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Tassieri, M., Laurati, M., Curtis, D., Auhl, D., Coppola, S., Scalfati, A., Hawkins, K., Williams, P. & Cooper, J. (2016). i-Rheo: Measuring the materials' linear viscoelastic properties "in a step"! *Journal of Rheology*, 60(4), 649-660.

<http://dx.doi.org/10.1122/1.4953443>

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i-Rheo: Measuring the materials' linear viscoelastic properties “in a step”!

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Citation: *Journal of Rheology* **60**, 649 (2016); doi: 10.1122/1.4953443

View online: <http://dx.doi.org/10.1122/1.4953443>

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i-Rheo: Measuring the materials' linear viscoelastic properties “in a step”!

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(Received 3 February 2016; final revision received 1 April 2016; published 14 June 2016)

Abstract

We present a simple new analytical method for educing the materials' linear viscoelastic properties, over the widest range of experimentally accessible frequencies, from a simple *step*-strain measurement, without the need of preconceived models nor the idealization of real measurements. This is achieved by evaluating the Fourier transforms of *raw* experimental data describing both the time-dependent stress and strain functions. The novel method has been implemented into an open access executable “i-Rheo,” enabling its use to a broad scientific community. The effectiveness of the new rheological tool has been corroborated by direct comparison with conventional linear oscillatory measurements for a series of complex materials as diverse as a monodisperse linear polymer melt, a bimodal blend of linear polymer melts, an industrial styrene-butadiene rubber, an aqueous gelatin solution at the gel point and a highly concentrated suspension of colloidal particles.

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The broadband nature of the new method and its general validity open the route to a deeper understanding of the material's rheological behavior in a variety of systems. © 2016 The Society of Rheology. [<http://dx.doi.org/10.1122/1.4953443>]

I. INTRODUCTION

Since the field of rheology was established, the linear viscoelastic (LVE) properties of materials have been successfully correlated, both theoretically and experimentally [1–4], to their topological structure; from a macroscopic length scale (of the whole sample) at relatively low frequencies, down to an atomic length scale for frequencies of the order of terahertz (THz). Hence, the importance of their knowledge over the widest possible range of frequencies to gain a full picture of the materials' structure.

The LVE properties of a material can be represented by its frequency-dependent complex shear modulus $G^*(\omega)$, which provides information on both the viscous and the elastic nature of the material. The conventional method of measuring $G^*(\omega)$ over a discrete range of frequencies is based on simple oscillatory measurements, where for each explored frequency, a sinusoidal stress (or strain) is imposed and the resulting oscillatory strain (or stress) is measured. This, despite its effectiveness, is a *time-consuming* procedure that commonly limits the number of explored frequencies to a few points per decade, often ranging from 0.1 to 100 Hz. Moreover, despite the continuous effort in developing new high performance rheometers, the range of accessible high frequencies remains still limited. Indeed, while high-end rheometers are capable of detecting/applying torques as low as a few nN.m and angular displacements as small as a few μrad , they still present an upper frequency limit of ≈ 100 Hz, at best, because of instrument inertia.

Alternative experimental procedures for measuring the material's LVE properties are the "multiwave" test [5] and the "step" measurement [1]. The former is an oscillatory test, where multiple sinusoidal (stress or strain) waves having

different frequencies and amplitudes are superimposed. The analysis of the resulting material's response (strain or stress, respectively) provides the values of the moduli only for the explored frequencies. The second test, which is at the heart of this article, allows the determination of material's LVE properties over a much wider (in principle infinite) range of frequencies and is achieved by "instantaneously" imposing a finite strain or stress (i.e., a Heaviside step function) to the material. Indeed, it is well known [6] that, given a generic system, the full frequency spectrum of its linear response [i.e., its transfer function $H(\omega) = \hat{y}(\omega)/\hat{x}(\omega)$, written in the Fourier domain], is given by the ratio between the Fourier transforms (denoted by the symbol " $\hat{\cdot}$ ") of the system's temporal response $[y(t)]$ to a time-dependent input $[x(t)]$ having the form of either a unit *impulse* $[\delta(t)]$ or a unit *step* $[u(t)]$ (with known Fourier transforms as schematically shown in Fig. 1).

Unfortunately, none of the above two ideal input functions are exactly reproducible in real experiments. However, while the $\delta(t)$ function is generally not an option, the *step*-function is well approximated with the exception of an initial nonlinear ramp of short duration (ε). In addition, it has been shown [7] that the evaluation of the above mentioned Fourier transforms, given only a finite set of data points over a finite time domain, is nontrivial [8–12] since interpolation and extrapolation from those data can yield artefacts that lie within the bandwidth of interest.

In this article, we present a new rheological "tool" to evaluate the materials' LVE properties over the *widest* range of experimentally accessible frequencies from a simple *step*-strain measurement, with neither the need of preconceived models nor the idealization of real measurements. This is achieved by evaluating the Fourier transforms of *raw* experimental data describing both the time-dependent stress and strain functions by means of the analytical method introduced by Tassieri *et al.* [7]. Notably, when compared with conventional oscillatory measurements, the proposed analytical procedure significantly extends the range of explored frequencies at both ends. The computational method has been implemented into an open access executable named i-Rheo and its effectiveness has been corroborated by direct comparison with conventional linear oscillatory measurements for a series of complex materials having significantly different viscoelastic nature, as described in Sec. III.

II. THEORETICAL BACKGROUND

A. Linear rheology

The material's complex shear modulus $G^*(\omega)$ is a complex number whose real and imaginary parts provide information on the viscoelastic nature of the material. This is defined as the ratio between the Fourier transforms of the stress $\sigma(t)$ and the strain $\gamma(t)$, whatever their temporal forms and regardless of whichever has been imposed or measured [1]

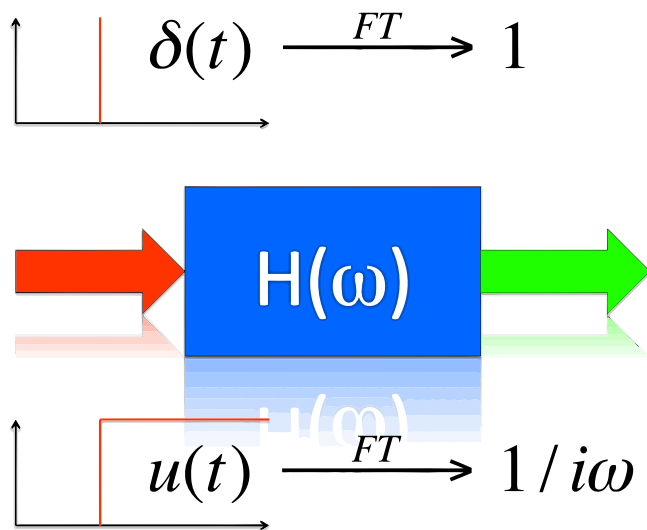


FIG. 1. Block diagram of a generic system where an input having the temporal form of either a unit *impulse* $[\delta(t)]$ or a unit *step* $[u(t)]$ function is used to educe the system transfer function $H(\omega)$. The Fourier transforms of the input functions [e.g., $FT[\delta(t)] = \int_{-\infty}^{+\infty} \delta(t)e^{-i\omega t} dt = 1$] are also shown.

$$G^*(\omega) = \frac{\hat{\sigma}(\omega)}{\hat{\gamma}(\omega)} = G'(\omega) + iG''(\omega), \quad (1)$$

where ω is the angular frequency, i is the imaginary unit (i.e., $i^2 = -1$), $G'(\omega)$ and $G''(\omega)$ are the material storage (elastic) and loss (viscous) moduli, respectively.

The standard method of measuring $G^*(\omega)$ over a finite set of frequencies is based on the imposition of an oscillatory stress $\sigma(\omega, t) = \sigma_0 \sin(\omega t)$ (where σ_0 is the amplitude of the stress function) and the measurement of the resulting oscillatory strain, which would have a form of $\gamma(\omega, t) = \gamma_0(\omega) \sin[\omega t + \varphi(\omega)]$, where $\gamma_0(\omega)$ is the strain amplitude and $\varphi(\omega)$ is the phase shift between the stress and the strain. From Eq. (1), it follows that

$$G^*(\omega) = \frac{\sigma_0}{\gamma_0(\omega)} \cos(\varphi(\omega)) + i \frac{\sigma_0}{\gamma_0(\omega)} \sin(\varphi(\omega)), \quad (2)$$

from which the expressions of the viscoelastic moduli can be inferred. Nevertheless, conventional rotational rheometers are limited in the range of accessible frequencies, mainly at the top end, because of the inertia carried by the electric motor that generates the torque [proportional to $\sigma(t)$] necessary to induce the material deformation. At low frequencies, the motor inertia is negligible and the measurements are mainly limited by the “patience” of the operator (when of course material’s related issues such as aging, evaporation, and mutational effects [13] have been already pondered). For instance, to perform an oscillatory measurement at $\omega = 10^{-3}$ rad/s (and considering “only” 1.5 of a cycle), a

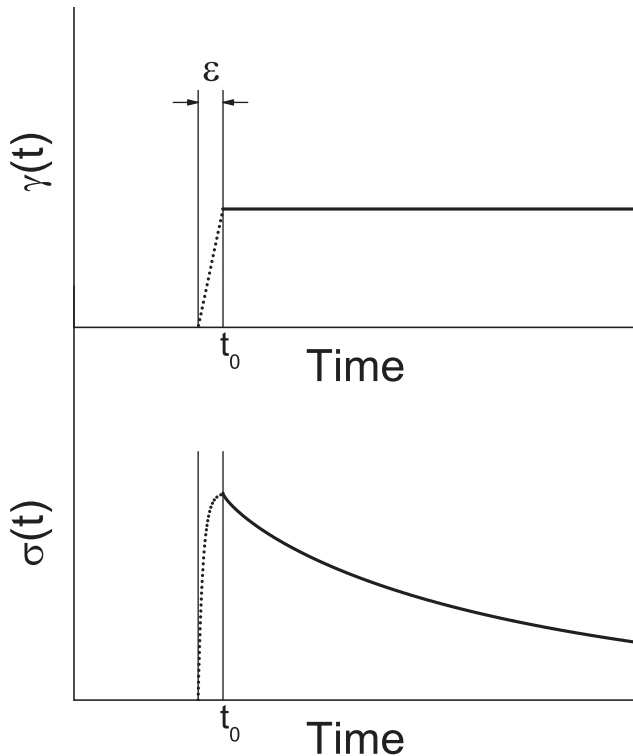


FIG. 2. Schematic representation of a step-strain measurement: (Top) A semi-idealized temporal behavior of the strain function $\gamma(t)$ and (bottom) description of the material’s stress function $\sigma(t)$ in response to the applied finite deformation.

rheometer would take $(1.5 \times 2\pi)/10^{-3} \simeq 10^4$ s (i.e., circa 3 h) to read a single value of $G^*(\omega)$.

A useful but *limited* tool for measuring the materials’ LVE properties over a wide range of frequencies is the time-temperature-superposition (TTS) method. This is an empirical procedure that combines the material’s LVE properties measured at different temperatures by means of a simple scale change. In terms of the complex modulus, one could write

$$G^*(\omega, T) = b_T G^*(a_T \omega, T_0), \quad (3)$$

where a_T and b_T are two adjustable parameters only function of the temperature (T) and not of frequency. Therefore, by performing a number (≥ 5) of measurements at different temperatures, it is possible to build a master curve of $G^*(\omega)$ that spans several decades of frequency, as shown for instance in the bottom graphs of Figs. 4 and 5 (symbols). However, it is important to remind that the TTS procedure works almost exclusively for amorphous polymer melts and there are no guarantees of its applicability to branched polymers, polymer blends, and rubbers. In the case of solutions and suspensions, its inapplicability is guaranteed.

B. Step-strain measurement

In the case of simple shear, a step-strain (or stress relaxation, SR) measurement is achieved by imposing a finite strain within a *brief* period of time ε (Fig. 2). In the unrealistic case that the finite strain is achieved with a constant rate of strain $\dot{\gamma} = \gamma/\varepsilon$, the following constitutive equation simplifies:

$$\sigma(t) = \int_{-\infty}^t G(t-t') \dot{\gamma}(t') dt' \equiv \int_{t_0-\varepsilon}^{t_0} G(t-t') \frac{\gamma}{\varepsilon} dt', \quad (4)$$

where $G(t)$ is the material’s shear modulus and t_0 is the time at which the strain is completed. By appealing to the Theorem of the Mean, Eq. (4) solves as

$$\sigma(t) = \left(\frac{\gamma}{\varepsilon}\right) \varepsilon G(t - t_0 + \phi \varepsilon), \quad 0 \leq \phi \leq 1, \quad (5)$$

which is indistinguishable from

$$\sigma(t) = \gamma G(t), \quad (6)$$

when t_0 is set equal to 0 and for times much longer than ε .

Equation (6) has been accepted by the rheology community because the data acquisition rates (AR) of rheometers were (until few years ago) slower than ε . However, nowadays, thanks to the development of sensitive and fast transducers, it is possible to acquire a significant number of experimental data within the time window defined by ε . Nevertheless, these data are commonly *discarded* because of the condition on which Eq. (6) relies on, i.e., $t \gg \varepsilon$. Moreover, the general approach of rheological studies based on step-strain measurements is to perform a best fit of $G(t) \equiv \sigma(t)/\gamma$ with a *preconceived* function having a known Fourier transform, such as a generalized Maxwell model. This is because $G^*(\omega)$ is simply related to $G(t)$

$$G^*(\omega) = F \left[\frac{dG(t)}{dt} \right] = i\omega \hat{G}(\omega), \quad (7)$$

where $\hat{G}(\omega)$ is the Fourier transform of $G(t)$. However, this common procedure presents some drawbacks: (i) it neglects the potential high frequency information contained in the initial time window defined by ε and (ii) it leaves some uncertainties related to the accuracy of the fitting procedure. Notably, both of the above issues are discarded by the method introduced in this paper.

C. Evaluating the Fourier transform of raw data

An analytical procedure for the evaluation of the Fourier transform of any generic function sampled over a finite time window was proposed by Evans *et al.* [11,12], to convert creep compliance $J(t)$ (i.e., a *step-stress* measurement) into $G^*(\omega)$ directly, without the use of Laplace transforms or fitting functions. This method is based on the interpolation of the finite data set by means of a piecewise-linear function. In particular, the general validity of the proposed procedure makes it equally applicable to find the Fourier transform $\hat{g}(\omega)$ of any time-dependent function $g(t)$ that vanishes for negative t , sampled at a finite set of data points (t_k, g_k) , where $k = 1 \dots N$, which extend over a finite range, and *need not* be equally spaced [11]

$$-\omega^2 \hat{g}(\omega) = i\omega g(0) + (1 - e^{-i\omega t_1}) \frac{(g_1 - g(0))}{t_1} + \dot{g}_\infty e^{-i\omega t_N} + \sum_{k=2}^N \left(\frac{g_k - g_{k-1}}{t_k - t_{k-1}} \right) (e^{-i\omega t_{k-1}} - e^{-i\omega t_k}), \quad (8)$$

where \dot{g}_∞ is the gradient of $g(t)$ extrapolated to infinite time and $g(0)$ is the value of $g(t)$ extrapolated to $t=0$ from above.

This method was improved by Tassieri *et al.* [7] while analyzing microrheology measurements performed with optical tweezers. The authors found that a substantial reduction in the size of the high-frequency artefacts, from which some high-frequency noise tends to spill over into the top of the experimental frequency range, can be achieved by an *over-sampling* technique. The technique involves first numerically interpolating between data points using a standard non-overshooting cubic spline, and then generating a new, over-sampled data set, by sampling the interpolating function not only at the exact data points but also at a number of equally spaced points in between. Notice that, over-sampling is a common procedure in signal processing and it consists of sampling a signal with a sampling frequency f_s much higher than the Nyquist rate $2B$, where B is the highest frequency contained in the original signal. A signal is said to be over-sampled by a factor of $\beta \equiv f_s/(2B)$ [6].

III. RESULTS AND DISCUSSION

Figure 3 shows the front panel of the executable i-Rheo, which implements the analytical method introduced by Tassieri *et al.* [7] to evaluate the Fourier transforms of both the measured stress and strain functions and therefore the material's complex modulus via Eq. (1). In particular, i-Rheo reads the experimental *raw* data (i.e., $[t_k, \sigma_k, \gamma_k]$) in the form of a tab-separated.txt file and generates a new over-sampled set of data [with a sufficiently high value of $\beta \equiv f_s/(2AR) \gg \omega/AR$, usually $f_s \cong 10$ MHz]; then it applies Eq.

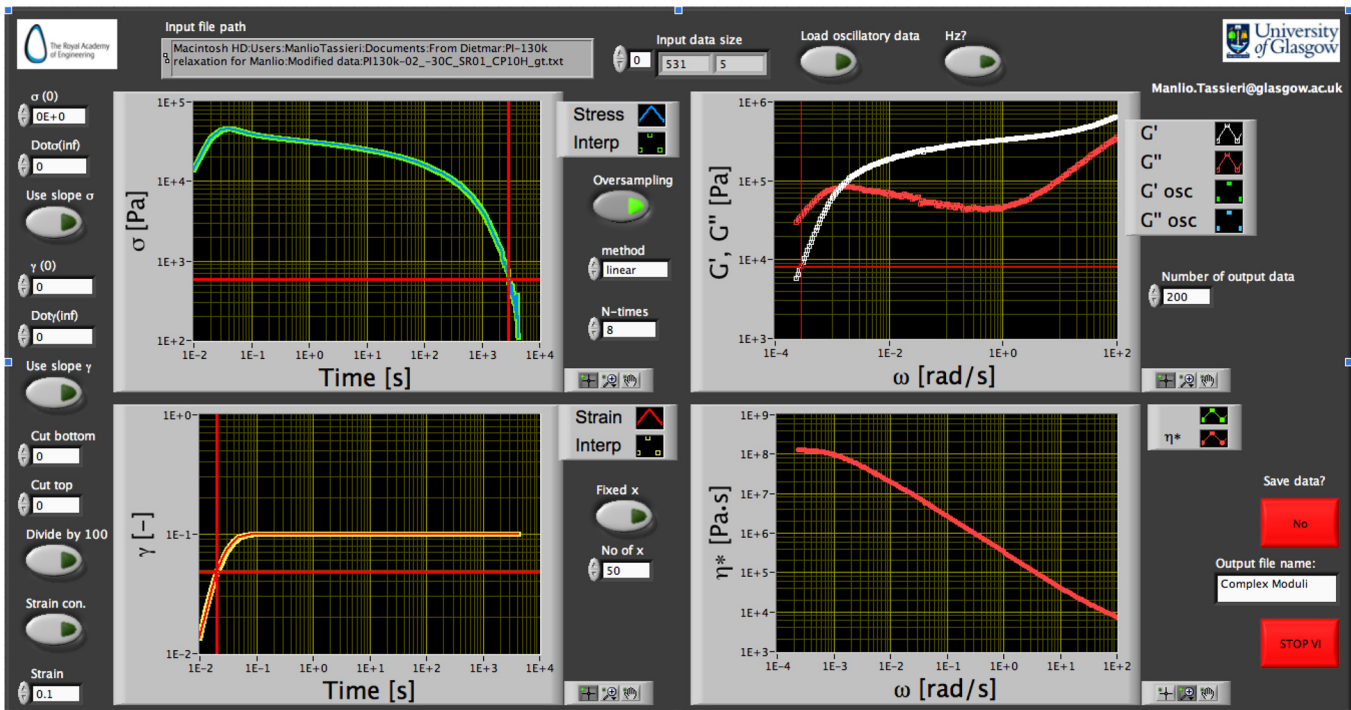


FIG. 3. Front panel of the LABVIEW (National Instruments) executable i-Rheo, which implements the analytical method introduced by Tassieri *et al.* [7] to evaluate the Fourier transforms of both the measured stress and strain functions in Eq. (1). The executable is free to download (together with the instructions) from the following link: <https://sites.google.com/site/manliotassieri/labview-codes>.

(8) to this new data set and returns the viscoelastic moduli of the material under investigation.

It is important to highlight that the default values of the two parameters \dot{g}_∞ and $g(0)$ required by Eq. (8) are set equal to zero for both the functions $\sigma(t)$ and $\gamma(t)$. Notably, this is an exact assumption for $\sigma(0)$ when the material is fully relaxed prior the start of the measurement [i.e., $\sigma(0) = 0$] and for both $\gamma(0)$ and $\dot{\gamma}_\infty$ given the specific nature of the step measurement. In the case of $\dot{\sigma}_\infty$, it is a sensible initial guess; however, its value depends on the viscoelastic nature of the material under investigation. Indeed, for viscoelastic fluids whose linear response is characterized by the existence of the terminal region at low frequencies [where $G'(\omega) \propto \omega^2$ and $G''(\omega) \propto \omega$ for $\omega \rightarrow 0$], the long-time behavior of the stress is expected to be: $\sigma(t) \propto G(t) \cong G'(1/t) \propto t^{-2}$ for $t \rightarrow \infty$ and therefore $\|\dot{\sigma}_\infty\| \rightarrow 0$ for $t \rightarrow \infty$. The same conclusion is achieved in the case of viscoelastic solids (VES) (e.g., gels and rubbers), for which $G(t)$ tends to the equilibrium shear modulus G_0 at long times. For generic complex materials (like the last two investigated in this work), i-Rheo allows the evaluation of $\dot{\sigma}_\infty$ from the actual experimental data by means of a linear fit of the long-time behavior of $\sigma(t)$.

The effectiveness of this novel rheological tool to evaluate the LVE properties of complex materials from conventional bulk rheology step-strain measurements has been corroborated by investigating the rheological properties of a series of complex materials as diverse as two linear polyisoprene melts (Sec. III A), an industrial styrene-butadiene rubber (SBR) (Sec. III B), an aqueous gelatin solution at the gel point (GP) (Sec. III C), and a highly concentrated suspension of colloidal particles (Sec. III D).

A. Linear polyisoprene melts

The LVE properties of monodisperse amorphous linear polymer melts and their blends [14–16] represent a *validation* tool for a number of constitutive models (e.g., [17–22]) aimed at predicting the rheological behavior of complex polymer systems (e.g., [23–25]). This is because of their “simple” topological structure (i.e., *entangled* polymer chains), which has allowed, over the past 40 years, the establishment of a solid theoretical framework built on the pioneering tube model developed by de Gennes [26] and Doi and Edwards [27].

From an experimental point of view, the advantage of using monodisperse amorphous linear polymer melts is based on the applicability of the TTS method, which allows the evaluation of the material’s LVE properties over a wide range of frequencies, as shown for instance in the graphs displayed at the bottom of Figs. 4 and 5 (symbols). However, in order to implement the TTS method, several measurements performed on the same sample at different temperatures are required. This is not only a time-consuming procedure, but it can be easily affected by experimental issues such as thermal degradation of the sample and instrument misalignment due to the thermal expansion of the tools that may compromise the quality of the results.

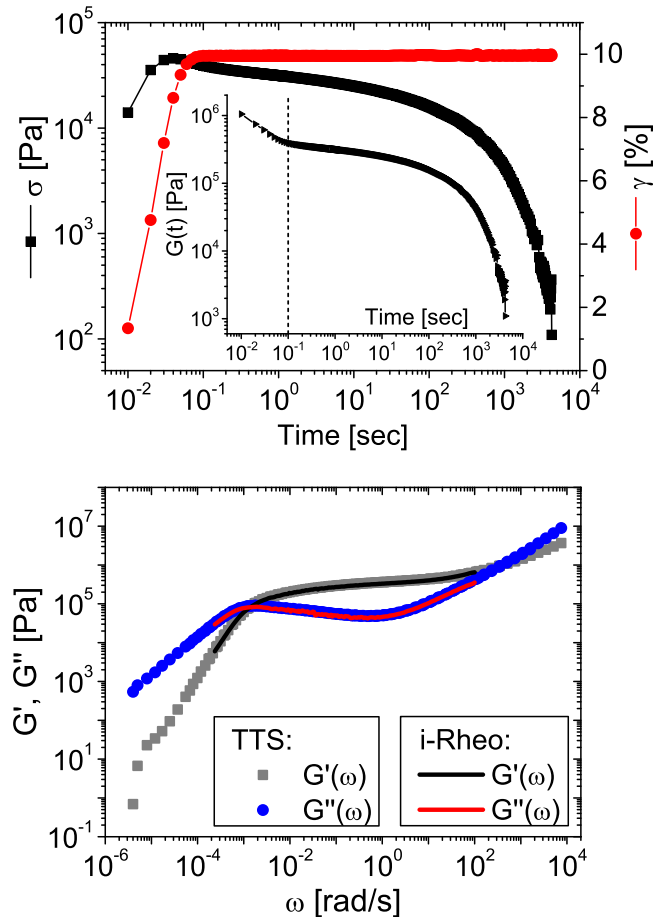


FIG. 4. (Top) The temporal behavior of the measured stress and strain functions when a shear step-strain of 10% is applied to a linear polyisoprene (PI-136k, see Table I for specifications) at a temperature of -30°C . The inset shows the temporal behavior of $G(t) = \sigma(t)/\gamma(t)$, where the dashed line indicates the time ($t_0 \neq 0$) at which the finite deformation is achieved [i.e., $\gamma(t_0) = \gamma$]. (Bottom) Comparison between the sample’s viscoelastic moduli derived by means of i-Rheo applied to the step-strain data shown at the top (continuous lines) and those obtained via the TTS method applied to conventional oscillatory shear measurements performed at eight different temperatures ranging from -45 to 50°C (symbols).

In contrast, the combination of the new analytical approach with the simplicity of execution of a step measurement (either strain or stress) performed at a single temperature allows the evaluation of the material’s LVE properties over a wide range of frequencies, but without the risk of incurring in any of the abovementioned experimental issues, as demonstrated by the results shown in this work.

1. Methods

Linear oscillatory measurements were performed with an ARES-L2 rheometer (Rheometric Scientific) equipped with a plate-plate geometry having a diameter of 10 mm and a gap of about 1 mm. The ranges of explored frequencies and temperatures were spanning from 0.1 to 50 rad/s and from -45 to 50°C , respectively. Off-line analysis of the measurements allowed the evaluation of the materials’ LVE properties over a wider range of frequencies by means of the TTS method implemented with a single set of parameters (a_T, b_T) [14]. The measurements were performed on two tailored polymers: (i) A linear polyisoprene PI-136k and (ii) a

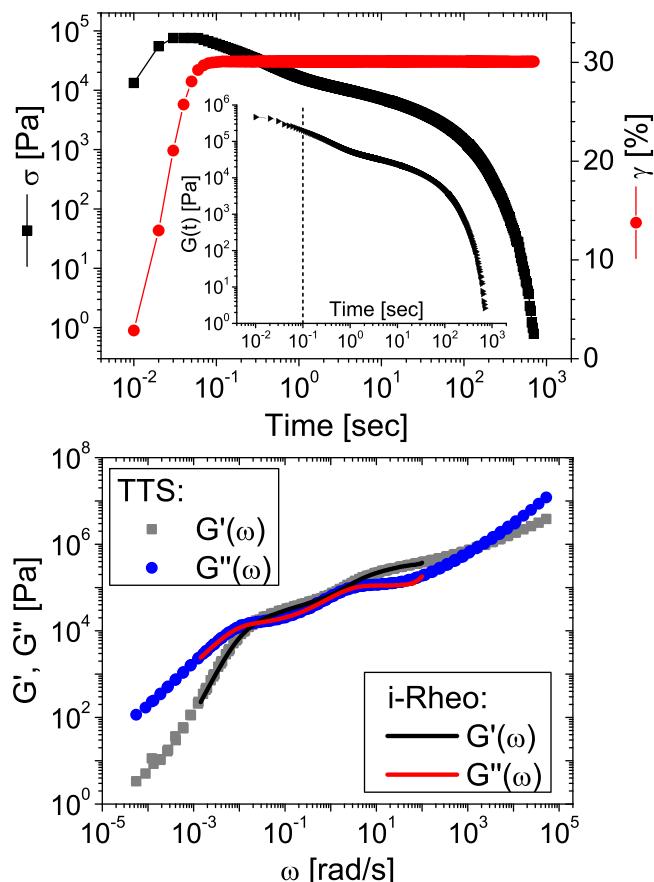


FIG. 5. (Top) The temporal behavior of the measured stress and strain functions when a shear step-strain of 30% is applied to a bimodal blend of linear polyisoprene melts (PI-20k and PI-136k, see Table I for specifications of the components) at a temperature of -20°C . The inset shows the temporal behavior of $G(t) = \sigma(t)/\gamma(t)$, where the dashed line indicates the time ($t_0 \neq 0$) at which the finite deformation is achieved [i.e., $\gamma(t_0) = \gamma$]. (Bottom) Comparison between the sample's viscoelastic moduli derived by means of i-Rho applied to the step-strain data shown at the top (continuous lines) and those obtained via the TTS method applied to conventional oscillatory shear measurements performed at eight different temperatures ranging from -45 to 40°C (symbols).

bimodal blend of linear polyisoprenes made of PI-136k at 40% weight fraction in PI-20k; see Table I for components specifications. The polyisoprenes were prepared by anionic polymerization with narrow-molecular-weight distributions and a similar microstructure of mainly *cis*-1,4 units (for details, see [14]). The blend was prepared by dissolving the components separately in cyclohexane at about 40°C in the presence of an antioxidant (BHT, about 10 wt. % vs polymer). When both polymers were dissolved, the low-MW solution was carefully poured into the flask containing the high-MW solution. The resulting solution was allowed to stir at 40°C for about 1 h. The blends were recovered by precipitation in cold methanol and dried under vacuum. Single step-

strain measurements were performed on the samples at single temperatures of -30 and -20°C , for duration of 5000 and 800 s, respectively. Linear oscillatory shear measurements were performed at eight different temperatures ranging from -45 to 50°C and -45 to 40°C , respectively.

2. Results

Figures 4 and 5 (top) show the temporal behavior of the measured stress and strain functions of two shear step-strain measurements. It is clear that, within the *brief* period of time ε , there exists a significant amount of useful data that contain valuable information on the “high” frequency LVE properties of the materials. These data are commonly neglected or discarded because of the condition on which Eq. (5) relies on (i.e., $t \gg \varepsilon$). Here, $t_0 \cong 10^{-1}$ s for both the measurements and data acquisition starts a decade before. Therefore, based on the general validity of Eq. (1), which is unconditioned by the temporal form of both the stress and strain functions [unlike Eq. (5)], we have analyzed the raw data (i.e., $[t_k, \sigma_k, \gamma_k]$) of the above mentioned step-strain measurements by means of i-Rho and compared the results with conventional oscillatory measurements.

The effectiveness of i-Rho is apparent in both Figs. 4 and 5 (bottom), where for each sample, the viscoelastic moduli obtained by means of i-Rho (continuous lines) are directly compared with those obtained via the TTS method (symbols). In both the cases, the moduli show good agreement between the two procedures over five decades of frequency. In particular, the range of accessible frequencies by means of i-Rho is dictated by two factors: (i) the data AR of the instrument and (ii) the measurement duration (P); i.e., the minimum and the maximum frequencies are $\omega_{min} = 1/P$ and $\omega_{max} = AR \equiv (t_0 - \varepsilon)^{-1}$, respectively. Notably, in both the cases, there is a gain in the range of explored high frequencies of one decade, when compared to a conventional SR measurement for which the maximum frequency would be $\omega_{max} \leq 1/t_0$.

The technique reported herein assumes that a constant velocity gradient is instantaneously established within the sample upon movement of the motor, i.e., the test operates under gap loading conditions during the initial transient part of the experiment. For oscillatory experiments, gap loading conditions may be confirmed by ensuring that the shear wavelength (λ_s) is at least greater than $10h$, where h is the geometry gap. The shear wavelength can be estimated as [28]

$$\lambda_s = \frac{1}{\cos(\varphi(\omega)/2)} \left(\frac{G^*(\omega)}{\rho} \right)^{1/2} \left(\frac{2\pi}{\omega} \right), \quad (9)$$

TABLE I. Specification of both the linear polyisoprene melts and of the industrial SBR used in this work. y_S and y_{Lin} indicate the mass fractions of styrene and its linear component within the blend, respectively.

Material	y_S (%w/w)	M_p linear (kg/mol)	M_p star (kg/mol)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	y_{Lin} (%w/w)	T_g ($^{\circ}\text{C}$)
PI-20k	—	—	—	22.8	23.5	1.03	—	≤ -53
PI-136k	—	—	—	148	152	1.03	—	≤ -53
SBR	25.3	94.7	366.1	110	143.1	1.30	77.2	-29.7

where ρ is the density of the medium. For each of the materials studied herein, this condition was met at all frequencies extracted using the novel technique, but it is foreseen that some material dependent limiting frequency will exist above which the gap loading criterion will not be satisfied.

It is important to highlight that, while a simpler analysis of the materials' SR curves performed in the time-domain [i.e., $G(t)$ as expressed by Eq. (6)] may provide supportive information on the materials' topological structure (e.g., see [25]), the knowledge of the frequency-dependent viscoelastic moduli provides richer information on the material's rheological properties, e.g., a direct reading of the materials' characteristic relaxation times (τ_i), which are identified by the abscissa values (ω_i) of the moduli crossover points, i.e., $\tau_i \equiv 1/\omega_i$ when $G'(\omega_i) \equiv G''(\omega_i)$.

The method presented in this manuscript sets new standards for analyzing step measurements (either strain or stress) and offers the opportunity to revise the results of a great number of rheological studies for a better understanding of the link between material topology and viscoelastic properties, without the need of preconceived models.

B. Styrene-butadiene rubber

Blends of linear and star styrene and butadiene random copolymers (also known as SBRs [29–31]) constitute a class of materials that has made a significant impact in modern industry, mostly because of their cost-effectiveness in replacing in many applications the natural rubber and its mechanical properties (e.g., resistance to abrasion) [32]. In SBRs, the butadiene can be enchainned as 1,4 *cis*, 1,4 *trans*, or 1,2. By tuning the relative amount of the styrene fraction and of 1,2 butadiene enchainment, it is possible to produce a wide range of materials having different glass transition temperatures (T_g). In Table I, a set of key properties of the industrial SBR sample used in this study are reported. SBRs are used for the production of a variety of products having markedly different mechanical properties such as automobile tyres [33], children's toys, and shoe soles. Therefore, the knowledge of their viscoelastic spectrum, over a wide range of frequencies, is an essential requirement not only for material characterization [34–36] but also for all those predictors aimed at revealing the final product's applicative behavior (e.g., grip, hysteresis). As mentioned before, the TTS method has some limitations of applicability, especially for those polymers that are able to crystallize at relatively high temperatures (thus raising the lower-end limit of accessible temperatures) or for those that have a low degradation/cross-linking temperature (hence reducing the higher-end limit of accessible temperatures). The industrial SBR sample used in this work has a relatively low maximum temperature of circa 150 °C. This is a common feature of all diene elastomers due to the high level of insaturation. It is important to note that, even if the measurements were performed in a nitrogen environment, when the temperature was set close to 150 °C, it was not possible to preserve the sample from cross-linking reactions. Therefore, in order to investigate the long-time relaxation processes of the amorphous SBR sample, long

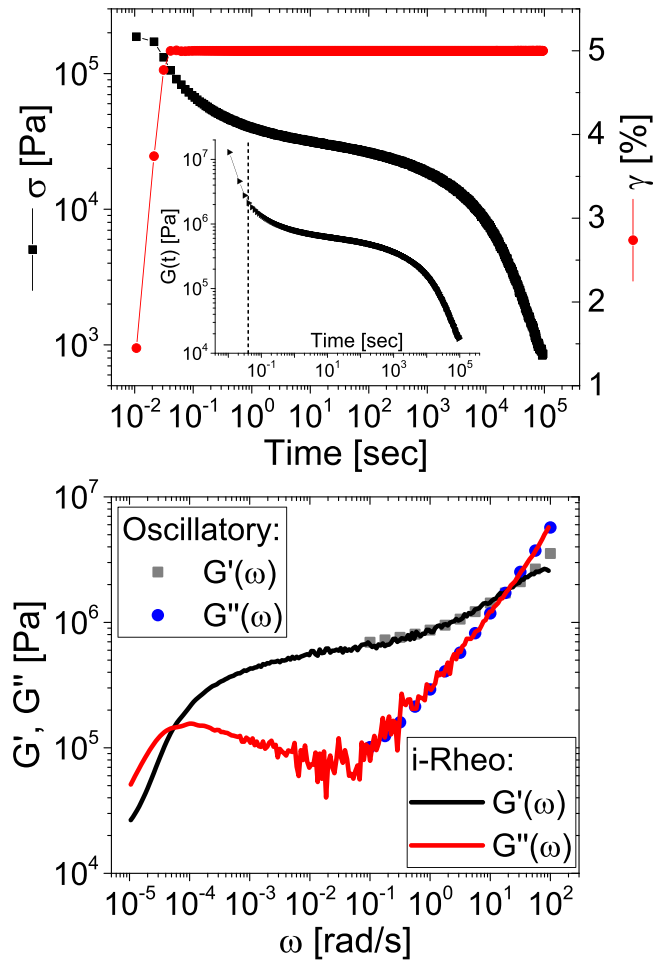


FIG. 6. (Top) The temporal behavior of the measured stress and strain functions when a shear step-strain of 5% is applied to the industrial SBR. The inset shows the temporal behavior of $G(t) = \sigma(t)/\gamma(t)$, where the dashed line indicates the time ($t_0 \neq 0$) at which the finite deformation is achieved [i.e., $\gamma(t_0) = \gamma$]. (Bottom) Comparison between the sample's viscoelastic moduli derived by means of i-Rheo applied to the step-strain data shown at the top (continuous lines) and those obtained via a conventional oscillatory shear measurement (symbols). Both the measurements were performed at -15 °C.

measurements were performed at temperatures significantly lower than 150 °C, as described below.

1. Methods

The measurements were performed with a MCR501 (Anton Paar-Physica) equipped with parallel plates (diameter 8 mm). The temperature control was achieved by a Peltier system combined with a nitrogen fed convection hood to ensure temperature uniformity inside the chamber and an inert environment. The polymer sample was loaded at high temperature (110 °C). The sample was kept for 20 min at 110 °C after loading in order to ensure polymer adhesion to the metal surfaces. The temperature was then changed to -15 °C by a continuous ramp while keeping a constant normal force to ensure contact between polymer and plates. After temperature equilibration, a test sequence made of a frequency sweep (i.e., 100–0.1 rad/s; 1% strain) and an SR (i.e., 5% strain; duration $\approx 10^5$ s) was performed (see Fig. 6).

2. Results

In this section, we compare the viscoelastic spectra of an industrial SBR sample measured by means of both a conventional frequency sweep test and a step-strain measurement analyzed by means of i-Rheo; both the measurements were performed at a temperature of -15°C , which is well below the sample cross-linking temperature of 150°C and few degrees above its T_g (see Table I). From Fig. 6, the agreement between the two experimental procedures is apparent. Moreover, it is worthy to note that the proposed method allows the evaluation of the SBR's LVE properties over "seven" decades of frequency spanning from frequencies as low as 10^{-5} to 10^2rad/s (i.e., the inverse of the step-strain measurement time-window limits). Notice that, accessing such low frequencies would be prohibitive for conventional oscillatory measurements, as a rheometer would take at best $(1.5 \times 2\pi)/10^{-5} \simeq 10^6\text{ s}$ (i.e., circa 11 days) to read a single value of $G^*(\omega)$.

In the particular case of branched polymers, broadband rheology is an essential requirement because of their broad relaxation spectrum, which is ruled by the exponential dependence of the longest relaxation time upon arm length [37]. In the specific case of the investigated SBR, the star arm is very well entangled (ca. 40 entanglements per arm) and the material has a very long relaxation time, even though almost 80% of the chains are linear (see Table I). In addition, the ability of measuring the relaxation spectrum at a single temperature is of critical importance when branched polymers showing thermorheologically complex behavior are investigated [38].

We envisage that the combination of a step-strain measurement with the novel analytical tool (i-Rheo) for the data analysis can prompt a better understanding of more complex systems of industrial interest such as filled SBRs [39,40], which are commonly used for tyres production and for which the TTS method is not applicable at all.

C. Aqueous solution of gelatin

During chemical or physical gelation, the materials' rheological properties undergo a transition between those characteristics of viscoelastic liquids (VEL) and those characteristics of VES. The critical extent of reaction at which the transition between VEL and VES behavior occurs is known as the GP and corresponds with the establishment of an incipient sample spanning gel network. The materials' rheological properties at the GP are distinct from those at their liquid or solid state and this has led to the definition of the critical gel state (CG) [41].

The viscoelastic properties of a CG are defined by the Winter–Chambon gel equation [41], which predicts power law SR over a wide range of time scales limited only by a minimum relaxation time λ_0 , according to

$$G(t) = St^{-\alpha} \quad \text{for } \lambda_0 < t < +\infty \quad (10)$$

or in the frequency domain to

$$G'(\omega) \propto G''(\omega) \propto \omega^\alpha \quad \text{for } 0 < \omega < 1/\lambda_0. \quad (11)$$

The CG state is identified by measuring (i) identical power law scaling exponents in $G'(\omega)$ and $G''(\omega)$ [see Eq. (11)] or equivalently, (ii) frequency independent loss tangent [$\tan(\varphi) = G''(\omega)/G'(\omega)$] [42]. Hence, in systems undergoing gelation, identification of a CG state requires the viscoelastic properties of a material to be monitored as a function of both time and frequency. This has been successfully achieved for a range of gelling systems through the sequential application of (i) a series of oscillatory waveforms with discrete frequency (a frequency sweep approach), (ii) a multicomponent waveform (FTMS) [42–44], and (iii) a frequency modulated waveform [45,46]. In this work, FTMS was used to monitor the approach to the CG before a step-strain experiment was performed on the material at the CG state.

1. Methods

Gelatin (20 wt. %), a model gelling system, was prepared by mixing appropriate amounts of (type I) deionized water (60°C) and general grade gelatin powder (Fisher G015053) and agitating vigorously. The solution was then placed in a waterbath at 60°C for 45 min with further agitation every 10 min to ensure complete dissolution of the gelatin powder [47]. The gelatin solution was then aliquoted and stored at 5°C for a maximum of 2 days. The gelatin aliquot was melted in a water bath at 60°C for 45 min and immediately transferred to the temperature controlled Peltier plate of an ARES-G2 rheometer (TA Instruments) fitted with a 50 mm titanium parallel plate geometry with a gap of $400\ \mu\text{m}$. The rheometer "zero gap" routine was performed at the test temperature (i.e., 31°C) prior to sample loading at 35°C (i.e., above the minimum gelation temperature of the material). Low viscosity silicone oil was then added to the free surface of the sample to prevent evaporation before the temperature was lowered to the test temperature. An FTMS waveform [42] was employed to monitor gelation and upon attainment of frequency independent φ (i.e., 63°), an SR experiment (with a step strain of 10%) was performed. The mutation number [43] over the duration of the step-strain experiment was calculated to be 0.1, thus confirming the quasistable nature of the material at the GP under conditions of slow gelation [42,43]. The absence of sample inertia and slip artefacts was confirmed using standard techniques [48,49]. All measurements were conducted using a level of strain within the LVE range of the material as determined by strain amplitude sweeps in both pre- and postgel states.

2. Results

Figure 7 (bottom) shows the frequency behavior of the viscoelastic moduli as derived from a step-strain measurement [Fig. 7 (top)] analyzed by means of i-Rheo. Weighted least squares fits of the data (spanning over more than four frequency decades) result in identical scaling exponents in $G'(\omega) \propto G''(\omega) \propto \omega^\alpha$ with $\alpha \simeq 0.71$, thus confirming the attainment of the CG state. The value of α obtained using this approach is in excellent agreement with previous studies [42,44]. Moreover, values of $G'(\omega)$ and $G''(\omega)$ measured using the FTMS technique immediately prior to acquisition of the SR data are also shown in Fig. 7 (bottom) and confirm the

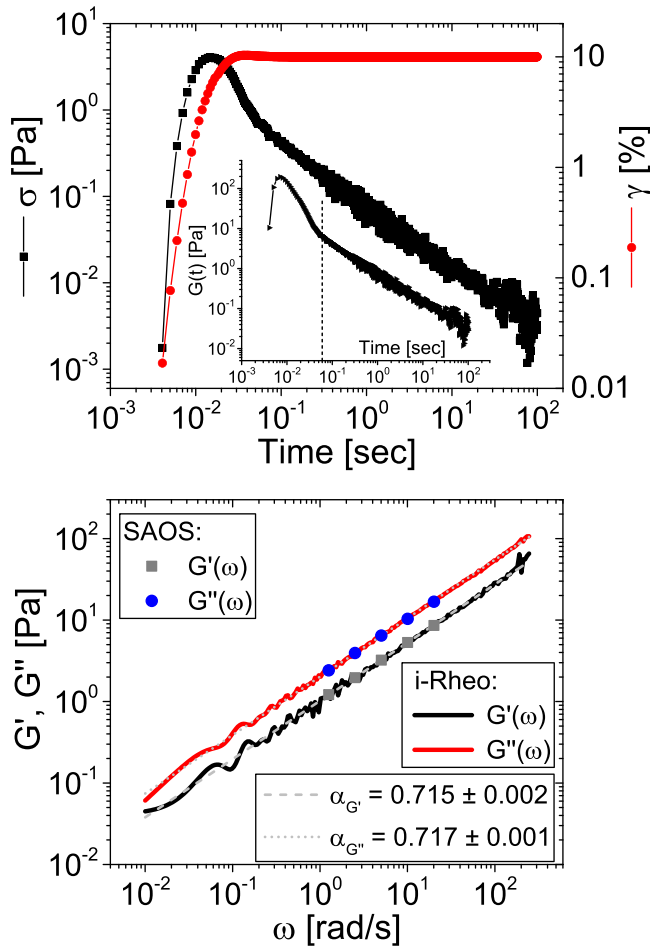


FIG. 7. (Top) The temporal behavior of the measured stress and strain functions when a shear step-strain of 10% is applied to the gelling system at the critical point. The inset shows the temporal behavior of $G(t) = \sigma(t)/\gamma(t)$, where the dashed line indicates the time ($t_0 \neq 0$) at which the finite deformation is achieved [i.e., $\gamma(t_0) = \gamma$]. (Bottom) Comparison between the sample's viscoelastic moduli derived by means of i-Rheo applied to the step-strain data shown at the top (continuous lines) and those obtained by performing a small amplitude oscillatory shear test that has been analyzed by using a proprietary software (TA Instruments, Trios) (symbols). Dashed and dot lines show the linear fits of the results obtained with i-Rheo.

excellent agreement between the two methods. These results provide the first confirmation of the validity of the analytical method introduced by Tassieri *et al.* [7] (here implemented in the executable i-Rheo) in converting step-strain data to the dynamic viscoelastic moduli for systems at a CG state.

D. Colloidal glass

A wide range of materials is often dispersed as colloidal particles for pouring or transporting them [50]. Dispersion paints are one familiar example of this class of materials. One-component dispersions of hard-sphere like colloids have been intensively used as a model system of more complex colloidal dispersions [51,52]. In this system, the volume fraction ϕ is the only control parameter. When the width of the size distribution of the colloidal particles exceeds about 7%, increasing ϕ above $\phi_g \approx 0.58$ leads to the formation of an amorphous solid state called glass [53]. The solidification of the dispersion is indicated by $G'(\omega) > G''(\omega)$ at all measurable frequencies [54,55]. The emergence of a solid-like

response arises from dynamical arrest of particles [53], which are permanently localized in cages formed by their neighbors and from which they can only escape through activated processes [56]. This activated relaxation is responsible for the minimum typically observed in $G''(\omega)$. Dynamical arrest is confirmed by measurements of the intermediate scattering function (ISF) from dynamic light scattering (DLS), which reveals a nondecaying component upon increasing ϕ beyond ϕ_g [53], and by an emerging plateau in the mean-squared displacements that can be derived from the ISF and can also be measured by confocal microscopy [57]. The mode-coupling theory (MCT) has been shown to accurately describe both the LVE moduli of the glass [54,55] and the experimentally determined ISF [53,58].

1. Methods

Polymethylmethacrylate spheres of radius $R = 175$ nm (polydispersity 15%), sterically stabilized with a layer of polyhydroxystearic acid (PHSA), were dispersed in octadecene, a solvent that evaporates very slowly and in which the particles behave like hard spheres [59]. A random close packed sample was obtained by sedimenting a dilute suspension in a centrifuge. The sediment, whose volume fraction was estimated using simulation and experimental results to be $\phi \approx 0.66$ [60–62], was subsequently diluted to a volume fraction $\phi = 0.60$. Rheological measurements were performed with an ARES G2 strain-controlled rheometer (TA instruments), using a cone and plate geometry of diameter $D = 25$ mm, angle $\alpha = 2^\circ$, and truncation $d = 0.048$ mm. A solvent trap was used to minimize solvent evaporation. The temperature was set to $T = 20^\circ\text{C}$ and controlled within 0.1°C via an advanced Peltier system. The effects of sample loading and aging were reduced by performing the following rejuvenation procedure before each test. Directly after loading, large amplitude oscillatory shear was applied to the samples for 200 s with frequency $\omega = 1$ rad/s and strain amplitude $\gamma = 500\%$, well above the yield strain, to liquify the sample. Subsequently, oscillatory shear at the same frequency and with $\gamma = 1\%$ (LVE regime) was applied until a steady-state response, i.e., a time-independent storage $G'(\omega)$ and loss modulus $G''(\omega)$, was achieved; which typically took about 300 s. This indicated that no further structural changes occurred and hence a reproducible state of the sample was obtained. The LVE moduli were directly measured using a conventional dynamic frequency sweep with amplitude $\gamma = 1\%$ in the frequency range $10^{-3} < \omega < 100$ rad/s. SR after a step strain of $\gamma = 1\%$ was measured for $T = 6 \times 10^4$ s using logarithmic sampling.

2. Results

The LVE moduli of the sample obtained from an SR experiment analyzed by means of i-Rheo show the typical response of a colloidal glass (Fig. 8, bottom): $G'(\omega)$ is larger than $G''(\omega)$ for all frequencies and both the moduli show a relatively weak frequency dependence [54,55]. The loss modulus shows the presence of a minimum which is typically associated with the presence of activated relaxation processes [56]. However, even at the lowest measured

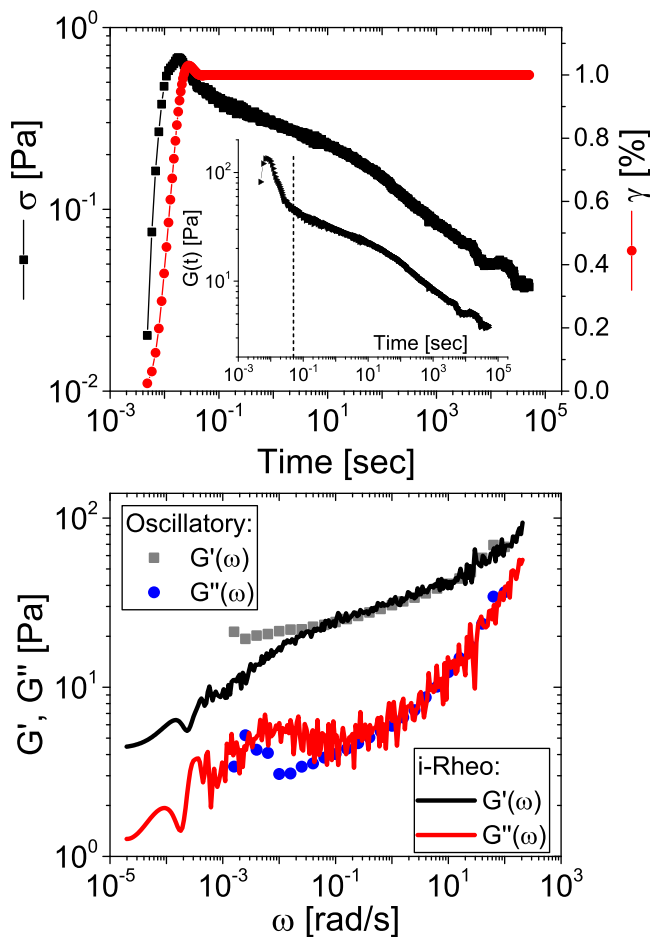


FIG. 8. (Top) The temporal behavior of the measured stress and strain functions when a shear step-strain of 1% is applied to the highly concentrated suspension of colloidal particles. The inset shows the temporal behavior of $G(t) = \sigma(t)/\gamma(t)$, where the dashed line indicates the time ($t_0 \neq 0$) at which the finite deformation is achieved [i.e., $\gamma(t_0) = \gamma$]. (Bottom) Comparison between the sample's viscoelastic moduli derived by means of i-Rheo applied to the step-strain data shown at the top (continuous lines) and those obtained via a conventional oscillatory shear measurement (symbols).

frequency, the two moduli do not cross, indicating the extremely long lifetime of the amorphous solid state. The agreement with data from conventional oscillatory measurements is excellent down to about $\omega \approx 10^{-2}$ rad/s. Some discrepancy at lower frequencies might be due to noise in the relaxation data, associated with the low values of the stress at long relaxation times (Fig. 8, top). In addition, the effects of aging might be different for the two methods, given the considerably longer measurement times of the conventional oscillatory test at low ω . The analysis of the SR data extends the frequency range of conventional measurements both in the low and high frequency ends. At high frequencies, this is the result of the faster sampling possible during the SR and at low frequencies of the possibility to avoid averaging over cycles, which prohibitively extends measurement times in conventional oscillatory measurements. Notice that the presence of a relatively small overshoot in the applied strain function does not compromise with the results at high frequencies.

Also, in this case, we envisage that i-Rheo opens up the route to a better determination of the extremely slow

relaxation of colloidal glasses, in particular, the investigation of the nature of activated processes, as well of a better characterization of the elasticity at high frequencies in relation to short-time in-cage motions.

IV. CONCLUSIONS

In this article, we present and validate a new analytical method, in the form of an open access executable named i-Rheo, for the evaluation of the materials' LVE properties, over the *widest* range of experimentally accessible frequencies, from a simple *step* measurement. The effectiveness of the method is corroborated by direct comparison with conventional linear oscillatory measurements for a series of complex materials as diverse as a monodisperse linear polymer melt, a bimodal blend of linear polymer melts, an industrial SBR, an aqueous gelatin solution at the GP, and a highly concentrated suspension of colloidal particles.

i-Rheo sets new standards for the evaluation of the linear response of any generic system (i.e., its transfer function) via the analysis of the system's response to an input having the temporal form of a *real* step-function. Moreover, it offers the opportunity to revise the outcomes of previous rheological studies where original measurements were either interpreted by means of theoretical models or "partially discarded" because of the absence of an effective tool for data analysis. This new *tool* allows the investigation of frequency regions previously "difficult" or "impossible" to access by conventional methods; thus, the opportunity to gather new insights on relaxation phenomena for a variety of materials, with particular attention to those for which the TTS method is not applicable (e.g., polymer solutions [63,64] and biological samples [65–67]). Indeed, we envisage the impact that this new analytical tool will have on all those biological systems (e.g., actin-fascin network [68]) for which the knowledge of their LVE properties, over a wide range of frequencies, can provide a better understanding of both the molecular structure and interactions at different length scales. Finally, the general validity of the proposed method makes it transferable to all those mechanical tests where both stress and strain data can be defined, but for which the ability of measuring the materials' LVE properties over a wide frequency spectrum is still an ambition, e.g., atomic force microscopy [69] and tensile tests [70].

ACKNOWLEDGMENTS

In memory of Alexei Likhtman. The authors thank Mike Evans, Dimitris Vlassopoulos, Giovanni Ianniruberto, and Giuseppe Marrucci for helpful conversations. The authors thank Pierre Chambon for kindly providing the polyisoprene samples, which were originally produced for the EPSRC project μ PP-2. M.T. acknowledges support via personal research fellowships from the Royal Academy of Engineering/EPSRC (10216/101). M.L. acknowledges funding by the Deutsche Forschungsgemeinschaft (DFG) through the research unit FOR1394, Project P2.

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