IOP PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS

J. Phys. D: Appl. Phys. **41** (2008) 215501 (5pp) doi:10.1088/0022-3727/41/21/215501

Post-crystallization increases in the mechanical strength of self-assembled fibrillar networks is due to an increase in network supramolecular ordering

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Received 19 June 2008, in final form 2 September 2008
Published 6 October 2008
Online at stacks.iop.org/JPhysD/41/215501

Abstract

Fibre–fibre interactions strongly influence the elastic properties of an organogel and are of critical importance to the ability of the network to entrain liquid oil. At 30 °C, there was a significant decrease in the storage modulus in time due to a decrease in the amount of crystalline material (i.e. a decrease in the free induction decay (FID) amplitude) and order of crystalline material (i.e. an increase in the FID T_2 relaxation time (i.e. a measure of proton mobility)). Conversely, at 5 °C, there was an increase in G' in time but no changes were observed in both the amount of crystalline material and its order. This increase in G' was accompanied by a significant increase in the enthalpy of melt and the melting temperature, which translated to a significant increase in the entropy of melt of the system. This decrease in the absolute entropy of the system in time probably arose due to an increase in the number of van der Waals interactions between 12-hydroxystearic acid fibres. Hence the increased order of the system is due to the fibre–fibre interactions which results in a significant increase in G' in time at 5 °C.

1. Introduction

The crystallinity, oil mobility and elastic properties of a self-assembled fibrillar network are a function of cooling rate and storage temperature which alter the degree of both permanent and transient junction zones [1–3].

As an organogelator is cooled in solution, a super-saturated solution forms eventually causing the gelator molecules to microscopically phase separate and to self-assemble via microscopic stochastic nucleation events [3, 4]. Organogelator molecules self-assemble in nucleation events with highly specific interactions promoting one-dimensional growth [4]. This one-dimensional expansion results in fibre formation which has been described as 'crystal-like' [5]. SAFiNs serve the same function as (polymer) chains in a polymer gel [5]. The main difference between polymer networks and SAFiNs are polymers are flexible networks while SAFiNs are rigid networks. The junction zones and branching between these polymer-like SAFiN strands are responsible for the rigidity of the networks [5].

There are three levels of structure described for SAFiNs, ranging from the microscopic scale to the macroscopic scale [6]. The aggregation of the gelator molecules builds the primary structures via non-covalent bonds, in the case of 12-hydroxystearic acid (12HSA) the primary structure is a consequence of hydrogen bonding between the carboxyl acids and hydroxyl groups at position 12. The ability for these molecules to self-assemble into rod-like structures requires a balance among opposing parameters such as solubility and those parameters that control epitaxial growth into axially symmetric elongated aggregates [4, 7].

SAFiNs create a three-dimensional network structure (secondary structure) by self-organizing the rods, tubes or

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sheets into three-dimensional networks through non-covalent interactions, including hydrogen bonding, van der Waals interactions, π–π stacking and metal coordination bonds [7]. The tertiary network structure relates to how the strands then interact to form the supramolecular structure. This is reportedly the most complicated level of structure to modify, but is the structure which affects the macroscopic properties of the material [6] such as hardness, stability and oil mobility.

There are two types of junction zones identified in SAFiNs, i.e. transient and permanent [6]. Transient bonds occur due to SAFiN fibres entangling and are able to break and reform and occur in 12HSA/canola oil gels and are based on two predominant forces, primarily van der Waals forces and secondarily hydrogen bonding. The permanent junction zones arise due to crystallographic mismatches at the interface of growing fibres, which result in a branched fibre [6]. The supersaturation-driven crystallographic mismatch branching (also called non-crystallographic branching) is governed by the nucleation and growth of a gel network [6], while transient junction zones are formed on the surface of the fibre, predominately via London dispersion forces and possibly by hydrogen bonding.

In this paper we demonstrate that the increase in the elastic modulus of an organogel is due to an increase in fibre–fibre interactions which lead to the formation of a greater number of transient junction zones, in turn leading to a more ordered system. This increase in the order of the system is associated with an increase in the oil binding capacity of the organogel.

2. Materials and sample preparation

A 99% pure racemic mixture of 12-Hydroxystearic acid (DL-12HSA) was obtained from Sigma-Aldrich (Catalogue Number 219967, St. Louis, MO, USA). Canola oil was obtained from Sunfresh Limited (batch 286G-C, Toronto, ON, CA) and used as received. 1–5 wt% samples of 12HSA in canola oil were prepared by heating the 12HSA in canola oil to 85 °C for 30 min. The samples were then stored at 5, 15, 20 or 30 °C for 1 day, 1 week and 1 month in a Sanyo MIR-153 incubator (Sanyo Incubator, Japan) prior to pNMR, DSC, rheology and image analysis to ensure that adequate time was given to anneal the network giving maximum structure.

3. Differential scanning calorimetry of 12HSA/canola oil gels

Samples of 3%HSA-canola oil were melted at 80 °C and a drop of sol ranging from 10 to 12 mg was placed in an Alod-Al hermetic DSC pans. The sample and the pan were then heated for 30 min at 80 °C and stored for 24 h. The DSC chamber (Q2000, TA instruments, New Castle, DE) was pre-cooled to the storage temperature before the sample was loaded and the chamber continually flushed with nitrogen (0.5 ml min^{-1}). The samples were cooled at an underlying cooling rate of 2 °C min^{-1} with a modulation of $\pm$0.032 °C min^{-1} to determine the transition enthalpy as well as the onset, peak and end of crystallization temperatures. The integration limits were determined using the inflection points on the first derivative of the heat flow curve. This was done because in dilute systems an asymmetric bell shaped transition if often observed making the onset and end points of the transition difficult to detect. Using the first derivative allowed for a clear inflection point at the onset and endpoint of the transition to be observed.

4. Time domain ^{1}H NMR measurements

Samples were subjected to T_2 relaxation measurements on a Bruker mq20 Series NMR Analyzer (Bruker, Milton, ON, CA). The temperature of the cell was maintained at 5 and 30 °C using a circulating water bath (Isotemp3006D, Fisher Scientific, Ottawa, ON, CA). A free induction decay (FID) was used to measure the T_2 relaxations of the solid crystalline component of the organogels. These liquid relaxations are very fast and thus there is no requirement to modify τ. However, the operations pulse length was obtained again using the calibration procedures recommended by the manufacturer.

5. Rheological measurements

An AR 1000 rheometer (Q2000, TA instruments, New Castle, DE) equipped with a 2 cm flat parallel plate with sandpaper epoxied to the surface and to the surface of the peltier plate was used to probe the rheological properties of the gels using oscillatory measurements. 12HSA/canola oil gels were produced in aluminium molds, 2 cm in diameter and 30 mm thick, and stored for 1 week, 24 h and 1 month at which point oscillatory rheology was employed to probe the G' within the LVR as well as the limit of linearity which was taken when the G' decreased by 5% of the value within the LVR.

6. Cryo-scanning electron microscopy of 12HSA/canola oil gels

A drop of molten fat was placed onto a gold coated glass coverslip and stored at 30 °C for 24 h. The sample was placed in a sealed metal container with 0.25 g osmium tetroxide (99.5% pure, Fisher Scientific, Pittsburg, PA) to fix the unsaturated fatty acids in the canola oil. Once the oil was fixed with osmium tetroxide vapours for 1 week at 30 °C the sample was removed and treated with isobutyl alcohol in order to remove unfixed surface oil and to expose the supramolecular network structure. The cover slip was mounted on a copper holder designed for the Emitech K550 Cryo-preparation unit (Ashford, Kent, UK) using Tissue-Tek®. The copper holder was plunged into a liquid nitrogen slush (−207 °C) which was prepared by pulling a vacuum on the liquid nitrogen.

The copper holder was withdrawn from the freezing chamber under an argon blanket to prevent frost from forming on the surface of the samples. They were transferred frozen, and under vacuum into the preparation chamber of the cryo-unit where the sample was sublimated at 80 °C for 30 min. The sample was then coated with 30 nm of gold.

The holders were then transferred from the preparation unit, frozen and under vacuum, onto the SEM (Hitachi S-570, Tokyo, Japan) cold stage held at −137 °C. Images were

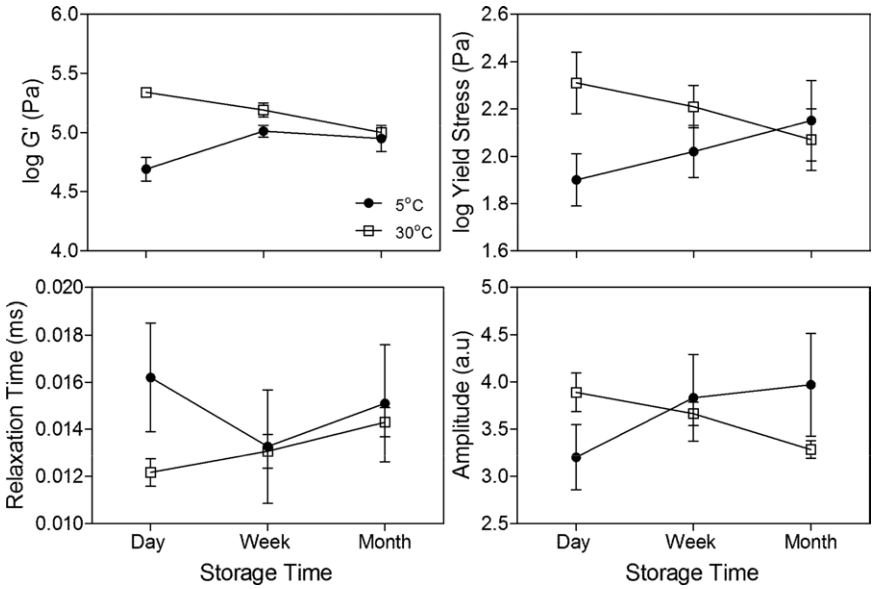

Figure 1. Changes in the storage modulus (*a*), the yield stress (*b*), pNMR FID measurements of the relaxation time (*c*) and the amplitude (*d*) of 3% HSA-canola oil organogels in time stored at 5 and 30 °C.

Table 1. Changes in the structural parameters of 3% 12-hydroxystearic acid organogels as a function of time and temperature. Values with the same superscript are not significantly different from each other ($p > 0.05$) in time at each storage temperature.

	5 °C			30 °C		
Parameter	Day	Week	Month	Day	Week	Month
Log G' (Pa)	4.69^{a}	5.01^{b}	4.95^{b}	5.34^{a}	5.19^{b}	5.00^{c}
Log Yield Stress (Pa)	1.9^{a}	2.02^{a}	2.15^{a}	2.31^{a}	2.21^{a}	2.07^{a}
FID T2 (ms)	0.0162^{a}	0.0132^{a}	0.0151^{a}	0.012^{a}	$0.013^{a,b}$	0.014^{b}
FID Amp (a.u.)	3.20^{a}	3.83^{a}	3.97^{a}	3.89^{a}	$3.66^{a,b}$	3.28^{b}
Enthalpy (kJ mol^{-1})	1.75^{a}	$2.08^{a,b}$	2.18^{b}	1.27^{a}	1.12^{a}	0.98^{a}
Onset of Melt (°C)	54.8^{a}	55.0^{a}	53.2^{a}	53.9^{a}	53.5^{a}	54.9^{b}
Entropy (kJ mol^{-1} K^{-1})	4.40^{a}	6.97^{b}	7.76^{c}	3.87^{a}	4.06^{a}	4.08^{a}

Note: values represent the means of three replicates.

captured digitally using the Quartz PCI imaging software (Quartz Imaging Corp. Vancouver, BC).

7. Oil mobility of 12HSA organogels

Samples stored at 5 and 30 °C were removed from the incubators after 24 h and were equilibrated at 20 °C for 1 h before being placed on Whatman filter papers (Whatman, number 5, 15 cm diameter) for 1 h. The sample was placed in the centre of the filter paper, suspended on an o-ring, to ensure the oil did not collect on the surface below the filter paper. The filter paper was maintained in a controlled environment at 20 °C under nitrogen gas. The distance of the oil migration front was measured after 10, 20, 40 and 60 min. The rate of radial diffusion of the oil migration front was used to determine the rate of oil migration.

8. Results and discussion

12HSA-canola oil gels have been shown to change as a function of time and storage temperature [3]. Translucent gels become opaque and opaque gels can exude oil depending on the storage temperature. It is important to understand what drives these systems to remain stable in some instances and destabilize in others [1, 2]. Figure 1 indicates how the elastic properties of the gel changes as a function of time when stored at 5 and 30 °C. Figure 1(*a*) indicates that gels produced at 30 °C are more elastic (have a higher storage modulus, G'), as previously reported [1]. However, at higher temperatures there was a reduction ($p < 0.05$) (table 1) in the G' as a function of time (figure 1(*a*)). In contrast, at 5 °C, the G' of the organogels increased during storage ($p < 0.05$) (table 1). Even though the yield stress displayed similar trends, the effects were not statistically significant due to the larger error ($p > 0.05$) (table 1). It has been well documented that the elasticity of organogels increases with the amount of crystalline material, the thickness of the fibres, and the number of permanent and transient junction zones [8–10]. Hence, the observed change in the elastic properties must be related to one or more of the following: the amount of crystalline material, the thickness of the fibres, and/or the number and type of junction zones present.

To examine if the change in the rheological properties was due to a change in the amount of crystalline material, FID measurements were carried out using pulsed nuclear

magnetic resonance (figures 1(*c*) and (*d*)). The T_2 relaxation is a measure of the order in the crystalline material [1, 2]. Shorter T_2 relaxations are indicative of a more crystalline network (i.e. more order in the crystalline fibre). This is generally interpreted as more perfect crystals with less solvent inclusions. We observed that at 30 °C the 12HSA protons in the crystalline network were initially more ordered than at 5 °C ($p < 0.05$) [1, 2]. In time, however, at 5 °C, no significant changes in crystalline order were observed at 5 °C, while an increase in the T_2 was observed at 30 °C, meaning that the degree of order in the crystalline network decreased as a function of time ($p < 0.05$) (table 1). The amplitude of the decay is related to the amount of crystalline material present in the system. Not only does the degree of order decrease in time at 30 °C but also the amount of crystalline material decreases as a function of time ($p < 0.05$) (table 1) (figure 2(*b*)). This may account for the observed decrease in the elastic modulus in time at 30 °C (figures 1(*a*) and (*b*)). This decrease in the amount of crystalline material was somewhat surprising. We cannot discard the possibility that the T_2 amplitude could also be sensitive to the amount of liquid oil entrained within the crystalline lattice. The signal from this immobilized liquid oil could be interpreted as a signal originating from solid protons. Upon recrystallization, this immobilized oil would be released, thus leading to a decrease in the T_2 amplitude. The increase in the amount of free liquid oil would lead to a fluidization of the system, with a lower storage modulus and enthalpy of melting.

Conversely, the elasticity increased as a function of time at 5 °C, but neither the T_2 relaxation time nor the amplitude of the signal changed, meaning that neither the amount of crystalline material nor the order in the crystalline material changed in time ($p < 0.05$) (table 1). Differential scanning calorimetry was employed to measure the enthalpy and the onset of melting of the organogels (figures 2(*a*) and (*b*)). From these values, the entropy change upon melting was determined from $\Delta S_f = \Delta H_f / T_o$ (figure 2(*c*)). The enthalpy of melting per gram of HSA was higher for gels set at 5 °C which was a result of a reduction in the critical concentration (i.e. HSA was more soluble at 30 °C than 5 °C) as observed from an increase in the FID amplitude ($p < 0.05$) (table 1) (figure 1(*d*)). The melting enthalpy is a function of the number of non-covalent interactions between 12HSA molecules in the crystal, as well as van der Waals interactions (and possibly some hydrogen bonding) between the crystalline fibres. At low temperatures, the enthalpy of melt continues to increase in time. It is unlikely that the 12HSA crystallization process was continuing during this month of storage since the amplitude of the FID signal did not increase during this period. It was thus somewhat surprising that there was a significant ($p < 0.05$) (table 1) increase in the enthalpy of melting of the system over the storage period. We would like to propose that this increase may be attributed to an increased number of interactions *between* fibres in the system (van der Waals interactions, hydrogen bonding) which would not change the amount of crystalline material, but would affect the total amount of energy required to melt the system. Now, returning to the entropy argument, in figure 3C we show that the change in ΔS_f was the same at 5 and 30 °C after one day ($p > 0.05$) (table 1). However, in

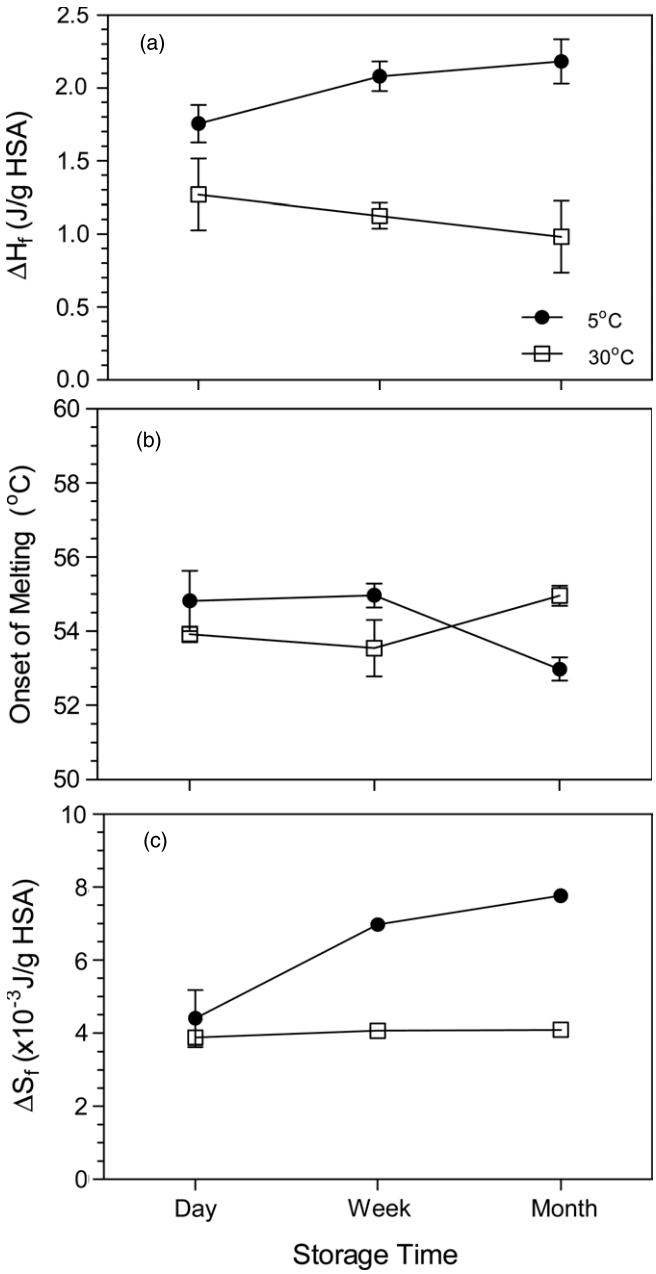

Figure 2. Changes in the enthalpy of melting (*a*), onset temperature of melting (*b*) and entropy of melting (*c*) of 3% 12HSA-canola oil organogels in time stored at 5 and 30 °C as determined using differential scanning calorimetry.

time, there was no change in ΔS_f at 30 °C ($p > 0.05$) (table 1), while ΔS_f significantly increased in time at 5 °C ($p < 0.05$) (table 1). This means that the system at 5 °C became more ordered in time, while it did not change at 30 °C. These results suggest that the absolute entropy of the system was lower at 5 °C than at 30 °C after one week, and this increase in the order of the system could only have come from the ordering of the supramolecular structure of the 12HSA organogels, possibly an increase in the number and strength of fibre–fibre interactions (junction zones).

Transient junction zones are depicted in figure 3 (i.e. T on the micrograph) as entangled fibres. Permanent junction zones can also be seen in figure 3 (i.e. P on the micrograph) which

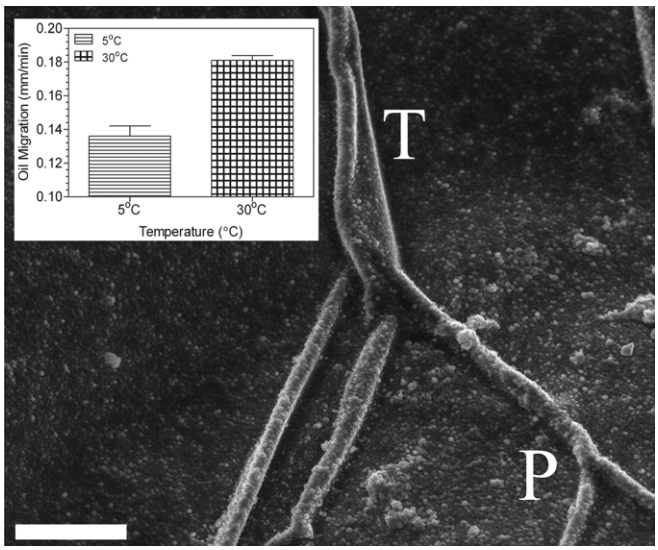

Figure 3. Cryo-SEM image of the 12HSA-canola oil organogel depicting transient (T) and permanent (P) junction zones. Magnification bar = 15 μm. Oil mobility measurements of 12HSA-canola oil organogels at 5 and 30 °C (inset).

arise due to crystallographic mismatches. These changes in the ability of the fibres to interact have consequences not only for the elastic properties of the gel but also on oil binding capacity (figure 3 inset). It would seem that gels which have more transient junction zones were able to entrain liquid oil more efficiently.

9. Conclusion

Storing 12-hydroxystearic acid-vegetable oil organogels at different temperatures affects the entropy state of the system which not only affects the critical concentration but also fibre–fibre interactions. Interactions between fibres (i.e. transient junction zones) strongly influence the elastic properties of an organogel which are also important in the ability of the network to entrain liquid oil.

At 30 °C, the storage modulus decreased significantly in time due to a significant decrease in the amount of crystalline material (i.e. a decrease in the FID amplitude) as well as the order of crystalline material (i.e. an increase in the FID T_2 relaxation time). At 5 °C, the storage modulus increased in time; however, there was no change in either the amount of crystalline material or its order. This increase in storage modulus was accompanied by a significant increase in the enthalpy of melt and the melting temperature which translated to a significant increase in the change in entropy of melting of the system. Here we propose that this decrease in the absolute entropy (increase in order) of the system arose due to an increase in the number of van der Waals interactions between 12HSA fibres. Hence, the increased order of the system was due to the fibre–fibre interactions resulting in a significant increase in the storage modulus.

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