Creep test observation of viscoelastic failure of edible fats

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Abstract A rheological creep test was used to investigate the viscoelastic failure of five edible fats. Butter, spreadable blend and spread were selected as edible fats because they belong to three different groups according to the Codex Alimentarius. Creep curves were analysed according to the Burger model. Results were fitted to a Weibull distribution representing the strain-dependent lifetime of putative fibres in the material. The Weibull shape and scale (lifetime) parameters were estimated for each substance. A comparison of the rheometric measurements of edible fats demonstrated a clear difference between the three different groups. Taken together the results indicate that butter has a lower threshold for mechanical failure than spreadable blend and spread. The observed behaviour of edible fats can be interpreted using a model in which there are two types of bonds between fat crystals; primary bonds that are strong and break irreversibly, and secondary bonds, which are weaker but break and reform reversibly.

1. Introduction
The creep-and-recovery test is an important tool for investigating the viscoelastic failure of soft solids. In the creep test the strain is measured under a constant stress as a function of time at different temperatures. The test consists of two phases: the strain is first measured as a function of time at constant shear stress in the creep phase; any change in strain that occurs when the stress is removed is then measured in the recovery phase. The Maxwell model of a viscoelastic material comprises a (purely viscous) Newtonian dashpot and a (purely elastic) Hookean spring connected in series, whereas the Kelvin–Voigt (or Voigt) model comprises a Newtonian dashpot and Hookean spring connected in parallel. The complete creep curve can be accounted for by a Burger model comprising one or more Kelvin–Voigt units in a series with the Maxwell unit [1]. The creep and recovery behaviour of a Burger system [2] has been described by

\[
\frac{\varepsilon(t)}{\sigma} = \frac{1}{G_0} + \frac{t}{\eta_0} + \sum_{i=1}^{n} \frac{1}{G_i} \left[ 1 - e^{-t/\tau_i} \right]
\]

where \(\sigma\) is the applied shear stress, \(\varepsilon(t)\) is the strain at time \(t\), \(G_0\) is the instantaneous elastic modulus, \(\eta_0\) is the viscosity characteristic of the Newtonian dashpot and \(G_i\) are elements of the spectrum of the retarded modulus associated with time constants \(\tau_i\). The time constant is related to the viscosity \(\eta_i\) of the \(i^{th}\) Voigt unit: \(\eta_i = G_i \tau_i\).

A Weibull distribution is often used to model the behaviour of composite solid substances and assess their reliability [2]. The Weibull density function [3]-[6] is given by

\[
f(x_i) = \frac{\beta}{\alpha} \left( \frac{x_i - \gamma}{\alpha} \right)^{\beta-1} e^{-\left( \frac{x_i - \gamma}{\alpha} \right)^{\beta}}
\]
where \( x_i \) is the breaking strength of the \( i^{th} \) element, \( \beta > 0 \) is the shape factor, \( \alpha > 0 \) and \( \gamma \geq 0 \) are scale parameters; \( \gamma \) is the location parameter or \( x \)-threshold, below which we take \( f(x_i) = 0 \).

Fancey [7] showed that equations based on the Weibull distribution functions can be used accurately to represent the creep and recovery behaviour of polymeric materials. The Weibull shape parameter \( \beta \) and scale parameter \( \alpha \) can both be estimated from creep test data represented by the equation
\[
\varepsilon(t) = \varepsilon_i + \varepsilon_c \left[ 1 - e^{-t/(\alpha \gamma)} \right]
\]
where \( \varepsilon_c \) is a constant and \( \varepsilon_i \) is the strain at time zero. The recovery of the sample following the removal of the load be used to estimate the same parameters can also be estimated based on the representation
\[
\varepsilon(t) = \varepsilon_i e^{-t/(\alpha \gamma)} + \varepsilon_f
\]
where \( \varepsilon_i \) and \( \varepsilon_f \) are constants [7].

Our present results have been obtained by conducting creep and recovery tests at refrigeration temperature (5 °C) and at room temperature (20 °C).

2. Materials and methods

2.1. Materials
Mainland butter and Anchor Spreadable blend (a butter and sunflower oil blend) (Fonterra Brands, Auckland, New Zealand), Pams butter (Pam’s Products Ltd, Auckland, New Zealand), Sunrise table spread and MeadowLea Original spread (Goodman Fielder New Zealand Ltd, Auckland, New Zealand) (both spreads contained 70% fat) were purchased from a supermarket and transferred chilled to a 5 ºC store.

2.2. Sample Preparation
Cylindrical samples (25 mm diameter) from each material were prepared using a cork borer. Using a stainless steel wire, the cylinders were sliced into discs approximately 3 mm in height for use on the rheometer and stored at 5 ºC until required.

2.3. Creep Test
A rheometer (Paar Physica UDS 200, Physica Messtechnik GmbH, Stuttgart, Germany) was used with parallel plate fixtures. The lower plate was fitted with a Peltier element that kept the temperature within 0.1 °C of the set value. To prevent the samples slipping, emery paper was fixed to the upper and lower plates. The instrument was set to the zero gap position and the lower plate set to 20 ºC. The upper plate was then raised and the gap set to 3 mm. A disc was placed on the lower plate and the top plate lowered to 3mm. Excess material was carefully removed and the sample allowed to equilibrate for 30 min after which a run was initiated. A digital laser thermometer (HLP Controls Pty Ltd, model 8859, Riverstone, NSW, Australia) was used to check the temperature of the upper plate prior to commencement of each run. For the samples tested at 5 ºC, the Peltier plate was set at 5 ºC and the run initiated immediately without an equilibration period. Stress of 250 Pa was applied to the samples in all cases.

3. Results and discussion
Figure 1 shows the creep behaviour for the five chosen edible fats, taken at two different temperatures where this was possible, fitted to the Burger model (Eq. 1). In all cases a satisfactory fit was obtained by using only one Voigt unit and use of two units did not significantly improve fit to the data. The values obtained for the rheological parameters are shown in Table 1. Results from three
replicate experiments were used to estimate the value of each parameter and its precision (quantified as the standard error of the mean).

## Table 1. Creep parameters of edible fat.

| Sample         | $G_0$ (Pa) | $G_1$ (Pa) | $\tau_1$ (s) | $\eta_1$ (Pa s) | $\eta_0$ (Pa s) |
|----------------|------------|------------|--------------|----------------|-----------------|
| Pams 5 °C      | $1.3 \times 10^6$ | $4.7 \times 10^5$ | 46.4         | $2.2 \times 10^7$ | $1.5 \times 10^8$ |
| Mainland 5 °C  | $1.7 \times 10^6$ | $5.6 \times 10^5$ | 46.6         | $2.6 \times 10^7$ | $1.6 \times 10^8$ |
| Anchor 5 °C    | $6.7 \times 10^4$ | $6.7 \times 10^4$ | 42.7         | $2.9 \times 10^6$ | $4.5 \times 10^7$ |
| Sunrise 5 °C   | $4.6 \times 10^3$ | $2.4 \times 10^4$ | 38.6         | $9.2 \times 10^5$ | $1.2 \times 10^7$ |
| Meadowlea 5 °C | $1.9 \times 10^5$ | $1.4 \times 10^5$ | 42.5         | $5.8 \times 10^6$ | $7.0 \times 10^7$ |
| Pams 20 °C     | $5.4 \times 10^4$ | $2.6 \times 10^4$ | 46.9         | $1.2 \times 10^6$ | $1.2 \times 10^7$ |
| Mainland 20 °C | $7.3 \times 10^4$ | $3.7 \times 10^4$ | 47.4         | $1.8 \times 10^6$ | $1.7 \times 10^7$ |

**Figure 1.** Creep behaviour for data fitted with one Voigt-unit for (a) Pams (×) and Mainland (+) at 5 °C, (b) Pams (×) and Mainland (+) at 20 °C, (c) Anchor (+) and MeadowLea (×) at 5 °C (d) Sunrise (+).
The recovery data was not robust enough to allow meaningful fitting of the 4-parameter Burger model.

The Burger model gives a good representation of the creep behaviour of viscoelastic materials. When stress is applied, elastic forces (represented by a series-connected Hookean spring element, elastic modulus \(G_0\)) give rise to the virtually instantaneous appearance of moderate strain due to simple molecular bond stretching. The appearance of further strain, beyond the elastic limit of these bonds and somewhat delayed, arises due to the operation of internal viscous forces (represented by Newtonian dashpot elements) as polymer molecules in close contact move relative to one another. Non-recoverable strain due to such effects is represented by the single series-connected dashpot (viscosity \(\eta_0\)). The Voigt unit represents that part of the process of structural change in which the secondary intermolecular bonds break and reform with a characteristic retardation time (\(\tau_1\)).

At 5 °C the butters have significantly higher intrinsic mechanical strength and viscosity. These higher values are also reflected in the parameters associated with the Voigt unit. It is notable that the viscosities (\(\eta_1\)) associated with the (parallel connected) Voigt unit are in all cases lower than those (\(\eta_0\)) obtained for the Newtonian dashpot in the (series connected) Maxwellian unit, whereas the opposite is true concerning the mechanical strength: \(G_0 > G_1\). This is consistent with the interpretation in which the Maxwellian unit represents the behaviour of stronger primary bonds which break irreversibly whereas the Voigt unit represents the behaviour of weaker secondary bonds that break and reform as continuous stress is applied and the sample is increasingly strained.

It is noteworthy that there are no significant differences between the retardation times \(\tau_1\) for the different samples, except perhaps for one of the spreads (Sunrise). This could be interpreted as an indication that the character of the secondary bonds is similar for the all of the materials tested whether they are butters, spreads or blends.

Non-linear curve fitting was applied to both the creep (not shown) and recovery test data (Figure 2) to obtain estimates of the relevant Weibull parameters (Eqs. 3 & 4). The goodness of fit for this curve-fitting procedure was very similar to that for the Burger model procedure (Figure 1). Results of the Weibull parameters obtained for the five samples are listed in Tables 2 and 3.

Table 2. Estimated Weibull parameters for the creep test.

| Samples         | \(\varepsilon_i\)   | \(\varepsilon_c\)   | \(\alpha\) (s) | \(\beta\)            |
|-----------------|--------------------|--------------------|----------------|----------------------|
| Pams 5 °C       | \((6.2 \pm 1.3) \times 10^{-2}\) | \(2.1 \pm 0.2\) | \(25.0 \pm 4.4\) | \((5.1 \pm 0.9) \times 10^{-1}\) |
| Mainland 5 °C   | \((11.3 \pm 2.6) \times 10^{-2}\) | \(1.9 \pm 0.2\) | \(55.5 \pm 24.7\) | \((6.9 \pm 0.8) \times 10^{-1}\) |
| Anchor 5 °C     | \((2.1 \pm 1.4) \times 10^{-1}\) | \(0.9 \pm 0.2\) | \(7.0 \pm 1.1\)   | \((4.6 \pm 1.3) \times 10^{-1}\) |
| Sunrise 5 °C    | \(3.3 \pm 0.5\)    | \(3.2 \pm 0.5\)   | \(3.2 \pm 0.4\)   | \((3.5 \pm 0.1) \times 10^{-1}\) |
| MeadowLea 5 °C  | \((0.8 \pm 0.2) \times 10^{-1}\) | \(0.5 \pm 0.2\) | \(9.9 \pm 2.2\)   | \((4.8 \pm 0.5) \times 10^{-1}\) |
| Pams 20 °C      | \((3.0 \pm 1.1) \times 10^{-1}\) | \(2.4 \pm 0.2\) | \(17.5 \pm 1.5\)  | \((5.4 \pm 0.3) \times 10^{-1}\) |
| Mainland 20 °C  | \((1.5 \pm 0.6) \times 10^{-1}\) | \(2.3 \pm 0.6\) | \(12.7 \pm 6.3\)  | \((5.0 \pm 1.5) \times 10^{-1}\) |
Figure 2. Weibull parameter plots using strain values for recovery test of (a) Pams (×) and Mainland (+) at 5 ºC, (b) Pams (×) and Mainland (+) at 20 ºC and Anchor (○) and (c) MeadowLea (×) at 5 ºC (d) Sunrise (×) at 5 ºC.
Table 3. Estimated Weibull parameters for the recovery test.

| Samples         | $e_r$        | $e_f$        | $\alpha$     | $\beta$  |
|-----------------|-------------|-------------|--------------|----------|
| Pams 5 °C       | $(3.1 \pm 0.2) \times 10^{-4}$ | $(6.9 \pm 0.5) \times 10^{-4}$ | $181.6 \pm 38.1$ | $(5.4 \pm 0.3) \times 10^{-1}$ |
| Mainland 5 °C   | $(5.2 \pm 0.3) \times 10^{-5}$ | $(8.5 \pm 0.7) \times 10^{-4}$ | $268.5 \pm 4.2$   | $(7.5 \pm 0.1) \times 10^{-1}$ |
| Anchor 5 °C     | $(3.2 \pm 0.2) \times 10^{-3}$ | $(4.8 \pm 0.3) \times 10^{-3}$ | $201.4 \pm 1.4$   | $(7.6 \pm 0.1) \times 10^{-1}$ |
| Sunrise 5 °C    | $(6.9 \pm 0.0) \times 10^{-3}$ | $(4.4 \pm 1.2) \times 10^{-2}$ | $183.4 \pm 40.2$  | $(6.9 \pm 0.4) \times 10^{-1}$ |
| MeadowLea 5 °C | $(6.6 \pm 0.3) \times 10^{-3}$ | $(2.8 \pm 0.2) \times 10^{-2}$ | $100.5 \pm 1.6$   | $(9.8 \pm 0.2) \times 10^{-2}$ |
| Pams 20 °C      | $(3.0 \pm 0.5) \times 10^{-3}$ | $(1.2 \pm 0.1) \times 10^{-2}$ | $137.6 \pm 24.7$  | $(8.2 \pm 0.6) \times 10^{-1}$ |
| Mainland 20 °C  | $(3.7 \pm 0.5) \times 10^{-3}$ | $(1.0 \pm 0.1) \times 10^{-2}$ | $133.5 \pm 6.8$   | $(8.5 \pm 0.4) \times 10^{-1}$ |

The value of the scale (life-time) parameter ($\alpha$) estimated from creep test data was highest for two brands of butter followed by MeadowLea Original spread, Anchor Spreadable blend and Sunrise spread. The life-time parameter was lower for Anchor Spreadable blend and Sunrise spread than for Pams butter and Mainland butter at 20 °C and for MeadowLea Original spread. These results indicate that mechanical failure is less likely in MeadowLea Original spread, Pams butter and Mainland butter than in Anchor Spreadable blend and Sunrise spread.

The Weibull shape parameter ($\beta$) indicates whether the failure rate of internal elements of the material is increasing ($\beta > 1$), constant ($\beta = 1$) or decreasing ($\beta < 1$) over time. The experimentally obtained value of $\beta$ was indistinguishable from unity for both brands of butter, indicating that the mechanical composition of these butters is, within the temperature range 5–20 °C, quite homogeneous. The other materials have values of $\beta$ slightly less than unity, indicating that the distribution of strengths of individual mechanical elements is skewed toward those which are weaker. This effect is much more marked in the “spreads” as opposed to the “blend”.

The results of Weibull fitting to the recovery test data indicate that the recovery process does not occur through exactly the same mechanism as the creep process. In the first place, all of the values of the shape parameter $\beta$ were found to be smaller than unity for the recovery data, indicating a decreasing rate of strain diminution over time; greater numbers of weaker bonds reforming at a slower rate. However, even more striking is the large increase (typically between one and two orders of magnitude) in the life-time parameter when the substances switch from creep to recovery behaviour. The rate of recovery under zero applied stress is very much slower than the rate of deformation under the constant applied stress of 250 Pa.

4. Conclusion

A comparison of the rheometric measurements of three different types of edible fat samples showed clear differences among the products. Overall the data suggest that the microstructure of Mainland butter at 5 °C is the most robust, while Anchor and Sunrise are the least robust. Furthermore, the microstructure of the Anchor and Sunrise products is more unstable at 5 °C than the microstructure of the Pams and Mainland products at 20 °C. These differences in failure characteristics are probably due to differences in the composition and manufacturing procedure of the all products, questions which are now under investigation.
5. References

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