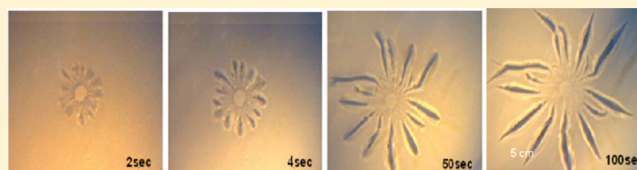


Surface Tension-Induced Gel Fracture. Part 2. Fracture of Gelatin Gels

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ABSTRACT: The spreading of surfactants on gel layers has been found to be accompanied by an intriguing instability which involves the formation of crack-like patterns on the surface of the gel. In an attempt to extend the findings on the spreading on agar gels presented in part 1 of this series, this paper examines the case of surfactant spreading on gelatin, which is a characteristic example of a protein-based gel.

Aqueous solutions of Silwet L-77 of varying concentrations were spread on thick gelatin layers of varying concentrations. The resulting pattern formation was found to have many similarities to the corresponding phenomenon on agar. In terms of spreading dynamics, the values of the spreading exponent, n , of the power law $L(t) \sim kt^n$, which describes the temporal evolution of the cracks, are similar to those of the agar case, within the predicted limits for surface tension gradient-induced spreading on thick films, highlighting the dominant presence of Marangoni stresses. However, the values of the spreading coefficient, k , are much smaller compared to those measured during the spreading on agar. Further observations are linked with the rheological properties of gelatin, which are also measured in detail.



1. INTRODUCTION

The spreading of uncontaminated and surfactant-laden liquids on the surface of condensed phases plays a key role over a wide range of industrial, biological, and daily life applications. These applications include coating flow technology, microfluidics, surfactant replacement therapy for neonates, film drainage in emulsions and foams, drying of semiconductor wafers in microelectronics, spreading of oils or enhanced spreading of pesticides, inkjet printing, and aerosol delivery of medication.^{1–8} The spreading process can exhibit an intriguing flow instability, which manifests itself by the formation of patterns that look like fingers, has been termed *fingering instability*. The formation of these fingers can be driven by intermolecular forces, by gravitational forces,⁹ and by surface tension gradients, which are the result of the presence of surfactants. In the latter case, these instabilities are the result of the so-called *Marangoni Effect*.^{10–12}

The understanding of Marangoni flow is important, as it is found in many common situations, and its high velocity makes it a popular transport mechanism in the field of medicine.¹³ Therefore, surface tension-gradient-driven fingering instability phenomena on the surface of liquids and solids have been the subject of a significantly large number of studies, both experimental and theoretical.^{14–34}

When the spreading occurs on the surface of an underlying compliant substrate, or a substrate of complex rheology, such as a polysaccharide agar gel, a different instability is observed; growing cracks are formed from the location of the deposition of a surfactant droplet and along the surface of the substrate.^{35,36} Investigating the specific type of instability is expected to provide improved understanding of the complex interactions between spreading liquids and underlying gellike

materials, which are central to numerous industrial and biomedical applications.^{13,37–41}

In part 1 of this study,⁴² it was shown that such gel surface fractures can occur during the spreading of different types of surfactants and inside a “window” of surfactant and agar gel concentrations. Apart from the “conventional” anionic SDS, the spreading of the nonionic Silwet L-77 was also investigated. Silwet L-77 belongs to a class of surfactants named “super-spreaders”, which are known for their ability to significantly reduce the surface tension of water and to promote highly rapid spreading, even on very hydrophobic substrates.^{43–50} The “superspreading” behavior of Silwet L-77 was also justified in the case of spreading on a gel, because it was observed that it can form cracks on a gel surface that grow much faster than the ones formed by the spreading of SDS.⁴² It was also suggested that, independently of the type of surfactant used, a fracture on an agar gel substrate occurs only within the experimental conditions where $S/\Delta w \geq G'$, with S being the surface tension between the surfactant and the gel, Δw being a change of the width of a crack, and G' being the storage modulus of the gel.

In this study, the case of the spreading on a different type of gel substrate is examined, to test the universality of the surfactant-driven gel fracture and to investigate the ways in which a substrate of different structural characteristics and rheology can potentially affect the observed pattern formation and the spreading dynamics. The substrate used consists of gelatin, which is a common example of a protein-based gel. As previously, droplets of aquatic Silwet L-77 solutions of

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concentrations below and above the cmc were deposited and subsequently spread on the surface of thick gelatin layers of different concentrations. The results for the different pattern morphologies and crack evolution rates are compared against the rheological characteristics of gelatin, which were obtained from appropriate and detailed rheological tests.

2. EXPERIMENTAL SECTION

2.1. Materials. The surfactant used in this study was the trisiloxane Silwet L-77 (polyalkylene oxide-modified heptamethyltrisiloxane 85%, from De Sangosse UK). Its cmc was measured with the Wilhelmy plate method and found to be $\approx 150 \pm 16$ mg/L at 20 °C. The surface tensions of all the surfactant and gel solutions were also measured using this technique. The surface diffusivity of Silwet L-77 was assumed to be on the order of 10^{-10} m²/s, which is characteristic of superspreading trisiloxane surfactants of similar molecular structure.⁵¹

The underlying substrates are made of gelatin, a protein-based gelling agent derived from the collagen present inside the skin and bones of animals. A gel is formed via the building of a triple-helix structure during the sol-gel transition.⁵² Aggregation of gelatin molecules takes place on cooling, and the system changes from a viscous solution to an elastic solid during gelation.⁵³ An increase in gelatin solution concentration results in a change from viscous fluids to gellike solids.⁵³

2.2. Experimental Procedure and Visualization Technique. The gelatin gel solutions were prepared by mixing gelatin powder (BDH Chemicals UK) with deionized water and heating the resulting mixture. After heating, the gels were allowed to set in a refrigerator at 4 °C for more than 24 h. To visualize and record the spreading, the experimental setup depicted in Figure 1 was used. This setup has been described in greater detail previously.⁴²

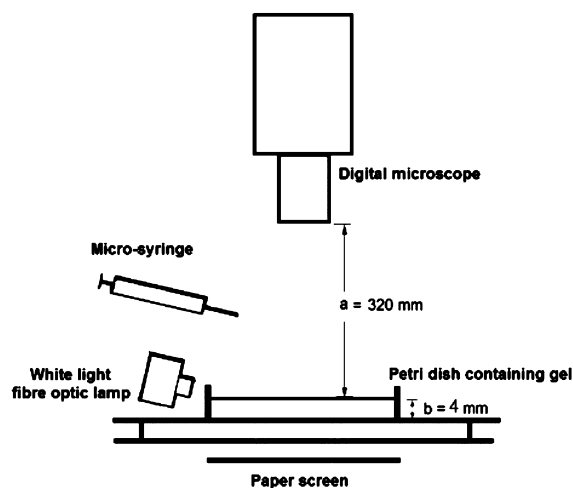


Figure 1. Schematic sketch of the experimental setup.

Five microliter drops of aqueous Silwet L-77 solutions were delivered to the surface of the gel using a 20 μ L precision microsyringe (from Hamilton UK). The gel rested inside 14 cm diameter circular glass Petri dishes, and the spreading was recorded at a rate of 30 frames per second, by a Dino X-Lite digital microcamera with a 1.3 megapixel resolution and a magnification capability of up to 500 \times (model AM-413M, from Dino-Lite Europe). The experiments were conducted at ambient temperature and humidity.

2.3. Rheological Characterization of Gelatin Gel Solutions.

The rheological properties of the gelatin gel solutions were measured with an AR-G2 rheometer (from TA Instruments USA), using parallel disks geometry and following the same technique that was described previously.⁴² The rheometer is equipped with a Peltier system which allows the temperature to be controlled with accuracy of ± 0.1 °C and with a 40 mm in diameter titanium rotating disk. The software of the rheometer depicts the applied and measured waveforms for each final

point of every oscillatory measurement, allowing a facilitated distinction between in-phase or out-of-phase results.

Any measurement for gelatin gels reported herein was made after the minimum time period of 24 h that the solution was left inside the refrigerator. Also note that the viscoelastic response of gelatin gels strongly depends on the thermal history of the sample and on the actual temperature of the measurement; for instance, the storage modulus of 1.1 wt % gelatin from 4 °C to 20 °C decreases from 19 to 3 Pa. Accordingly, for 1.7 wt % gelatin from 4 °C to 20 °C, it decreases from 100 to 20 Pa. Another difference from the agar gels was the fact that the adequate gap for nondistorted waveforms was smaller, i.e., 650 μ m for the 0.7 wt % gelatin, 850 μ m for the 1.1 wt % gelatin, and finally 1000 μ m for the higher concentration of 1.7 wt %. Concerning the effect of time over the values of G' and G'' for dense gels, the observed drift to higher values of G' and G'' in 0.14 wt % agar was also observed in gelatin gels; indeed, it is more pronounced. Results for 1.1 wt % over approximately 4 days are shown in Figure 2.

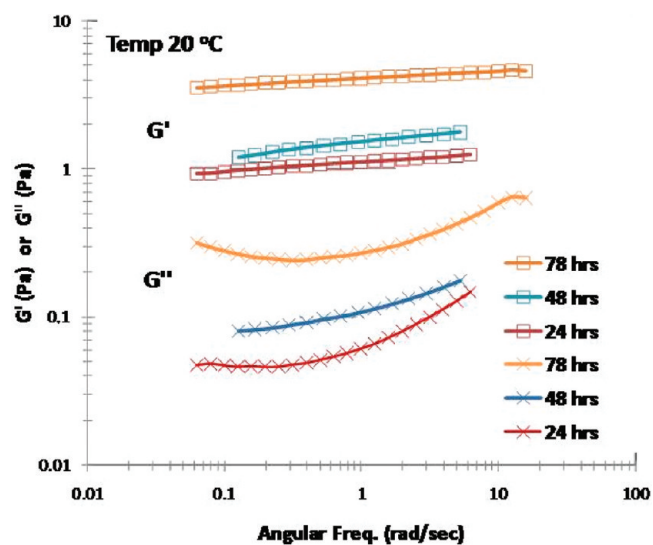


Figure 2. Effect of time over the values of G' and G'' for gels of 1.1 wt % gelatin. In this and subsequent figures, the lines connecting the data points are for guidance of the eye.

It must also be pointed out that the gelatin storage modulus G' was about 1 order of magnitude higher than the loss modulus G'' for applied frequencies of 0.08 to 10 rad/s. For the higher concentration of 1.7 wt % gelatin, however, a greater divergence between G' and G'' was observed, while for the lower concentration (0.7 wt % gelatin), the G' was higher than the G'' only by a factor of 2.5. These results are presented in Figure 3. For the concentrations of 1.1 wt % and 1.7 wt % gelatin, the raw phase difference between the applied strain and the resultant stress of the gels was between 1.5° to 3.5°, indicating fairly elastic behavior; yet, in the lower gelatin concentration of 0.7 wt %, the raw phase difference was approximately 20°. This observation is in line with the increased applied strain of 15% for the lower gelatin concentration; the higher the strain for clear and nondistorted waveforms, the more reduced the gellike behavior of the fluid. As Figures 2 and 3 show, for the concentrations of 1.1 wt % and 1.7 wt %, the storage modulus is constant over wide ranges of frequencies, while the loss modulus appears more affected by the measurement parameters.

Most of the reported results for gelatin correspond to concentrations over 1% and to lower temperatures, e.g., 16 °C. Direct comparison with these results is difficult to make because the thermal history of the gels plays a crucial role in rheological behavior of gelatin gels. Hence, by using the terminal values for the mechanical properties of the gelatin gels in Figure 3, the effect of gelatin concentration on the G' and G'' can be illustrated (Figure 4).

By comparing the corresponding results of the rheological characterization of agar⁴² with the ones presented here, and by taking

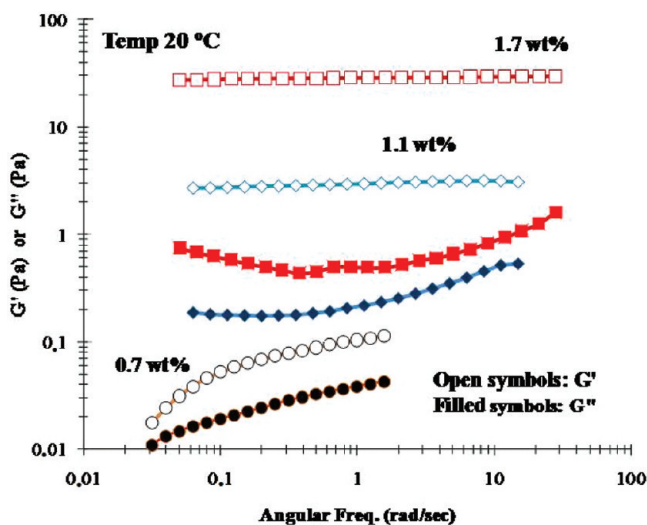


Figure 3. Frequency sweeps for gelatin of 0.7 wt %, 1.1 wt %, and 1.7 wt % gelatin.

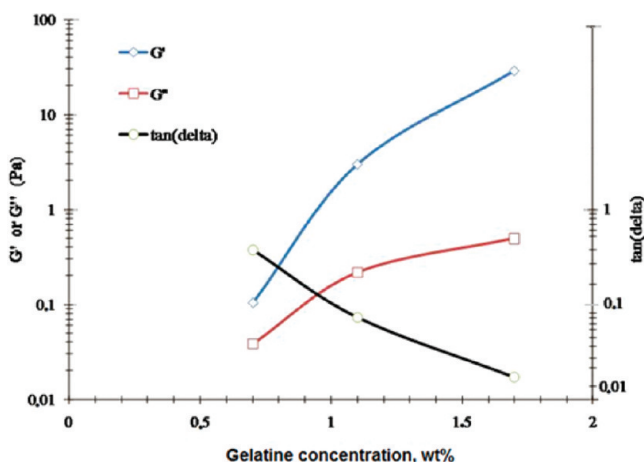


Figure 4. The effect of wt% gelatin concentration on G' and G'' .

the G' as a measure of elastic behavior, the same G' values will be expected for gelatin concentrations of 1 order of magnitude higher than the agar concentrations. In addition, the more sensitive parameter of $\tan \delta$ (where $\tan \delta = G''/G'$) shows that there is more balanced correlation of G' to G'' for the agar gels. It is postulated from the data trend in Figure 4 that also the gelatin data will reveal this balanced correlation of G' to G'' (or $\tan \delta$ almost constant) after 2% to 3% in gelatin concentration.

Finally, the steady-state flow curves of the gelatin gels, for the investigated concentrations, are presented in Figure 5. These “down” curves (decreasing $\dot{\gamma}$ -values) reveal extensive plateau values over 3 orders of magnitude of $\dot{\gamma}$, i.e., $10^{-4} \text{ s}^{-1} < \dot{\gamma} < 10^{-1} \text{ s}^{-1}$. Although the shape of the curves related to higher concentrations is not smooth, yield stress values of 1 and 10 Pa could be associated with 1.1 wt % and 1.7 wt %, respectively, while a good approximation for the yield stress for the 0.7 wt % gelatin would be a value of 0.08 Pa. The ascending curves (not shown here) were similar to the ones of agar, having a negative slope around $10^{-1} \text{ s}^{-1} < \dot{\gamma} < 1 \text{ s}^{-1}$, indicating that these highly structured fluids begin to flow by forming bands, and after an increased $\dot{\gamma}$ -value, the sample behaves as a homogeneous material.

3. RESULTS

Spreading of Silwet L-77 on Gelatin Gels. After the deposition and subsequent spreading of aqueous Silwet L-77 solution droplets on the surface of gelatin gel substrates, and

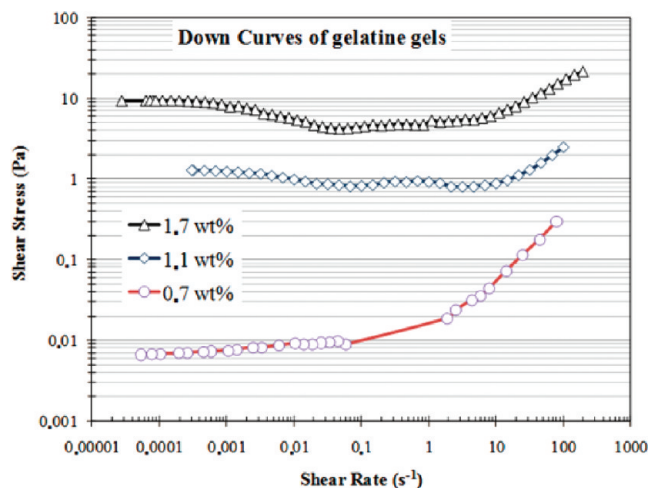


Figure 5. The steady-state flow curves of gelatin samples of different concentrations.

under specific surfactant and gel concentration regimes, crack-like patterns were observed. These are, in general, morphologically similar to those reported on agar,^{35,36,42} because they are shaped and grow in “starburst” formations.

The main difference compared to the spreading on agar is that the cracks are now formed for much higher gel concentrations. More specifically, visible crack patterns can be observed for gel concentrations between 0.7 wt % to 1.7 wt %, 1 order of magnitude higher than the 0.04 to 0.14 wt % limits reported so far for agar. Cracks are seen for a very wide range of surfactant concentrations, from below the cmc, to well above the cmc. However, the quantitative characteristics of the patterns do not change much after the surfactant concentration exceeds 10 cmc. The results obtained from the deposition and spreading of Silwet L-77 droplets on the surface of gelatin gels are summarized in the pattern map presented in Figure 6. Changes in the system parameters, which are the surfactant and gel concentrations, promote discernible variations in the morphologies observed. Lower gel concentrations such as 0.7 wt % and 0.9 wt % show wider and more clearly visible major arms. Intermediate gel strengths such as 1.1 wt % and 1.3 wt % give interesting crack patterns with a large number of “arms”. Branching arising from the major spreading “arms” is also observed in these concentration regions. For gelatin concentrations between 1.5 wt % and 1.7 wt %, the “arms” are much thinner and fewer in number with minimal branching. For gelatin concentrations outside the range of 0.7 wt % to 1.7 wt %, no visible crack patterns or other signs of deformation are observed. On extremely weak gel samples below 0.7 wt %, surfactant droplets spread as they would on any liquid substrate. Also, on high gel strength samples above 1.7 wt %, the droplets remain essentially axisymmetric.

Varying the surfactant concentration also gives interesting comparative results. Lower surfactant concentrations such as 0.5 cmc and 2 cmc give relatively thinner and fewer arms. However, higher concentrations, between 10 cmc and 100 cmc, are characterized by patterns with much wider “arms” and considerable branching. Similarly to agar, the presence of ridges along the “arms” is common among gelatin concentrations below 0.9 wt % (Figure 7), and branching wisps are also common among gelatin concentrations above 0.9 wt % (Figure 8). Elements of both of these morphologies can be seen in gelatin concentrations of 0.9 wt %.

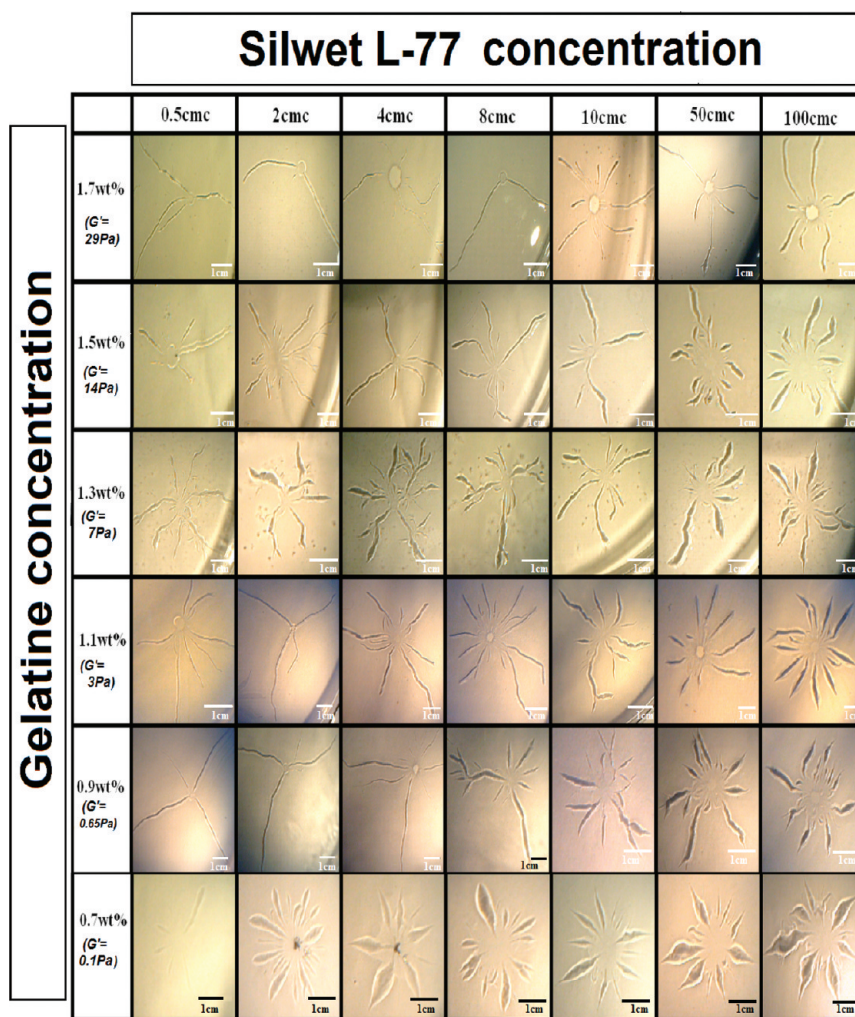


Figure 6. Pattern map showing fully developed patterns from Silwet L-77 droplets of different concentrations which have spread on approximately 4 mm thick gelatin gel layers of varying concentrations.

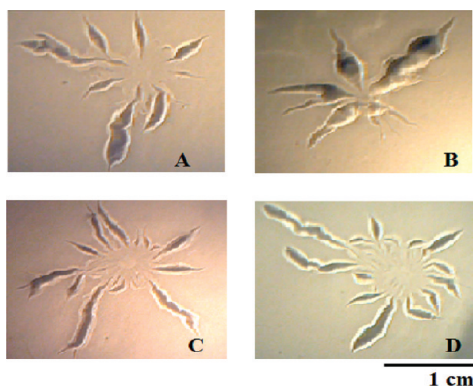


Figure 7. Ridges flanking the “arms” of fully developed patterns after the spreading of (A) Silwet L-77 10 cmc on 0.8 wt % gelatin, (B) Silwet L-77 30 cmc on 0.8 wt % gelatin, (C) Silwet L-77 50 cmc on 1.5 wt % gelatin, and (D) Silwet L-77 100 cmc on 0.9 wt % gelatin.

A typical example of the spatiotemporal evolution of the patterns on gelatin is shown in Figure 9. The evolution of the patterns can last for much longer times compared with agar, even up to 100 s. Another strikingly interesting observation in the case of gelatin only is what seems to be a rapid “self-healing” behavior. The cracks formed by the spreading of Silwet

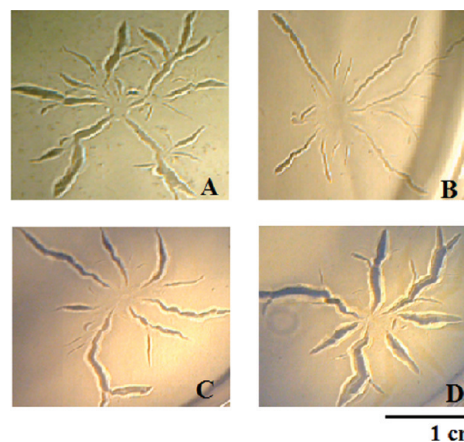


Figure 8. Branching wisps observed on fully developed patterns after the spreading of (A) Silwet L-77 4 cmc on 1.3 wt % gelatin, (B) Silwet L-77 2 cmc on 1.5 wt % gelatin, (C) Silwet L-77 10 cmc on 1.1 wt % gelatin, and (D) Silwet L-77 30 cmc on 0.9 wt % gelatin.

L-77 on gelatin layers close in just a short span of time after their formation. In some cases, it is observed that the cracks begin to close while the major arms are still propagating outward from the point of deposition (see Figure 10). The

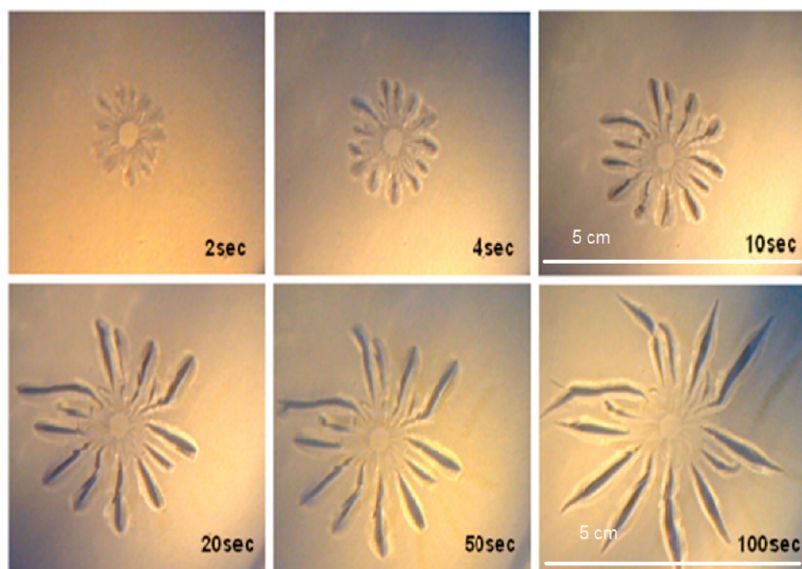


Figure 9. Spatiotemporal evolution of a pattern formed on the surface of a 1.1 wt % gelatin gel after the deposition and spreading of a Silwet L-77 100 cmc droplet. After $t = 100$ s, the evolution was completed.

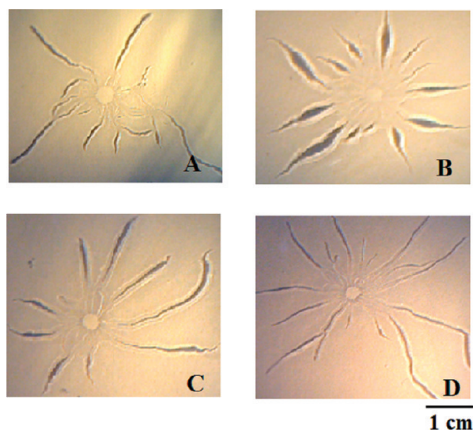


Figure 10. "Self-healing" of patterns formed from the spreading of (A) Silwet L-77 20 cmc on 1.1 wt % gelatin, (B) Silwet L-77 30 cmc on 0.9 wt % gelatin, (C) Silwet L-77 50 cmc on 1.1 wt % gelatin, and (D) Silwet L-77 8 cmc on 1.1 wt % gelatin.

gelatin layer heals itself, and this phenomenon begins to occur from the drop deposition spot outward.

During a typical spreading process of liquids on liquids or on solids, the spreading front advances with time following a power law that is generally accepted to have the following form:

$$L(t) \sim kt^n \quad (1)$$

where $L(t)$ denotes the radial extent of spreading, k is a prefactor, t is the spreading time, and n is the spreading exponent. The value of the spreading exponent can give an indication of the balance of forces that are involved in the spreading.⁵⁵ Herein, L will denote the length of a spreading crack or "arm". The values of n and k are obtained from logarithmic plots of the evolution of the length of each one of the cracks of each pattern observed. Because a crack can have a different exponent value compared to other cracks of the same pattern, a single spreading exponent for each pattern is determined through averaging the various spreading exponent values of the individual cracks. The results are shown in Figure 11.

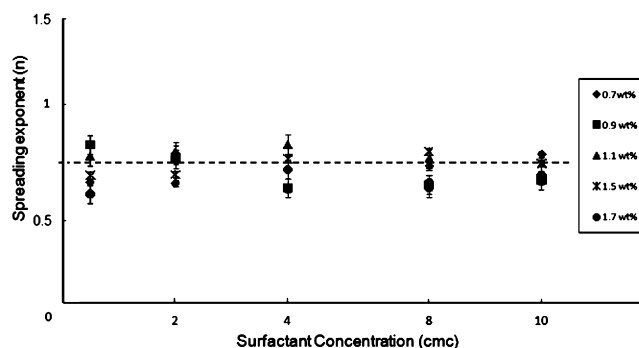


Figure 11. Variation of the spreading exponent with Silwet L-77 concentrations, for spreading on gelatin gel layers of different concentrations. These points represent the average of multiple runs. The dashed line is the theoretically predicted value of $3/4$ which is characteristic of Marangoni-driven spreading on thick films.^{55–57}

Independently of gel and surfactant concentrations, the majority of the values of n were found to be very close to $3/4$, similarly to the case of Silwet L-77 spreading on agar gels.⁴² This highlights an agreement with the $t^{3/4}$ scaling prediction, associated with the Marangoni-driven spreading of a finite mass of surfactants on thick films^{55–57} and suggests that Marangoni forces play a significant role in the spreading.

The crack evolution rate is determined by differentiating eq 1, which gives:

$$\frac{dL}{dt} = nkt^{n-1} \quad (2)$$

where dL/dt is the velocity of evolution of a crack, and by fitting $n = 3/4$ in eq 2, which gives:

$$\frac{dL}{dt} = \frac{3}{4}kt^{-1/4} \quad (3)$$

From eq 3, k can provide a measure of the crack propagation velocity. On this basis, the values of k , and thus the crack propagation velocities measured for gelatin substrates, are the lowest reported in either parts of this study. This is

demonstrated by the fact that the values of k measured here are smaller than those measured for the spreading on agar.⁴² Figure 12

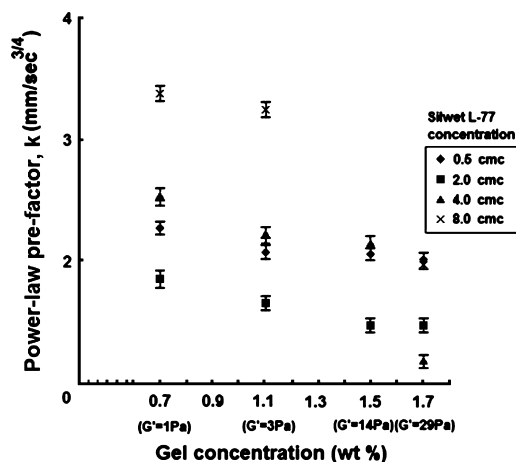


Figure 12. The dependence of the power-law prefactor k on gelatin gel concentration for spreading of Silwet L-77 droplets.

summarizes the different values of k found for different gelatin gel and Silwet L-77 concentrations. The minimum value of k is observed for a 4 cmc Silwet L-77 drop spreading on a 1.7 wt % gel, and the maximum value of k is reported for a 8 cmc Silwet L-77 drop spreading on a 0.7 wt % gel. Therefore, the velocities related to spreading on gelatin are slightly smaller than those related to SDS spreading on agar and much smaller than those related to Silwet L-77 spreading on agar.⁴² Similarly to the previous cases, it is observed that k decreases with increasing gel concentration and strength.

The evolution of the “arms”/cracks is faster for weaker substrates. This is also demonstrated in Figure 13 where dL/dt

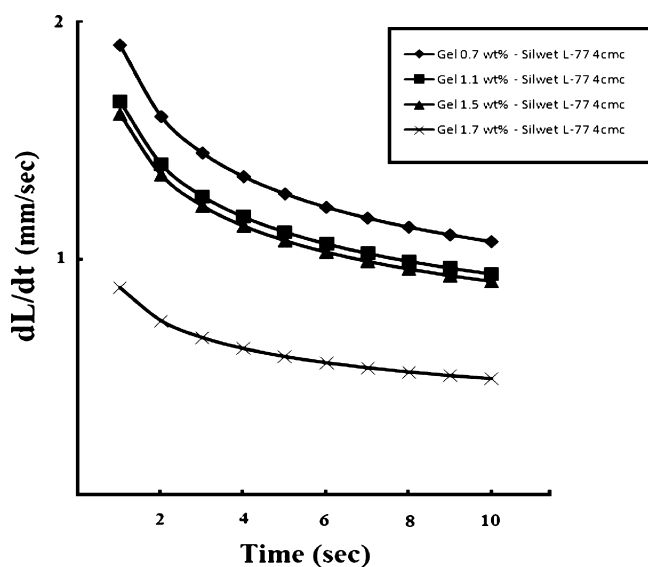


Figure 13. Plot of dL/dt against time for spreading of a 4 cmc Silwet L-77 droplet on gelatin gels of varying concentrations.

is plotted against time for different gelatin gel concentrations. It is observed that dL/dt decreases with increasing gel concentration and that it achieves its highest values for early times in each case.

Neither an increased Silwet L-77 concentration nor an increased gelatin concentration seems to affect the number and the length or the “arms” formed. However, as Figure 14 shows,

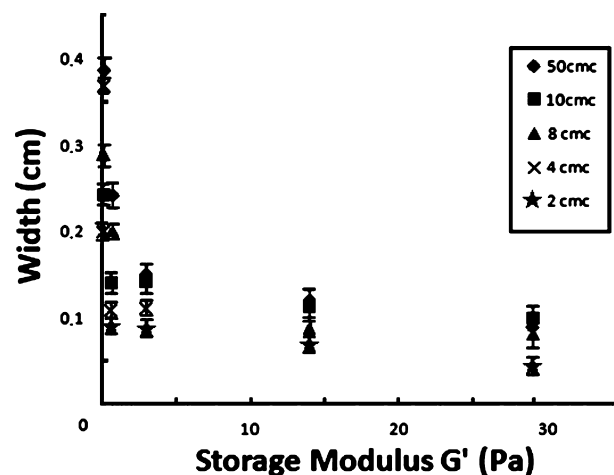


Figure 14. Dependence of the width of the pattern “arms” on storage modulus of gelatin. Each width was measured after the completion of any self-healing process, and each point represents the average of multiple runs. $G' = 0.1$ Pa corresponds to 0.7 wt % gelatin, $G' = 0.65$ Pa corresponds to 0.9 wt % gelatin, $G' = 3$ Pa corresponds to 1.1 wt % gelatin, $G' = 14$ Pa corresponds to 1.5 wt % gelatin and $G' = 29$ Pa corresponds to 1.7 wt % gelatin.

the width of a crack decreases with increasing gelatin gel concentration (strength). The same behavior was reported for the spreading of surfactants on agar, in part 1 of this study.⁴² For gel concentrations of 1.7 wt % ($G' = 29$ Pa), the “arm” widths are the smallest observed on both substrate types.

4. DISCUSSION

Compared to the spreading of the Silwet L-77 on agar, the most evident difference is that the cracks can now be seen for gel concentrations 1 order of magnitude higher than in the case of agar. However, this is to be expected because these gelatin concentrations used here, namely 0.7 wt % to 1.7 wt %, have associated storage moduli similar to the ones attributed to the agar concentrations tested previously, namely 0.04 wt % to 0.14 wt %, suggesting that both substrates are broadly of the same strength for the relevant concentration limits and therefore offer similar resistance to spreading and crack formation. The only exception is the 1.7 wt % gelatin concentration, where the value of the storage modulus is somewhat higher ($G' = 29$ Pa) than the ones observed usually on agar, and in this concentration region the thinnest “arms” are reported.

Another notable difference is the “self-healing” tendency of the gelatin, with the cracks being able to close even before the pattern has been fully developed. “Self-healing” can be seen also in the case of agar; however, it takes much longer times and it starts only after the “arms” have developed fully. One may expect that the fast “self-healing” behavior of gelatin is linked to its rheological properties; however, the gelatin concentrations tested here represent storage modulus values similar to those associated with the agar concentrations tested in the previous parts of this study. The only exception is the 1.7 wt % concentration region, where $G' = 29$ Pa, which is larger than the modulus of the highest agar concentration (15 Pa). Therefore, the roots of this difference should be attributed to the loss

modulus (G'') of gelatin which, for the concentrations studied here, varies from 0.04 to 0.5 Pa. These values are smaller compared with the corresponding values for agar, which vary from 0.14 to 2 Pa. Gelatin exhibits a lower loss modulus, and hence a lower viscosity compared to agar, which can lead to a faster flow that occurs simultaneously with crack propagation and therefore result in healing. In agar such healing is slower because of the higher loss modulus and hence viscosity of the gel.

On the same pattern, not all “arms”/cracks were found to grow following a scaling relationship $L(t) \sim kt^n$ with the same value of n . This can be explained by the high degree of local heterogeneities on the surface of the same gel. The reason behind these local heterogeneities should be attributed to the structure of the gel, which is formed from heterogeneous populations of molecules with different properties.⁵⁸ In addition, as a crack evolves, it can prevent the evolution of a neighboring crack, by altering the local growth conditions, such as the concentration gradients. However, as Figure 11 shows, when a single spreading exponent value is considered for each pattern, n constantly achieves values very close to 3/4 in the majority of instances, independently of surfactant and gel concentrations. Hence, there is an agreement with the $t^{3/4}$ scaling prediction, characteristic of Marangoni-driven spreading of a finite mass of surfactant on thick films^{55,56,59–62} indicating that Marangoni forces are dominant in the Silwet L-77–gelatin system. Even though most previous studies consider spreading on viscous liquids, the $t^{3/4}$ prediction is still confirmed for the spreading on gelatin gels and is in agreement with the corresponding values for spreading on agar gels.^{35,36,42} Therefore, considering only the spreading exponent as a means of describing the “arm” propagation, it would be concluded that the spreading dynamics of surfactants are similar on agar and gel substrates. However, the consideration of the power-law prefactor, k , reveals a different picture, which is more suitable with what the experimentalist observes; the “arm” evolution velocities on gelatin are the lowest observed in both parts of these study. Figure 12 demonstrates that the maximum value that k achieves in all the spreadings on gelatin is lower than 4 mm/s^{3/4}, while the corresponding values for spreading on agar can exceed 15 mm/s^{3/4}.⁴²

Considering the dominant presence of Marangoni stresses in Silwet L-77–gelatin systems, it can be suggested that the main driving force behind the cracking process is the presence of surface tension gradients between the surfactant and the gel. The spreading coefficient determines whether a drop will spread on the gel surface and is defined as:⁶³

$$S = \sigma_g - \sigma_d - \sigma_{gd} \quad (4)$$

where σ_g , σ_d , and σ_{gd} denote the surface tensions for the gel–vapor, droplet–vapor, and gel–droplet, respectively. Equation 4 can be written as $S \equiv \sigma_g - \sigma_d$ because σ_{gd} can be considered almost equal to zero because the surfactant droplet and the gel consist mainly of water.^{35,36} In all cases, $S \geq 0$ for the droplet to be allowed to spread. The surface seems to be cracked only when the surface tension gradient can generate Marangoni stresses that are strong enough to overcome the resistance of the rigidity of gelatin. The cracks appear only inside a certain “window” of surfactant and gel concentrations. To quantify this, the width or the “arms”/cracks are considered to play an important role in the cracking process; this is highlighted by the fact that from the physical characteristics of a crack, only its width seems to have a correlation with the rheological characteristic of the gel substrate, because the width seems to

decrease while the shear modulus of the gel increases (Figure 14). This is also evident on agar. The difference in surface tensions over a change of the width of a crack (Δw) can represent a stress that compares with the storage modulus of the substrate. A surface tension gradient can overcome the rigidity of the substrate when:

$$\frac{S}{\Delta w} \geq G' \quad (5)$$

A comparison of $S/\Delta w$ against G' for Silwet L-77 spreading on gelatin, illustrated in Figure 15, shows that inequality 5 is

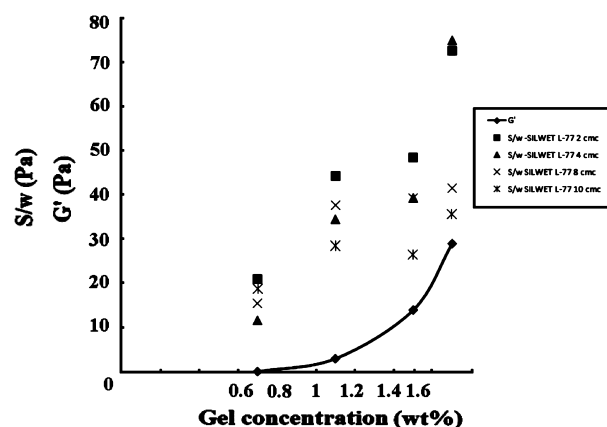


Figure 15. $S/\Delta w$ and G' against gelatin gel concentration, with Silwet L-77 concentration varying parametrically. $S/\Delta w$ is consistently greater than G' wherever cracking patterns are observed.

valid for all the surfactant and gelatin gel concentrations that allowed a cracking pattern formation. This is also the case for SDS and Silwet L-77 spreading on agar gels, as shown previously;⁴³ hence, there is indication that inequality 5 can be universal for surface tension-induced cracking formation on gellike substrates. It might be also possible to use inequality 5 to estimate the width of a crack, by dividing S by G' .

While Marangoni stresses are dominant, other forces might play an important role in the system. The surface Peclet number, defined as $Pe_s = SH_o/\mu D_s$, where H_o and μ denote the thickness and the viscosity of the underlying substrate, respectively, and D_s denotes the surface diffusivity, can reveal the relative strength of Marangoni stresses over surface diffusion effects. Here S achieves values between 33 to 45 mN/m, and L varies from 0.005 to 0.046 m; therefore, Pe_s is of the order of 10^8 . This indicates that Marangoni stresses dominate surface diffusion. The bulk Peclet number, Pe_b , defined as $Pe_b = UH_o/D_b = \varepsilon(SH_o/\mu D_b)$, where $\varepsilon = H_o/L_o$ is the developed crack aspect ratio, is a measure of the relative strength of Marangoni stresses to bulk diffusion effects. Here Pe_b is in the order of 10^6 , suggesting that Marangoni stresses dominate bulk diffusion as well.

The Bond number, Bo , can reveal the relevant strength of Marangoni stresses over hydrostatic pressure and is defined as $Bo \equiv \rho H_o^2 g/S$,⁶⁴ where ρ denotes the density of the underlying fluid and g denotes the gravitational acceleration. Bo can usually have a high value for low surfactant concentrations on thick underlying substrates. Here Bo varies between 3.5 to 4.8, indicating that gravitational forces are significant, similar to the case of Silwet L-77 spreading on agar. The significance of gravitational forces might be responsible for preventing further growth of the cracks, through a flow reversal effect that can

occur when hydrostatic forces overwhelm the relaxed Marangoni stresses with time.⁶⁴

5. CONCLUSIONS

The results presented here provide insight into the interactions between spreading surfactant-laden liquids and underlying gelatin gel substrates. This can contribute to the control and improvement of a large number of processes that involve systems of gellike materials and liquids. The spreading of aqueous Silwet L-77 solution droplets on gelatin gel layers was found to be accompanied by the formation of cracking patterns, in “starburst” formations. The universality of the surfactant-driven gel fracture is demonstrated; this phenomenon is reported not only on agar, as shown previously, but also on gelatin, which is a protein-based gel. It is therefore possible that surface instabilities or cracks can occur on gellike materials of any type, including the mucus-laden films in the human lung. By using surfactants, it could be possible to crack such mucus and clear the airways of the lung, improving respiration.

Most characteristics of the spreading found for agar were also observed here, with the main difference being the crack evolution velocity, which is much lower in the case of gelatin, as indicated by the small values of the spreading coefficient, k , of the $L(t) \sim kt^n$ power law. Marangoni stresses are dominant during the spreading in all cases examined, because the spreading exponent, n , was found to have values close to 3/4 in majority, resembling the prediction for Marangoni-driven spreading on thick layers and similar to what was the case for spreading on agar.

It is evident that the cracking patterns can be formed only inside a “window” of surfactant and gel concentrations, which represents an “intermediate” state of the gel, where it exhibits both solid-like and liquid-like behaviors. Inside this window, the surface tension gradient between the surfactant and the gel can generate a stress which is higher than the rigidity of the gel. There is also evidence that the width of the cracks plays a significant role in the cracking. Via the suggested inequality $S/\Delta w \geq G'$ that was found to be valid for all the gel and surfactant concentration pairings which lead to crack formation, it may be possible to control the width of the cracks by changing S and G' . The gel concentrations within which the cracking was possible were much higher than the corresponding ones for agar; however, the concentrations of both substrates correspond to similar values of the storage modulus, G' . The spreading and cracking dynamics, however, cannot be affected by the high degree of local heterogeneities that exist within the gel. These heterogeneities also result in the patterns being asymmetrical.

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Notes

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