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ORIGINAL CONTRIBUTION

# Viscoelastic measurement of complex fluids using forced oscillating torsion resonator with continuously varying frequency capability

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**Abstract** Traditional torsional resonators, often obtaining the viscoelastic moduli of complex fluids only at one or several given discrete frequencies, lack the continuously varying frequency capability. This is an obvious disadvantage of the traditional torsional resonator technique. This paper presents an improved strategy, based on our previous discrete-frequency-measuring method (Wang et al., J Rheol 52:999–1011, 2008), to overcome such restriction and thus accomplish the continuously varying frequency capability of the traditional torsional resonator for measuring the viscoelastic properties of complex fluids. The feasibility of this strategy is demonstrated with the Newtonian fluids (several water–glycerol solutions) of viscosities varying from 10 to 1,400 cp by using our homemade torsion resonator apparatus in the 10 ∼ 2,500 rad/s frequency range (continuous frequencies). Some results for typical viscoelastic polymers (two polyethylene oxide (PEO) aqueous solutions) are also given. Additionally, a comparison of the PEO results is made with the common rheometer technique. It is demonstrated that this improved strategy could enable the traditional torsional resonators, with one oscillating resonance mode, to work as the microrheological technique and the common rheometer technique in the continuous frequency range.

**Keywords** Viscoelastic measurement · Complex fluids · Torsion resonator · Continuously varying frequency

## Introduction

Rheology measurements of complex fluids are important in both industrial production and scientific research. Over the last 50 years, there has been some significant progress in the innovation of conventional viscoelastic measuring techniques (Ferry 1980; Lakes 2004; Hou and Kassim 2005; Waigh 2005; Willenbacher and Oelschlaeger 2007). A wide variety of viscoelastic measurement devices, such as conventional rheometers (Ferry 1980), microrheological techniques (Mason and Weitz 1995a, b; Mason et al. 1996; Mason 1999), torsional resonators (Ferry 1980; Blom and Mellema 1984; Fritz et al. 2003; Romoscanu et al. 2003), and so on, have been developed. The torsional resonator, providing access to the high frequency rheological properties of the dilute and low-viscous complex fluids, is considered as one of the most popular and important rheological techniques in rheometry (Willenbacher and Pechhold 2000).

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To investigate the rheological properties of macromolecular solutions, Mason et al. (Mason and Murray Hill 1947; Mason et al. 1948, 1949) first proposed the torsional resonator method, that the complex characteristic impedance and shear moduli of liquids were obtained through detecting the shifts of the resonance frequency and a broadening of the resonance curve of the immersed resonator compared to its behavior in air. Much effort was then invested in developing this technique, and various corresponding experimental designs were employed. Initially, the resonator exhibiting one resonance frequency was considered, only the viscoelastic properties of the detected liquid at the resonance frequency could be obtained. A different resonator is thus required for each frequency studied, which makes the corresponding measurements of the frequency-dependent viscoelastic properties of complex liquids more tedious and inconvenient. In order to overcome this experimental restriction, Schrag and Johnson (1971) designed the multiple lumped resonators (MLR) based on Birnboim's concept (Birnboim and Elyash 1966) that the resonator could exhibit multiple different resonance frequencies corresponding to their different normal modes of torsional oscillation. This technique was later modified and developed by Hvidt and coworkers (1982), the Amis group (Amis et al. 1986; Hair and Amis 1989; Hair et al. 1989), the Elgsaeter group (Ellingsrud et al. 1992; Mikkelsen et al. 1992; Naken et al. 1994, 1995), the Willenbacher group (Willenbacher and Pechhold 2000; Fritz et al. 2002, 2003; Willenbacher et al. 2007), and so on. Apart from the MLR technique, other techniques, such as the torsional nickel resonator (Glover et al. 1968; Oosterbroek et al. 1980) and the McSkimin-type torsional rod apparatus (Stokich et al. 1994), were also proposed. Despite excellent improvement obtained due to these efforts, whatever the original or developed torsional resonator techniques obtain the storage and loss modulus of complex fluids only at one or several given discrete frequencies, lacking the continuously varying frequency capability. Consequently accomplishing the continuously varying frequency capability of the torsional resonators can greatly promote the development of the torsional resonator techniques in rheometry, being of greater industrial and academic significance.

Recently we have proposed a new method (Wang et al. 2008) to extend the conventional torsion resonator available for investigating the concentrated and large-viscous liquid in the low frequency range ($\leq$100 Hz) with a better precision. This method avoids the restriction of the common method that the resonator should have the high quality factor both in air and in liquid samples, and thus enables the torsional resonator apparatus to accurately achieve not only the high frequency rheology of the low-viscous and dilute liquid but also the low frequency rheology of the concentrated and large-viscous liquid when in the surface loading limit. Nevertheless, this method, working only at the resonance frequency, also lacks the continuously varying frequency capability.

The purpose of this paper is to propose a simple but novel measurement strategy, based on our recently-proposed method (Wang et al. 2008), to accomplish the continuously-varying-frequency capability for the traditional torsional resonator only exhibiting one oscillation resonance frequency. Viscoelastic behaviors of both the Newtonian fluids (the glycerol–water mixtures; Wang et al. 2008) and the typical non-Newtonian fluids (the polyethylene oxide (PEO); Cooper et al. 1991; Dasgupta et al. 2005) at two different concentrations above the overlap concentration $c^*$) are investigated by using our homemade oscillating-cup torsion pendulum apparatus (Zhang et al. 2003; Wang et al. 2008, 2010) to demonstrate the validity of this strategy. Moreover, to further check the viscoelastic measurements of PEO–water solutions by our torsional resonator apparatus employing the new strategy, we compare the corresponding results with those by the conventional rheometer. Emphasis should be placed that all the rheological measurements reported in this paper, performed by our homemade torsional resonator apparatus and the commercial rheometer, were repeated several times to check their reproducibilities.

## Theoretical analysis

As the theoretical descriptions in the previous studies (Schrag and Johnson 1971; Blom and Mellema 1984; Wang et al. 2008), the motion of a forced oscillating-cup resonator, having only one torsional oscillation mode, is described by

$$I\ddot{\theta} + (Z + D)\dot{\theta} + K\theta = M \tag{1}$$

in which $\theta$ is the angular displacement, $M$ is the driving torque exerted on the pendulum, $I$ is the equal effective momentum of inertia of the resonator, $Z = R + iX$ is the torsion impedance due to the surrounding liquid, $D$ is the damping of the torsion pendulum itself, and $K$ is the torsion-spring constant. If the driving torque is given by $M = M_0 e^{i\omega t}$ (where $M_0 = |M|$ and $\omega$ is the radian frequency), the angular displacement $\theta$ will be $\theta = \theta_0 e^{i(\omega t - \varphi)}$ (where $\theta_0 = |\theta|$ and $\varphi$ is the phase angle by which $\theta$ lags $M$), and the response equations are given by (Wang et al. 2008)

$$\theta_0 = \frac{M_0/I}{\sqrt{\left(\omega_0^2 - \omega^2 - \omega X/I\right)^2 + \omega^2 \left(R + D\right)^2 / I^2}} \tag{2}$$

and

$$\tan\varphi = \frac{\omega\left(R + D\right)/I}{\omega_0^2 - \omega^2 - \omega X/I} \tag{3}$$

where $\omega_0 = \sqrt{K/I}$. From Eqs. 2 and 3 one can obtain,

$$R = \frac{M_0}{\omega\theta_0}\frac{1}{\sqrt{1 + 1/\tan^2\varphi}} - D \tag{4}$$

$$X = -\frac{M_0}{\omega\theta_0}\frac{1}{\tan\varphi\sqrt{1 + 1/\tan^2\varphi}} + \frac{I}{\omega}\left(\omega_o^2 - \omega^2\right) \tag{5}$$

According to the previous analysis (Glover et al. 1968; Blom and Mellema 1984; Wang et al. 2008), for an oscillating-cup with the wall far thinner than two spacing between the resonator and the sample holder, the relation between $Z$ and the characteristic plane wave shear impedance ($Z_{pl}$) approximately satisfies (Wang et al. 2008)

$$Z \approx A_0 Z_{pl} \tag{6}$$

where $Z_{pl} = R_{pl} + iX_{pl}$ is defined as the ratio of the force per unit area to the linear velocity of the surface being considered, and $A_0 = 4\pi a^3 l$ (at which $a$ is the radius of the oscillating cup, and $l$ is the length of the cup inserted into the liquid) is the apparatus constant. Then, from Eqs. 4~6, it can follow that from a measurement in air (or in vacuum) and in liquid, respectively, the components of the characteristic plane wave shear impedance is determined by

$$R_{pl} = E_4\left[\frac{1}{\omega\theta_{0l}\sqrt{\left(1/\tan\varphi_l\right)^2 + 1}} - \frac{1}{\omega\theta_{0\mathrm{air}}\sqrt{\left(1/\tan\varphi_{\mathrm{air}}\right)^2 + 1}}\right] \tag{7}$$

$$X_{pl} = A_4\frac{\omega_0^2 - \omega^2}{\omega} - E_5\frac{1}{\omega\theta_{0l}\tan\varphi_l\sqrt{\left(1/\tan\varphi_l\right)^2 + 1}} \tag{8}$$

where $\varphi_{\mathrm{air}}$ and $\varphi_l$, $\theta_{0\mathrm{air}}$ and $\theta_{0l}$, as well as $\omega$, are the phase angle, the angular displacement, and the continuously varying frequency in vacuum and in liquid, respectively; and $A_4 = I/4\pi a^3 l$, $E_4 = E_5 = M_0/4\pi a^3 l$ are the apparatus constants. Note that, for simplicity the subscripts of the varying frequency in Eqs. 7 and 8 denoting, respectively, the situations in air or in liquid have been neglected, since both the measurements in air and in liquid are taken by using the same sinusoidal varying external torque.

Obviously, Eqs. 7 and 8 indicate that after determining values of apparatus constants ($A_4$,$E_4$,$E_5$) by calibration, values of $R_{pl}$ and $X_{pl}$ at every excited frequency ($\omega$) can be calculated from the corresponding phase angle and angular displacement data (that is, values of $\varphi_{\mathrm{air}}, \varphi_l, \theta_{0\mathrm{air}}$, and $\theta_{0l}$) measured both in liquid and in vacuum. Finally, viscoelastic properties of liquid can be obtained from the relation between the components of the complex shear modulus $G^* = G' + iG''$ and both $R_{pl}$ and $X_{pl}$, given by Ferry (1980)

$$G'\left(\omega\right) = \frac{\left(R_{pl}\left(\omega\right)\right)^2 - \left(X_{pl}\left(\omega\right)\right)^2}{\rho} \tag{9a}$$

$$G''\left(\omega\right) = \frac{2\left(R_{pl}\left(\omega\right)\right)\left(X_{pl}\left(\omega\right)\right)}{\rho}, \tag{9b}$$

as well as the one for the Newtonian fluid (Ferry 1980)

$$\eta\left(\omega\right) = \frac{2\left(R_{pl}\left(\omega\right)\right)\left(X_{pl}\left(\omega\right)\right)}{\omega\rho}. \tag{10}$$

It can be thus concluded that through detecting the resonance curve data both in air and in liquid, the torsion resonators with one vibrating mode, often employed for the discrete frequency measurement, can have the continuously varying frequency capability to measure the frequency-dependent viscoelastic properties of complex liquids by using Eqs. 7–10.

## Experimental details

In order to validate the above theoretical analysis, several glycerol–water mixtures with various glycerol concentrations and two PEO solutions at different concentrations have been examined to determine their frequency dependences of viscosity or viscoelastic modulus at room temperature respectively by using our home-made torsional resonator (Zhang et al. 2003; Wang et al. 2008, 2010) with ultra-high precision and an advanced rheometric extended system (ARES. TA Co.) (Wang and Zhang 2007, 2009) in an oscillation mode with a double-walled couette geometry. Thereunto, measurements by our torsion resonator apparatus were performed on approximate 20 × $10^{-6}$ $\mathrm{m}^3$ of the liquid sample, and the temperature was set with an accuracy of ±0.05°C.

Instruments and calibration

Our homemade torsion resonator apparatus is developed from the resonant absorption mechanical spectrometer (Zhang et al. 2003; Wang et al. 2008). It can work at frequencies between 0.1 and 1,000 Hz. Its torsion resonator with the effective inertia of approximately $3.0 \times 10^{-5}\ kg\ m^2$ is a two-thin-walled cup joined by a cylindrically shaped torsion spring fixed to the base plate and is suspended by a neglecting-effect silk thread. The resonators, having the torsion springs of different rigidity, can have the different $Q$ value in air. As stated in previous references (Hong and Lu 1995; Wang et al. 2008), such unique-designed resonator makes viscoelastic measurements with better reproducibility and stability. Nevertheless, one drawback of this technique in factual experiments (Hong and Lu 1995; Zhang et al. 2003; Wang et al. 2008) should also be emphasized that the measurements with the thin and soft torsion spring might be vulnerable to the interference from the external or parasitic vibration (Brodt et al. 1995), having a worse displacement and phase measuring accuracy. Especially when for the dilute and less-viscous liquid samples, the influence from such interference on the torsional oscillation of the thin and soft torsion spring will be larger. To alleviate such limitation, a resonator with a rigid torsion spring and having large $Q$ value is necessary. Consequently, in order to increase the viscosity and viscoelasticity accuracy of our apparatus, in this work, some dense and viscous glycerol–water samples with glycerol concentration of 60–100% are only concerned, and to provide a good comparison with the PEO results obtained by commercial rheometer, when for measuring the water–PEO samples, a more rigid torsion spring was used.

The resonators used in the experiments were calibrated by measuring several standard Newtonian liquids with known viscosity at 20°C, including Milli-Q-water, Baysilone siliconoil M 10 and silicon oil AP 100 (AP 100 Wacker chemie), in a strict calibration process as reported in previous references (Ferry 1980; Blom and Mellema 1984; Stokich et al. 1994; Fritz et al. 2003). Values of the apparatus constants $A_4$, $E_4$, and $E_5$ have been given in Table 1.

As such, similar to the previous torsion methods (Schrag and Johnson 1971; Blom and Mellema 1984; Fritz et al. 2003; Wang et al. 2008), the proposed method based on Eqs. 7 and 8 should work in the surface loading condition. This requires that the propagating shear wave excited by the forced oscillating cup should be damped out when it reaches the inner sample holder walls (Wang et al. 2008). According to Mason et al. (1949) and Thurston (1964), the distance ($\delta$), at which the amplitude of the shear wave is damped out by 1/e in the liquid medium, satisfies

$$\delta = \frac{1}{\omega}\sqrt{\frac{2}{\rho}\left(\frac{G'^2 + G''^2}{\sqrt{G'^2 + G''^2} - G'}\right)}. \tag{11}$$

The penetration depth for all samples has been checked and was typically less than 200 μm and in all cases less than 4.0 $mm$.[1] Such penetration is considerably smaller than the width of the gap from the sides of the oscillating cup to the sample holder walls ($d \approx 20.0$ mm), thus ensuring that the torsional oscillation works in the surface loading limit.

In terms of the maximum deformation of the surrounding fluid estimated by Mason et al. (1949) and Fritz et al. (2003)

$$\gamma_{\max} = \Omega\delta^{-1} = \Omega\sqrt{\frac{\rho\omega^2}{2}\frac{\sqrt{G'^2 + G''^2} - G'}{G'^2 + G''^2}}, \tag{12}$$

at which $\Omega$ is the oscillation amplitude of the resonator, to make sure the torsional resonator measurements work in the linear viscoelastic region, typical working angular displacements in liquids are controlled to be within the order of ±0.01° or less at the resonance frequencies. In addition, when employing the advanced rheometric extended system (Wang and Zhang 2007, 2009), a dynamic strain sweep was conducted prior to the frequency sweep, and the strains were controlled to sufficiently low to ensure the corresponding measurements within a linear viscoelastic region.

Samples preparation

The glycerol–water mixtures were prepared carefully by mixing the tri-deionized water and pure glycerol of 1,420 cp at room temperature in terms of the designated preparation criterion (Chen 1994), so that the viscosities and densities of these mixtures could be obtained theoretically by using the calculation method of the standard Newtonian-liquid preparation (Chen 1994; Wang et al. 2008). The relative measured accuracy of our homemade torsional resonator apparatus employing this strategy can thus be quantitatively analyzed through comparing the measured results with the calculated ones, as the previous treatment (Wang et al. 2008).

Two PEO solutions with different concentrations that are greater than the overlap concentration,

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[1] The 4.0 mm penetration depth was estimated by Eq. 11 for a pure glycerol ($\eta = 1420$ cp, $\rho = 1.26$ Kg/m$^3$) at a frequency of 20.0 Hz. Wang et al. (2008)

**Table 1** Apparatus constants

| | $Q$-factor in air | $M_0$ $(10^{-6}\ N.m)$ | $A_4^{Cacu}$ $(kg/m^2)$ | $E_4^{Cacu}$ $(N/m^3)$ | $E_5^{Cacu}$ $(N/m^3)$ | $A_4^{Exp}$ $(kg/m^2)$ | $E_4^{Exp}$ $(N/m^3)$ | $E_5^{Exp}$ $(N/m^3)$ |
|---|---|---|---|---|---|---|---|---|
| (a) | 701 | 2.5 | 2.49 | 2.12 | 2.12 | 2.65 | 2.32 | 2.21 |
| (b) | 805.5 | 5.0 | 2.49 | 4.24 | 4.24 | 2.51 | 4.53 | 4.45 |

(a) is for the resonator with the rigid copper rod (used as the torsion spring) of 1.5 mm in diameter (Wang et al. 2008) and used for measurements of water-glycerol solutions; and (b) is for the one with a thicker and more rigid copper rod of 2.2 mm in diameter and used for water–PEO solutions. Note deviations of experimental values of $A_4$, $E_4$, and $E_5$ from the calculated ones are within approximately 5% of the calculated ones

$c^*$ (approximately 0.16 wt.%) (Cooper et al. 1991; Devanand and Selser 1991), were prepared by using PEO with the molecular weight of 900 kDa (purchased from *Changchun-Dadi-Fine Chemical Co.,Changchun,China*) and the tri-deionized water. The two PEO solutions, the pH of which were typically about 5.5, begin to exhibit significant viscoelasticity due to the entanglement of the polymer coils, and corresponding preparations follow a rigorous process (Cooper et al. 1991; Dasgupta et al. 2005), which requires great care and patience. First, the PEO powder and the tri-deionized water were occasionally gently stirred by using a magnetic stirrer for about 2 h at room temperature; and a drop of chloroform was added to prevent bacterial growth, and sodium chloride was also added to ensure consistent salt concentration for all our samples, the salt concentration of which was 25 mM. Then the well-prepared stock solutions, wrapped in an aluminum foil to avoid photodegradation of the polymer, were kept in an incubator for 10 days at ∼ 40°C to allow the polymer to dissolve completely.

## Experimental results

### Newtonian samples: water–glycerol mixtures

The first step to validate the above-presented strategy is to investigate the viscosity of water–glycerol mixtures at room temperature by using our homemade torsional resonator. Figure 1 shows the measuring torsional resonance curves when loading and unloading the samples. Evidently, the resonance frequency, the bandwidth, and the maximal angular velocity of the resonance curves become smaller, broader, and lower as the glycerol concentration increases. Such behavior coincides well with our previous results (Wang et al. 2008), illustrating the quality of the measurements presented here.

According to the above theoretical analysis, from the resonance curves data in Fig. 1, together with calibration data given in Table 1a, the mechanical resistance and reactance ($R_{pl}$ and $X_{pl}$) can be calculated by using Eqs. 7 and 8. Figure 2 presents plots of the frequency dependence of the resulting $R_{pl}$ and $X_{pl}$ values. Also presented are the theoretical curves obtained by using $R_{pl} = X_{pl} = \sqrt{\omega\rho\eta_{\text{theo}}/2}$, where $\rho$ and $\eta_{\text{theo}}$ are, respectively, the theoretical density and viscosity of the glycerol–water mixtures calculated in terms of the designated preparation criterion (Chen 1994; Wang

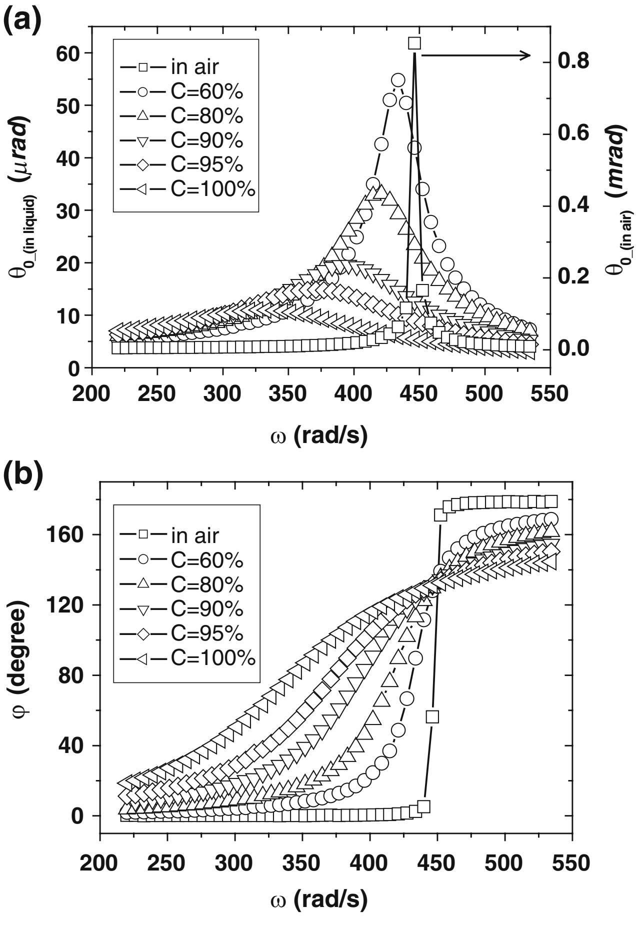

**Fig. 1** The resonance behaviors for measurement of different water-glycerol mixtures detected using our home-made torsion pendulum apparatus. **a** Angular-displacement amplitude versus driving frequency; **b** phase shift $\phi$ versus driving frequency. *C* volume fraction of glycerol in the mixtures

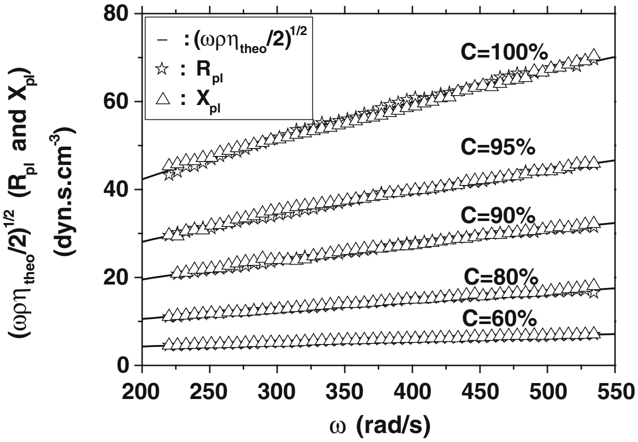

**Fig. 2** Resistance and reactance values for different water-glycerol mixtures plotted as a function of frequency. *C* is the volume fraction of glycerol in the mixtures

et al. 2008). Obviously, there is good agreement between the measured and theoretical values of the shear mechanical impedance of Newtonian samples, which hence demonstrates the validity of Eqs. 7 and 8. From the mechanical resistance and reactance data of Fig. 2, the resultant viscosities, plots of which against the frequency shown in Fig. 3a, are then obtained through using Eq. 10. This result exhibits a good agreement with the previous ones obtained by the PAV apparatus (Grassous et al. 2005), further demonstrating the feasibility of our proposed strategy to measure the Newtonian liquids.

Figure 3b shows the corresponding relative measured errors ($|\eta^M - \eta_{\text{theo}}|/\eta_{\text{theo}}$). From Fig. 3b, it is clear that the measurements by using our homemade apparatus have a high measuring precision better up to 4.0% for investigating the Newtonian liquids with the viscosity range of approximate 10∼1,420 cp at the frequency range of 200∼550 rad/s during the vicinity of the resonance frequency. Apart from systematic errors due to changes in the materials of the resonator (Ferry 1980; Blom and Mellema 1984; Wang et al. 2008), from Eq. 10, it can be seen that the primary error source to the measuring viscosity accuracy is located in the uncertainties to calculate $R_{pl}$ and $X_{pl}$, i.e., $^{\square}(R_{pl})$ and $^{\triangle}(X_{pl})$, which are approximate within 2.0% indicated from Fig. 2. From Eqs. 7 and 8, $^{\square}(R_{pl})$ and $^{\triangle}(X_{pl})$ originate in the measured errors of both the phase angle ($tg\varphi$) and angular displacement data ($\theta_0$) both when in air and in liquid. This suggests that a better accuracy can be obtained by increasing the displacement and phase resolution of the torsion resonator apparatus.

Furthermore, in terms of the above analysis and from the forced oscillation resonance curves shown in Fig. 1, we find that $\theta_0 \rightarrow (\theta_0)_{\max}$ and $tg\varphi \rightarrow \infty$ when close to the resonance frequency (Thereunto, $(\theta_0)_{\max}$ denotes the maximal angular displacement at the resonance frequency), so that for the constant uncertainties of the displacement and phase angle measurements (i.e., $^{\triangle}(\theta_0)$ and $^{\square}(tg\varphi)$), the relative measuring errors of the $\theta_0$ and $tg\varphi$ data during the vicinity of the resonance frequency (i.e., $^{\triangle}(\theta_0)/\theta_0$ and $^{\square}(tg\varphi)/tg\varphi$) are to be the smallest, since $^{\triangle}(\theta_0)/\theta_0 \rightarrow {}^{\triangle}(\theta_0)/(\theta_0)_{\max}$ and $^{\square}(tg\varphi)/tg\varphi \rightarrow 0$ as the driving frequency approaches the resonance frequency. Consequently, measurements at the vicinity of resonance frequency would have better viscosity accuracy than those at other frequencies, as clearly demonstrated in Fig. 3b.

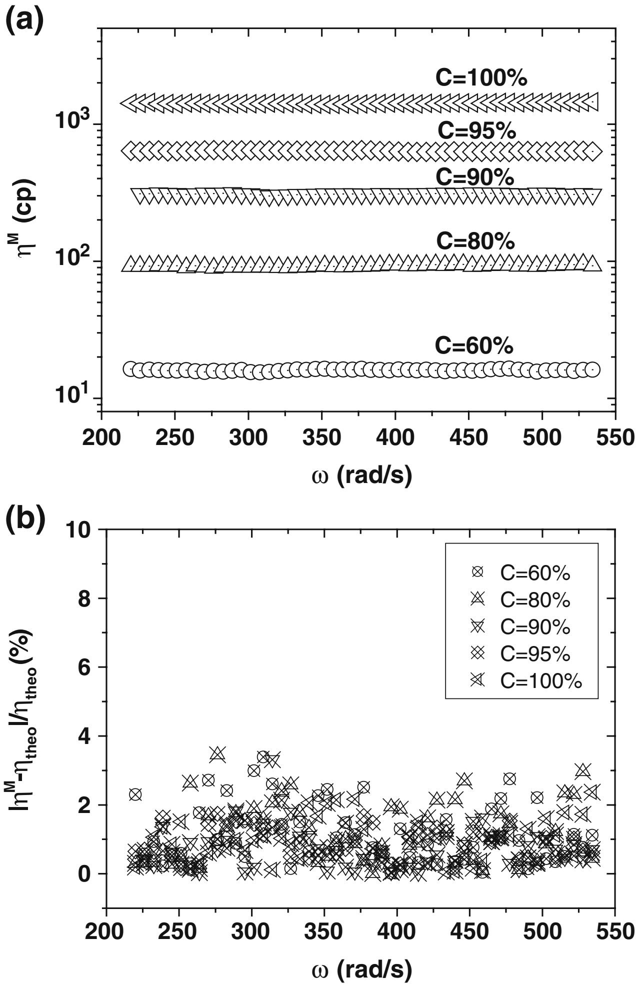

**Fig. 3** Measured viscosity data and corresponding measured errors. **a** Plots of measured viscosities $\eta^M$ versus frequency for different water–glycerol mixtures. **b** Plots of the measured error $|\eta^M - \eta_{\text{theo}}|/\eta_{\text{theo}}$ versus the varying frequency. *C* volume fraction of glycerol in the mixtures

### Non-Newtonian samples: water–PEO solutions

Next, we consider the frequency dependence of two different water–PEO solutions in the semidilute region, which exhibit significant viscoelasticity due to the entanglement of the polymer coils. Figure 4 shows the corresponding resonance curves detected by our torsional resonator apparatus. Examining these resonance curves and comparing with the ones shown in Fig. 1, it is seen that with increasing the PEO concentration, the resonance curves in Fig. 4 also become lower and broader as those in Fig. 1, but the phase shift curves (in Fig. 4b) do not intersect at the frequency point at $\phi = 135^\circ$, values of which increase contrarily. Such behavior indicates that the water–PEO solutions might have the configurational shear elasticity, which has a dependence on PEO concentration. This indication can be illustrated from the frequency dependence of the corresponding mechanical impedances and viscoelastic moduli shown in Figs. 5 and 6, respectively.

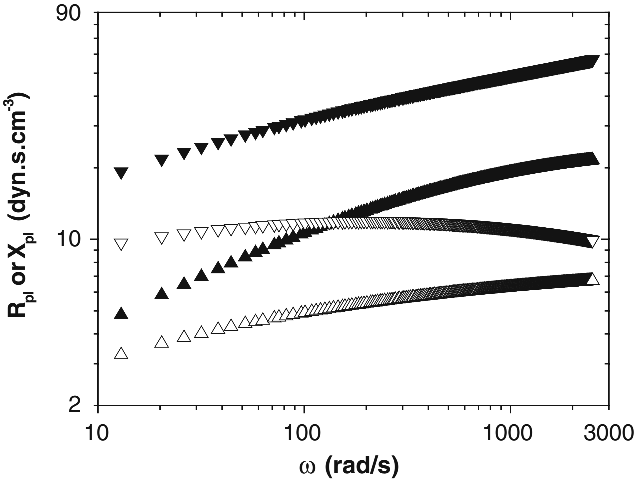

**Fig. 5** Resistance (*solid symbols*) and reactance (*open symbols*) values for two 900-kDa PEO aqueous solutions with different PEO concentrations of 3.7 wt.% (*solid and open triangles*), 8.1 wt.% (*solid and open inverted triangles*)

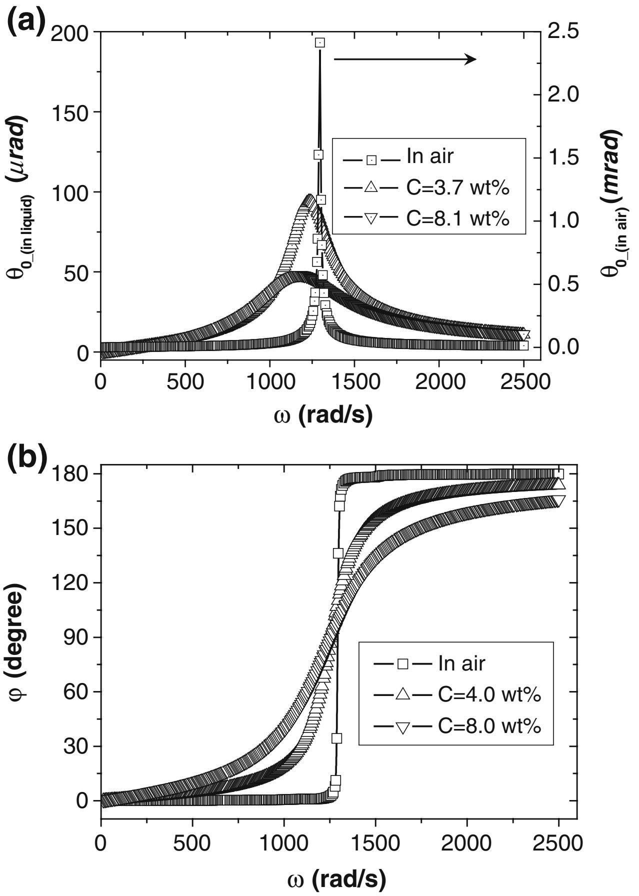

**Fig. 4** The resonance behaviors for measurement of different concentrations of 900 kDa PEO sample solutions. **a** Angular displacement versus driving frequency; **b** Phase shift $\phi$ versus driving frequency. *C* weight fraction of PEO in the PEO–water solutions

Similar to the data handling process for Newtonian liquids discussed above, Fig. 5 is obtained from resonance curves data in Fig. 4 and through using Eqs. 7 and 8. From Fig. 5 it is obvious that the resistance and reactance terms are not equal (which are different from those in Fig. 2); and the resistance terms are quite larger than the reactance ones as the PEO concentration or shear frequency increases. In terms of previous studies (Mason et al. 1949; Ferry 1980; Dasgupta et al. 2005), it is the increase of both the elasticity and viscosity in the water–PEO solutions as increasing the PEO concentration that results in the increase of the mechanical impedances and the divergence between the resistance and reactance terms. Thereunto, the elasticity is considered to result from the elastic deformation of the PEO network in solutions. Figure 6, obtained from curves data in Fig. 5 and through using Eqs. 9a and 9b, provides a more robust and straightforward support to the analysis mentioned above. Note that, for the viscoelastic measurements of the water–PEO solutions by using our homemade torsional resonator employing the new strategy, $G''$ has a relative uncertainty of about 4.0% or less, with the $G'$ relative uncertainty being about 8.0% for solutions for which $G'$ is greater than 0.04 Pa.

In addition, the comparison to the viscoelastic results of water–PEO solutions detected by the strain-controlled commercial rheometer (Wang and Zhang 2007, 2009), is also shown in Fig. 6. Results from the

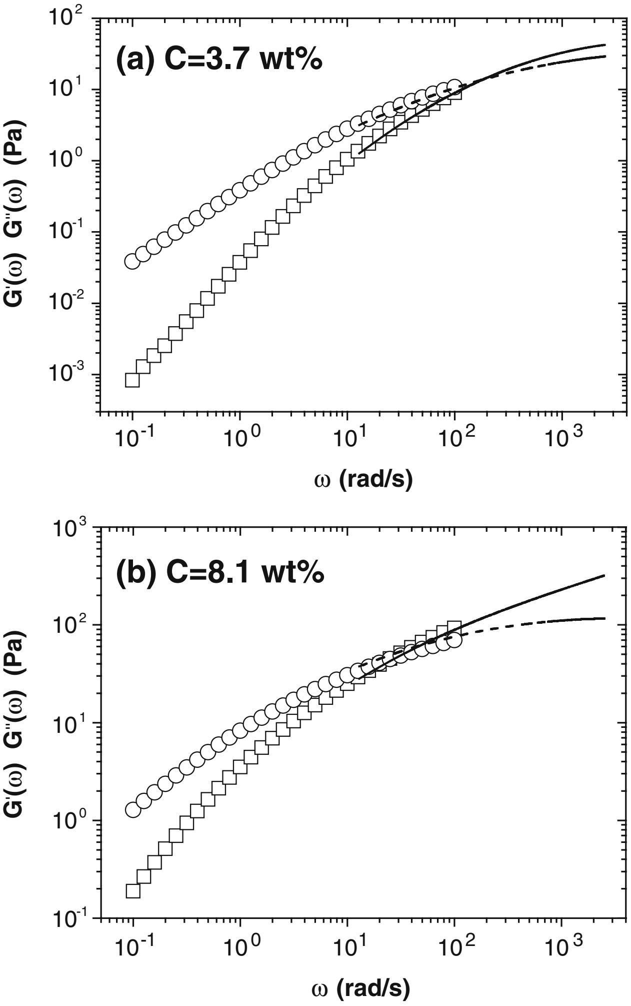

**Fig. 6** Storage and loss moduli for two 900 kDa PEO solutions of **a** 3.7 wt.% and **b** 8.1 wt.% concentrations obtained, respectively, from conventional mechanical rheometer ($G'$ (*unfilled squares*); $G''$ (*unfilled circles*)) and our homemade torsion pendulum apparatus ($G'$, *solid line*; $G''$, *dashed line*). $C$ is the weight fraction of PEO in the PEO–water solutions

torsional resonator apparatus are shown by the solid lines for the elastic moduli and dashed lines for the viscous moduli; and the bulk rheology measurements using the strain-controlled rheometer are plotted as open symbols using squares for the elastic moduli and circles for the viscous moduli. Obviously, the viscoelastic moduli, respectively, obtained by the two techniques coincide very well in the region of frequency in which they overlap. This excellent accordance illustrates the ability of the torsional resonator employing the presented new strategy to precisely obtain the viscoelastic results for polymer solutions in the continuous frequency range.

## Conclusion remarks

A novel strategy for accomplishing the continuously varying frequency capability of the traditional surface-loading torsion resonator apparatus with one resonance mode to measure the viscoelastic properties of the complex fluids is introduced in this paper. The feasibility of this strategy was then validated by measurements of the water–glycerol solutions and water–PEO solutions through using our homemade torsion resonator, which despite were performed only at the audio-frequency range (10∼2,500 rad/s) due to the short frequency range restriction of our homemade apparatus. As such, the viscoelastic spectra of the PEO solutions by using our homemade apparatus agree with the results obtained from the commercial rheometer, further validating this strategy. Besides, the torsional resonator employing this strategy can have a better viscoelasticity-measuring precision during the vicinity of the resonance frequency.

However, some limits of this new strategy should be also mentioned. In the first place, the accuracy is limited by the changes and parasite vibrations in the torsion spring of the resonator and the fluctuation of the driving torque, for which an appropriate torsion spring made of the materials with a smaller linear thermal expansion coefficient and a higher quality driving torque are substituted. Second, the corresponding measurement requires better precisions of the phase lags and the displacement amplitude of torsional resonator apparatus, as well as a better precision of varying driving-frequency. Third, accuracies of measurements at frequencies far from the resonance frequency are poorer, different resonators with various higher $Q$ value are also required for investigating the viscoelastic properties of liquids at a wider frequency range. Additionally, further experiments are also required to explore the full range of its validity in the future, such as the studies of the rheological properties of wormlike micelles, the colloidal suspension, the emulsion or the (900 kDa) PEO–water samples with lower PEO concentration, and so on.

To sum up, although the new strategy presented here is seemingly just an extension of our previous work (Wang et al. 2008) and further improvements to this work are also required in the future, it has been demonstrated convincingly that employment of the novel strategy presented here can enable the traditional forced torsion resonator, only exhibiting one resonance mode, to precisely measure the viscoelastic properties of complex fluids with the continuously varying frequency capability. We believe that this new technique will be of great innovation and significance in rheometry to advance the traditional torsional resonators.

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