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Describing the firmness, springiness and rubberiness of food gels using fractional calculus. Part I: Theoretical framework.

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Abstract

Constitutive models for soft solids that quantitatively relate the state of the stress in the material to the deformation history have the potential to be used in a structure-texture engineering context, but successful examples are scarce. In the present work we define equations for the firmness $F$, springiness $S$, and rubberiness $R$, of semi-soft food gels such as cheeses that exhibit broad power-law stress relaxation over a wide range of timescales. The equations contain only two material properties, which have their origin in the food microstructure: a fractional exponent, which quantifies the frequency and temporal response and secondly a scale factor or “quasi-property”, which sets the magnitude of the stress in the material. Together they form a constitutive element, known as the ‘springpot’ or Scott Blair element which can accurately capture the viscoelastic properties of food gels such as semi-hard cheeses. Using this model it becomes possible to provide clear and unambiguous definitions of textural parameters such as firmness, springiness and rubberiness, and to quantify their time- and interpendency. The magnitude of the firmness and springiness are inversely related through the fractional constitutive model. Our FSR-equations can be used in a texture engineering context to guide effective product reformulation of soft-solid, hydrocolloidal gels.

Keywords: rational reformulation, food gels, structure-texture engineering, constitutive model, fractional calculus, Scott Blair

1. Introduction

Product reformulation is a major theme in the food industry, which is driven by raw material costs, carbon footprint, or health incentives (Norton et al., 2006; Almeida-Rivera et al., 2007; Foegeding and Davis, 2011; Renard et al., 2006). However, when replacing or removing ingredients, sensory texture, shelf life and processability can be negatively affected (Renard et al., 2006). It is the task of the food product engineer to deliver solutions that overcome
these trade-offs. Macro-scale food properties such as sensory texture are, to a large extent, determined by the microstructure of the food (Aguilera, 2005; Lucey et al., 2003). A wealth of engineering solutions are available to modify food microstructure based on insights from soft matter and colloidal science (Van der Sman and Van der Goot, 2009; Mezzenga et al., 2005; Stokes and Frith, 2008; Mezzenga and Fischer, 2013; Dickinson, 2012; Ubbink et al., 2008; Norton and Frith, 2001) as well as from process technology (Foegeding and Davis, 2011; Jousse, 2008; Almeida-Rivera et al., 2007). Transitioning between the micro- and the macro-scale and dealing with a multitude of constraints requires a rational and integrated product and process design approach (Norton et al., 2006; Almeida-Rivera et al., 2007), using models that can quantitatively relate food formulation and structure to processing and sensory texture.

The fields of rheology and soft matter science have the potential to deliver such models (Bourne, 2002a; Scott Blair, 1958; Mohsenin, 1970; Foegeding et al., 2003) especially when expressed in the form of a general frame-invariant constitutive relationship (Gallegos et al., 2004) for the essential rheological properties (Reiner, 1971) describing the material response to deformation. For non-food materials (e.g., in the polymer processing industry), application of rheological models to improve process throughput and product performance has now become standard; however, successful examples in the texture engineering field are scarce. Probable causes are the additional non-rheological factors that contribute to sensory judgment, such as phase transformations (Bourne, 1978), interaction with saliva (Kapsalis and Moskowitz, 1978; Choi et al., 2014) and repeated macroscopic fracture while the food material is orally processed (Bourne, 1975; Chen, 2009).

The firmness $F$, springiness $S$, and rubberiness $R$, of food gels, are examples of what Reiner (1971) called ‘technological properties’ rather than true material properties and these texture attributes are typically assessed solely by pressing and depressing the material by hand (Fig. 1) (Szczesniak and Bourne, 1969; Goh et al., 2003; Foegeding and Drake, 2007). Such manually-evaluated texture attributes can also be measured instrumentally using bulk rheological testing (Stokes et al., 2013) which makes these texture attributes excellent candidates for a quantitative structure-texture model which is based on analysis of the imposed kinematics using appropriate constitutive equations (or equations of state) for the material. These constitutive relationships should also then predict how well the product performs under handling conditions other than those of sensory texture assessment (Scott Blair and Coppen, 1940c), such as whether the product retains its intended shape when stacked and stored (Bourne, 1975) (Fig. 1), as well as provide insight into possible product reformulation strategies.

Firmness is one of the most researched texture attributes for a wide variety of foods (Szczesniak and Bourne, 1969). The most common route to enhance the firmness of a food
product is by transforming one or more of the hydrocolloidal food constituents into a gel. A second important function of gelation is to keep water and fat in the product, implying that firmness and composition are intrinsically related (Foegeding and Davis, 2011). Examples of gelled foods are numerous and include yoghurt, cheese, starch puddings (Sala et al., 2008), hotdogs and sausages (Sala et al., 2008; Salvador et al., 2009), seafood analogues (Herranz et al., 2012) and tofu (Sato, 2003). When consumed, these food gels are masticated into smaller pieces and mixed with saliva to form a bolus that can be swallowed (Chen, 2009; Hutchings and Lillford, 1988). The sensations arising when the product is touched and squeezed are good predictors for the sensations perceived in the first steps of mastication (Barrangou et al., 2006; Drake et al., 1999).

Firmness ($F$) is determined while the food material is being pressed, whereas the texture attribute of springiness ($S$) is measured after depressing the piece of food (Szczesniak, 1963a; van Vliet, 1991; Foegeding and Drake, 2007; Barrangou et al., 2006; Çakir et al., 2012). In former days, craftsmen in cheese production used to assess both the firmness as well as the ‘spring’ of the cheese curds to determine if this precursor in the cheese-making process was ready to proceed to the next stage of processing (Scott Blair and Coppen, 1940a,b). For bread, springiness is a desired property (Matos et al., 2014) and this texture attribute is used as a measure for being fresh or stale (Purhagen et al., 2011). Springiness and rubberiness are two texture attributes that are often intertwined (Jowitt, 1974) and for both terms the synonym elasticity is sometimes used (Davis, 1937; Scott Blair, 1973; Hayakawa et al., 2014; Devezeaux de Lavergne et al., 2015; Brenner et al., 2015). Rubbery, springy, or elastic food gels are very popular in Japan (Brenner et al., 2015); however, they are also linked to eating difficulties (Funami et al., 2012; Hayakawa et al., 2014). In cheese, a Muenster type is allowed to be springy, whereas a Parmesan is not (Foegeding and Drake, 2007). ‘Rubbery’ has been used as a negative descriptor for cheese that has reduced fat content (Yates and Drake, 2007).

George William Scott Blair, who is considered by many to be the founding father of food rheology (Szczesniak, 2002; Bourne, 2002b), had a special interest in the subjective aspects of firmness, which led to ground breaking panel studies (Scott Blair and Coppen, 1940c). He laid the foundations of a special branch of rheology called psychorheology (Scott Blair, 1947), which later evolved into the field of texture studies (Scott Blair, 1974). His central question was: What material property gives rise to key texture properties like the ‘body’ of dough and the ‘firmness’ of cheese? His approach was as simple as it was effective: ask panels to squeeze two graspable complex materials with known material constants and which are purely viscous (bitumen), purely elastic (rubber) or viscoelastic (cheese, unvulcanized rubber). He asked the panelist to judge which of the two materials they squeezed was softest with the
restriction that the two objects were pressed at the same time, and for a well-defined period.

The conclusions were threefold. First, human touch is very sensitive in discriminating between softer and firmer objects, even if one is purely elastic and the other purely viscous. Second, firmness is a time-dependent property and is judged dynamically, which is in line with the notion that the perception of sensory texture is the result of measuring a dynamic process rather than measuring a final state (Hutchings and Lillford, 1988; Devezeaux de Lavergne et al., 2015). Finally, Scott Blair demonstrated that the time-dependence of the firmness for many of the complex materials he studied has the form of a power-law in time.

Thus in rheological terms the firmness, springiness, and rubberiness of food gels can be considered as viscoelastic texture attributes. This suggests the use of constitutive models that correlate these attributes to true linear viscoelastic (LVE) material parameters characterizing the materials of interest. Various models have been fitted to material property data of cheese obtained from rheometry in the LVE region to correlate composition and processing conditions to cheese material properties. The most popular model is the generalized Maxwell model (Tschoegl, 1989), that has been applied by numerous authors (Hort and Le Grys, 2000; Sadowska et al., 2009; Subramanian and Gunasekaran, 1997; Muliawan and Hatzikiriakos, 2007; Campanella and Peleg, 1997; Subramanian et al., 2006; Li Yuet Hee et al., 2008; Bertola et al., 2000; Venugopal and Muthukumarapppan, 2001). To describe measured LVE behavior accurately over two decades of time, at least three relaxation modes (with six model parameters) are typically needed, from which it is hard to derive insight into structure-texture relations. Furthermore, the fitted results are not valid outside the domain of measurement making extrapolation difficult and thus the extracted model parameters lack a strong physical underpinning (Kollmannsberger and Fabry, 2011; Jaishankar and McKinley, 2013) which is essential for a connection to the underpinning microstructure. One approach to reduce the number of parameters in the mechanical model is to fit a continuous spectrum of relaxation times to the material functions determined in the LVE regime (Winter and Mours, 1997; Del Nobile et al., 2007; Sadowska et al., 2009; Lorenzo et al., 2013). Again the spectral distribution parameters that are obtained lack physical meaning.

When a creep/recovery test is performed to measure the temporal response of a food gel to deformation, the Burgers model is widely used to interpret the material properties that are measured (Scott Blair and Burnett, 1959; de Faria et al., 2013; Dolz et al., 2008; Harrington and Morris, 2009; Korus et al., 2009; Lorenzo et al., 2013; Meng et al., 2014; Moreira et al., 2011; Olivares et al., 2009). This four-parameter model is capable of describing viscoelastic deformation and the unrecoverable strain at the end of recovery (Scott Blair and Burnett, 1959). It comprises of a spring and dashpot in series (Maxwell model) attached to a spring and
dashpot in parallel (Kelvin-Voigt model). Scott Blair (1973) proposed to measure springiness $S$, by a dimensionless number composed from the characteristic relaxation time $\tau_r$ and retardation time $\tau_{ret}$ in the Burger model, $S = \tau_r/\tau_{ret}$. However he also concluded that to capture more complex relaxation behaviour, the addition of an extra Kelvin-Voigt body is necessary, which makes the modeling increasing phenomenological in nature (Scott Blair and Burnett, 1959).

Various authors have independently recognized the power-law relaxation characteristics in food gels when performing Small Amplitude Oscillatory Shear (SAOS) tests and they have fitted empirical models of the form $G'(\omega) = A\omega^b$ and $G''(\omega) = C\omega^d$ (where $G'(\omega)$ and $G''(\omega)$ are the storage and loss modulus, respectively) to the measured frequency data. Here $A$, $b$, $C$ and $d$ are constants and $\omega$ the imposed oscillatory frequency. (Subramanian et al., 2006; Korus et al., 2009; Moreira et al., 2011; Ronda et al., 2013; Zhou and Mulvaney, 1998; and Gabriele et al., 2001) further reduced the number of constitutive fitting parameters from four to two by fitting a similar model to the magnitude of the complex modulus $|G^*(\omega)|$. In all these papers no attempt was made to represent these functional forms in the form of a constitutive model that could be applied in a predictive form to describe other deformations.

Scott Blair (1947) was the first to focus on developing constitutive equations where the stress $\sigma(t)$ is related to the strain $\gamma(t)$ or strain rate $\dot{\gamma}(t)$ in the form of a power-law. He started with the Nutting equation (Nutting, 1921; Scott Blair and Coppen, 1942), $\Psi = \sigma^\beta \gamma^{-1} t^k$, where $t$ is the time, $\beta$ and $k$ are constants and $\Psi$ a “firmness intensity” (Scott Blair, 1943). From his experiments he concluded that the number of parameters in this equation could be reduced by writing the stress in terms of a fractional differential equation $\sigma = \Psi(\frac{d^\beta \gamma}{dt^\beta})$. He called attention to two novel rheological concepts, the use of a fractional derivative with a fractional exponent ($\beta$), and the existence of a ‘quasi-property’ $\Psi$ (Scott Blair et al., 1947). Scott Blair argued that such a quasi-property is intermediate between a shear modulus $G$ and a viscosity $\eta$ and is a measure of the dynamic relaxation processes within a material rather than of an equilibrium state. The magnitude of this quasi-property (here a “firmness intensity”) sets the scale of the stress in the material, whilst the fractional exponent quantifies the frequency and temporal response. The fractional constitutive framework was further developed in the 1980’s by Bagley and Torvik (1983a,b) and Koeller (1984). The latter introduced a new mechanical element, the springpot, also referred to as the Scott Blair element (Mainardi and Spada, 2011), which is quantified by two material parameters; the quasi-property and the fractional exponent.

Successful fitting of a fractional constitutive model to measured linear viscoelastic responses can be found for red blood cells (Craiem and Magin, 2010), lung tissues (Suki et al., 2001), and many other materials.
and arteries (Craiem and Armentano 2007). A selective number of other examples can be found for describing food ingredients like gums (Jaishankar and McKinley 2013) emulsifiers (Ma and Barbosa-Canovas 1996; Chen and Kim 2004) and melon (Xu and Chen 2013). Bagley and Torvik (1983b) proved that at sufficiently high frequencies, the Rouse theory for polymer melts can also be compactly expressed in terms of an equivalent fractional constitutive equation containing a springpot with exponent $\beta = 1/2$. Several works (Heymans and Bauwens 1994; Schiessel et al. 1995) have built constitutive models by hierarchically ordering springs and dashpots in self-similar structures, like those encountered in biological materials, and showed that the hierarchical model asymptotically approaches a springpot.

The microstructural origins of the power-law relaxation commonly observed in complex materials can also be found in the distribution of lengths in dangling chains in imperfectly cross-linked elastomers (Curro and Pincus 1983), the distribution of energy wells around the interacting elements that form soft glassy materials (Sollich et al. 1997; Jaishankar and McKinley 2013) and in the continuous distribution of waiting times for a particle that diffuses in a heterogeneous structure (Bouchaud and Georges 1990; Amblard et al. 1996). Tracking the trajectory of such a particle, as it diffuses through the heterogeneous structure, is a form of micro-rheology. Caggioni et al. (2007) used this technique in combination with shear rheology to characterize gellan gum micro gels. They showed that both bulk- and micro-rheological measurements displayed power-law frequency sweeps with identical slopes, and that this power-law slope changed when the microstructure was altered.

In the remainder of the paper we build on the efforts of Davis and Scott Blair to link cheese texture attributes to essential rheological properties that can be extracted from rheometry and we proceed through the steps of building a structure-texture model based on a fractional constitutive framework. First we introduce the main mathematical relations that are required to construct this framework. We show that from these parameter values we can correctly predict the evolution of both the relaxation modulus $G(t)$ and creep compliance $J(t)$. We next introduce exact definitions of the firmness $F$, springiness $S$, and rubberiness $R$, of food gels in terms of specific points on the creep / recovery curve. Using the tools of fractional calculus this allows us to derive expressions for the material’ firmness, springiness, and rubberiness in terms of the quasi-property and the power-law exponent that characterize the cheese. We show that we can quantitatively predict springiness and rubberiness from the measured /fitted creep curve which demonstrates that firmness, springiness, and rubberiness are interrelated and all governed by the two material parameters we determine in the linear viscoelastic regime. We finally outline how our equations can be used in the context of structure-texture design. In part II of this work we extend these texture engineering ideas to characterizing a full-fat, reduced-
fat, and zero-fat cheese products over a wide range of temperatures and water / protein ratios.

We also quantify the effect of large loadings that exceed the linear viscoelastic limit, common in oral processing (Goh et al., 2003), on the measured magnitude of firmness, springiness and rubberiness.

2. Fractional constitutive framework

To construct fractional constitutive equations in an identical fashion as classical constitutive models (e.g. the Maxwell model), Koeller (1984) defined a rheological element whose stress is proportional to the fractional derivative of the strain. He called this two-parameter viscoelastic element the ‘springpot’:

\[
\sigma_{springpot} = G \frac{d^\beta \gamma}{dt^\beta}
\]  

(1)

This constitutive response is a generalization of the classical dashpot and spring: for \(\beta = 1\), the springpot behaves as a dashpot, whereas for \(\beta = 0\) it describes a linear elastic spring, as depicted in Figure 2(a). The front factor, denoted \(G\), is equivalent to Scott Blair’s quasi-property (originally denoted \(\Psi\)) and has units of \(Pa \ s^\beta\). The exponent \(\beta\) is a measure of the frequency or temporal dependence of the material response, as well as the relative degree of viscoelasticity, and, as such is related to the phase angle, \(\tan(\delta)\) in the material. The latter parameter is more commonly used to describe the solid- or liquid- like nature of semi-solid food gels such as cheese (Foegeding et al., 2011). Various material responses can be described with constitutive models derived from mechanical analogues that are constructed with the springpot, and comprehensive reviews can be found in Schiessel et al. (1995) and Friedrich et al. (1999).

The fractional constitutive framework builds on ideas from fractional calculus, that incorporate integrals and derivatives of arbitrary order (Podlubny, 1999; Mainardi, 2010; Jaishankar and McKinley, 2014). For compactness these derivatives are called fractional derivatives and we give models, expressions and parameters derived from these derivatives the adjective ‘fractional’ as well as materials that can be mechanically described by these entities.

There are several alternative definitions for the fractional operator generically indicated by Eq. (1). To conform to the initial condition for appropriate rheological tests of \(\gamma|_{t=0} = 0\), we use the Caputo derivative, which reformulates the fractional derivative into a fractional integral through integro-differentiation (Surguladze, 2002). The derivative in Eq. (1) with order \(0 < \)
\[ G \frac{d^\beta \gamma}{dt^\beta} \equiv \frac{G}{\Gamma(1-\beta)} \int_0^t (t-t')^{\beta-1} \dot{\gamma}(t') dt' \] (2)

The constitutive response of the springpot \cite{Koeller, Torvik and Bagley} is thus equivalent to a Boltzmann memory integral with a power-law relaxation kernel, rather than the more familiar Maxwell-Debye exponential form (or sum of exponentials) commonly used in viscoelastic models \cite{Ferry}. The Caputo derivative has a Laplace transform, which for \(0 < \beta < 1\) is defined as \cite{Podlubny, Surguladze}:

\[ \mathcal{L} \left\{ \frac{d^\beta}{dt^\beta} \gamma(t); s \right\} = s^\beta \tilde{\gamma}(s) \] (3)

This enables us to derive analytical expressions for two standard linear viscoelastic shear material functions \cite{Bird}: the relaxation modulus \(G(t)\) and the creep compliance \(J(t)\). In a stress relaxation experiment, a sudden step in shear strain \(\gamma(t) = \gamma_0 H(t)\) is imposed (where \(H(t)\) is the Heaviside step function \cite{Abramowitz and Stegun}), and the resulting evolution of the stress \(\sigma(t)\) in the material is measured. This provides the relaxation modulus \(G(t) \equiv \sigma(t)/\gamma_0\) for the material. By analogy the creep compliance, \(J(t) \equiv \gamma(t)/\sigma_0\) is obtained, by imposing a step in the shear stress acting on the sample, \(\sigma(t) = \sigma_0 H(t)\), and following the evolution of the strain \(\gamma(t)\) in the material over time.

Other standard linear viscoelastic shear material functions, such as the storage and loss moduli \([G'(\omega), G''(\omega)]\), are obtained by harmonic excitations in shear, also denoted as small amplitude oscillatory shear (SAOS) experiments. To find the appropriate fractional expression for these functions we use the Fourier transform of the Caputo derivative of the function \(\gamma(t)\), which is given by \cite{Schiessel et al.}:

\[ \mathcal{F} \left\{ \frac{d^\beta}{dt^\beta} \gamma(t); \omega \right\} = (i\omega)^\beta \tilde{\gamma}(\omega) \] (4)

where \(\tilde{\gamma}(\omega) = \mathcal{F} \{\gamma(t); \omega\}\).

Equations (2), (3) and (4) provide the mathematical framework to build fractional constitutive equations from mechanical analogues and solve them analytically. In this paper we will use fractional models consisting of a single springpot, (i.e. the canonical Scott Blair model (SB)) as well as two springpots arranged in series, which we call the Fractional Maxwell model (FMM). In the latter four-parameter model each element is described by a quasi-property (which we denote \(V\) or \(G\)) and an exponent \((\alpha\ or\ \beta)\), where we take \(\alpha > \beta\) without loss of generality. This constitutive model is schematically depicted in Fig. 2(b). In the Maxwell model the stresses in each element are equal \((\sigma = \sigma_1 = \sigma_2)\) and the strains are
additive ($\gamma = \gamma_1 + \gamma_2$). With the constitutive relation for each springpot (Eq. (1) and Fig. 2(b))
this gives the fractional Maxwell model (FMM):

$$\sigma(t) + \int_0^\alpha \frac{V}{G} \frac{d^{\alpha-\beta} \sigma(t)}{dt^{\alpha-\beta}} = \int_0^\beta \frac{V}{G} \frac{d^{\beta-\gamma}(t)}{dt^{\beta-\gamma}}$$

(5)

where $0 \leq \beta \leq \alpha \leq 1$.

Materials that are described by a single power-law (e.g. Eq. (2)), have no characteristic
timescale that can be identified. A discrete spectral representation of the power-law kernel
in Eq. (2), requires an infinitely broad spectrum of time constants [Ng and McKinley, 2008].
However for a material displaying two power-law regimes, as described by the FMM, we can
unambiguously define one single characteristic timescale $\tau_c$ by the parameter combination:

$$\tau_c = \left(\frac{V}{G}\right)^{1/(\alpha-\beta)}$$

(6)

This time corresponds to the characteristic time (or frequency $\omega_c = 1/\tau_c$) at which the local
power-law in the material response, transitions from one exponent ($\alpha$) to the other ($\beta$). This
expression also reduces to the expected value for the limit of a classical Maxwell model for
which $V \to \eta$, $G \to G$, $\alpha \to 1$ and $\beta \to 0$, so that $\tau_c = \eta/G$.

3. Results

3.1. Rheological definitions of firmness, springiness, and rubberiness

There is no consensus on a unique definition of the firmness, springiness, and rubberiness
of food gels such as cheese, nor its method of assessment [Foegeding and Drake, 2007], which
hampers correlation of these texture attributes to essential material properties. The firmness $F$,
can be judged while deforming a piece of cheese with the mouth (tongue and palate, incisors,
front teeth or molars) or by hand (Fig. 1(a)). During the assessment, the cheese can be slightly
pressed or completely bitten through [Drake, 2007]. When choosing a method of assessment,
panelists tend to make a choice that depends on the level of firmness itself [Szczesniak and
Bourne, 1969].

Correlative studies between panel test results and instrumental measurements do not pro-
vide additional clarity on how firmness should be defined. It has been correlated to rheologi-
cal properties covering the regimes of linear to non-linear rheology up to fracture [Foegeding
et al., 2003; van Vliet, 1991]. Since the development of the Texturometer [Friedman et al.,
1963] and the entrance of the Instron Universal Testing Machine in texture measurements
[Bourne, 1968], the uniaxial compression experiment has become very popular to assess firm-
ness and is still deployed regularly (e.g. Liu et al. (2015); Çakir et al. (2012)). In this ex-
periment (Fig. 1(b)), a cylindrical sample is crushed between two parallel plates either at a
constant rate of displacement (Friedman et al., 1963; Bourne, 1968) or at constant strain rate (Luyten, 1988; Goh et al., 2003). In an alternative configuration, firmness is determined with a penetration test, where the upper plate is replaced by an indenter and the test material is left to rest in the cup or beaker in which it was prepared (e.g. Li Yuet Hee et al. (2008); Oliver et al. (2015); Bot et al. (2014)). Such indentation tests deform the material locally and are of specific relevance when the materials with the lowest firmness are too weak to hold their own weight. When using maximal force as a measurement for firmness, it appears that the relative firmness of two types of cheese depends both on the rate and the degree (or extent) of compression (Shama and Sherman, 1973; Bourne and Comstock, 1981). This gives an indication that when measured instrumentally, firmness has both a viscoelastic as well as a plastic (or flow) component.

Firmness is often intertwined with hardness (Jowitt, 1974; Peleg, 1980; van Vliet, 1991). Jowitt (1974) prefers the term firm over hard and defines it as ‘high resistance to deformation’. Reiner and Scott Blair (1967) define hardness as a ‘resistance to penetration’, i.e. the resistance to a specific type of deformation, which can be instrumentally quantified with the indentation test described above. They use ‘suppleness’ as an antonym for ‘hardness’ whereas ‘soft’ is the antonym for ‘firm’ (Jowitt, 1974). Van Vliet (1991) proposes the use of firmness for recoverable viscoelastic deformations only and hardness for non-recoverable plastic deformations. This is in line with Scott Blair’s findings that firmness is a time-dependent texture attribute.

Two alternative studies indicate that firmness can indeed be measured with loading conditions that remain within the linear viscoelastic regime of the food material. The first is a series of comparative experiments on Monterey Jack and Mozarella cheese between an expert panel and rheometry. Brown et al. (2003) showed that the maximum compliance, \( J_{\text{max}} = \max \{ J(t) \} \), determined in a 600 s creep test (Fig. 1(c)) in the linear viscoelastic region had a strong negative correlation with both hand- and mouth-evaluated firmness. Ewoldt (2013) demonstrated that by plotting the creep compliance \( J(t) \), the best discrimination between a soft and firm grade of therapy putty could be made. Ewoldt also showed that firmness is a sensory texture attribute that cannot only be measured with tactile senses but also by vision (Bourne, 2002b) as long as one probes the property over long time-scales. A soft material will lose shape rapidly over time, an undesirable feature for a cheese that needs to be sliced (Fig. 1(a)).

In Fig. 3 we have summarized the findings from Scott Blair and Coppen (1940c), Scott Blair (1947), Brown et al. (2003) and Ewoldt (2013). In Fig. 3(a) we plot the compliance against time for a creep / recovery experiment (see also Fig. 1(c)) on two hypothetical materials.
Firmness $F$, is defined as a resistance to creep, and can be expressed by the inverse of the maximum compliance $J(t)$ measured at the end of the creep phase. The time at which we measure a texture attribute is generically called the time of observation $t_o$. For firmness this time is denoted as $t_f = t_o$. Thus the firmness $F$ is defined as

$$F \equiv 1 / \max\{J(t)\} = 1 / J(t_f)$$

and has units of Pa. The datapoints that are used to calculate the firmness $F$, of materials A and B are indicated by the filled, colored square on the creep/recovery curve in Fig. 3. The corresponding time of observation $t_f$ is indicated by the hollow square on the time-axis. The two hypothetical materials A and B are equally firm at the time of observation $t_f = 10$ s, however the two creep curves approach $J(t_f) \equiv \max\{J(t)\}$ differently. In Fig. 3(b) we have plotted the creep phase of the same experiment on a double logarithmic scale and extrapolated the curves beyond the time of observation $t_f$ (dashed line). It shows that the two materials each have the form of a power-law with different slopes $\beta$. The plot also emphasizes the importance of the time of observation in measuring firmness. If we had chosen a smaller observation time, material A would have been considered firmer than B and vice versa at longer times.

The term ‘elastic’ is often used as a synonym for ‘springy’ (Davis, 1937; Devezeaux de Lavergne et al., 2015; Scott Blair, 1973). The word ‘elasticity’ was taken up in the list of primary parameters in the Texture Profile Analysis (TPA) (Szczesniak, 1963a). Davis (1937) pointed out that the use of ‘elasticity’ is not correct and that should be reserved for the assessment of a modulus by hand. More recently ‘elasticity’ has been replaced by ‘springiness’ (Szczesniak, 2002) in Texture Profile Analysis and it is defined in TPA as ‘the rate at which a deformed material goes back’ to its undeformed condition after the deforming force has been removed (Szczesniak, 1963a). Davis and Blair argued that springiness is related to a time of relaxation (Davis, 1937; Scott Blair, 1973) and that the sensation involved is an amount of recovery instead of a rate. Based on the graphical definition of springiness in Friedman et al. (1963), van Vliet (1991) concluded that the springiness $S$ indeed should be defined as an ‘extent’ to which a deformed material returns to its undeformed state. In their review of texture definitions, Foegeding and Drake (2007) identify authors that speak of ‘a rate at which sample “springs” back’, as well as those who speak of an ‘extent of recovery’.

Van Vliet (1991) combines both rate and extent of deformation in one definition by proposing ‘the tendency to instantaneously and completely recover from a large deformation after removal of the deforming force’, however he prefers to use the term rubberiness instead of springiness. Foegeding and Drake (2007) link rubberiness to springiness by defining it as ”the degree of rubberiness experienced when biting in a sample”. We propose that from a rheolog-
ical perspective and based on the competing definitions above, it is justifiable and necessary to have two separate, distinct definitions for the springiness \( S \) and rubberiness \( R \). Intuitively, the word ‘springiness’ deals with sudden responses that are evaluated over a short period of time and thus the use of a rate is appropriate. As a consequence the term ‘rubberiness’ is used to relate to the total extent of strain that is recovered at the end of the creep / recovery experiment. In polymeric theories, rubbery materials are assumed to be purely elastic or perfectly cross-linked; in other words any applied deformation is reversed upon cessation of the application. By analogy, the term ‘rubberiness’ is used to relate to the amount of strain recovered at the end of a creep-recovery experiment.

Our precise, rheological definitions for the springiness \( S \) and rubberiness \( R \), follow from the location of the three markers on each creep / recovery curve in Fig. 3(a). For convenience we define the elapsed time of recovery as \( \Delta t = t - t_f \) (denoted by the dashed, horizontal black line in Fig. 3(a)). The springiness \( S \) is defined as the absolute secant rate of recovery just after the stress is released and is judged at a time of observation \( t_s = t_f + \Delta t_s \). The springiness is thus unambiguously and mathematically defined as:

\[
S \equiv \frac{|J(t_s) - J(t_f)|}{t_s - t_f} = \frac{|J(t_f + \Delta t_s) - J(t_f)|}{\Delta t_s}
\]

(8)

and has units of 1/Pa s, which is equal to the inverse of the units of viscosity. In practice one judges the springiness of a material such as cheese, by looking at the instantaneous response when the stress is released. It is thus logical to take \( \Delta t_s << t_f \). We will use \( \Delta t_s = 0.1 \) s when we report values for springiness in the remainder of this paper, which is a time close to the response time of a modern rheometer at the time of publication. The location of the time of observation for measuring springiness is denoted on the time-axis is indicated by the hollow triangle in Fig. 3(a), which visually overlaps with the hollow square representing \( t_f \), indicating that the elapsed time of recovery is very small. Note, that although the recovery time is short, the creep compliance of Material A (red triangle) has decreased considerably. This is reminiscent of a very springy material and is expressed by a secant (red dashed line) that is more steeply negatively sloped than the secant of material B (blue dashed line). Thus the materials A and B are equally firm, but not equally springy for a fixed time of observation \( t_f \).

The rubberiness \( R \), is defined as the extent to which a cheese returns to its original shape during the interval \( (t_f, t_r] \), where \( t_r \) is the time we take for measuring rubberiness. If the strain is fully recovered at the time \( t = t_r \), then \( R = 1 \). If there is no strain recovery at \( t = t_r \), then the rubberiness \( R = 0 \). Thus \( R \) is mathematically defined as:
which is a dimensionless quantity, and where $\Delta t_r$ is the elapsed time of recovery for measuring rubberiness. In this paper we will use values of $\Delta t_r = 10$ seconds (hollow circle on the time axis in Fig. 3(a)) and $\Delta t_r = 100$ seconds, a time convenient to measure in the rheometer and which corresponds to practical times of judging the attribute. By choosing $\Delta t_r \gg \Delta t_s$ we distinguish between the key features of the short and intermediate time response of power-law materials and make springiness and rubberiness two distinct attributes.

To conclude, we want to address the suggestion that the definition of an antonym of a texture attribute [Jowitt, 1974] or the definition of an inverse of a rheological property [Reiner and Scott Blair, 1967] helps the comprehension of the differences between terms used. We propose to follow Jowitt [1974] and call a food gel with a low level of firmness ‘soft’. Foegeding and Drake [2007] defines ‘softness’ as easily ‘moldable’, we propose to use the latter term as an antonym for the rubberiness $R$. For the springiness $S$ [Jowitt, 1974] proposes to use the antonym ‘plastic’, but this is a synonym for ‘moldable’ and has no sense of rate. We suggest the use of ‘squishy’ instead [Yates and Drake, 2007].

In this section we have given precise rheological definitions of firmness, springiness, and rubberiness both in words as well as in terms of specific points on the creep compliance curve, $J(t)$, of a creep/recovery experiment (Fig. 3). We will now use these rheological definitions to derive expressions for firmness, springiness, and rubberiness using the fractional constitutive framework. We subsequently refer to these definitions as the FSR-equations.

### 3.2. Fractional equations for firmness, springiness, and rubberiness (FSR)

For the analytical expressions of the creep compliance $J(t)$, Laplace transformation (Eq. (3)) of the constitutive equation for the springpot (Eq. (1)) is performed with a step shear stress as the input and then solving for the strain $\gamma(t)$ by inverse Laplace transformation. For the Scott Blair model this gives the following expression for the compliance [Jaishankar and McKinley, 2013]:

$$J(t) \equiv \frac{\gamma(t)}{\sigma_0} = \frac{1}{G} \frac{t^\beta}{\Gamma(1 + \beta)}$$  \hspace{1cm} (10)

and for the fractional Maxwell model

$$J(t) = \left( \frac{1}{V} \frac{t^\alpha}{\Gamma(1 + \alpha)} + \frac{1}{G} \frac{t^\beta}{\Gamma(1 + \beta)} \right)$$ \hspace{1cm} (11)

As before $V$ and $G$ are quasi-properties, and $0 \leq \beta \leq \alpha \leq 1$ are the fractional exponents.

For materials probed at strains within the linear viscoelastic limit which can be described by a single power-law, or springpot element, the compliance is given by Eq. (10). Using the
definition of firmness in Eq. (7), the fractional equation for the firmness $F$ of a Scott Blair element becomes

$$F(t_f) = \frac{1}{J(t_f)} = \frac{G}{\Gamma(1 + \beta)} t_f^\beta$$

(12)

This expression for firmness is in line with Scott Blair’s observations: it is a time-dependent texture attribute that depends on two material properties, the quasi-property $G$ and the power-law exponent $\beta$, as well as on the time of observation $t_f$. We have defined the firmness $F$, as being independent of the stress applied, which also corresponds to Scott Blair’s findings: although the stresses applied by panelists varied by a factor two, it did not affect their judgments of differences in firmness. Since the time of observation is essential for quantifying numerical values of the firmness, any measurement should always be provided together with the observation time $t_f$ and the characteristic power-law exponent $\beta$, to enable extrapolation to practical situations. The time dependency of the firmness $F(t_f)$, favours a stress-controlled creep measurement (Fig. 1 (c)) over the more common practice of reporting a modulus from a strain-rate-controlled compression experiment (Fig. 1 (b)); the former experiment naturally exposes time effects and allows us to interconnect the firmness to situations where stressess are applied for short times, such as sensory texture measurement, or for long times, such as in storing cheese (Fig. 1 (a)).

The definition of the springiness $S$ is given in Eq. (8). The point $J(t_s)$ lies at the end of the creep curve and is given by the inverse of Eq. (12). The point $J(t_s)$ lies on the recovery curve and requires an appropriate fractional calculus expression for this part of the creep-recoil experiment, which is derived by [14]; the Scott Blair element:

$$J(t) = \frac{t^\beta - (t - t_f)^\beta}{\Gamma(1 + \beta)}, \text{ for } t > t_f$$

(13)

When we divide both nominator and numerator in Eq. (13) by $t_f^\beta$ and substitute the equation for firmness, Eq. (12), and our definition for the recovery time, $\Delta t = t - t_f$, we get

$$J(t) = \frac{t_f^\beta (t_f^\beta - \Delta t)^\beta}{F(t_f)}, \text{ for } t > t_f$$

(14)

To derive an expression for the springiness $S$, we first define the elapsed recovery time at which we measure as $\Delta t_s = t_s - t_f$. The numerator of Eq. (8) is then expressed as

$$J(t_s) - J(t_f) = \frac{t_f^\beta (t_f^\beta - \Delta t_s)^\beta}{F(t_f)} - \frac{1}{F(t_f)}$$

(15)

Substituting this in Eq. (8) and writing out $t_s = t_f + \Delta t_s$ gives
\[
S = \frac{|(1 + \Delta t_s/t_f)^\beta - (\Delta t_s/t_f)^\beta - 1|}{F(t_f)\Delta t_s}
\]  

(16)

The springiness equation reveals that this attribute is indeed inversely related to firmness. The time dependency of a springiness measurement is two-fold, it depends on the duration \(t_f\) of the creep phase and the time \(\Delta t_s\) over which the secant rate is measured. We have depicted this two-fold time dependency in Fig. 4 where we have plotted springiness for the two hypothetical materials A and B from the previous section (Fig. 3). Recall that at a time \(t_f = 10\) s these two materials were equally firm, and that material A (with the smaller fractional power-law exponent) was the most springy. This is in line with what we read out from the solid lines in Fig. 4(a) when we take \(\Delta t_s = 0.1\) seconds (for the elapsed time at which we measure springiness). However if we increase the value of the elapsed time \(\Delta t_s\), we arrive at a point where we measure approximately equal springiness for both materials. For \(t_f > 10\) s even a crossover point appears as shown by the dashed lines for \(t_f = 10^6\) s. This crossover point shifts towards smaller time with increasing \(t_f\) (data not shown). For small values of the elapsed recovery time \(\Delta t \approx t - t_f\) the springiness becomes independent of the total creep time \(t_f\). If we substitute the expression for firmness from Eq. (12) in Eq. (16) for times \(\Delta t_s\) that are small compared to the time of measuring firmness, \(t_f\), the latter time indeed cancels out:

\[
S \approx \left| \frac{-(\Delta t_s/t_f)^\beta}{G(1 + \beta)t_f^\beta\Delta t_s} \right|, \text{ for } \Delta t_s << t_f
\]  

(17)

To derive an expression for the rubberiness \(R\) of the Scott Blair element, we begin with the definition given in Eq. (9). Substituting the time \(t_r\) in Eq. (14) and subsequently defining this time in terms of elapsed recovery time, using \(t_r = t_f + \Delta t_r\) gives:

\[
J(t_r) = \frac{t_r^\beta \left((t_f + \Delta t_r)^\beta - \Delta t_r^\beta\right)}{F(t_f)}, \text{ for } t > t_f
\]  

(18)

When we substitute this equation for the compliance at the time at which we measure rubberiness, \(J(t_r)\), into the mathematical definition of rubberiness, given by Eq. (9), we obtain the following expression:

\[
R = 1 - t_r^\beta \left((t_f + \Delta t_r)^\beta - \Delta t_r^\beta\right)
\]  

(19)

It thus appears that rubberiness is not a function of the quasi-property \(G\) of the material directly, but of the two times \(\Delta t_r\) and \(t_f\), and the fractional exponent only. This two-fold time dependency is reflected in Fig. 4(b) where we have plotted the rubberiness \(R\), for the same materials A and B as in Fig. 3 and Fig. 4(a). For rubberiness we do not observe a cross-over.
point of the two materials. However the plots of the rubberiness reveal another remarkable
feature of this texture attribute: all power-law materials probed in the linear viscoelastic region
will ultimately show a rubberiness approaching unity. Distinctions between the two materials
only comes from differences in the fractional time exponent and the combination of values
of $t_f$ and $\Delta t_r$ chosen. In rheological terminology this means that the long term compliance
of the recovery phase, modeled with a single springpot, will approach zero, so that all of the
imposed strain is recovered elastically. Jaishankar and McKinley (2014) showed that this long
term behaviour for $J(t)$, Eq. (13), is approximated by

$$J(t) \approx \frac{\beta f}{\Gamma(\beta)} \left( \frac{t}{t_f} \right)^{\beta - 1}$$ (20)

Since $\beta < 1$, the compliance thus monotonically approaches zero, which confirms the
response in Fig. 4(b). The full elastic recovery of strain after a small applied deformation
within the linear viscoelastic regime is a hallmark of protein gels (Leocmach et al., 2014).

Our FSR-equations consist of only these material parameters and a specification of the
time of measurement. This suggests that we may perform a a single firmness measurement
(i.e. a creep test), determine the quasi-property $G$ and fractional exponent $\beta$, and then obtain
values for both springiness and rubberiness as long as we stay within the linear viscoelastic
region; a separate recovery measurement is not required.

Using fractional calculus, we have developed equations that enable the texture attributes of
firmness, springiness, and rubberiness to be defined in terms of two constitutive material pa-
rameters, which can be extended to four parameters if an even more accurate description over
a much wider time scale is necessary. The FSR-equations show that in the linear viscoelastic
regime these three texture attributes all time-dependent and coupled (to an extent that depends
on the total experiment duration). From a single measurement of the linear viscoelastic creep
compliance function $J(t)$ we can accurately determine the magnitudes of the quasi-property $G$
and fractional exponent $\beta$ describing the material, and then predict values of the firmness, the
springiness and the rubberiness. The firmness and springiness of a sample are anti-correlated
through the magnitude of the quasi-property $G$, which sets the scale of the stresses in the
material. By contrast, the rubberiness is not a function of the quasi-property, but only of the
fractional exponent $\beta$. Note that if equal test times are used to measure firmness during creep,
and to measure rubberiness during recovery, i.e. so that $t_f = \Delta t_r$, Eq. (19) gives

$$R = 2 - 2^\beta$$ (21)

and the rubberiness becomes time-independent.
We emphasize that the FSR-equations (12), (16), (19) allow us to quantify the three texture attributes from any of the standard linear viscoelastic material functions, as we demonstrate in Fig. 5(a). Here we display a frequency sweep performed on zero-fat Gouda cheese, a soft-solids, hydrocolloidal gel, at a temperature of $T = 10^\circ \text{C}$ and water/protein ratio of $w/p = 1.8$.

The linear viscoelastic properties of the cheese show the typical power-law behaviour of a critical gel [Winter and Mours, 1997]: a line of constant slope on a log-log plot over a wide range of frequencies for both the storage and loss modulus, {$G'(\omega), G''(\omega)$}, with both curves nearly parallel. To retrieve the quasi-properties and exponents from these plots, we need an expression for the storage and loss modulus for the Scott Blair model. The complex modulus is obtained by Fourier transforming the constitutive equation for the springpot, Eq. (1), which results in:

$$G^*(\omega) = G(i\omega)^\beta$$

Following the procedure for separating out the real and the imaginary part, outlined by Friedrich et al. [1999] and Schiessel et al. [1995], one can readily find for the storage modulus

$$G'(\omega) = G\omega^\beta \cos \left(\frac{\pi \beta}{2}\right)$$

and for the loss modulus

$$G''(\omega) = G\omega^\beta \sin \left(\frac{\pi \beta}{2}\right).$$

The magnitude of the complex modulus, $|G^*(\omega)|$, can be calculated from

$$|G^*(\omega)| = \sqrt{(G\omega^\beta \cos (\pi \beta/2))^2 + (G\omega^\beta \sin (\pi \beta/2))^2} = G\omega^\beta.$$  

This set of equations shows that $G'(\omega)$ can be predicted from $G''(\omega)$ and vice versa and that we can either fit equations (23), (24) or (25) to our dataset of $G'(\omega)$, $G''(\omega)$, or $|G^*(\omega)|$ respectively. We choose Eq. (25) in combination with a least square optimisation procedure to obtain $G$ and $\beta$, since it gives the least bias towards either the $G'(\omega)$ or $G''(\omega)$ data points.

The reconstituted curve of the SB model, using magnitudes of $G = 4 \times 10^5 \text{ Pa s}^\beta$ and $\beta=0.18$, is depicted by the solid lines in Fig. 5(a). It shows that the model gives a good fit for both the elastic and storage moduli, with only the two constitutive parameters, the quasi-property $G$ and the fractional exponent $\beta$.

The inset in Fig. 5(a) demonstrates that the phase angle is independent of the frequency $\omega$, which is a second typical feature of critical gels. This corresponds to what the Scott Blair model predicts:

$$\tan(\delta) = \frac{G''(\omega)}{G'(\omega)} = \tan \left(\frac{\pi \beta}{2}\right)$$

i.e. the phase angle is a function of the fractional exponent $\beta$ only.
In Fig. 5(b) we show the creep/recovery curve of a sample from the same zero-fat cheese (blue circles) as used in Fig. 5(a), at the same temperature of $T = 10^\circ C$. The dashed line denotes the prediction of the compliance $J(t)$, which is obtained by substituting the acquired material parameters (from the SB fit to the data for the complex modulus depicted in Fig. 5(a).) into the SB model expressions for $J(t)$ in the creep phase, Eq. (10), and in the recovery phase, Eq. (13), respectively. The hollow symbols in Fig. 5(b), and in the log-log representation of the creep phase in Fig. 5(c) and the recovery phase in Fig. 5(d), show that we accurately predict the evolution of $J(t)$, from which we can then calculate the firmness $F$ (circle), springiness $S$ (triangle), and rubberiness $R$ (circles) of zero-fat cheese. Both measured responses in Fig. 5(c) and Fig. 5(d) show some ‘creep ringing’ at very short times due to coupling of the elasticity with the moment of inertia of the instrument. Fig. 5(d) demonstrates that the compliance ultimately approaches zero, as predicted from Eq. (20).

3.3. Texture engineering

We have demonstrated how a framework based on fractional equations can be used to characterize and quantify the linear viscoelastic (LVE) response of hydrocolloidal gels. This framework is compact and effective and only one constitutive element, the two-parameter springpot or Scott Blair element (Eq. (1)) (Koeller, 1984), is required to describe the LVE material functions of cheese over a broad range of frequencies or times. The springpot is characterized by the quasi-property, $G$, and the fractional exponent, $\beta$, both introduced to rheology by Scott Blair et al. (1947). The quasi-property can be viewed as an ‘intermediate’ material property that is appropriate for characterizing soft materials and which sets the scale of the stress in the material. It smoothly interpolates between an elastic shear modulus $G$ and a Newtonian viscosity $\eta$. The fractional exponent quantifies the frequency and temporal response of the material and ranges from purely elastic ($\beta = 0$), to purely viscous ($\beta = 1$).

Our measurements show that its magnitude is related to the underlying microstructure and composition of the material.

From the descriptions of the manipulations and observations required to evaluate the firmness, springiness, and rubberiness of cheese from textural analysis (Szczesniak 1963b; Davis 1937; Foegeding and Drake 2007; van Vliet 1991) we have deduced that the rheological analogues of these attributes are all defined by specific points on the creep/recovery curve (Fig. 3). We have demonstrated that the fractional constitutive framework allows us to obtain quantitative descriptions of this rheological experiment that can be expressed explicitly in terms of the quasi-property and the fractional exponent of the model. By substituting the appropriate timescales of observations we are able to predict the textural measures of firmness.
F, springiness S, and rubberiness R, from the material properties G and β. We refer to our predictive equations based on essential material properties as the FSR-equations (Eq. (12), (16), (19) respectively). They guide the effective reformulation of semi-soft food gels such as cheese, while keeping the product at a desired level of firmness, springiness, and rubberiness.

In Fig. [6] we sketch out one example of our FSR-equations being used as a design tool. The markers in Fig. [6(a)] represent two sets of material parameters \(G, \beta_A\) and \(G, \beta_B\). These sets describe the hypothetical materials A and B from Fig. [3] and are mapped onto firmness contours, which are calculated with Eq. (12) and plotted on a logarithmic scale. In Fig. [6(a)] we take the same time of observation \(t_f = 10\) s as in Fig. [3], which results in the materials A and B being equally firm, i.e. \(F_A = F_B\). The markers in Fig. [6(a)] thus lie on the same iso-firmness line, and we take the magnitude of \(F = 6 \times 10^4\) Pa at \(t_f = 10\) s represented by these markers, as our desired level of firmness.

When we increase the time of observation in Fig. [6(b)] from \(t_f = 10\) s to \(t_f = 10^6\) s, the iso-firmness lines rotate counterclockwise, from a more horizontal to more vertical orientation. This tells us that at short times, the magnitude of the quasi-property G dominates firmness assessment, whereas at long times of observation it is dominated by the fractional exponent β of the material. This results in material A being the firmer of the two materials at \(t_f = 10^6\) s. It has the lowest quasi-property but also the lowest fractional exponent giving \(F_A = 6 \times 10^3\) Pa as compared to \(F_B = 2 \times 10^1\) Pa at \(t_f = 10^6\) s. If retaining shape after long times of loading (e.g. during storage) is a product requirement, material A is preferred over material B.

In Fig. [6(c)] we map these same two materials A and B onto a springiness contour plot. This figure shows that a more elastic material with a low value of the quasi-property is the most springy. Fig. [6(d)] demonstrates that there is no significant effect of the observation time \(t_f\) on the magnitude of springiness assessed in the material, provided that we use small values for the elapsed recovery time \(\Delta t_s \ll t_f\). This corresponds to our analysis of the springiness equation in section 3.2, the bulk of the elastic strain energy stored in the material is accumulated (and returned) at short time scales. For values of the fractional exponent \(\beta > 0.8\), the springiness rapidly drops and the material becomes very 'squishy'. If low springiness is preferred over retaining shape, than we chose material B. For rubberiness, similar plots to those shown in Fig. [6(a)-(d)] can also be created. If we take equal times of observations for firmness and rubberiness, \(t_f = \Delta t_s\), then equation (21) applies and all iso-rubberiness lines are vertical: the magnitude of the rubberiness is independent of the magnitude of the quasi-property G. The most rubbery material will be material A, which has the lowest fractional exponent.

Design plots such as Fig. [6] reflect graphical representations of how rheology can, and should, be used in the context of structure-texture engineering. The foundations for this ap-
approach were laid more than 60 years ago by Davis (1937) and Scott Blair (1947, 1959), two pioneers in food rheology. They both combined well-defined deformations of food-stuffs with a central question: which essential material property gives rise to a specific texture attribute.

We favour their approach over the more undirected approach of statistically correlating large amounts of rheological data to the results from Quantitative Descriptive Analysis (QDA) of multiple texture attributes. Our reservations to the latter approach are for two reasons. First the deformations and observations in QDA that lead to the texture judgment are ill-defined and may vary from panel to panel. This \textit{a priori} weakens correlations with the measurements obtained from the carefully designed rheological experiment. Our second argument to favour the Scott Blair / Davis approach, is that material properties are intrinsic properties whereas texture attributes are extrinsic in nature \cite{Reiner1971}. This essential difference is clearly demonstrated by the plots in Fig. 6. Whereas the coordinates of the markers that indicate the material properties of materials A and B do not change from plot (a)-(d), the grade and orientation of the contours that represent texture vary, depending on the attribute of interest and the timescale of observation chosen. The extrinsic nature of such sensory texture attributes makes it very hard, if not impossible, to make an unambiguous connection from a panel judgment to material models representing the food microstructure, when a purely statistical model is used as an intermediate. Once dynamic and quantitative relations between texture and the essential material properties are established (such as the FSR-equations developed in this study), one can build on the long track record of quantitative rheological testing for probing structure-property relations.

4. Conclusion

We have created a structure-texture engineering model which can help guide the rational reformulation of semi-soft food gels while maintaining reference levels of firmness $F$, springiness $S$, and rubberiness $R$. The central features of the model are rheological definitions of these texture attributes in the linear viscoelastic regime. Firmness is defined as the inverse of the compliance at the end of the creep regime, springiness as the secant rate of change of the compliance during the first 0.1 seconds of recovery, and rubberiness as the relative amount of strain recovered at the end of the creep recovery period. The firmness, springiness, and rubberiness (FSR) equations are constructed using a fractional constitutive framework, which can be visualized pictorially in terms of a mechanical element known as a springpot \cite{Koeller1984}. This framework compactly and effectively captures the predominant power-law relaxation and retardation of complex multi-scale materials such as cheese.
The FSR-equations contain only two material parameters, the quasi-property $G$, and the fractional exponent $\beta$ \cite{Scott Blair 1947}, and the resulting stress or strain in the material depends on an experimental time of observation $t_o$. These two material parameters can be extracted from measurements of any of the standard linear viscoelastic material functions: the complex modulus, $G^* (\omega) = G'(\omega) + i G''(\omega)$, the relaxation modulus, $G(t)$, or the creep compliance, $J(t)$.

Our FSR-equations are derived from linear viscoelastic theory and predict time-dependent responses for the firmness \cite{Scott Blair et al. 1947} (as demonstrated by Scott Blair et al. \cite{1947}) and also for the springiness and rubberiness assessed for a material. Firmness is linearly related to the quasi-property $G$, whereas springiness is inversely related to $G$. This rationalizes the anti-correlation between the two texture attributes commonly found experimentally. We have chosen to measure springiness at very short times of observation after the imposed shear stress is released, which results in a texture attribute that is independent of the time of observation for measuring firmness, $t_f$. Rubberiness is not a function of the quasi-property (i.e. the magnitude of the stress in the material), but only of the fractional exponent $\beta$, $t_f$, and the elapsed recovery time for measuring rubberiness, $\Delta t$. For the specific case where both times are equal, $t_f = \Delta t$, time cancels out and rubberiness is merely a function of the fractional exponent $\beta$ that characterizes the timescale of the material response.

The viscoelastic nature of the firmness implies that for specific pairs of power-law materials, the experimental conditions of creep and recovery can be chosen such that different materials appear to be equally firm. For values of the creep times that are common in judging cheese texture, one material can be assessed as the firmest, whereas for creep times relevant to storage the same material may be regarded as the softest. If one waits for the materials to recover from the imposed stress for long times, both power-law materials will fully recover from the applied stress and will be judged to be completely rubbery, however at shorter times the sample will appear to have different rubberiness. For all three examples of viscoelastic time-dependency outlined above, our FSR-equations can calculate if and when these transitions occur, provided the material parameters $G$ and $\beta$ of each material are known. The food engineer must be keenly aware of the temporal dependencies in these textural attributes before performing a rheological test.

Although there has been a long standing promise for rheology to deliver quantitative structure-texture relations for foods, successful examples are rare. In this paper we have implicitly formulated three prerequisites for a successful structure-texture model for food gels, based on shear rheometry. The first is selecting texture attributes that can be measured with bulk rheology and thus are assessed at first touch or bite (before mastication disrupts sample
homogeneity). This holds for all three of the attributes firmness $F$, springiness $S$, and rubberiness $R$, defined here. The second is to have rheological definitions that leave no room for selective interpretation and can be directly evaluated from well-defined rheological experiments. We have done so by defining realistic observation times and by revisiting the early creep / recovery experiments performed by Davis (1937) and argue that $J(t)$ should be the standard rheological curve for measuring and defining firmness, springiness, and rubberiness.

The third prerequisite is to have a constitutive model which accurately describes the material response to a deformation with as few material parameters as possible and from which the creep / recovery curve can be reconstituted. The model parameters should be intrinsic material constants and thus be obtainable from an independent rheological experiment, e.g. small amplitude oscillatory shear (SAOS). Fractional constitutive equations, such as the Scott Blair and fractional Maxwell model, based on the ideas of fractional calculus meet these requirements. The key to a successful structure-rheology-texture model is to determine material parameters that predict complex, time-dependent (and often subjectively-defined) properties such as texture which are founded in the material structure; Scott Blair’s (1947) original ideas of quasi-properties and fractional exponents do just that.

In Part II of this paper (Faber et al., 2016), we will show that the FSR-equations ((12), (16), (19)) will also quantify the firmness, springiness, and rubberiness in the viscoelastic regime from a measurement of the relaxation modulus $G(t)$. We also address the over-prediction by the Scott Blair model of the rate of recovery of cheese subjected to loadings that exceeds the linear viscoelastic limit and which therefore result in irreversible plastic flow events occurring.

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References


Shama, F. and Sherman, P. (1973). Evaluation of some textural properties of foods with the


Three methods of assessing the firmness, springiness, and rubberiness of cheese: (a) with human senses using touch (mouth or hands) or sight (eyes) or (b, c) with rheological measurements. (b) Monotonic uniaxial compression is the most commonly used test protocol but involves complex kinematics: nonlinear viscoelastoplasticity and fracture. In this paper we use (c) creep/recovery in simple shear to quantify firmness, springiness, and rubberiness in the linear viscoelastic limit.

Schematic representation of the springpot, a mechanical element defined by the quasi-property $G$ and the power-law exponent $\beta$, which we call the fractional exponent (adapted from Jaishankar and McKinley (2013)). For a material characterized by a single power-law only one element is needed to capture its linear viscoelastic response, we call this the Scott Blair model (SB). The arrows demonstrate how the springpot interpolates between a Newtonian dashpot with viscosity $\eta$ ($\beta = 1$) and a Hookean spring with modulus $G$ ($\beta = 0$). The corresponding constitutive equations are given below each element. (b) Mechanical analogue of the Fractional Maxwell Model (FMM) constructed from two springpots. The FMM has four material parameters: two quasi-properties ($G$ and $\mathcal{V}$) and two fractional exponents ($\beta$ and $\alpha$).

(a) Schematic representation of the springpot, a mechanical element defined by the quasi-property $G$ and the power-law exponent $\beta$, which we call the fractional exponent (adapted from Jaishankar and McKinley (2013)). For a material characterized by a single power-law only one element is needed to capture its linear viscoelastic response, we call this the Scott Blair model (SB). The arrows demonstrate how the springpot interpolates between a Newtonian dashpot with viscosity $\eta$ ($\beta = 1$) and a Hookean spring with modulus $G$ ($\beta = 0$). The corresponding constitutive equations are given below each element. (b) Mechanical analogue of the Fractional Maxwell Model (FMM) constructed from two springpots. The FMM has four material parameters: two quasi-properties ($G$ and $\mathcal{V}$) and two fractional exponents ($\beta$ and $\alpha$).

Creep/recovery curves of two hypothetical materials A (red) and B (blue) with identical firmness and different springiness and rubberiness. Specific values of the compliance for each material indicated with filled markers are used to calculate firmness $F$ (squares), springiness $S$ (triangles), and rubberiness $R$ (circles). Their corresponding times of observations, $t_f$, $t_s$, and $t_r$ are plotted as hollow markers on the time-axis. We define the elapsed time of recovery as $\Delta t = t - t_f$ (black dashed line). Firmness is the inverse of the maximal creep compliance max $\{J(t)\}$ and thus has units of Pa. Springiness has units of $(\text{Pa s})^{-1}$ and is defined as the secant rate of recovery just after the stress is removed at $t = t_f + \Delta t_s$, where $\Delta t_s \ll t_f$. For each material, the dashed, colored, secant line goes through the correspondingly colored filled square and triangle. The absolute magnitude of the slope of the secant is equal to the springiness $S$. Rubberiness is defined as the relative extent to which the compliance recovers from the stress applied. If $J(t) = 0 \text{ Pa at } t = t_r$ then the rubberiness $R = 1$. We have chosen $t_r$ such that $\Delta t_r >> \Delta t_s$. Material A (red) is more springy and more rubbery than material B (blue). (b) The same experiment as in (a) but now plotted on a log-log scale, without the recovery phase and with the creep phase extrapolated (dashed line). The plot shows that A and B are power-law materials: $J(t) \propto t^\beta$, where $\beta$ is the power-law exponent. This plot emphasizes the importance of controlling and reporting time when assessing firmness: only at $t_f$ are the two materials equally firm, before or after this point the material with the lowest compliance is the firmest. In the text we also demonstrate that the magnitude of the springiness and firmness are also dependent on the time of observation chosen.

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4 Effect of measurement time on the values of (a) springiness and (b) rubberiness. The colors represent the two hypothetical materials A (red) and B (blue) from Fig. 3. The solid and dashed line represent a time $t_f$ for measuring firmness of $t_f = 10$ s and $t_f = 10^6$ s respectively. The springiness $S$ and rubberiness $R$, are functions of both $t_f$, and the elapsed time of recovery $\Delta t$ at which we calculate $S$ and $R$. The markers denote the elapsed recovery times we have chosen to calculate springiness, $\Delta t = 0.1$ s (triangles in (a)) and rubberiness, $\Delta t = 10$ s (circles in (b)). Our choice of $\Delta t << t_f$ makes the springiness $S$ independent of the time for measuring firmness $t_f$. Our choice of $\Delta t << \Delta t_f$ makes springiness and rubberiness two distinct properties.

5 (a) Determining the quasi-property $G$ and fractional exponent $\beta$ of zero-fat cheese with a water/protein ratio $w/p = 1.8$ and a temperature of $T = 10^\circ C$. The material parameters are obtained by fitting the Scott Blair model (SB, black line) for the complex modulus, Eq. (25), to the storage and loss modulus measurements $\{G'(\omega),G''(\omega)\}$ (filled and unfilled symbols respectively). The SB model gives a good fit demonstrating that the relaxation behaviour of cheese is well described by a single power-law over frequencies $1 \leq \omega \leq 100$ rad s$^{-1}$. Inset: phase angle as a function of the frequency. (b) Creep/recovery experiment ($\sigma_0 = 100$ Pa) of zero-fat cheese at $T = 10^\circ C$. Dashed line: prediction of the compliance $J(t)$ during creep and recovery using the Scott Blair element, Eq. (10) and Eq. (13), with $t_f = 10$ s and $\Delta t_f = 10$ s, and the material properties from the fit in (a). The hollow symbols are the specific points from the predicted creep/recovery curve which are used to calculate the firmness $F$, (square), springiness $S$, (triangle), and rubberiness $R$, (circle). (c,d) Same experiment and predictions as in (b) plotted on a log-log scale and with the creep phase (c) and the recovery phase (d) separated. (d) The compliance ultimately approaches zero, as predicted from Eq. (20). These plots demonstrate that our equations correctly predict the firmness, springiness, and rubberiness of power-law materials such as cheese, from the two constitutive parameters $G$ and $\beta$ describing the material.

6 Contour plots of the magnitude of the firmness $F$, Eq. (12), and the springiness $S$, Eq. (16), of power-law materials such as cheese. The magnitude of the firmness and springiness are functions of the quasi-property $G$ and fractional exponent $\beta$ describing the material. The times of observation $t_f$ and $\Delta t_f$, at which the firmness and springiness are measured are indicated above each plot. The scale bars and contour lines are spaced logarithmically. The material properties of the hypothetical materials A and B from Fig. 3 and Fig. 4 are mapped onto each contour plot as red and blue markers respectively. (a) At $t_f = 10$ s, materials A and B are equally firm and the iso-firmness lines are close to horizontal, meaning the firmness $F$ is dominated by the magnitude of the quasi-property $G$. (b) At $t_f = 10^6$ s, the iso-firmness lines are inclined to be almost vertical and the magnitude of the fractional exponent $\beta$ dominates the magnitude of the firmness $F$. For times $t_f > 10$ s, material A is firmer than material B, which corresponds to what we have depicted in Fig. 3(b). (c,d) Springiness is hardly affected by the value of $t_f$. All iso-springiness lines slope downwards as the exponent $\beta$ increases. For materials with equal fractional exponent $\beta$, the material with the smallest value of the quasi-property $G$ is the most springy.
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