# Measurement techniques for steady shear viscosity of Mozzarella-type cheeses at high shear rates and high temperature

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## Abstract

While measuring steady shear viscosity of Mozzarella-type cheeses in a rotational rheometer at 70°C, three main difficulties were encountered; wall slip, structural failure during measurement and viscoelastic time dependent effects. Serrated plates were the most successful surface modification at eliminating wall slip. However, even with serrated plates shear banding occurred at higher shear rates. Because of the viscoelastic nature of the cheeses, a time dependent viscous response occurred at shear rates <1 $s^{-1}$, requiring longer times to attain steady shear conditions. Prolonged continuous shearing altered the structure of the molten cheeses. The effects of structural change were greatly reduced by minimising the total accumulated strain exerted on the sample during flow curve determination. These techniques enabled successful measurement of steady shear viscosity of molten Mozzarella-type cheeses at 70°C at shear rates up to 250 $s^{-1}$.

## 1. Introduction

Accurate measurement of the rheological properties of food materials is important for equipment design, product development, quality control and process modelling. Mozzarella cheese is rheologically complex over its processing and consumption conditions because it is viscoelastic, exhibiting varying amounts of solid- and liquid-like character depending upon temperature, rate of deformation and extent of working during manufacture. Many studies have been reported on small angle oscillatory shear measurements on Mozzarella-like cheeses (Tunick et al., 1993; Hsieh, Yun, & Rao, 1993; Ak & Gunasekaran, 1996; Subramanian & Gunasekaran 1997; Guinee, Feeney, Auty & Fox 2002;  Venugopal & Muthukumarappan, 2003; Karoui, Laguet & Dufour, 2003; Joshi, Muthukumarappan & Dave, 2004; Rock et al., 2005; Udayarajan, Horne & Lucey, 2007; Hussain et al., 2012; Ma, Balaban,  Zhang, Emanuelsson-Patterson & James, 2014) as it is relatively easy to perform such experiments on rotational rheometers. However, there are fewer reports on steady shear viscosity measurements on such cheeses with rotational rheometers because of the difficulty in performing steady shear experiments (Lee, Imoto & Rha, 1978; Ruegg, Eberhard, Popplewell & Peleg, 1991; Guinee & O’ Callaghan 1997; Yu & Gunasekaran, 2001). Most of the steady shear reports were conducted using empirical methods or devices, and did not produce data at shear rates >10 $s^{-1}$. Capillary rheometers have been used successfully to achieve higher shear rates but various flow instabilities were noted during their use (Smith, Rosenau & Peleg, 1980; Cavella, Chemin, & Masi, 1992; Taneya, Izutsu, Kimura & Shioya, 1992; Muliawan & Hatzikiriakos, 2008; Bahler & Hinrichs, 2013).

We are commencing a study on the cooking/stretching stage in Mozzarella manufacture as it is poorly understood. The deformation regime in rotational rheometers is closer to the processing conditions in this process stage than that in capillary rheometers. Reported average shear rates during cooking/stretching vary from ~40 $s^{-1}$ for a batch pilot-scale twin screw cooker (Glenn & Daubert, 2003; Glenn, Daubert, Farkas & Stefanski, 2003) to 70-150 $s^{-1}$ for a laboratory scale, single impeller mixing device (Lai, Steffe & Ng, 2000; Kapoor, Lehtola & Metzger, 2004). We estimate maximum shear rates between the screw tip and the wall in a batch pilot-scale Blentech cooker to be about 200 $s^{-1}$. It is therefore useful to determine shear viscosity of molten cheese at higher shear rates.

The presence of a no-slip condition at the wall is an important pre-requisite in accurately measuring steady shear viscosity. In the case of Mozzarella-like cheeses in the molten state, liquid fat at the cheese surface starts lubricating the wall (Ruegg et al., 1991; Muliawan & Hatzikiriakos, 2008). This lubrication violates the classical no-slip boundary condition, leading to erroneous viscosity data (Yoshimura & Prud'homme, 1988) particularly at shear rates $> 10$ $s^{-1}$. A rheologically complex material such as Mozzarella cheese exhibits time dependency arising from two separate phenomena: 1. The viscoelastic nature of the material which is important at low shear rates ($<1$ $s^{-1}$) and 2. Structural change as a result of shearing which is important after prolonged shearing at higher shear rates (Steffe, 1996; van Vliet, 2014). We use the term viscoelastic time dependency to refer to the first and structural change to refer to the second. Because of these difficulties of wall slip and time dependency, a limited amount of work has been conducted on steady shear rheology of Mozzarella cheese.

It is desirable to have a method that takes account of the viscoelastic time dependency and measures the viscosity before significant structural change has occurred. The main aim of this study was to develop such a method that is suitable at higher shear rates and higher temperatures. A secondary aim was to understand the physical phenomena that occur during shear viscosity measurement as these same phenomena will also occur in processing equipment that imparts shear.

## 2. Materials and Methods

### *2.1 Materials*

Samples of commercial Mozzarella cheese, a model Mozzarella cheese and renneted casein gel were obtained as frozen blocks from Fonterra Co-operative Group Limited, Palmerston North, New Zealand. Model Mozzarella cheese was prepared by mixing and working renneted casein gel, cream, water and salt at 70 $^{o}$C in a twin screw batch cooker (Blentech, model CC-0045, Blentech Corporation, Rohnert Park, CA, USA). Renneted casein gel was a dewatered, renneted and acidified curd made from skim milk. The compositions of the cheeses were determined by the Analytical Services Group of Fonterra Research and Development Centre (Table 1). Each cheese block was thawed at 4 $^{o}$C for at least 24 h before use in experiments.  Cheese cylinders of 20 mm diameter were drawn from a cheese block using a cork borer. Discs 2-3 mm thick were cut from the cheese cylinder using a wire cutter. Cheese discs were wrapped in food wrap to prevent moisture loss and stored at 4 $^{o}$C.

### *2.2 Rheological properties*

Initial experiments (as noted in figure legends) were conducted on a stress controlled AR-G2 rheometer (TA Instruments, New Castle, DE, USA) using parallel plate geometry (diameter 20 mm). Unless otherwise noted in figure legends, all other rheological measurements were conducted on a MCR 301 rheometer (Anton Paar, Graz, Austria) using a Peltier temperature hood (H-PTD 200), a 20 mm serrated parallel plate geometry and using the following conditions.

Cheese discs were equilibrated to room temperature (21 $^{o}$C) for at least 30 min and then placed between the parallel plates of the rheometer. To ensure good rheometer/sample contact the measurement gap was set by closing the gap at room temperature until the normal force was 5 N. While closing the gap, the velocity of the rheometer moving head was 50 µm/s. The sample was then heated to 70 °C using the in-built Peltier heating system for both the bottom plate and the upper temperature hood. The sample was then held at 70 °C for 2 min to ensure isothermal conditions and to allow some stress relaxation. To avoid drying soybean oil was applied around the edges of the cheese disc. All rheological measurements were performed at 70 °C. Oscillatory rheological measurements on renneted casein gel were conducted in the linear viscoelastic range using 1 Hz frequency and 0.5% amplitude at 70 °C.

Temperature gradients across the samples were explored using a temperature probe (Q1437 digital thermometer, Dick Smith Electronics, Auckland, New Zealand) and a high viscosity standard oil (Viscosity reference standard N4000, Cannon Instrument Company, State College, PA, USA).

### *2.3 Image acquisition to illustrate wall slip*

To visualize wall slip a digital camera, Canon EOS 650D (Canon, Tokyo, Japan), was used in video mode. The camera was operated remotely by computer using software EOS digital version 25.2 (Canon, Tokyo, Japan). The camera was fixed at the same height as the rotating plate and sample and was able to capture the wall slip event. A reference mark was drawn vertically on the sample and upper plate. The sample was heated to 55 °C using the in-built Peltier heating system. The rheometer was run at a shear rate of 0.04 $s^{-1}$. A video-clip was captured at 50 frames $s^{-1}$ and 1280 x 720 resolution for 69 s. Still images were extracted from the video using the software Windows Live™ Movie Maker (Microsoft Corporation, Redmond, WA, USA).

### *2.4 Environmental scanning electron microscopy*

To explore the effect of shearing on microstructure, environmental scanning electron microscopy (ESEM) was conducted on cheese samples obtained before and after shearing in the rheometer. For the unsheared sample, a specimen was cut assuming random protein fibre orientation. However, for the sheared fibrous-looking sample, protein fibre orientation was assumed to be along the length of the sample and the specimen was cut in the longitudinal direction. Specimens were cut with dimensions 4x4x1 mm. ESEM was conducted in a variable pressure FEI Quanta 200F scanning electron microscope (FEI, Hillsboro, OR, USA) equipped with a Schottky field emission gun and a Peltier cooling stage in environmental mode. Water vapour (imaging gas) was used as a gas medium for secondary electron signal amplification. The chamber was pumped for four to five cycles with minimum pressure 3.2 Torr and maximum pressure 7 Torr to stabilise the water vapour pressure. A spot size of 3, accelerating voltage of 10 kV and working distance of approximately 5-6 mm were used. In order to ensure wetness of the sample, the relative humidity of the chamber was maintained at 60% by controlling pressure at 3.2 Torr and temperature at 2.0 °C.

## 3. Results and Discussion

### *3.1 Wall slip and shear banding*

In an initial attempt to determine a flow curve of model Mozzarella cheese at 70 $^{o}$C using smooth plate geometry, a flow discontinuity was observed, evidenced by a sudden drop in apparent viscosity and shear stress at shear rates ~5 $s^{-1}$ (Fig. 1). Yu and Gunasekaran (2001) reported a similar drop in viscosity in the shear rate range 2-5 $s^{-1}$ while measuring steady shear viscosity of Mozzarella cheese at 60 $^{o}$C. For Mozzarella-like cheeses at temperatures above 30 $^{o}$C, the fat will be molten and so the cheese surface will tend to be slippery (Ruegg et al., 1991; Muliawan & Hatzikiriakos, 2008). The molten fat and slippery surfaces are likely to cause loss of grip resulting in early wall slip.

To confirm the hypothesis that molten fat was causing wall slip, a movie was filmed using a high resolution camera (Fig. 2). Even at the very low shear rate of 0.04 $s^{-1}$, the images show that the mark at the top of the cheese became displaced from that on the top plate by 35 s and was progressively displaced further after 45 s and 55 s. This displacement was a clear visual indication of wall slip. From the polymer literature, the picture of wall slip is that of accumulated strain/stress building up in polymeric chains, reaching a critical value and eventually leading to permanent detachment from the interface. The molten fat in Mozzarella cheese may have worsened this situation. For an isothermal sample of a Newtonian liquid or Hookean solid the marker line would be expected to be linear. We suggest the curve formed with little distortion near the upper plate (Fig. 2) is caused by a temperature gradient in the sample from 55 $^{o}$C on the lower Peltier plate to a lower temperature at the upper plate.

We modified the cheese contact surfaces in an attempt to eliminate or minimize the wall slip effect. Best results were obtained with serrated plates, followed by sandpaper and then sandblasted plates (Fig. 3). The viscosity values with the serrated plates (Fig. 3) are about 5 times those with smooth plates (Fig. 1) even at low shear rates indicating the large effect of wall slip on the results. Flow discontinuities were still observed at shear rates > 100 $s^{-1}$, so surface modification has just changed the location of the apparent slip or sample fracture from the walls to within the material. Patarin, Galliard, Magnin and Goldschmidt (2014) described similar behaviour as macroscopic failure or fracture when a cheese sample having good contact with upper rotating and bottom stationary plates was sheared in a rheometer. This apparent slip or fracture within the sample is referred to as shear banding, shear localisation or melt fracture in the polymer literature (Ancey, 2005).

A temperature gradient across the samples was observed while conducting tests on the AR-G2 rheometer. When the temperature of the Peltier bottom plate was 70 $^{o}$C a temperature gradient of ~ 5 $^{o}$C was recorded across the sample with the temperature probe. The high viscosity standard oil showed that the measured viscosity was accurate at 20 $^{o}$C but high at 70 $^{o}$C indicating that the average sample temperature was lower than the 70 $^{o}$C set temperature.

### *3.2 Transient viscoelastic effects and measurement duration*

At low shear rates (<0.1 $s^{-1}$) and 70 $^{o}$C, model Mozzarella cheese exhibited a transient viscosity peak, a localized maximum of viscosity on the flow curve (Fig. 3). Viscoelastic materials exhibit non-steady state flow conditions at low shear rates (<1 $s^{-1}$) if the timescale of deformation is too small. This effect is related to the slow rate of stress dissipation within the material resulting in slow development of steady flow conditions. In the literature, these effects are termed start-up effects or time-dependent transition effects (Mezger, 2011; van Vliet, 2014).

The apparent viscosity of Mozzarella cheese at 0.01 $s^{-1}$ and 70 $^{o}$C was found to be time dependent (Fig. 4). Viscosity increased with measurement time and eventually reached a relatively constant steady state value at around 100 s. At a higher shear rate (10 $s^{-1}$) apparent viscosity attained a constant value in less than 2 s.

Mezger (2011) proposed a rule of thumb that measurement duration at each point should be at least as long as the reciprocal of shear rate, i.e. $t > 1/\dot{\gamma}$. Fig. 4 agrees with this rule of thumb. Attaining steady shear conditions at each shear rate step is important for obtaining an accurate flow curve for viscoelastic materials such as cheese. Van Vliet (2014) provides an excellent description of the role of time scale in food rheology including cheese examples. The duration of shear rate application plays a vital role in the stress response of the material. Reaction to applied stress is nearly instantaneous for a rigid elastic material but is time-dependent for soft solids (van Vliet, 2014; Malkin, 2013). For viscoelastic materials time dependency is related to the disruption and reformation of molecular interactions and to the spectrum of relaxation times of these processes (van Vliet, 2014).

### *3.3 Structural changes/failure during shearing*

Continuous shearing of Mozzarella cheese at higher shear rates eventually resulted in structural failure and expulsion of some of the sample from the rheometer measurement gap in the form of a thick strand (diameter about the same as the measurement gap) with aligned protein fibres. The unsheared sample had a random ESEM structure (Fig. 5). On the other hand, the sheared sample exhibited alignment of the protein and fat structure, presumably in the direction of shearing. These observations plus observations on model Mozzarella cheese manufactured in pilot-scale equipment led us to the conclusion that shearing of Mozzarella-type cheese led to changes in the structure of the material. Similar observations were reported by Manski (2007), who created fat filled protein structures by shearing calcium caseinate-fat dispersions and showed that shearing led to structural orientation initially and then with a further increase in shear rate also resulted in failure of the material.

Steady-state viscosity measurement for Mozzarella cheeses therefore changes the structure of the cheese thus changing the viscosity that we are trying to measure. Although viscosity measurements can be used as probing tools for changes in structure we wish to measure steady shear viscosity before any significant structural change has occurred.

### *3.4 Optimum flow curve*

One way to limit structural changes during rheological measurement is to minimize shearing of the sample during the measurement. Fig. 6 indicates that this strategy was certainly an improvement. The default shear rate settings for flow curve determination resulted in an early breakdown of the flow curve at a shear rate near 10 $s^{-1}$. The flow curve with only 5 shear rate steps with shorter measurement durations resulted in successful measurement of shear viscosity up to a shear rate of 150 $s^{-1}$. The power law model fitted the data well ($R^2$=0.998).

The practical limit of the method appeared to be about 150 $s^{-1}$ with the chosen steps as only one reliable data point was obtained at 150 $s^{-1}$ from the triplicate runs.

To further check the robustness of the method two different shear step series with lower accumulated strain units were attempted on commercial Mozzarella cheese. The data obtained from both series also fitted very well to the power law model ($R^2$=0.998) and the flow curves for the two series were virtually identical (Fig. 7). The maximum shear rate achieved was 250 $s^{-1}$. Thus, a smooth flow curve up to 250 $s^{-1}$ was obtained for Mozzarella cheese by allowing longer measurement durations at low shear rates to avoid transient viscoelastic effects and selecting only a few shear rate steps in order to limit total accumulated shear strain (<50 strain units).

Values of the flow behaviour index for commercial Mozzarella cheese were similar (~0.74) in figures 6 and 7 indicating similar moderate shear thinning behaviour. However, the consistency coefficient shown in Fig. 7 is lower (~122 Pa.$s^n$) than that in figure 6 (~211 Pa.$s^n$). Fig. 7 was performed on the same material as Fig. 6 but after storage at 4$^o$C for two weeks. The lower consistency coefficient in Fig. 7 was possibly attributed to softening caused by proteolysis during storage of the cheese at 4 $^o$C. The effect of proteolysis on softening of Mozzarella cheese is well reported (Metzger, Barbano & Kindstedt, 2001; Guinee *et al.*, 2002; Kindstedt, Hillier & Mayes, 2010).

Rheological data obtained by Muliawan & Hatzikiriakos (2007) for Mozzarella cheese at 25 $^o$C using both capillary and sliding plate rheometers were described by the Herschel-Bulkley model (i.e. Power law with yield stress) with a higher consistency coefficient (K=3.34 kPa.$s^n$), a lower flow behaviour index (n=0.25) and a yield stress (1.93 kPa). Muliawan & Hatzikiriakos (2007) reported the absence of a yield stress above 60 $^o$C and suggested this was because of complete melting of the protein structure and hence easier initial flow of the cheese. Our fit of data to the power law model therefore agrees with Muliawan & Hatzikiriakos (2007) but absolute values of the model parameters were different because of our higher test temperature.

### *3.5 Flow properties of molten renneted casein gel*

Some experiments were conducted with molten renneted casein gel, effectively a fat-free, low salt Mozzarella cheese, to explore the role of the protein phase in the flow instabilities such as wall slip or structural failure. Fig. 8 indicates a discontinuity occurred in the flow curve for molten renneted casein gel at around 25 $s^{-1}$ with a sudden decrease in viscosity. Fat is absent here so the occurrence of flow instability suggests breakdown of protein structures upon shearing rather than wall slip.

### *3.6 Applicability of the Cox-Merz rule*

The Cox-Merz rule is an empirical rule that seeks to relate oscillatory rheological data to steady shear data. The Cox-Merz rule is represented by following equation:

$$\eta\,(\dot{\gamma}) \;=\; |\eta * (\omega)| = \frac{G"}{\omega}\sqrt{1+\left(\frac{G'}{G"}\right)^2}\,\Bigg|_{\omega\,=\,\dot{\gamma}} \tag{1}$$

Where, $\eta(\dot{\gamma})$ is shear viscosity in Pa.s, $\eta^*(\omega)$ complex viscosity in Pa.s, ω rotational speed in rad.$s^{-1}$, G', storage modulus and G" loss modulus in Pa.

Reasonably good agreement was observed between complex viscosity and shear viscosity with our data almost superimposing over the shear rate range 0.01-25 $s^{-1}$ (Fig. 8). This agreement suggested that the Cox-Merz rule was applicable to renneted casein gel and also suggested the possible use of oscillatory data to estimate shear viscosity at higher shear rates beyond which wall slip or structural breakdown would have occurred in rotational steady shear mode. Muliawan & Hatziriakos (2007) compared complex and shear viscosities of

Mozzeralla cheese at various temperatures from 25 $^{o}$C to 60 $^{o}$C and reported poor agreement at temperatures up to 50 $^{o}$C suggesting non-compliance to the Cox-Merz rule. They suggested this lack of agreement was caused by the solid-like structure and by the presence of a yield stress at temperatures of 50 $^{o}$C and below. However, at 60 $^{o}$C or above where the cheese is more molten Muliawan & Hatziriakos (2007) reported agreement between oscillatory and steady shear data in agreement with Fig. 8.

### *3.7 Structural origins of rheological behaviour*

Flow instabilities have been widely reported and discussed in the polymer melt rheology literature. Two of the most common terms used for structural failure of the material during rheological measurement are shear banding and melt fracture. Entangled polymeric chains or aggregated gel networks both show shear banding in simple shear (Boukany & Wang, 2010). Polymer chain entanglement and disentanglement (also known as the coil and stretch phenomena) in concentrated polymer dispersions are the usual phenomena that have consequences for rheological measurements (Ferry, 1980; Graessley, 1974; Boukany & Wang, 2010). Entanglement of polymer chains may lead to an initial elastic deformation before the molten material actually starts flowing. If the rate of external deformation is higher than the chain relaxation rate, the chain or gel network may collapse to facilitate flow. This collapse may be a localized event giving rise to a shear banding type of flow discontinuity. This is a complex type of time dependency in that it is shear rate dependent and also results in structural change with time. Shear banding could also arise from breakage of polymeric interactions above a critical shear stress or shear rate (Callaghan & Gill, 2000). Melt fracture is a stress induced structural failure of material perhaps arising from stress-induced disentanglement among bulk polymer chains (Wang & Drda, 1997; Koopmans, den Doelder & Molenaar, 2011).

Casein structures in Mozzarella-like cheeses can be viewed as entangled polymers, as while stretching at higher temperature, they form macroscopic fibers because of calcium mediated casein-casein interactions (Lucey, Johnson & Horne, 2003). These polymeric chains may also have cross links to further strengthen the protein network. Self-association of α and β-caseins may form worm-like polymeric chains and hedgehog-like micelles, respectively (Horne, 1998). Casein gels have also been considered as a heterogeneous network structure consisting of strands of aggregated casein particles (van Vliet, Roeffs, Zoon & Walstra, 1989). In relatively concentrated and close packed conditions such as cheese these casein aggregates may interact with neighboring casein aggregates through entanglement (Horne, 1998).

The fact that casein structures in Mozzarella-like cheeses can be considered as either entangled polymers or aggregated gel networks suggests that insights from the polymer literature are relevant. High shear rates applied to molten Mozzarella cheese in a capillary rheometer result in melt fracture, which can be caused either by fat-protein separation or by a stick-slip type of behaviour (Muliawan & Hatzikiriakos, 2008; Bahler & Hinrichs, 2013). However, a critical shear stress or shear rate was necessary to cause melt fracture. Yu & Gunasekaran (2001) reported a sharp drop in shear viscosity at 2-5 $s^{-1}$ for molten Mozzarella cheese and suggested that the cheese undergoes structural breakdown above some critical shear rate.

## 4. Conclusions

Steady shear viscosity measurements are possible on molten Mozzarella-like cheeses at higher shear rates. The best methods to obtain reliable and consistent data up to 250 $s^{-1}$ on steady shear viscosity of Mozzarella cheese were: 1. Use of 20 mm serrated plates with a Peltier temperature hood; 2. Using longer measurement duration for low shear rates and; 3.

Using fewer shear rate steps in the flow curve to limit the total accumulated shear strain. The flow curves obtained for Mozzarella-type cheeses at 70 $^{o}$C were found to follow the power law model. At higher shear rates flow inconsistencies may arise from the combined effect of wall slip and structural failure of the material. The Cox-Merz rule was found to be applicable for renneted casein gel at 70 $^{o}$C and is recommended as a possible tool to predict steady shear viscosity from oscillatory rheological data.

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## Figure Legends

**Fig. 1.** Flow curves of model Mozzarella cheese showing wall slip obtained in the AR-G2 (TA Instruments) rheometer using smooth plates. Shear viscosity (–●–), Shear stress (–○– ).

**Fig. 2.** Visualization of wall slip of model Mozzarella cheese at 55 $^{o}$C using smooth parallel plates on the AR-G2 (TA Instruments) rheometer at 0.04 s$^{-1}$ shear rate. The black marker line on the cheese becomes displaced from that on the upper plate suggesting wall slip. The images were taken at 0, 10, 25, 35, 45 and 55 s from the start of shearing.

**Fig. 3.** Effect of surface modification of the rotating parallel plates on the flow curves of model Mozzarella cheese. Experiments used 40 grit sand paper (–●–) on the AR-G2 (TA Instruments) rheometer and sandblasted plates (–○–) or serrated plates (–▼– ) on the MCR301 (Anton Paar) rheometer.

**Fig. 4.** Transient start-up effects on shear viscosity of commercial Mozzarella cheese at constant shear rates 0.01 s$^{-1}$ (–●–) and 10 s$^{-1}$ (–○–).

**Fig. 5.** Environmental scanning electron microscopy (ESEM) images of unsheared model Mozzarella cheese (upper row) and of a thick strand of sheared cheese that had come out from the measurement gap of the rheometer after shearing for 3529 strain units (bottom row). Globular structures represent fat globules.

Fig. 6. Two flow curves for commercial Mozzarella cheese using different shear rate sequences: continuous flow curve using default settings of the Anton Paar MCR301 to give uniform spacings on the log shear rate axis (□) and flow curve using only five selected shear rates (♦). For the default settings measurement duration decreased at a logarithmic rate from 25 s to 2 s as the shear rate increased from 0.01 to 200 s$^{-1}$ accumulating 1572 total strain units. The selected shear rates were 0.01, 0.1, 10, 100 and 150 s$^{-1}$ for measurement durations

of 100, 25, 5, 0.1 and 0.05 s respectively accumulating only 71 total strain units. For clarity only one flow curve is shown using the default settings. The flow curve with selected shear rates was performed in triplicate.

**Fig. 7.** Two flow curves of commercial Mozzarella cheese using different series of shear rate steps; Series 1: 0.01-0.1-1-10-100-200 s$^{-1}$ (■) with measurement durations of 100, 12.5, 5, 0.05, 0.05, 0.05 s respectively, performed in duplicate; Series 2: 0.05-0.5-5-50-150-250 s$^{-1}$(▲) with measurement durations of 50, 6.25, 2.5, 0.05, 0.05, 0.05 s respectively. The dotted line represents the power law regression model fitted on the pooled series. Total accumulated strain was 23 units for series 1 and 41 units for series 2.

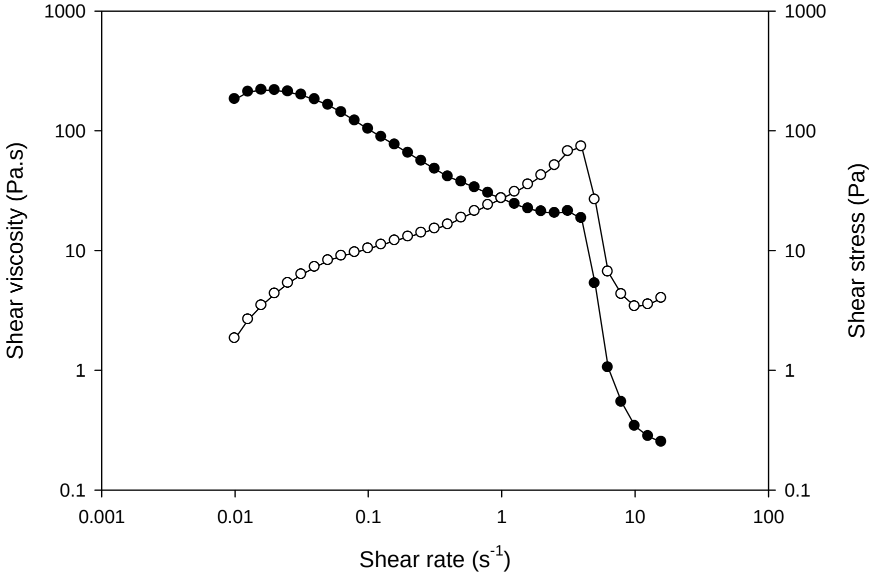
**Fig.8.** Shear viscosity, $\eta$ (♦) and complex viscosity, $|\eta^*|$ (□) as a function of shear rate and angular frequency to explore the applicability of the Cox-Merz rule to molten renneted casein gel. For oscillatory measurements the strain amplitude was 0.5%.

**Revised Table**

Table 1. Composition of Experimental Cheeses

| | Model Mozzarella | Commercial Mozzarella | Renneted Casein Gel |
|---|---|---|---|
| Moisture (g 100 g$^{-1}$) | 53.9 | 48.7 | 56.1 |
| Fat (g 100 g$^{-1}$) | 22.2 | 22.4 | 0.2 |
| Protein (g 100 g$^{-1}$) | 22.3 | 24.7 | 41.6 |
| Salt (NaCl) (g 100 g$^{-1}$) | 1.13 | 1.25 | - |
| pH | 5.5 | 5.4 | 5.6 |

**Revised Figure**



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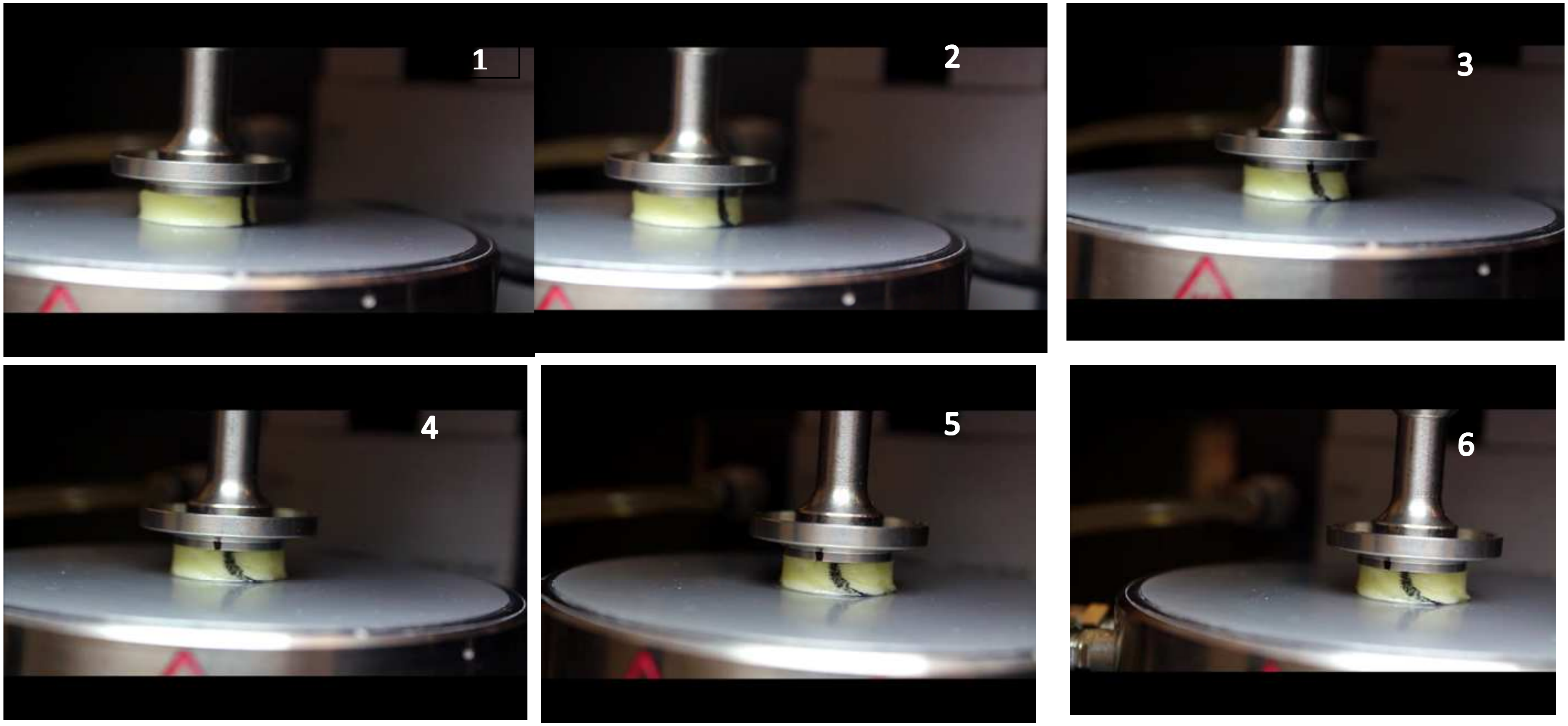

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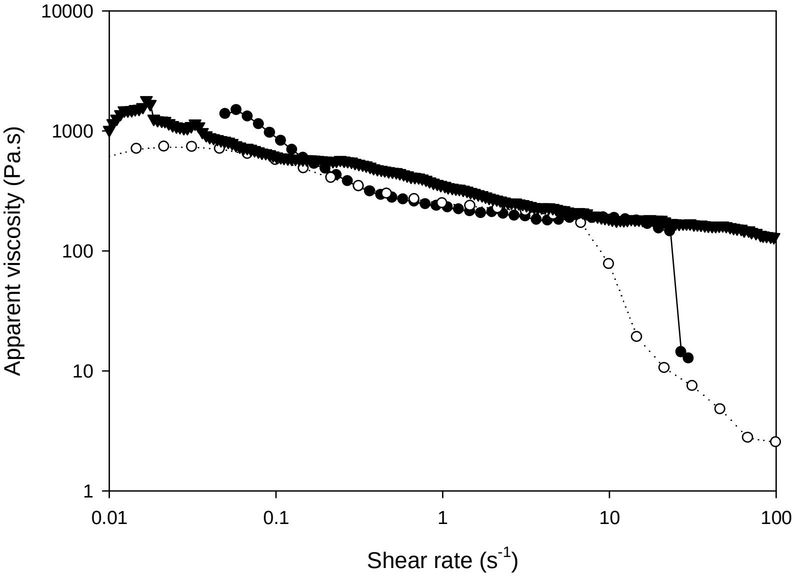

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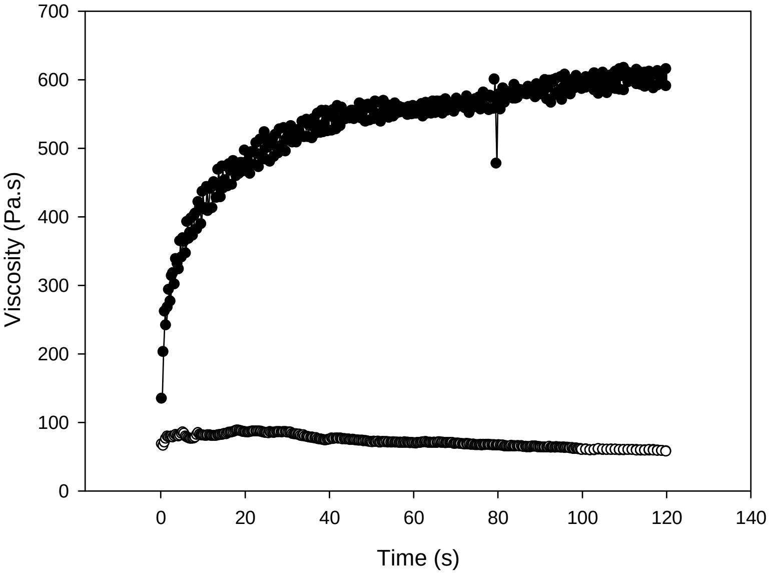

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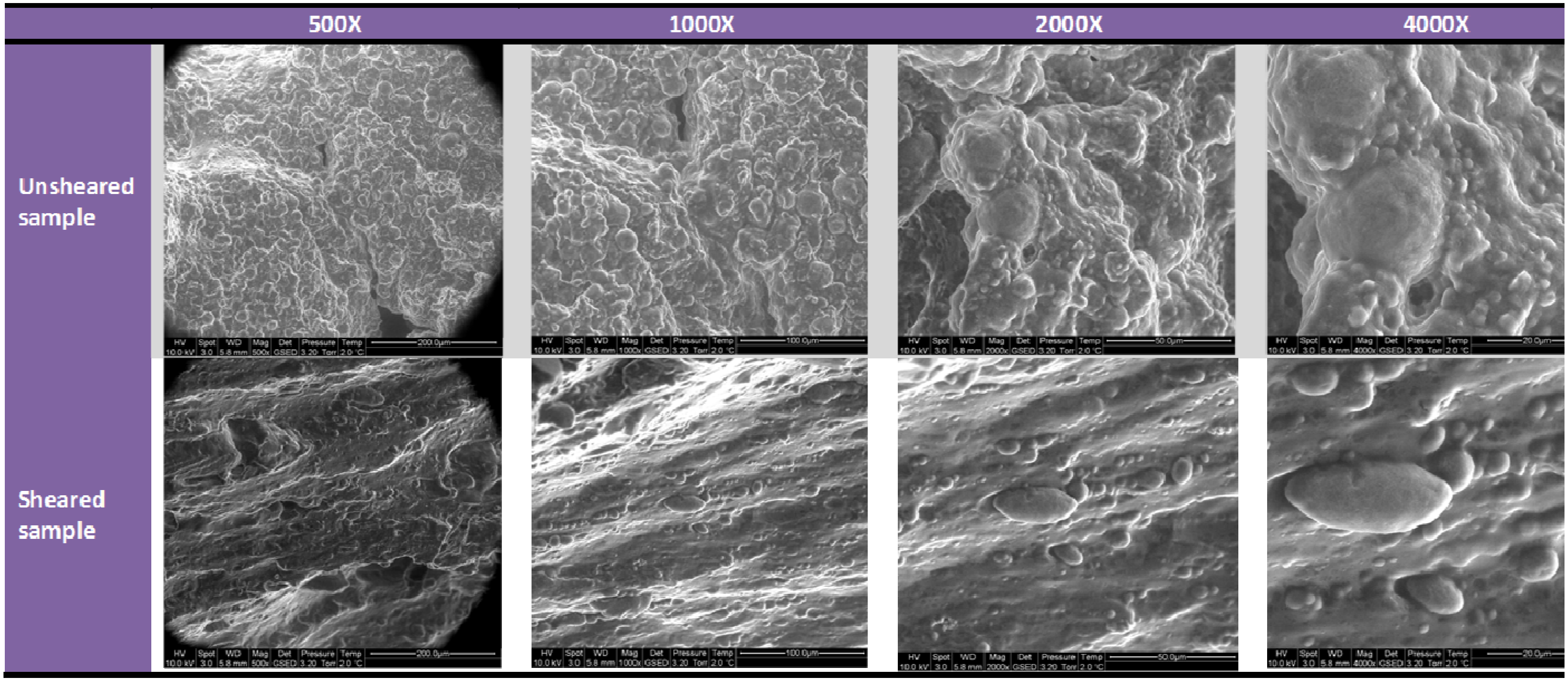

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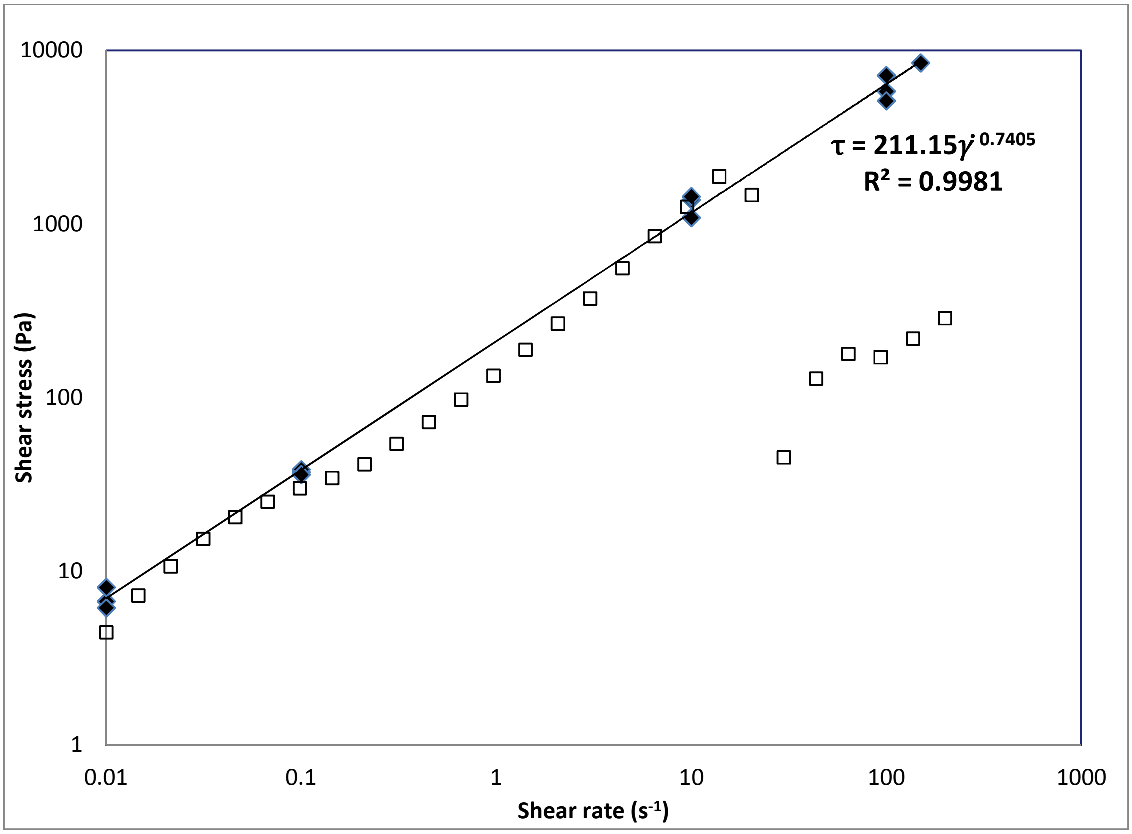

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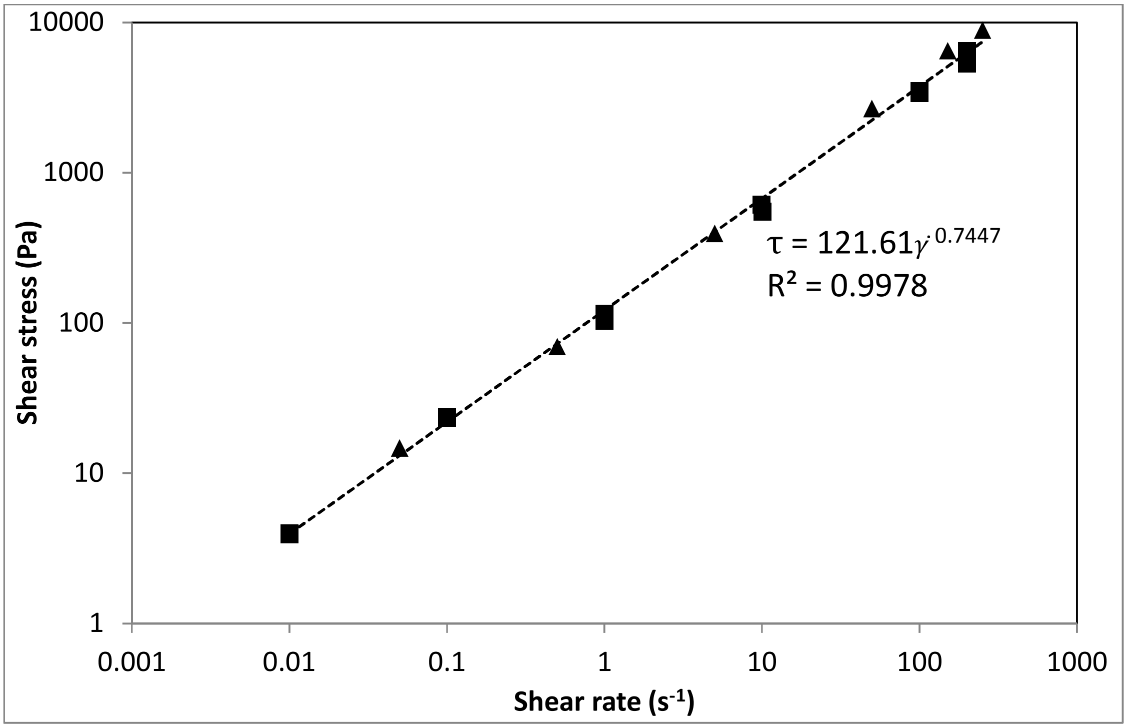

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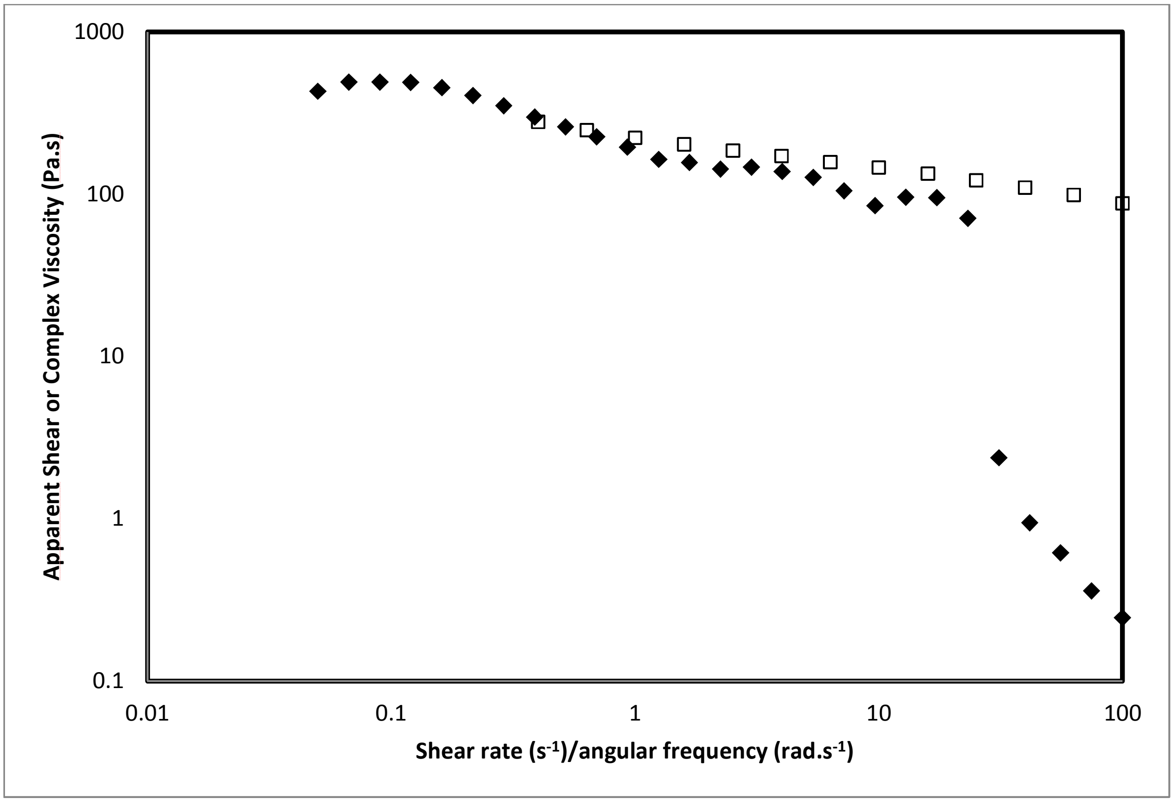

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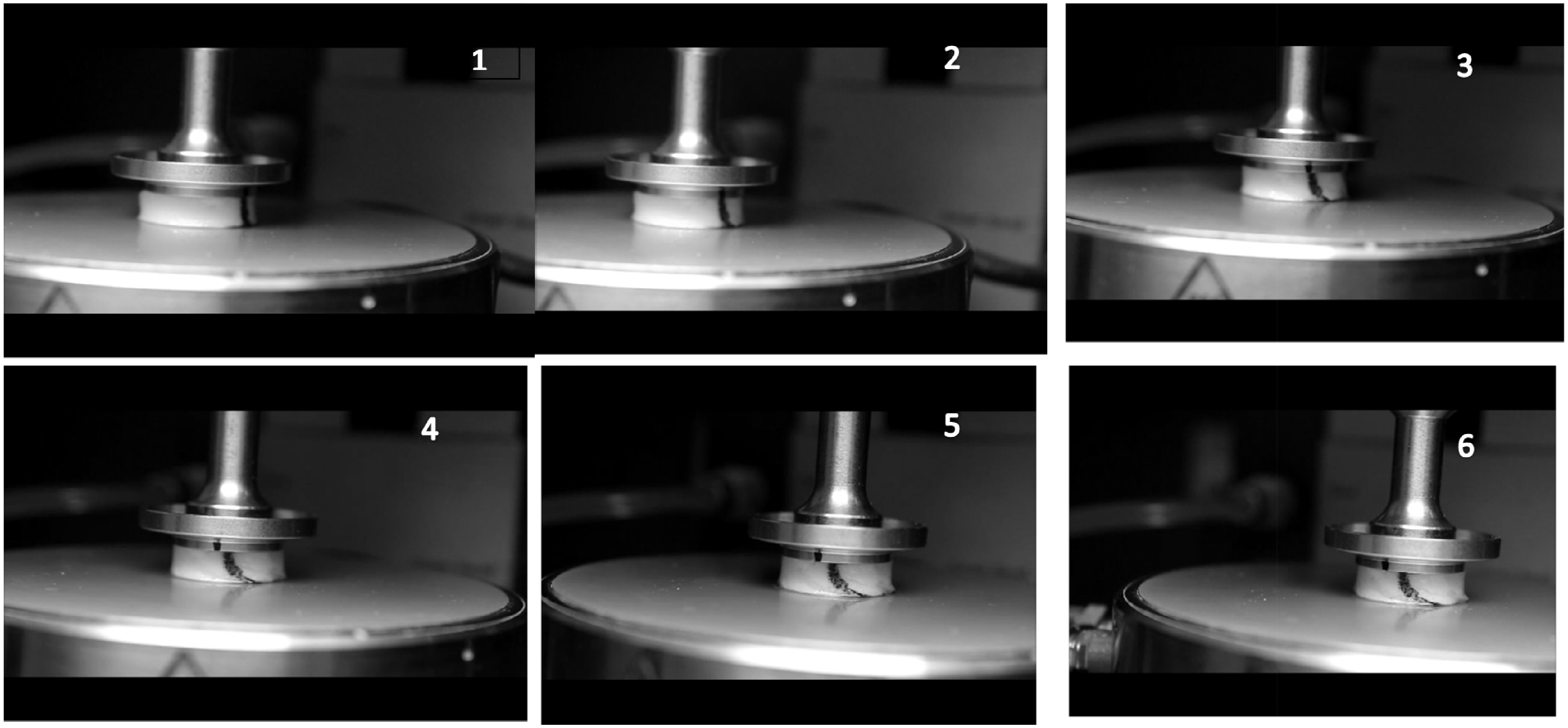
## Black and white version of Fig. 2



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