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## An enhanced rheometer inertia correction procedure (ERIC) for the study of gelling systems using combined motor-transducer rheometers

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# An enhanced rheometer inertia correction procedure (*ERIC*) for the study of gelling systems using combined motor-transducer rheometers

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The rheological characterisation of viscoelastic materials undergoing a sol-gel transition at the Gel Point (GP) has important applications in a wide range of industrial, biological, and clinical environments and can provide information regarding both kinetic and microstructural aspects of gelation. The most rigorous basis for identifying the GP involves exploiting the frequency dependence of the real and imaginary parts of the complex shear modulus of the critical gel (the system at the GP) measured under small amplitude oscillatory shear conditions. This approach to GP identification requires that rheological data be obtained over a range of oscillatory shear frequencies. Such measurements are limited by sample mutation considerations (at low frequencies) and, when experiments are conducted using combined motor-transducer (CMT) rheometers, by instrument inertia considerations (at high frequencies). Together, sample mutation and inertia induced artefacts can lead to significant errors in the determination of the GP. Overcoming such artefacts is important, however, as the extension of the range of frequencies available to the experimentalist promises both more accurate GP determination and the ability to study rapidly gelling samples. Herein, we exploit the frequency independent viscoelastic properties of the critical gel to develop and evaluate an enhanced rheometer inertia correction procedure. The procedure allows acquisition of valid GP data at previously inaccessible frequencies (using CMT rheometers) and is applied in a study of the concentration dependence of bovine gelatin gelation GP parameters. A previously unreported concentration dependence of the stress relaxation exponent ( $\alpha$ ) for critical gelatin gels has been identified, which approaches a limiting value ( $\alpha = 0.7$ ) at low gelatin concentrations, this being in agreement with previous studies and theoretical predictions for percolating systems at the GP. © 2017 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/>). [<http://dx.doi.org/10.1063/1.4993308>]

## I. INTRODUCTION

Inertial effects can dominate rheological measurements performed by combined motor-transducer (CMT) rheometers (also known as controlled stress rheometers) on low viscosity systems or samples with weak gel network structures (Krieger, 1990), such effects being most severe at high frequencies (Klemuk and Titze, 2009; Krieger, 1990; Lauser and Stettin, 2016; and Walters, 1975). The design of CMT rheometers requires the torque developed by the instrument to both deform the sample under investigation and accelerate the moving components of the rheometer. Standard practice requires that the instrument is calibrated without the sample present in order to determine the inertial characteristics of the rheometer-geometry assembly and to allow subsequent correction of the raw data. Separate motor-transducer (SMT) rheometers (also known as controlled strain) are not susceptible to instrument inertia artefacts since the torque sensing element remains static during data acquisition (Franck, 2003).

An inertia correction is routinely applied to raw storage modulus data ( $G'_{raw}$ ) by the software controlling CMT rheometers such that

$$G' = G'_{raw} - I_c \omega^2 k_g, \quad (1)$$

where  $G'$  denotes the apparent storage modulus of the material,  $I_c$  denotes a calibrated inertia constant,  $\omega$  denotes the angular frequency, and  $k_g$  denotes a geometry factor (Franck, 2005). However, the inertia constant can only be determined to finite precision and there will always be some uncertainty regarding the accuracy of  $G'$  extracted from the raw waveforms where the magnitude of the term  $I_c \omega^2 k_g$  may represent a dominant part of  $G'_{raw}$  (Ewoldt *et al.*, 2015). Further, a momentum balance can be used to show that the inertial term has no imaginary component (Klemuk and Titze, 2009), and hence the loss modulus,  $G''$ , is unaffected by the presence of instrument inertia (Franck, 2005). The raw phase angle,  $\delta_{raw}$ , measured by the instrument is often used as a measure of the extent to which the inertial artefacts pollute the raw data. Instrument manufacturers recommend caution where  $\delta_{raw}$  exceeds a stated value that is dependent on the rheometer model, e.g., the TA Instruments

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AR-2000ex model has a limiting raw phase angle of  $150^\circ$  (TA Instruments, 2016).

Motivated by a significant discrepancy between gel point (GP) data obtained using CMT and SMT rheometers ( $\delta_{GP} = 72.8^\circ \pm 6.9^\circ$  and  $62.7^\circ \pm 1.0^\circ$ , respectively, for low concentration gelatin samples, see Sec. IV), we exploit the characteristic rheological behaviour of the critical gel (i.e., frequency independent phase angle,  $\delta$ ) (Chambon and Winter, 1987) to develop an Enhanced Rheometer Inertia Correction (ERIC) procedure. The ERIC procedure can be used to correct GP data in the post-acquisition phase. In the present work, the ERIC procedure was used in a study of the concentration dependence of the stress relaxation properties of bovine gelatin at the GP.

Characterisation of the sol-gel transition, which occurs at the GP of a material undergoing gelation, can provide information concerning the evolving microstructural properties of the material under investigation (Curtis *et al.*, 2011 and Lawrence *et al.*, 2015). At the GP the storage and loss moduli scale as identical power laws in frequency ( $G' \sim G'' \sim \omega^\alpha$ ) (Chambon *et al.*, 1986) with the parameter  $\alpha$  ( $0 < \alpha < 1$ ), termed the stress relaxation exponent, which is sensitive to the microstructure of the sample spanning incipient gel network that forms at the GP. The measurement of  $\alpha$  is often challenging and is limited by sample mutation (Mours and Winter, 1994) and, as demonstrated in the present work, instrument inertia artefacts (when using CMT rheometers). Examples of the utility of GP data are widespread in terms of physical and chemical gels (Djabourov *et al.*, 1988a; Hawkins *et al.*, 2008; Hsu and Jamieson, 1993; Djabourov *et al.*, 1988b; and Michon *et al.*, 1993). Recently, GP characterisation of coagulating blood has been shown to provide a novel biomarker for healthy coagulation (Evans *et al.*, 2010) and a predictor of clot microstructure (Curtis *et al.*, 2013).

Gelatin is a common biopolymer derived from the hydrolysis of collagen. Whilst at temperatures above the maximum gelation temperature ( $\sim 33.6^\circ\text{C}$ ) (Tosh and Marangoni, 2004), gelatin displays near Newtonian rheological properties, upon cooling, a thermoreversible gelation process occurs to form a physically crosslinked biopolymer network (Boedtger and Doty, 1954; Tosh and Marangoni, 2004; and Wolf and Keller, 1996). The thermoreversible nature of gelatin gelation makes the system an ideal test material for studies involving the validation of novel rheometric approaches (Curtis *et al.*, 2015a; Curtis *et al.*, 2015b; and Hawkins *et al.*, 2008).

## II. MATERIALS AND METHODS

### A. Gelatin preparation

Appropriate quantities of gelatin powder (Fisher G/0150/53) and type I deionised water were combined and shaken vigorously for 5 min before being placed in a  $60^\circ\text{C}$  water bath for 45 min to ensure complete dissolution. The solutions were agitated for 1 min every 10 min and retained at  $60^\circ\text{C}$  for no longer than 45 min to prevent degradation. Aliquots of each concentration ( $2.5 \text{ wt. } \% \leq c \leq 30 \text{ wt. } \%$ ) of gelatin were stored in a refrigerator ( $4^\circ\text{C}$ ) and melted at  $60^\circ\text{C}$  for 45 min prior to being loaded to the rheometer.

## B. Rheometry

### 1. CMT rheometers

Rheological measurements were conducted using a 60 mm acrylic plate geometry fitted to a TA Instruments AR-2000ex rheometer or a 60 mm aluminium plate geometry fitted to a TA Instruments AR-G2 rheometer; both systems used Peltier plate temperature control. Gelatin samples were loaded onto the rheometer at  $34^\circ\text{C}$  before the upper geometry was lowered into place and the test commenced at which point the temperature was quenched to the test temperature. To satisfy the gap loading condition (Schrag, 1977), which ensures that the velocity gradient across the geometry gap is uniform thus confirming negligible sample inertia effects, a shearing gap of  $150 \mu\text{m}$  was used. Inertia correction studies were completed using 2.5 wt. % gelatin. A sequence of gel point experiments was performed with each experiment covering a decade of frequency, the highest frequency being systematically increased from 1 Hz to 12 Hz (with the corresponding lowest frequencies being 0.1 Hz–1.2 Hz, respectively). All tests were performed at  $19^\circ\text{C}$  such that gelation occurred over approximately 900 s to minimise sample mutation effects at the GP (Mours and Winter, 1994). The mutation number is calculated for the lowest frequency using  $N_{mu} = \frac{\Delta t}{G'} \frac{dG'}{dt}$  (Mours and Winter, 1994), where  $\Delta t$  denotes the data point acquisition time. Under the conditions presented above, a typical mutation number would be 0.062.

Concentration dependence of gelatin gelation was studied using the AR-2000ex rheometer fitted with a 60 mm acrylic plate geometry. A frequency range of 0.3–3.0 Hz was used for all experiments. Since the gel time of gelatin is strongly dependent on both concentration and gelation temperature, it was infeasible to maintain a constant temperature for this set of experiments. Hence, the temperature was varied from  $19^\circ\text{C}$  (for 2.5 wt. % Gelatin) to  $32.5^\circ\text{C}$  (for 30 wt. % Gelatin). No temperature dependence of the stress relaxation characteristics of the gels was observed in preliminary tests, in agreement with the literature data (Hawkins *et al.*, 2008). Sample mutation was assessed and data omitted where the mutation number was found to exceed 0.15 (Mours and Winter, 1994). Furthermore, for all experiments linear viscoelastic measurements were confirmed by ensuring that the magnitude of the third harmonic of the displacement signal remained insignificant at the gel point (Hawkins *et al.*, 2010). A thin layer of low viscosity silicone oil (9.8 mPas, Brookfield) was applied to the free surface of the sample to prevent evaporation during the experiment.

### 2. SMT rheometer

A TA Instruments ARES-G2 rheometer fitted with a 40 mm parallel plate geometry (and Peltier plate temperature control accessory) was loaded with an appropriate volume of 2.5 wt. % gelatin. During loading, the Peltier plate temperature was set to  $30^\circ\text{C}$ . As for the CMT rheometer studies, a gap of  $150 \mu\text{m}$  was employed to ensure the gap loading assumption was valid. A pre-shear of  $100 \text{ s}^{-1}$  for 10 s was applied to ensure symmetrical loading before multiple consecutive frequency sweeps were performed (0.9–3.5 Hz) at  $20^\circ\text{C}$ . The transient nature of the gelation process requires that the strain amplitude

decreases throughout the experiment to (i) achieve a resolvable torque signal at all stages of gelation and (ii) maintain linear viscoelastic measurements. Hence, the strain amplitude was decreased by 25% (from an initial value of 100%) where the torque exceeded  $3 \mu\text{Nm}$ , harmonic analysis of the signals at the GP revealed no higher harmonic contribution to the stress waveform confirming linear conditions (Hawkins *et al.*, 2010).

### C. Enhanced rheometer inertia correction (ERIC)

Following Eq. (1), the value of  $G'$  reported by the instrument is dependent on the both the true value of the storage modulus,  $G'_t$ , and the calibrated inertia constant,  $I_c$ . The value of the latter is routinely determined during preparation of the instrument but the finite precision and accuracy of this calibration can cause the true inertia constant, which characterises the instrument-geometry assembly ( $I_t$ ), to differ from the calibrated Inertia Constant ( $I_c$ ) by a small deviation of  $\Delta I$ . Hence it can be written from Eq. (1) that

$$G'_t(\omega) = G'(\omega) + (I_t - I_c)\omega^2 k_g = G'(\omega) + \Delta I \omega^2 k_g. \quad (2)$$

A MATLAB routine was used to incrementally change the value of  $\Delta I$  in Eq. (2) whilst monitoring the standard deviation of the roots of the gel point data (Evans *et al.*, 2010). A root can be defined as the time and phase angle of the intersection between each pair of frequencies [see Fig. 1(a)] with the deviation in the positions of the roots providing a measure of the accuracy of the GP data. The procedure was coded as a MATLAB (The MathWorks, Inc., 2016a). GUI (ERIC) and is freely available from the corresponding author. Briefly, the procedure involved fitting a 5 parameter logistic equation to the  $\delta(t)$  data for each frequency and determining the location of the intersection between each pair of fitted curves (i.e., each root), the apparent GP was then defined at the mean phase angle and mean time of all roots. The standard deviation (with respect to time) of the roots was taken as a measure of the accuracy of the GP. The procedure was repeated for  $-0.2 \mu\text{Nms} \leq \Delta I \leq 0.2 \mu\text{Nms}$  with the true GP being identified where varying  $\Delta I$  caused a minimum in the standard deviation of the GP roots.

The  $\omega^2$  dependence of the inertia correction [Eq. (2)] prevents the ERIC procedure from generating an erroneous pseudo-GP if the material does not display this phenomenon. This can be demonstrated by assuming hypothetical (and valid) non-GP data in which  $G'$  and  $G''$  display separate power law dependencies on angular frequency such that

$$G' = k_1 \omega^\alpha, \quad G'' = k_2 \omega^\beta, \quad (\alpha \neq \beta).$$

From Eq. (2) a corrected value of  $G'$  would be expressed as

$$G'_c = k_1 \omega^\alpha + \Delta I \cdot K_g \cdot \omega^2.$$

A pseudo-GP would require frequency independent  $\tan\delta$ , i.e.,

$$\frac{G''(\omega)}{G'_c(\omega)} = \frac{k_2 \omega^\beta}{k_1 \omega^\alpha + \Delta I \cdot K_g \cdot \omega^2} = c,$$

where “c” is a constant. Rearranging for  $\Delta I \cdot k_g$  gives

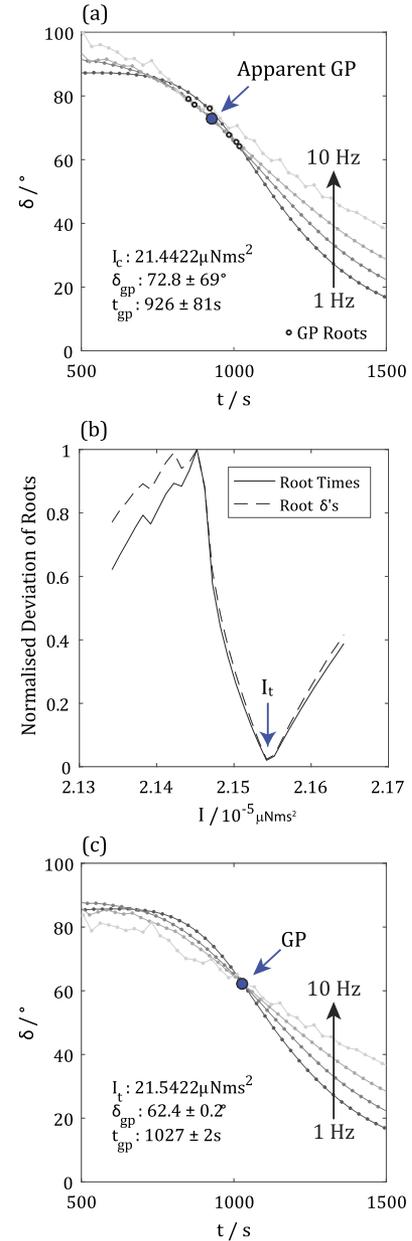


FIG. 1. (a) An apparent gel point (1.0–10 Hz) before correction showing the large deviation in the “roots” position and resultant difficulty in defining the GP as a consequence of inertia induced artefacts (*lines refer to data recorded at different frequencies*); (b) optimisation data for determination of  $I_t$ ; and (c) a corrected gel point with converged roots.

$$\Delta I \cdot k_g = \frac{k_2}{c} \omega^{(\beta-2)} + k_1 \omega^{(\alpha-2)},$$

and since  $\Delta I$  and  $k_g$  are, by definition, independent of frequency, pseudo-GP data can only exist where  $\alpha = \beta = 2$  or  $k_1 = k_2 = 0$ , neither of which are viable GP conditions [since at a GP  $0 < (\alpha = \beta) < 1$ , and both  $G'$  and  $G''$  must be non-zero], hence the ERIC procedure cannot generate a GP if one does not exist.

### III. RESULTS AND DISCUSSION

Figure 1(a) shows typical uncorrected GP data (acquired over a frequency range of 1.0 Hz–10 Hz) as reported by the instrument with an apparent GP at  $72.8^\circ \pm 6.9^\circ$ . This value is

significantly above the value of  $62.7^\circ \pm 1.0^\circ$  obtained using an SMT rheometer (ARES-G2 in the present study) and displays a high degree of uncertainty reflective of the large deviation of the positions of the GP roots. The deviation in the root positions ( $\pm 6.9^\circ$ ) should alert the experimentalist to inadequacies in the GP acquisition procedure, which may be caused by several experimental issues, for example; sample mutation (Hawkins *et al.*, 2010 and Mours and Winter, 1994); sample inertia (Schrag, 1977); evaporation of the sample (Hellström *et al.*, 2015); under/over/asymmetric loading (Ewoldt *et al.*, 2015) or instrument inertia. In the present study, the effect of inaccurate instrument inertia calibration has been isolated by careful experimental design and data verification (see Sec. II). The corrected instrument inertia constant ( $I_t$ ) was determined using ERIC; Fig. 1(b) shows the deviation in the root positions for a range of  $I_t$  with the “optimum” value being determined as  $21.5422 \mu\text{Nm}^2$  (this representing a 0.46% change from the calibrated value). Figure 1(c) shows the “corrected” GP data (after application of the ERIC routine) with an apparent GP at  $62.4^\circ \pm 0.2^\circ$  in excellent agreement with the SMT rheometer results.

Figure 2 shows both uncorrected (circles) and corrected (squares) GP data for gelatin acquired over increasing frequency intervals (with the minimum frequency being a decade lower than the maximum frequency reported on the abscissa). It can clearly be seen that increasing the frequency window over which the data are acquired drives the uncorrected data to higher values of the  $\delta$  at the GP with increasing deviation in the root positions (leading to less precise GP determination). However, appropriate correction of the data (using ERIC) allows both accurate and precise GP determination over the entire range of frequency windows studied herein. The result has important applications in the analysis of rapidly evolving strain sensitive gelling systems for which the use of techniques such as Fourier transform mechanical spectroscopy has been shown to be inappropriate (Hawkins *et al.*, 2008).

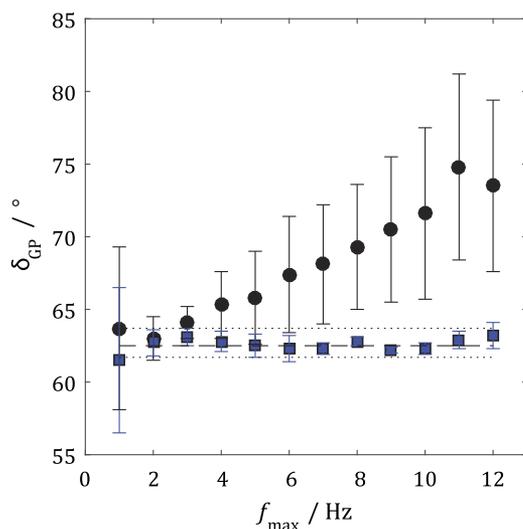


FIG. 2. Phase angle of the raw GP data (circles) collected over a range of frequencies, along with the corrected GPs for the same data sets (squares). The corrected data are shown to be back within the acceptable limit for the concentration of gelatin. In order to reflect the uncertainties associated with the measurements, error bars reflect the larger of either (i) the standard deviation between repeats or (ii) the deviation of the root positions.

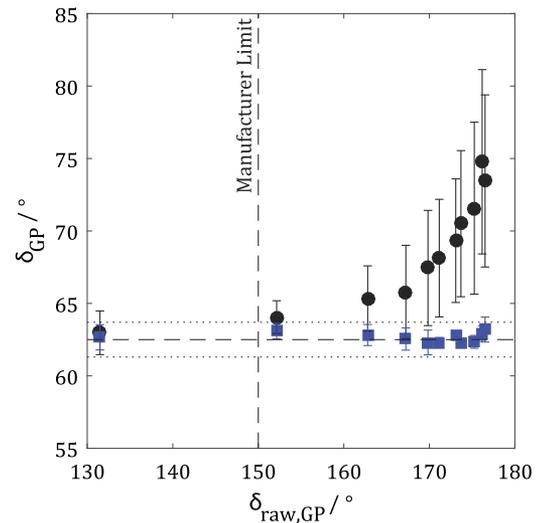


FIG. 3. Apparent (black circles) and corrected (blue squares) GP data as a function of  $\delta_{raw}$  at the apparent GP (highest frequency). Horizontal lines show the SMT rheometer mean (dashed) and standard deviation (dotted). The vertical line shows the manufacturer's stated limiting  $\delta_{raw}$  (TA Instruments, 2016). In order to reflect the uncertainties associated with the measurements, error bars reflect the larger of either (i) the standard deviation between repeats or (ii) the deviation of the root positions.

It should be noted that the dramatic improvement in both the precision and accuracy of the GP data has been achieved by an average 0.46% change in the calibrated inertia constant, whilst repeated calibration of the instrument inertia was found to generate a 0.15% deviation in this value. Hence, some systematic error in the calibrated inertia constant appears to exist for the AR-2000ex used in the present study, which limits the validity of data where the raw phase angle is in excess of  $150^\circ$  (see Fig. 3), thus preventing comparison of rheometric data obtained using other rheometers. This is in agreement with the manufacturer's stated limitation of the AR-2000ex instrument (TA Instruments, 2016).

To test the hypothesis that the ERIC procedure could be applied to correct this systematic error, thus allowing valid data to be acquired at high raw phase angles, two TA Instruments AR-G2 rheometers were used to determine the apparent GP using a frequency range of 1–10 Hz, both rheometers had undergone manufacturer servicing and calibration within a period of 12 months prior to the present study. Using standard instrument inertia calibrations, a significant difference between the data obtained using the two instruments was apparent (AR-G2 I:  $61.5^\circ \pm 2.0^\circ$ /AR-G2 II:  $69.0^\circ \pm 4.4^\circ$  - see Fig. 4). The ERIC procedure was then performed on all data obtained using these two instruments, and a Student t-test ( $n = 8$ ) was used to compare the distribution of  $\delta_{GP}$  obtained using standard inertia calibration (SIC) procedures and ERIC. No significant difference was observed between the distributions of  $\delta_{GP}$  using SIC and ERIC for AR-G2 I ( $p = 0.39$ ) indicating that the standard procedure was sufficiently accurate for this rheometer. However, for AR-G2 II, a significant difference ( $p = 0.003$ ) was found between the distributions indicating that the accuracy of the SIC protocols appears to be instrument-specific. Following the application of the ERIC procedures, no significant difference was observed between the data acquired using the two AR-G2 instruments ( $p = 0.16$ ).

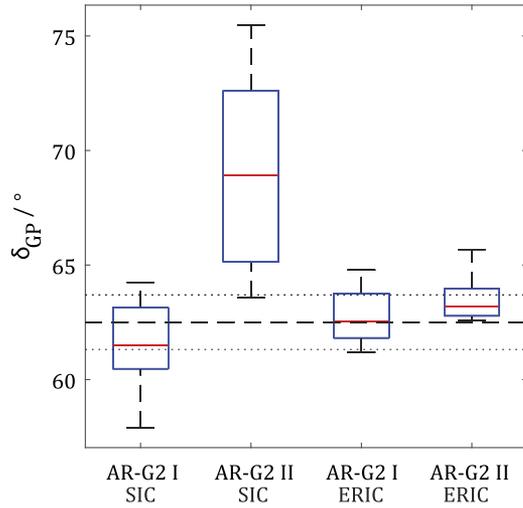


FIG. 4. Comparison of gel point results from two AR-G2 rheometers using standard inertia calibration (SIC) and ERIC. A significant difference between the rheometers is apparent using the SIC ( $p = 0.0004$ ), whilst no significant difference is apparent after the application of the ERIC routine ( $p = 0.16$ ). Horizontal lines show the mean and standard deviation of data acquired using the SMT rheometer.

In the present study, the concentration dependence of gelatin gelation has been studied (see Fig. 5) using a CMT rheometer with data processing using both the SIC and ERIC procedures, the use of ERIC allowing the concentration range to be extended as low as 2.5 wt. %. Figure 5(a) shows the data obtained in the present study (and corrected using the SIC procedure) with the literature data from both Hawkins *et al.* (2008) and Curtis *et al.* (2015a; 2015b). Both studies show excellent agreement with the present data despite the fact that the studies have been using differing techniques. In the latter study, Curtis *et al.* used an SMT rheometer to study gelatin at 30 wt. % using multi-frequency rheometric techniques that allowed data to be accessed up to 10 Hz. Good agreement between the present data and the data of Curtis *et al.* should be expected given the high concentration of gelatin. This causes the torque generated by the (significantly more viscous) material to dominate the measurement thus reducing the raw phase angle (in the present CMT data) to within acceptable limits. Hawkins *et al.* employed Fourier Transform Mechanical Spectroscopy (FTMS) (implemented using a CMT rheometer) to obtain data. Their data agree with that presented herein at low concentrations and is likely to suffer from the same instrument inertia artefacts as described above, leading to the aforementioned discrepancy between data obtained using SMT and CMT rheometers.

Post-acquisition application of the ERIC procedure has allowed the data presented in Fig. 5(a) to be corrected to account for the inaccuracy in the inertia constant [as shown in Fig. 5(b)]. Agreement between the SMT and CMT rheometers is then recovered (CMT:  $63.1^\circ \pm 0.6^\circ$ /SMT:  $62.7^\circ \pm 1.0^\circ$ ) confirming the validity of the ERIC procedure. Further, the corrected data appear to show that a maximum phase of angle of  $63^\circ$  is approached as gelatin concentration is decreased. This limiting value corresponds to a limiting stress relaxation exponent ( $\alpha = \delta/90$ ) commensurate with theoretical predictions for percolating systems ( $\alpha = 0.7$ ) (Adam *et al.*, 1981; Martin *et al.*,

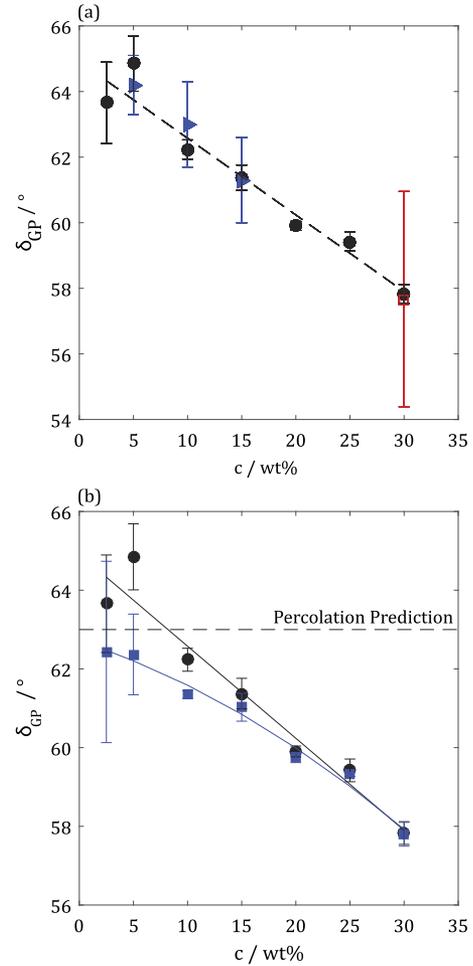


FIG. 5. Concentration dependence of  $\delta_{GP}$ . (a) shows data from the present study (0.3–3 Hz, black circles) using standard instrument correction procedures, Hawkins *et al.* (0.2–3.2 Hz, SAOS and Fourier Transform Mechanical Spectroscopy, blue triangles) (Hawkins *et al.*, 2008) and Curtis *et al.* (0.1–10 Hz, Optimal Fourier Rheometry and Fourier transform mechanical spectroscopy, red squares) (Curtis *et al.*, 2015a; 2015b). Excellent agreement between these CMT rheometer based studies is observed, but a clear discrepancy is also evident at 2.5 wt. % with data obtained using a SMT rheometer ( $62.7^\circ \pm 1.0^\circ$ , herein, shown as a red circle with error bars). (b) shows the effect of applying the ERIC procedure to data from the present study (standard inertia correction—black circles, ERIC—blue squares) along with the percolation theory prediction of the value of  $\delta_{GP}$ .

1988; and de Gennes, 1979) and experimental observations of other biopolymer systems (Audebrand *et al.*, 2003; Axelos and Kolb, 1990; Werner *et al.*, 2006; and Yu *et al.*, 1997).

#### IV. CONCLUSIONS

The ERIC inertia correction procedure reported herein offers the experimentalist enhanced precision and accuracy of GP measurements and has facilitated the acquisition of valid GP data at previously inaccessible frequencies (where instrument inertia effects dominate the measurement). The typical modification to the inertia constant (of the order  $0.1 \mu\text{Nm}^2$ ) is larger than the precision of the inertia constant as determined through repeated calibrations. This suggests that there may be an underlying inaccuracy associated with this form of instrument calibration procedure and that application of the

ERIC procedure may provide a basis for identifying discrepancies between results obtained on different CMT instruments. A previously unreported concentration dependence of the stress relaxation exponent for critical gelation gels has been reported with a limiting value  $\delta_{GP}$  of  $63^\circ$  (corresponding to  $\alpha = 0.7$ ) being identified at low gelatin concentrations.

## ACKNOWLEDGMENTS

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