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Caroline E. Giacomina) and Peter Fischerb)

AFFILIATIONS
ETH Zürich, Department of Health Science and Technology, Institute of Food Nutrition and Health, Zürich 8092, Switzerland

Note: This paper is part of the special topic, Kitchen Flows.
a) Authors to whom correspondence should be addressed: caroline.giacomin@hest.ethz.ch and peter.fischer@hest.ethz.ch

ABSTRACT
An interfacial phenomenon can be observed in the kitchen in a cup of black tea. When tea is left to cool after steeping, a thin film at the air–water interface can form. In certain conditions, this film is observable by naked eye and, when disturbed, cracks visibly like sea ice. The mechanical properties of this interfacial film are assessed using bicone interfacial rheometry. Water hardness, acidity, the presence of sugar or milk, tea concentration, and brewing temperature all affect the formation of this film. Interfaces formed in hard water (200 mg CaCO3/L) exhibit increased elastic modulus vs those in moderately hard water (100 mg CaCO3/L), soft water (50 mg CaCO3/L), and Milli-Q water. All films formed in chemically hardened water exhibit yielding point behavior in the interfacial oscillatory shear. Film physical thickness shows no correlation with measured physical strength. Conditions forming the strongest film, chemically hardened water, may be industrially useful in packaged tea beverages for preferable shelf stability and for emulsion stabilization of milk tea products. Conditions forming weakened films, addition of citric acid, may be useful for dried tea mixes. In lab conditions, the film visibility is obscured due to purity of tea ingredients and careful washing. However, the film physically forms and can still be measured through interfacial rheometry.

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INTRODUCTION
An interfacial phenomenon can be visually observed in a cup of tea. The surface film that forms is brittle and mildly iridescent, and it cracks like ice floes when disturbed, see Fig. 1. Anyone can produce a cup of tea with just water and tea leaves, but the film may seem to randomly form in eyes of the everyday tea drinker. However, in a lab setting, this film can be carefully controlled. We investigate the rheological properties of tea film with varied calcium carbonate concentrations and the effect of additions provoked by some cultural tea practices.

Early work on tea films focused on thickness, kinetic formation, and composition of the film and was limited to black tea. Popular tea additions were also tested, including sugar, milk, and lemon juice. Spiro and Jaganyi uptook research on this film to evaluate the popular belief that this film came from the waxy coating on the tea leaves and concluded that the film does not come from the waxy coating. They focused on the chemical composition and physical thickness and then evaluated these films based on how transport phenomena and pH changes predicted the thickness deviations. The tea films were found to consist of oxidized tea polyphenols, calcium carbonate, and other salts; however, there are but two ingredients of a cup of tea: leaves and water.

All tea leaves come from the same plant, the Camellia sinensis (L.). While different cultivars of the Camellia sinensis (L.) exist, the leaf processing is what determines the tea variety produced, such as, fermentation, oxidization, rolling, steaming, and drying (see Fig. 2 of Ref. 6). Globally, 63% of tea consumed is black tea, while another 30% is green tea.

Water quality can be judged on a number of properties, including pH, total dissolved solids (TDS), and hardness. Dissolved calcium carbonate is the primary component considered in water hardness measurements. Water hardness has natural variability in groundwater and can vary widely depending on the local water resources and treatment. Across regions, and even within cities, the calcium carbonate of water samples can vary. Soft water is classified as having less than 60 mg CaCO3/L. 61–120 is classed as moderately hard, 121–180 is classed as hard, and beyond 180 mg CaCO3/L as very hard. When tea brewing is the goal, the ideal CaCO3 concentration is considered to be between 17 and 68 mg CaCO3/L. Below this, tea is astringent, while above 120 mg CaCO3/L, flavor is reduced.
The earliest known monograph on tea is a series of scrolls entitled Cha Jing (Classic of Tea) prepared by Lu Yu in the year 762 C.E.11
In his writings on tea preparation, Lu proposes the following "During the first boil, add a measure of salt appropriate to the amount of water to harmonize the flavor." Salted tea is still commonly made in Mongolian, Tibetan, Kazakh, and Himalayan traditions, though it has not become widespread beyond these regions. While Yu (from Hubei Province) was not from a region that currently has a large tradition for salted tea, it is assumed that the purpose of salt in the preparation by Yu was to clarify the water more than to provide salty flavor.10 No one knows why Yu proposed the salting step. We speculate that this step salted-out proteins, killed microbes, or balanced pH. The water–salting step will have a large effect on the ion content of the water. Salt addition holds the pH more constant during the brewing and changes the salts available for the film composition. Brewing tea itself reduces pH of the solution as tea polyphenols disperse in the solution.14 While water has been shown to affect the turbidity, color, and flavanol content of the brewed tea,17 most everyday tea drinkers continue to use local tap water. Tap water regionally varies; however, the European Union Drinking Water Directive specifies 40 and 80 mg Ca/l (equivalent to 100–200 mg CaCO3/l when all calcium comes from CaCO3) as optimal from a health point of view.13 Ion content of the water used has been shown to have an effect on the mass of the tea film formed such that de-ionized water forms no collectable film.14

The film is primarily composed of oxidized polyphenols, salts, and calcium carbonate.1 Lowering pH has been shown to have a positive effect on the extraction of theaflavin, a polyphenol, from black tea leaves.18 Since hydrogen ion rich environments allow for improved extraction of theaflavin, one could assume that more potential surface film forming material can be found in more acidic tea brews. However, the surface film contains other compounds that have not yet been fully elucidated.16 Moreover, from Eq. (3) of Ref. 2, we know that a lower pH actually leads to a thinner tea film. The addition of lemon juice forms an even thinner film than this equation predicts due to complexation of calcium ions with citric acid.2

CaCO3 is known to be a critical component in the formation of the tea film, but the film physical thickness has not been measured at varied CaCO3 concentration.2 The addition of sugar also has a thinning effect on the physical thickness of the tea film formed.2 Milk addition affects the composition of the formed film, but the film that is formed has been shown to be thicker for small additions of milk to tea.23 We study the effect of CaCO3 on tea film strength by measuring interfacial rheological properties and evaluate how the strength of films with additives compares to the prior work on physical thickness of the tea films formed with additives.

We perform rheological measurements for interfacial elastic and viscous moduli, G′ and G″, on the air–water interface of the tea film to enhance understanding about the brittle nature of the formed film. We identify the duration for formation, the rheological moduli of a stable film, and the force needed to crack the tea film in a variety of hardness conditions. Sugar, milk, and citric acid effects on the film are also measured. The insights to the tea film strength may be useful in the production of commercial tea beverages, and the film residues and stains left behind on the industrial tea brewing equipment.

**METHODS**

The effect of sample components on the tea film strength is determined with a 68.25 mm diameter, 2° bicone interfacial geometry on an MCR 702 TwinDrive Rheometer (Anton Paar, Graz, Austria).15 Strength is quantified with oscillatory rheology and expressed as interfacial elastic and viscous moduli. An interfacial time sweep experiment is run for 2 h with 0.3% interfacial shear strain at an angular frequency of 1 rad/s. This is followed by an amplitude sweep (approximately 0.5 h) from 0.1% to 100% shear strain at 1 rad/s to determine the interfacial shear strain break point of the film.

Surface tension was investigated with a bubble pressure tensiometer (BP59, Krüss GmbH, Germany) using capillaries of a 0.5 mm diameter.

ISO protocol 3103 outlines brewing instructions for tea preparation for sensory panels.17 Some modifications were made to ISO 3103 to facilitate the film formation and prevent film disruption. Loose leaf Ceylon black tea (Demet, Sri Lanka) was used for all experiments. The standard brew time was extended to the experiment duration (2.5 h). Leaves were removed at the standard 6 min, and the surface film forming is disrupted. Additionally, the mass of tea leaves added was reduced by half from ISO 3103 to be 1 g leaves per 100 ml water to prevent leaves from unfurling and disrupting the surface or touching the bicone underside. Brew temperature was also reduced to 60 °C to prevent the surface height drop caused by evaporation. Loose leaf tea is used to avoid any undesired effects from tea bag materials.18

We prepared six aqueous CaCO3 solutions: 0, 10, 25, 50, 100, and 200 mg/l. As appropriate citric acid, sugar, or UHT 3.25% milk fat (m.f.), milk was added to simulate lemon, sugar, and milk addition, respectively. The citric acid solution was made to mimic the citric acid concentration in lemon juice (48 g/l).19 Citric acid or milk each at 3 vol. % was simultaneously added with the water to brew. An assumption was made that slice of lemon is approximately one tenth of a lemon. Sugar was added at 1 g per 100 ml also at brewing onset. Each tea additive was individually measured and stirred using a spatula until either fully dissolved or dispersed to a uniform color throughout.

When interfacial forces are sufficiently large, the bulk effects can be neglected. The Boussinesq number, as well as the subphase drag subtraction, is used to make this determination.16,20 The viscosity of bulk tea was found to be 2.4 mPa s and Newtonian using a Couette-cup geometry with the 27.0 mm diameter on the same MCR 702. Other tea viscosities have been found to be on this same order of
Corrections for the subphase viscosity based on these methods were performed using RheoCompass software (Anton Paar, Graz, Austria).\textsuperscript{16,20}

RESULTS AND DISCUSSION

Effect of CaCO\textsubscript{3}

In water devoid of ions, Milli-Q water, supplemental CaCO\textsubscript{3} addition does not lead to a visible film. Tea made in the home with tap water has many other ions that contribute to the visible film. In lab conditions, the film visibility is obscured due to purity of tea ingredients, careful washing, and isolation of a single tap water component, CaCO\textsubscript{3}. However, this work addresses the role of CaCO\textsubscript{3} only, and with this, a non-optically observable film still forms and can still be rheologically measured (see Fig. 2).

In Fig. 2(a), the interfacial elastic and viscous moduli for a 2-h time sweep of the brew are shown. For 10, 25, 50, 100, and 200 mg CaCO\textsubscript{3}/L, the plateaus form after the first hour. Instabilities of interfacial moduli curves in the first hour are not investigated further in this work, but surface formation kinetics and cooling or drying may be involved. For the Milli-Q water, 0 mg CaCO\textsubscript{3}/L, no plateau is formed. Interfacial elastic modulus gives the elastic component of film strength. At an interfacial shear strain amplitude of 0.3%, elastic forces dominate over viscous forces for the concentrations of 50, 100, and 200 mg CaCO\textsubscript{3}/L and viscous forces are dominant for 0, 10, and 25 mg CaCO\textsubscript{3}/L. The inversion indicates a more flexible film microstructure at lower CaCO\textsubscript{3} concentrations.

When Milli-Q water is used to brew black tea, there is no perceptible film formed optically or rheologically. This confirms the work of Spiro and Jaganyi\textsuperscript{4} where a lack of ions dissuaded surface migration and formation of a tea film. A film can form that is optically imperceptible but still show surface strengthening in the time sweep. Surface strengthening is the formation of interfacial elastic and viscous moduli plateaus. Figure 2(a) confirms that there is no surface strengthening observed for Milli-Q brews with black tea. Figure 2(b) shows the time sweep stabilized plateau values for both interfacial elastic and viscous moduli. When the interfacial elastic modulus of the Milli-Q water brew is adjusted to remove the subphase flow,\textsuperscript{16,20} the value becomes negative and is not present on the logarithmic scale. A negative value here means that the subphase rheological influence is greater than the interfacial forces that can be detected.

Effect of additives

Figure 3 provides insights on how citric acid, milk, or sugar affect the elastic and viscous properties of the film formed when the tea is brewed with water and 200 and 100 mg CaCO\textsubscript{3}/L. The greater the interfacial moduli are, the stronger the film is. Figures 3(a) and 3(b) show that, when sugar is added, the film strength does not show a large difference in either the interfacial elastic or viscous moduli. These findings contrast with the prior work that demonstrated that tea film thickness decreases with sugar addition\textsuperscript{2} and the presumption that a thinner film would be rheologically weaker and confirm that physical thickness and strength are not directly related. This presumption was based on film composition being sparingly affected by the sugar due to the hydrophilicity of sugar, discouraging sugar presence at the surface. Thickness reductions exceed the predicted mass transfer corrections;\textsuperscript{2} however, Fig. 3 shows that this thickness reduction found by Spiro \textit{et al.} does not affect film physical strength. Citric acid caused moduli strength decreases of two orders of magnitude for both 200 and 100 mg CaCO\textsubscript{3}/L brews. Physical film thickness was also reduced in earlier work by adding lemon juice.\textsuperscript{2} This was explained by Eq. (3) of Ref. 2 and by complexation of calcium ions with citric acid.

Milk additions have been shown to increase film thickness\textsuperscript{15} but did not increase film strength. In these experiments, tea brewed with milk additions were the only samples to form visually observable films. This observation does not convey any information about physical thickness only that the refractive index of the milk tea film was visibly different from the milk tea subphase. Both Figs. 3(a) and 3(b) show milk addition weakening the interfacial moduli to unreliably surpass the lower instrument limit. This is suspected to be from the contributions of

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**FIG. 2.** (a) Interfacial moduli of black tea brews with varied CaCO\textsubscript{3} concentration measured during time sweeps with the shear strain of 0.3% and the angular frequency of 1 rad/s. (b) Moduli plateaus of the concentrations shown in (a). Closed circles are interfacial elastic modulus, $G'$, and open circles represent interfacial viscous modulus, $G''$. 

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milk lipids or proteins altering the chemical composition of the film proposed by Spiro and Chong, and we leave discernment of the effects of specific component to a later date.

**Mechanical film strength**

Amplitude sweeps are run for tea brews with the angular frequency 1.0 rad/s, and the results can be seen in Fig. 4. Concentrations of 100 and 200 mg CaCO₃/L require nearly identical shear strain (0.5–0.6%) for viscous losses to exceed elastic, therefore, for the interface to break. For the 50 mg CaCO₃/L brew, a slightly greater shear strain was required, of 0.8%, though the surface itself was weaker by almost one order of magnitude. Concentrations of 10 and 25 mg CaCO₃/L do not exhibit a distinct yielding point. In films for these concentrations, the interfacial viscous forces always exceed the interfacial elastic forces; therefore, there is no crossover to serve as a yielding point. The film is less deformable at higher CaCO₃ concentrations, but more brittle. Films with 50 mg CaCO₃/L are still elastically dominate and are the most resilient films for CaCO₃ concentrations measured herein. Additional amplitude sweeps beginning with the interfacial shear strain of 0.01 still did not yield an elastically dominant region for 10 and 25 mg CaCO₃/L; therefore, these films are entirely deformable.

Figure 5(a) shows that the addition of citric acid causes a 200 mg CaCO₃/L brew to behave like the 50 mg CaCO₃/L brew in Fig. 4, breaking at a larger shear strain of 1.5%, and presenting both moduli one full order of magnitude lower. Sugar did not affect the shear strain required for surface fracturing but showed greater difference between elastic and viscous moduli measured in the small-amplitude oscillatory interfacial shear region. For 100 mg CaCO₃/L brews with additions shown in Fig. 5(b), the citric acid behaved like the 200 mg CaCO₃/L brew, and the addition of sugar also showed greater difference between interfacial elastic and viscous moduli in the small-amplitude oscillatory shear region. However, sugar in 100 mg CaCO₃/L required a larger shear strain amplitude of 1.0% to break. This demonstrates more resilience of the sugared tea film in 100 mg CaCO₃/L. Though we also undertook surface tension measurements by bubble pressure tensiometry, we found no differences related to water hardness or additives. From this, we learn that tea film thickness and strength are determined by interfacial rheology rather than surface energy.

**CONCLUSION**

Interfacial rheological measurements can detect films imperceptible to the human eye. Tea film thickness does not directly correlate with film strength. In our oscillatory interfacial shear strain sweeps, tea films break at shear strains of about 1%. Citric acid can be added to tea to soften tea films and make them less brittle, breaking only at an interfacial shear strain of about 2%. Adding sugar does not generate a
more-glassy film than tea from hard water alone, leaving the strain at break unaffected. Conditions forming the strongest film may be industrially useful in packaged tea beverages for preferable shelf stability and for emulsion stabilization of milk tea products. The authors suggest making tea with hard tap water and without additives to best observe this interfacial phenomenon in the kitchen. Removing the tea leaves once brewing is complete affords best visibility. To view the phenomena without hard water, one can also neglect to wash the tea-cup and let the dissolvable minerals build up over a few uses.

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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