]\). The data clearly fit the exponential relationship predicted by Eq. (6) with the FT-CSPS data \( (\bullet) \) significantly enhancing the range of microstructures (and corresponding critical gel strengths) over which the relationship [Eq. (6)] is known to apply \((0 \text{ Pa} \leq \sigma_s \leq 30 \text{ Pa})\). \((\sigma_s \leq 20 \text{ Pa})\). Figure 7 shows \( \delta_{\parallel} \) at the GP as a function of \( \sigma_s \) for SDGs in which increasing \( \sigma_s \) is seen to cause a decrease in \( \delta_{\parallel} \) up to \( \sigma_s = 30 \text{ Pa} \); in previous work, mutation artefacts limited the study of these gels to \( \sigma_s \leq 20 \text{ Pa} \).\(^6\) 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 \( \sigma_s \), which appear in Fig. 7, are symptomatic of the sensitivity of the SDG system to the experimental variations in the gel composition when measured under CSPS conditions.

### 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
The FT-CSPS technique has been implemented in the study of flow-induced microstructural changes in the incipient gelatin network that appears at the gel point (as $\dot{\gamma}_s \rightarrow 0$) and provides identical “processibility metrics” ($G'_\parallel$ and $G''_\parallel$, 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 toward (i) an improved understanding of how products respond to imposed flows and how changes in formulation affect manufacturability and (ii) the deployment of advanced rheometric techniques in process-control applications.

ACKNOWLEDGMENTS

This work was supported by EPSRC (UK) Grant Nos. EP/K03099X/1 and EP/L024799/1. All data are provided in full in Secs. III and IV of this paper.

1. E. Holly, S. Venkataraman, F. Chambon, and H. Winter, “Fourier transform mechanical spectroscopy of viscoelastic materials with transient structure,” J. Non-Newtonian Fluid Mech. 27, 17–26 (1988).
2. K. Hawkins, M. Lawrence, P. Williams, and R. Williams, “A study of gelatin gelation by fourier transform mechanical spectroscopy,” J. Non-Newtonian Fluid Mech. 148, 127–133 (2008).
3. B.-S. Chiou, R. J. English, and S. A. Khan, “Rheology and photo-cross-linking of thiol-ene polymers,” Macromolecules 29, 5368–5374 (1996).
4. M. In and R. Prud’homme, “Fourier transform mechanical spectroscopy of the sol-gel transition in zirconium alkoxide ceramic gels,” Rheol. Acta 32, 556–565 (1993).
5. J. Dealy, “Official nomenclature for material functions describing the response of a viscoelastic fluid to various shearing and extensional deformations,” J. Rheol. 39, 253–265 (1995).
6. D. Curtis, N. Badiei, A. Holder, J. Claypole, D. Deganello, M. Brown, M. Lawrence, P. Evans, P. Williams, and K. Hawkins, “Assessment of the stress relaxation characteristics of critical gels formed under unidirectional shear flow by controlled stress parallel superposition rheometry,” J. Non-Newtonian Fluid Mech. 222, 227–233 (2015).
7. N. Badiei, A. M. Sowedan, D. J. Curtis, M. R. Brown, M. J. Lawrence, A. I. Campbell, A. Sabra, P. A. Evans, J. W. Weisel, I. N. Chemshy, C. Nagaswami, P. R. Williams, and K. Hawkins, “Effects of unidirectional flow shear stresses on the formation, fractal microstructure and rigidity of incipient whole blood clots and fibrin gels,” Clin. Hemorheol. Microcirc. 60, 451–464 (2015).
8. M. Yamamoto, “Rate-dependent relaxation spectra and their determination,” Trans. Soc. Rheol. 15, 331–344 (1971).
9. I. Vermant, L. Walker, P. Moldenaers, and J. Mewis, “Orthogonal versus parallel superposition measurements,” J. Non-Newtonian Fluid Mech. 79, 173–189 (1998).
10. H. Booj, “Influence of superimposed steady shear flow on the dynamic properties on non-Newtonian fluids. I. Measurements on non-Newtonian solutions,” Rheol. Acta 5, 215–221 (1966).
11. I. Macdonald and R. Bird, “Complex modulus of concentrated polymer solutions in steady shear,” J. Phys. Chem. 70, 2068–2069 (1966).
12. P. Boukany and W.-Q. Wang, “Nature of steady flow in entangled fluids revealed by superimposed small amplitude oscillatory shear,” J. Rheol. 53, 1425–1435 (2009).
13. E. Somma, O. Valentino, and G. Titomiano, “Parallel superposition in entangled polydisperse polymer melts: Experiments and theory,” J. Rheol. 51, 987–1005 (2007).
14. K. Hawkins, P. A. Evans, M. Lawrence, D. Curtis, M. Davies, and P. R. Williams, “The development of rheometry for strain-sensitive gelling systems and its application in a study of fibrin–thrombin gel formation,” Rheol. Acta 49, 891–900 (2010).
15. F. Chambon and H. Winter, “Linear viscoelasticity at the gel point of a crosslinking PDMS with imbalanced stoichiometry,” J. Rheol. 31, 683–697 (1987).
16. M. Mours and H. Winter, “Time-resolved rheometry,” Rheol. Acta 33, 385–397 (1994).
17. D. Curtis, A. Holder, N. Badiei, J. Claypole, M. Walters, B. Thomas, M. Barrow, D. Deganello, M. Brown, P. Williams, and K. Hawkins, “Validation of Optimal Fourier Rheometry for rapidly gelling materials and...
its application in the study of collagen gelation,” J. Non-Newtonian Fluid Mech. 222, 253–259 (2015).

18 J. Scanlan and H. Winter, “Composition dependence of the viscoelasticity of end-linked poly (dimethylsiloxane) at the gel point,” Macromolecules 24, 47–54 (1991).

19 S. Jatav and Y. M. Joshi, “Phase behavior of aqueous suspension of laponite: New insights with microscopic evidence,” Langmuir 33, 2370–2377 (2017).

20 T. Vermonden, N. A. M. Besseling, M. J. van Steenbergen, and W. E. Hennink, “Rheological studies of thermosensitive triblock copolymer hydrogels,” Langmuir 22, 10180–10184 (2006).

21 The MathWorks, Inc., MATLAB, The MathWorks, Inc., Natick, Massachusetts, 2016.

22 R. E. Hudson, A. J. Holder, K. M. Hawkins, P. R. Williams, and D. J. Curtis, “An enhanced rheometer inertia correction procedure (ERIC) for the study of gelling systems using combined motor-transducer rheometers,” Phys. Fluids 29, 121602 (2017).

23 M. Laronda, A. Rutz, X. Shuo, K. Whelan, F. Duncan, E. Roth, T. Woodruff, and R. Shah, “A bioprosthetic ovary created using 3D printed microporous scaffolds restores ovarian function in sterilized mice,” Nat. Commun. 8, 15261 (2017).