

Dynamic oscillatory shear testing of foods — selected applications

Sundaram Gunasekaran^{a,*}
and M. Mehmet Ak^b

^aBiological Systems Engineering Dept., University of Wisconsin-Madison, Madison, Wisconsin, USA
(tel: +1-608-262-1019; fax: +1-608-262-1228;
e-mail: guna@facstaff.wisc.edu)

^bDepartment of Food Engineering, Istanbul Technical University, Istanbul, Turkey

An ideal solid material will respond to an applied load by deforming finitely and recovering that deformation upon removal of the load. Such a response is called “elastic”. Ideal elastic materials obey Hooke’s law, which describes a direct proportionality between the stress (σ) and strain (γ) via a proportionality constant called modulus (G), i.e., $\sigma = G\gamma$. An ideal fluid will deform and continue to deform as long as the load is applied. The material will not recover from its deformation when the load is removed. This response is called “viscous”. The flow of simple viscous materials is described by Newton’s law, which constitutes a direct proportionality between the shear stress and the shear rate ($\dot{\gamma}$), i.e., $\sigma = \eta\dot{\gamma}$. The proportionality constant η is called the shear viscosity. From energy considerations, elastic behavior represents complete recovery of energy expended during deformation, whereas viscous flow represents complete loss of energy as all the energy supplied during deformation is dissipated as heat. Ideal elastic and ideal viscous behaviors present two extreme responses of materials to external stresses. As the terms imply, these are

* Corresponding author.

only applicable for “ideal” materials. *Real* materials, however, exhibit a wide array of responses between viscous and elastic. Most materials exhibit some viscous and some elastic behavior simultaneously and are called “viscoelastic”. Almost all foods, both liquid and solid, belong to this group. The viscoelastic properties of materials are determined by transient or dynamic methods. The transient methods include stress relaxation (application of constant and instantaneous strain and measuring decaying stress with respect to time) and creep (application of constant and instantaneous stress and measuring increasing strain with time). Though such methods are fairly easy to perform, there are several limitations. Major among them is that the material response cannot be determined as a function of frequency. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Dynamic tests

The dynamic test is performed applying a small sinusoidal strain (or stress) and measuring the resulting stress (or strain). These small-amplitude oscillatory tests are commonly performed in shear and hence the abbreviation SAOS, for small-amplitude oscillatory shear, is commonly used to represent dynamic viscoelastic tests. Though not yet very popular, the dynamic tests are also performed in compression/tensile mode [1,2] and in large amplitude shear mode (at strains in excess of 100%) [3]. It is important to emphasize that the strains (and stresses) used in SAOS tests are very small, often in the order of 1 to 3 or 5%. This is to assure that the material response is in the linear range—the range within which the stress is proportional to the applied strain, and the theory described below is applicable. The focus of this paper is to present only the linear viscoelasticity as measured by the SAOS tests.

The stress response of a linear viscoelastic material to a sinusoidal strain input is given as:

$$\sigma(t) = \gamma_0 G'(\omega) \sin(\omega t) + \gamma_0 G''(\omega) \cos(\omega t)$$

The frequency dependent functions $G'(\omega)$ and $G''(\omega)$ are shear elastic (storage) modulus and shear elastic (loss) modulus, respectively. G' is a measure of the energy stored and subsequently released per cycle of deformation per unit volume and. It is the property that relates to the molecular events of elastic nature. G'' is a measure of the energy dissipated as heat per cycle of

deformation per unit volume. G'' is the property that relates to the molecular events of viscous nature. Another commonly used dynamic viscoelastic property, the loss tangent [$\tan\delta(\omega) = G''/G'$] denotes relative effects of viscous and elastic components in a viscoelastic behavior. Some times the complex modulus G^* [$|G^*| = \sqrt{G'^2 + G''^2}$] is also used to describe dynamic test data.

Similarly, complex viscosity (η^*) can also be defined in terms of real (η') and imaginary (η'') parts of viscosity. The quantities G' , G'' and η' , η'' enable the rheological characterization of a viscoelastic material on the basis of an SAOS test.

The SAOS measurement is popular and useful for many reasons:

- It is a non-destructive technique enabling measurements to be made without incurring structural damage to the sample. This allows researchers to relate dynamic rheological parameters to the sample's molecular structure. These tests also provide a very sensitive means of studying the molecular motions that give rise to the phenomenon like glass transition temperature.
- It allows selective probing of molecular events by choosing a proper frequency range [4] since, in a dynamic mechanical experiment, the stress response is dominated by relaxation processes with a time constant near $1/\omega$.
- The linear viscoelastic region can be determined easily in dynamic testing by changing the amplitude of the input strain or stress function [5].
- Two quantities, usually G' and G'' , are measured simultaneously which provide a check on experimental error and applicability of time-temperature superposition [5].
- When applicable, data from oscillatory tests can be utilized in time-temperature superposition technique to expand the frequency range which otherwise would be inaccessible experimentally [6].
- Knowledge of dynamic properties such as G' and G'' allows computation of all other linear viscoelastic properties as well as the material behavior in other types of deformations such as tension.
- It is generally faster to perform oscillatory tests than to perform other linear viscoelastic experiments such as creep and relaxation. However, this depends on the selected range and number of frequencies [5].
- Sudden change of the displacement (stress relaxation test) or load (creep test) is not required in oscillatory shear experiments [7].
- Since it is a frequency domain rather than a time domain test, the amplitude of the deformation γ_0 and the time scale $1/\omega$ can be independently varied [7].

Although linear viscoelasticity is ideally suited to provide information to improve our understanding of material structure and its organization, most food processing operations (e.g., extrusion, pumping, mixing, spreading, chewing) involve large and rapid deformations that cannot be modeled using the theory of linear viscoelasticity alone. However, this is not a drawback for SAOS tests since it is the structure that controls the rheological response of the material, even in such large and rapid deformations. Moreover, many nonlinear constitutive equations for modeling response of materials in large deformations contain parameters derived from linear viscoelastic data [6]. For additional detailed information on the theory of linear viscoelasticity and measurement techniques the readers are referred to the classical work of Ferry [8] and others [9,10].

Due to both its many advantages and recent rapid improvements in measurement hardware and software, the SAOS tests are used now routinely in a wide variety of applications. Therefore, an exhaustive review of all applications is beyond the scope of this paper. Our goal is to present results of some selected applications. As such, there are many obvious omissions, starch and dough systems and muscle foods for example. Nonetheless, the topics discussed herein should provide the readers a broad overview of some major SAOS test applications.

Selected applications

Generally speaking, an investigation employing SAOS method should begin with the determination of strain or stress limit for which the linear viscoelasticity theory is applicable. For this, a strain or stress sweep test must be performed at a low frequency (e.g., 1 Hz) by increasing the amplitude of the imposed strain/stress. This test is schematically illustrated in Fig. 1. Once the linear viscoelastic limit is determined, we can proceed with further experiments (e.g., frequency-sweep) made at strains (or stresses) within this limit. It is highly recommended to repeat the strain sweep test at the extremes of experimental variables, for there are data indicating that the linear viscoelastic region can vary with test frequency, temperature, sample age, and composition etc. [11–13].

Dairy products

The SAOS technique is commonly used to measure linear viscoelastic properties of materials during gelation and aging. In a gelling system we usually observe sudden increases in G' and G'' after an initial lag period. This is often followed by a gradual decrease in rate of increase of G' and G'' which eventually levels off in most cases. Moreover, once the mature (or fully cured) gel is obtained, it is common practice to take further measurements such as: (a) strain sweep (G' and G'' vs. γ) to determine the linear viscoelastic region, (b) frequency

sweep (G' and G'' vs. ω) to determine the elastic character of the gel and (c) temperature sweep (G' and G'' vs. T) to evaluate thermal characteristics.

One immediate concern arises when we want to determine viscoelastic properties of a system going from viscous milk to elastic gel. This is whether the applied strain or stress amplitude affects the aggregation process. Dejmek [14] measured G' and G'' during rennet coagulation of milk. When the applied shear strain was high (i.e., $\gamma_0 = 0.2$), the resulting G^* from the continuous oscillation mode was significantly greater than that from the intermittent oscillation mode. Apparently, continuous oscillation affects the aggregation process. He also reported that the coagulation process was not affected by continuous shear strains below 0.05 at 1 Hz. To avoid disturbing the skim milk gel network, Zoon *et al.* [15] started oscillatory shear measurements at 1 rad/s (~ 0.16 Hz) only after a weak gel formed (i.e. $G' \approx 2$ Pa).

Dejmek [14] reported that the linear viscoelastic strain limit for mature rennet gels was 0.05. For rennet-induced skim milk gels, 0.03 was the corresponding limit [15]. Paulsson and Dejmek [16], applied strain amplitude of 0.02 at 1 Hz to stay in the linear viscoelastic region while monitoring formation of heat-induced

β -lactoglobulin gels. Most studies on dairy gels have been performed using strain amplitudes less than 0.05 and a frequency of 1 Hz.

A typical curve obtained during gelation (or curing) is schematically illustrated in Fig. 2. The beginning of time axis ($t = 0$) usually refers to the addition of rennet or acid to the milk. There is generally a lag period before dynamic properties attain values greater than the minimum torque of the rheometer. After the initial lag period, both G' and G'' increase with a rate that depends on the experimental conditions. Whether dynamic properties reach a plateau value or not also depends upon experimental conditions such as the temperature at which the gel is formed and aged [17].

Bohlin *et al.* [18] investigated effects of calcium chloride and rennet concentrations along with temperature on coagulation of milk. They showed that higher concentrations of rennet and calcium chloride and elevated temperature resulted in an earlier start of coagulation and a faster gelation rate, leading to stiffer gels (i.e., higher G^* values). The start of coagulation was identified as the time at which G' and G'' began to deviate from zero (see Fig. 2). Nakamura and Niki [19] studied the influence of calcium concentration on rheological

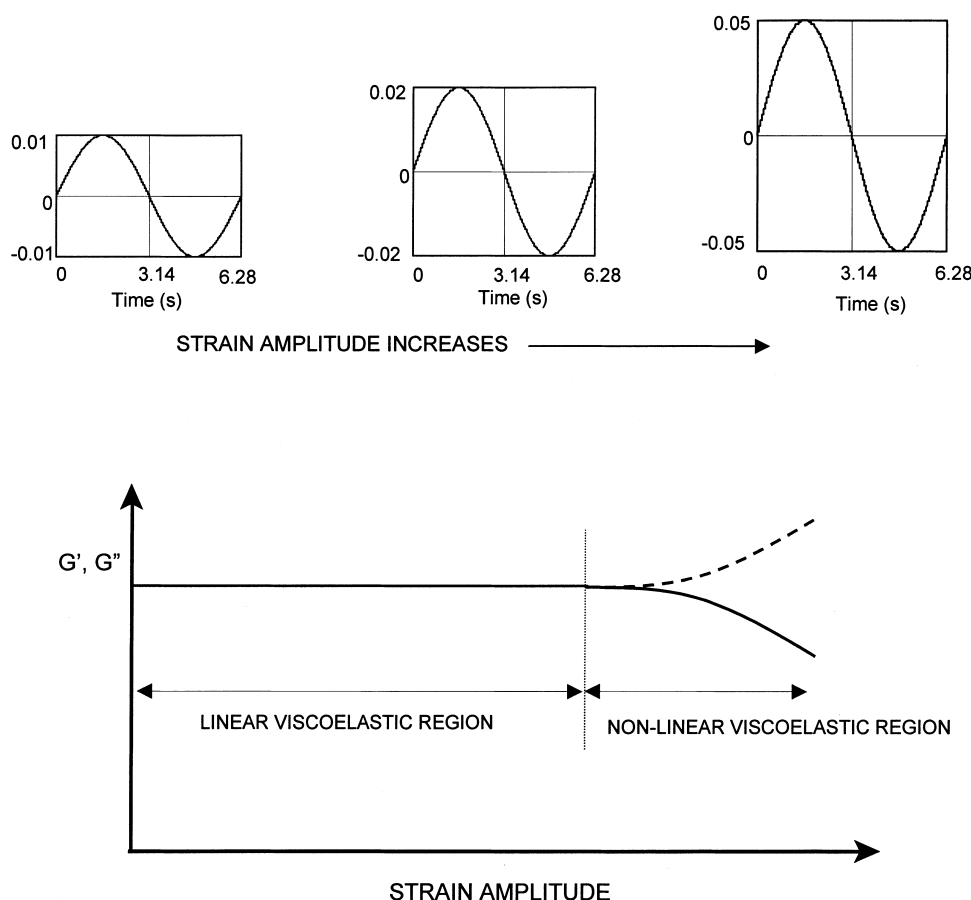


Fig. 1. Schematic illustration of the strain sweep test used in determining the linear viscoelastic region. Strain amplitude is increased, at a selected frequency, until the storage (G') or loss (G'') modulus ceases to be interdependent of the applied strain.

properties of casein micelles during gelation. They concluded that changing calcium concentration affects gelation rate but not the mechanism of gelation.

SAOS measurements have also been used to characterize behavior of dairy products (e.g., yoghurt, cheese, whey gels) as well as to evaluate effects of many factors on viscoelastic properties of these products. Skriver [20] conducted SAOS tests on stirred yoghurt to assess effect of technological parameters such as culture type, fermentation temperature, and dry matter content on rheological characteristics of the product. Based on dynamic shear data, stirred yoghurt was characterized as a weak gel. The main properties of weak gels are given by Ross-Murphy [21] as $G' > G''$, both G' and G'' are largely independent of frequency, and the linear viscoelastic strain limit is small ($\gamma < 0.05$). Moreover, Skriver [20] found that exo-polysaccharide produced by the ropy culture did not contribute to the dynamic gel stiffness of stirred yoghurt. This finding was in contrast to the viscometry (large deformations) results where the contribution of exo-polysaccharide to shear stress was reported to be significant [22]. Paulsson and Dejmek [16] studied gelation of heat-induced β -lactoglobulin by oscillation rheometry at different pH levels (4.5, 5, 7) and protein concentrations (3, 4, 5% mass/vol). They reported that the temperature at the start of gelation was mostly independent of pH and protein concentration but the value of G^* was influenced mainly by the protein concentration and to a lesser degree by the pH. It is interesting to note that the exponent n in the relation $|G^*| \propto (c)^n$, where c is the protein concentration, varied between 2.2 and 2.6 for rennet and acid milk gels [15] as well as heat-induced β -lactoglobulin gels when pH was below 7. When pH was 7, a higher value for n was reported [16].

Another use of SAOS test was demonstrated by Ozer et al. [23] where rheological properties of six different labneh (concentrated yogurt) samples were compared

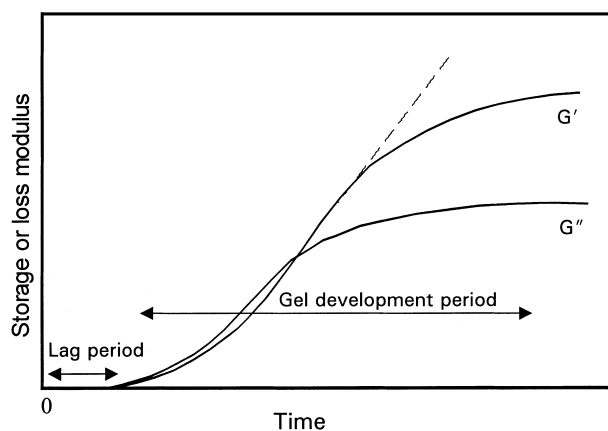


Fig. 2. Illustration of typical storage (G') and loss (G'') moduli data as a function of time during gelation of milk showing the initial lag period and the subsequent gel development period.

using data from SAOS, penetrometer, and viscosity tests. The destructive penetrometer and viscosity measurements failed to reveal expected differences among labneh samples prepared after different treatments. However, dynamic tests clearly differentiated between the samples and, therefore, were considered to be more reliable to determine rheological properties of labneh.

Food emulsion gels

Different types of emulsions are widely encountered in such food products as ice cream, margarine, butter, beverages, sauces, salad dressings and mayonnaise [24]. The stability of food emulsions is a rather important and complex phenomenon that greatly influences the quality and performance of a product. Good emulsion stability means that the size distribution and the spatial arrangement of droplets do not change significantly during the observation time. Rheological properties of food emulsions play an important role in stability as well as in the texture and mouthfeel of these products.

Muñoz and Sherman [25] measured the viscoelastic properties of commercial mayonnaise, reduced calorie mayonnaise, and salad creams using SAOS tests with a controlled stress rheometer (1 Hz, 8.96–18.51 Pa). They have explained the observed differences in viscoelastic properties by variations in the ingredients of these emulsions. For instance, the lower G' value of one mayonnaise compared to another was due to the presence of sugar in the former, as sugar molecules exerted a shielding effect on protein groups which are involved in interaction and network formation among the oil droplets. Peressini *et al.* [26] reported that G' increased with increasing fat content in the 48 to 76% range.

The lowest G' values for salad creams were attributed to the lower oil content, yielding a lower concentration of oil droplets in the emulsion. This was in accord with the results of Dickinson and Golding [27] that even when protein concentration was high ($> 8\%$ by mass) emulsion made with lower volume fraction of dispersed phase (oil) had a weaker structure. Other studies by Gallegos *et al.* [28] and Ma and Barbosa-Cánovas [29] confirm that higher oil contents result in higher dynamic moduli for commercial and model mayonnaise samples. Moreover, the strain sweep measurements at 10 rad/s on model mayonnaise samples indicated a narrower linear viscoelastic region for samples with lower oil content [28]. Small size oil droplets have a more dramatic filler effects than larger droplets. Matsumura *et al.* [30] reported that emulsion gels made from a fine emulsion, containing small oil droplets, exhibited higher G' and G'' than the gels made from coarse emulsion, containing larger oil droplets.

Past work on whey proteins has shown that co-homogenization or pre-emulsification of the oil with lecithin reduces significantly the strength of heat-set emulsion gels [31]. Consequently, Dickinson and

Yamamoto [32] used SAOS method (1 Hz, maximum strain amplitude of 0.5%) to examine thoroughly the effect of varying amounts of lecithin addition after emulsion formation on the properties of heat-set β -lactoglobulin emulsion gels. The dynamic data (G' and G'') clearly showed that the addition of lecithin at a concentration of 4.4% by mass increased G' of the heat-set β -lactoglobulin emulsion gel by at least 10 times. It was suggested that once β -lactoglobulin becomes adsorbed at the surface of oil droplets, the role of lecithin is then to form complexes with adsorbed and free β -lactoglobulin to reinforce the heat-set emulsion gel network [32]. The positive effect of lecithin was also observed in G' of heat-set β -lactoglobulin gel (no oil) but to a lesser extent. It was concluded that the lecithin-containing emulsion gels behaved more like a “strong” gel since G' was less frequency-dependent in the range 10^{-3} to 2 Hz as compared to the β -lactoglobulin gels made without lecithin. Goff *et al.* [33] reported the effect of stabilizers on the dynamic rheological properties of ice cream. Unstabilized samples had significantly higher G' and G'' at temperatures less than -8°C . It was clear that the dynamic shear testing can provide insights into the structure development in ice cream.

Chen and Dickinson [34] used SAOS measurements to investigate the effect of interfacial ageing of the β -lactoglobulin monolayer at the droplet surface on the viscoelasticity of heat-set whey protein isolate emulsion gel. They demonstrated that the ageing monolayer contributed to a smaller G' compared to the fresh emulsion gel. Apparently because the emulsion droplets covered by the aged β -lactoglobulin monolayer are not well integrated into the gel matrix.

Emulsion droplet structure information is also obtainable for the dynamic measurements. For example the nature of the $G''(\omega)$ curve can be related to the mono or polydispersity of the emulsion; and from the G' at 1 Hz vs. volume fraction data “close-packing limit” for the droplets in a highly concentrated emulsion can be determined [13].

Gel point determination

Another area of research where SAOS method has found wide use is in determining gel point, i.e., the moment at which a polymer/biopolymer system changes from a viscous liquid (sol) to an elastic solid (gel) during the course of the gelation process.

Determining the gel point from rheological properties such as steady shear viscosity for the liquid state and equilibrium shear modulus for the solid state requires extrapolation and suffers from singularity at the transition [35]. SAOS method, however, provides continuous rheological data for the entire gelation or curing process. Hence, SAOS has become widely used to investigate the sol/gel transition and the properties of mature gels [36].

Ross-Murphy [37] listed a number of rheological measures to detect gel point or gel time: (1) when the signal from gelling system becomes just greater than the background noise, (2) when G' becomes higher than a chosen threshold value, (3) when G' becomes just greater than G'' (the cross-over method), and (4) when $\tan\delta$ becomes independent of frequency (the Winter–Chambon method). Method 1, though simple, suffers from being dependent on the instrument’s minimum torque value which may vary among commercial rheometers. Method 2 requires prior knowledge of the proper value for gel strength. Method 3, as Tung and Dynes [38] pointed out, depends on the frequency of the oscillation test. Method 4, based on fundamental arguments that have been experimentally supported, appears to be the most preferred way in recent studies. But not all methods are suitable for all the food biopolymer gel systems. For example, entanglement network systems (weak gels) show a strong G' vs. frequency dependence and even a $G' - G''$ crossover. Crosslinked network gels (strong gels or chemical gels) show very little G' vs. frequency dependence. Physical gels which are intermediate between strong and weak gels show G' vs. frequency dependence but no $G' - G''$ crossover [39, 40]. They proposed the following relationship for the frequency (f) dependency of G' :

$$\log G' = n \log f + K$$

where, K and n are constants. For crosslinked gels $n = 0$ and physical gels $n > 0$. Therefore, n can be used as a measure of how close the gel is to being a covalent gel.

Tung and Dynes [38] suggested that the time at which G' and G'' curves cross each other (i.e. $\tan\delta = 1$) can be used for determining the gel point. Bryant and McClements [41] used this criterion to determine the gel point of heat-denatured whey protein isolate. However, this criterion becomes difficult to use in complex mixed systems such as a starch paste [39, 42]. Winter [43] examined the validity of $G' - G''$ crossover as the gel point. He stated that if $G' - G''$ crossover coincides with gel point, then the polymer should have a power law relaxation at the gel point, $G_t \propto t^{-n}$ for $n = 1/2$. If $n > 1/2$, the gel point occurs earlier than $G' - G''$ crossover. Doublier *et al.* [44] state that in some cases, $\tan\delta = 1$ at a given frequency can be regarded as a rather good criterion to detect the gel point if the chosen frequency is sufficiently low. But it is better to consider a range of frequencies. Therefore, the independence of $\tan\delta$ on frequency leads to the best estimate.

Stading and Hermansson [39] also give another method of defining gel point—at maximum G'' . This maximum is, however, not easily detectable due to excessive signal noise. Te Nijenhuis [45] reported a G'' maximum for gelatin just after the gel point. For gelation of

β -lactoglobulin, the gel point determined based on $G' > \text{noise}$ and $\tan\delta = 1$ were very close but the G'' maximum gave a higher value [39]. For some low viscosity systems, eg. milk, G'' may not be measurable with some low-sensitivity rheometers. In such cases, gel point is often determined to be when $G' > \text{noise}$ [46].

According to the Winter–Chambon method, $\tan\delta$ is independent of frequency at the gel point for chemical gels [36] (Fig. 3). The cross-over method is a special case of the Winter–Chambon method [35,47]. However, gelation time determined by this criterion does not necessarily correspond with that for the $G' - G''$ cross-over in a single frequency experiment [35]. It has been shown that the same criterion can be used to determine critical condition during either gelation or melting in *i*-carrageenan gel, a physical gel [44]. It has been extended to other biopolymer gels systems, gelatin and xanthan-locust bean gum mixtures [48]. Lopes da Silva and Gonçalves [49] studied rheological properties of curing high methoxyl pectin/sucrose gels at different temperatures using SAOS experiments. The $G' - G''$ crossover method could not be used as a criterion to identify the gel point. They instead applied the Winter–Chambon criterion. Michon *et al.* [50] applied the Winter–Chambon criterion to determine critical parameters of gelation (e.g., time, temperature) at different polymer concentrations for systems involving iota-carrageenan and gelatin. When gelatin was cooled from 60°C, the gelling time was found to be 44 min. In another set of experiments, the gelation temperature of iota-carrageenan was determined to be 53.5°C based on the same criterion. These researchers provided phase diagrams where critical temperature of sol–gel transition was charted against concentration of the polymers. These graphs showed that at a given temperature, a gelatin with mean molecular mass of 70,000 daltons would require a much higher concentration for the sol–gel

transition than that with a mean molecular mass of 182,000 daltons.

Gel forming ability of whey protein isolate (WPI) dispersions subjected to different heat treatments and other processing variables (e.g., pH, concentration) has been investigated by Labropoulos and Hsu [51] using SAOS method. Employing the Winter–Chambon method of gel point detection, a wide range of gelation times from 12 to 164 min were obtained depending on the experimental conditions. Information from such studies is expected to allow processors to obtain desired gel properties by controlling the variables during gelation of WPI dispersions. One additional advantage of applying the Winter–Chambon criterion, where possible, is that it is not necessary to have a constancy of the viscoelastic properties all along a frequency sweep, a condition which will not be met during fast gelation or melting, and it is even possible to obtain gel point by interpolation [44]. Recently, Petrofsky and Hosney [52] reported the need for using a temperature correction for probe frequency in the sample in evaluating sol–gel transition based on their studies with starch paste.

During heating of some gels, the $G' - G''$ cross over can also be used to identify gel melting transitions. For example, the $G' - G''$ cross over was considered a good indicator of process and imitation cheese meltability as determined by traditional tests [53,54].

For more detailed description of viscoelastic properties of food and biopolymer gels the readers are referred to Doublier *et al.* [44] and Clark and Ross-Murphy [55]

Determining glass transition temperature

Materials with amorphous or partially amorphous structures undergo a transition from a glassy solid state to a rubbery viscous state at a material-specific temperature called the glass transition temperature, T_g [2,56]. Glass transition in amorphous food materials generally occurs over a range of temperature rather than at a single temperature [56–58].

The technological importance of the glass transition phenomenon for different types of foods has been discussed in detail in the literature [56,59–65]. The glass transition or the associated parameter T_g has a great effect on processing, properties, quality, safety, and stability of foods [66]. T_g or the difference between the temperature of a material and its T_g (i.e., $T - T_g$) affects the physical and textural properties of foods (e.g., stickiness, viscosity, brittleness, crispness or crunchiness), the rates of deteriorative changes (e.g., enzymatic reactions, nonenzymatic browning, oxidation) and the success of many processes (e.g., flavor encapsulation, crystallization). Hence, the knowledge of T_g is essential in assuring quality, stability and safety of various foods such as confectionery products, breakfast cereals, baked goods, coated flavors, frozen products, and food powders [57,59,62,63,66–75].

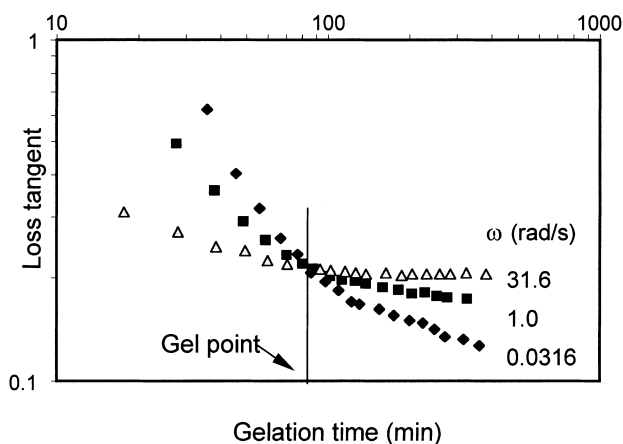


Fig. 3. Illustration of gel point determination per Winter–Chambon criterion. At the gel point, loss tangent ($\tan\delta$) is independent of frequency (ω) [data from ref. 36].

At glass transition temperature,¹ properties such as the thermal expansion coefficient, the dielectric constant (for polar materials) and the heat capacity exhibit a discontinuity. Thus, techniques measuring such property changes have been developed for experimental determination of T_g (e.g., dilatometry, calorimetry) [2]. Differential scanning calorimetry (DSC) is probably the most commonly used technique for determining T_g . Besides DSC, the utility and advantages of other techniques such as the nuclear magnetic resonance (NMR), the electron spin resonance spectroscopy (ESR), and the dynamic mechanical (thermal) analysis (DMA or DMTA) have been increasingly appreciated [77–82]. Kalichevsky *et al.* [80] stated that the dynamic mechanical techniques are more sensitive than DSC to the molecular motions around T_g and the relaxations below T_g .

When dynamic mechanical spectroscopy is employed within the linear viscoelastic regime to determine T_g , the storage and loss moduli (G' and G'' or E' and E'') and loss tangent ($\tan\delta = G''/G'$ or E''/E') are measured as a function of temperature at a constant frequency and a selected heating or cooling rate. In glass transition, the storage modulus of biological and synthetic polymers exhibits a sharp drop with temperature, whereas the loss modulus or $\tan\delta$ shows a characteristic peak [2,55,81,83–86]. The decrease observed in modulus of amorphous synthetic polymers is typically about three orders of magnitude, whereas that observed in biopolymers is about one order of magnitude [77,80–82]. Moreover, as Peleg [87] demonstrated, the plot of stiffness or rigidity (E' , G') vs temperature in the transition region of biomaterials has a downward concavity, which cannot be described by conventional models, such as WLF [88], developed for synthetic polymers. Peleg, therefore, suggested another model and demonstrated its applicability to describe the stiffness or rigidity vs temperature relationship of biopolymers at the transition region [58,84,87,89–91].

Different definitions have been used to facilitate experimental determination of T_g from the dynamic mechanical data: (a) temperature corresponding to the onset of drop in storage modulus T_{onset} , (b) temperature corresponding to the midpoint of the glass transition region for storage modulus T_{midpoint} , (c) temperature where the extrapolated line of the initial modulus intersects that of the steepest slope $T_{\text{intersect}}$, (d) temperature corresponding to the loss modulus G'' peak $T_{G''}$, and (e) temperature corresponding to the $\tan\delta$ peak $T_{\tan\delta}$. These are schematically illustrated in Fig. 4. It must be noted that values of T_g for the same material may differ slightly or significantly depending on the definition, the experimental conditions (e.g., heating/cooling rate in

DSC, and test frequency in DMA or DMTA), and the technique (e.g., DSC vs DMA) [82,83]. Hagen *et al.* [92] reported that T_g values, for instance, of an unfilled natural rubber, differ by about 10°C when determined by using two commercial dynamic mechanical instruments (DMA vs DMTA).

Frequently, the temperature corresponding to G'' or $\tan\delta$ peak is used as a marker of T_g [77,78,82,93]. However, Peleg [86] showed by the computer simulations and the published experimental data that the $\tan\delta$ peak location does not always correspond to the transition zone even for the same material with different moisture contents. Peleg [86] has instead suggested, as a more meaningful index of T_g , to use the temperature at which 50% of the initial stiffness (i.e., storage modulus, G') is lost.

Several factors, such as composition,² molecular weight, and features of chemical structure (e.g., cross-links, side groups) can alter the glass transition temperature of materials. Among the constituents of foods,

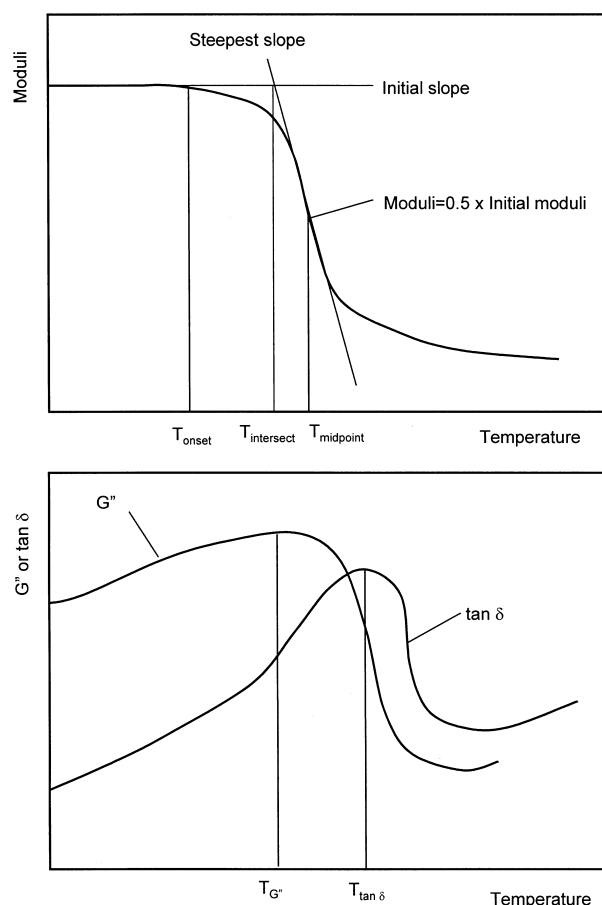


Fig. 4. Schematic drawing of different ways of obtaining glass transition temperature from dynamic mechanical data.

¹ No phase is involved as the word *transition* may possibly imply [76].

² It is interesting to note here that Matveev *et al.* [94] calculated T_g of proteins from the amino acid composition and reported good agreement with the experimental results.

water is an effective and ubiquitous plasticizer, which lowers the Tg of most biological materials [63]. Plasticizers are relatively low molecular weight materials that, when added to amorphous polymers, lead to a large increase in mobility and thus make it easier for changes in molecular conformation to take place.

Cocero and Kokini [77] demonstrated the plasticizing (or softening) effect of water, as measured by the storage modulus G' , on the major protein component (i.e., glutenin) in wheat flour. Hallberg and Chinachoti [95] used DMA to study phase transitions in shelf-stable MRE (“meal, ready-to-eat”) bread. Three distinct transitions are reported in fresh MRE bread and among those the main transition temperature decreased from about 160°C to –11°C as the moisture content increased from about 2.6% to 28.8%. It is also found that transition temperatures remained nearly constant throughout three years of storage [95]. Gontard *et al.* [96] reported on the strong plasticizing effect of water and glycerol on mechanical and barrier properties of edible wheat gluten films. Kalichevsky and Blanshard [93] studied effect of fructose and water on the glass transition of amylopectin to find that the effect of fructose on the Tg of amylopectin is greater at lower water contents.

The depression of Tg, due to plasticization of amorphous components by water or other plasticizers, to the vicinity of ambient temperatures may have significant effect on the shelf-life and stability of foods [57,97]. The importance of plasticization by water becomes more evident when one considers the hygroscopic nature of most dehydrated foods. A typical manifestation of water plasticization is the loss of crunchiness or crispness in snack foods and breakfast cereals [90,98,99]. It is important to note that, the loss of crispness in the corn flour extrudates and in the corn cakes occurred within the glassy state, meaning that the knowledge of Tg alone may not be sufficient to predict crispness [25,100].

Water can also exert an antiplasticizing effect particularly in the low moisture or low a_w region by causing an increase in puncture strength, modulus, and brittleness [96,101]. Moreover, addition of low molecular weight diluents other than water (e.g., fructose, glycerol) to glassy polymers (e.g., amylopectin, starch), on one hand lowers Tg but at the same time exerts an antiplasticizing effect on the mechanical properties of the polymer [101–104].

Estimating steady shear viscosity (Cox–Merz relationship)

Ideally, it should be possible to interrelate “true material properties” obtained from different experiments. This is useful because experimental limitation of one type of experiment (slippage, migration of sample constituents, etc.) can be overcome by using a different experiment and then relating those material properties

back to the framework of interest, also for independent comparison of results for validation.

Several investigations on the rheological properties of polymer solutions have shown that there is a correlation between the functions describing the dynamic properties and those characterizing the properties in steady shear flow. An important feature of this is the establishment of a correlation between one regime in which the deformations may be infinitely large and basically non-linear (steady shear flow), and another one, in which the deformations are small and linear (SAOS). Phenomenological theories, using various differential operators of complex structure, make it possible to obtain different forms of correlation between the dynamic and steady-shear characteristics of viscoelastic systems [105]. Similar results can be obtained using molecular-level models [8, 106]. However, it has been demonstrated that the Cox–Merz empirical method [107] is the most reliable method to correlate dynamic and steady shear rheological data.

The Cox–Merz rule (Fig. 5A) supports the superposition of shear rate dependence of steady-shear viscosity (η) and frequency dependence of complex viscosity amplitude ($|\eta^*|$) at equal values of angular frequency (ω) and shear rate $\dot{\gamma}$:

$$|\eta^*|(\omega) = \eta(\dot{\gamma})|_{\omega=\dot{\gamma}}$$

or

$$|G^*|(\omega) = \sigma(\dot{\gamma})|_{\omega=\dot{\gamma}}$$

This empirical correlation has been confirmed experimentally for several synthetic polymers [8, 108], and for several solutions of random-coil polyaccharides [109]. It is also noted that in many cases [110] polymers follow the same general behavior introduced above when a shift factor is introduced to give the following form [104]:

$$|\eta^*|(\omega) = \eta(a\dot{\gamma})|_{\omega=c\dot{\gamma}}$$

where, a is the shift factor. This is called extended or modified Cox–Merz rule (Fig. 5B).

Doraiswamy *et al.* [112] presented theoretical treatment for data on suspensions of synthetic polymers, they suggested by using effective shear rates, the Cox–Merz rule can be applied to products exhibiting yield stress. Rao and Cooley [113] reported that this is true for tomato paste.

For food materials, Cox–Merz rule has been observed to hold in some cases (i.e. dilute starch solution, polysaccharide solution, concentrated dextran solution, locust bean gum and low methoxyl pectin) [114–117]. Extended Cox–Merz rule has been also established for

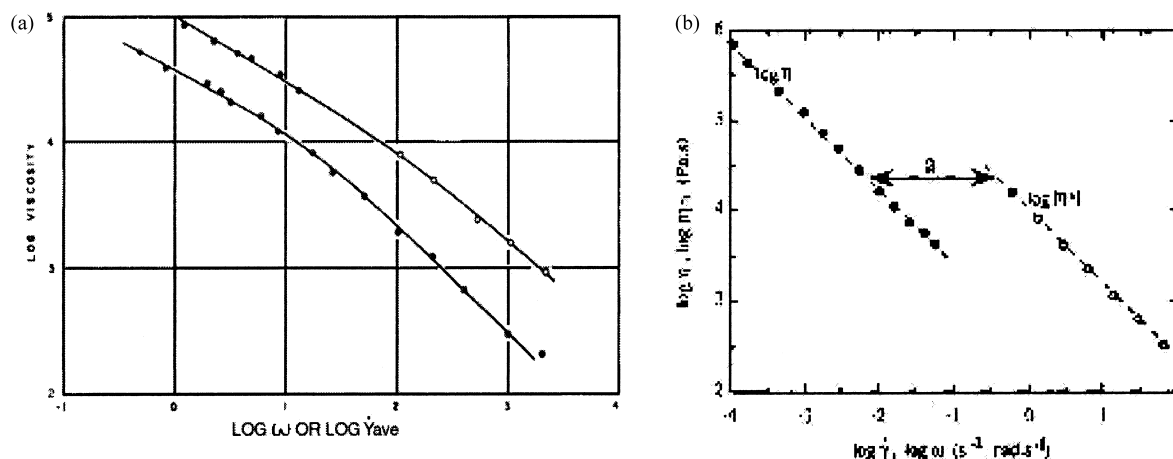


Fig. 5. Illustration of (A) Cox–Merz rule [107] and (B) Modified Cox–Merz rule [111].

some food materials (i.e. tomato paste, wheat flour dough) [111, 113]. A generalized Cox–Merz relation was observed to hold for several commercial food samples (i.e. apple butter, mustard, margarine) [118], which has the following form:

$$|\eta^*(\omega)| = K\eta(\dot{\gamma})^\alpha|_{\omega=\dot{\gamma}}$$

where, K and α are constantly decided experimentally. In most cases, both η^* vs. ω and η vs. $\dot{\gamma}$ can be approximated by a power-law, thus when $\alpha = 1$, this relation reduces to the modified Cox–Merz rule.

Some of the most difficult material properties of fluid and semi-solid foods to determine experimentally are viscometric functions or steady shear rheological properties. This is particularly true in the cone and plate geometry where slippage and outward migration of the sample make it often very tedious to obtain reliable results. On the other hand, SAOS test can be performed fairly easily and accurately by using modern dynamic rheometers. Since steady shear rheological properties, which decide the flow property of the material, are critical to understanding some important engineering processes such as mixing and extrusion, it is obvious that Cox–Merz rule is valuable to predict steady shear properties from SAOS data. The physical or structural reasons why Cox–Merz rule applies are still not clear. However, there are some clues from which we can extract useful structure information based on whether or not Cox–Merz rule applies. Schieber [106] proposed a molecular level constitutive model for long straight-chain polymer which predicts Cox–Merz rule, this is demonstrated to be true by Chamberlain and Rao [114] in their work on straight and highly-branched starch solutions. Most of the described departures from Cox–Merz rule are attributed to structural decay due to the extent of strain applied. By definition, applied strain is

low in SAOS, but is high enough in steady shear to break down structured inter and intramolecular associations. In this case, the complex viscosity is usually higher than the steady shear viscosity [119–121]. Thus departure from Cox–Merz rule may imply strong inter and intramolecular associations. As da Silva *et al.* [117] suggested, departure from Cox–Merz rule of waxy maize starch dispersions might imply a weak gel structure instead of a simple solution.

Determining sensory perception

Linear viscoelastic tests have also been applied to study the interaction between texture, flavor, and taste. It has been shown that measurements of η^* measured in dynamic tests rather than steady shear viscosities give better correlation with sensory thickness for weak gel systems such as liquid and semisolid foods [122–125]. They investigated the relationship between the perceived (sensory) thickness, taste and flavor and rheological parameters of a lemon pie filling. They established a general linear relationship between perceived thickness and η^* over the viscosity range of 1000 to 70,000 mPa.s. (Fig. 6). Whereas, Richardson *et al.* [122] covered the

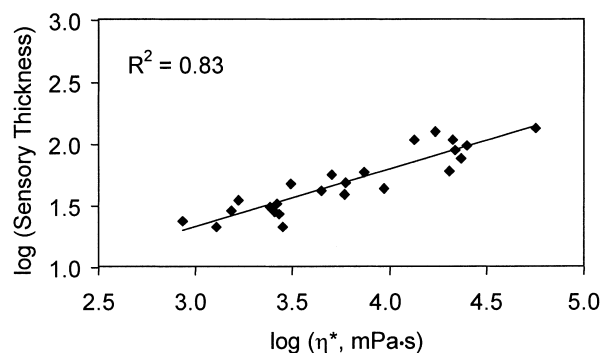


Fig. 6. Linear relationship between perceived sensory thickness and complex viscosity [data from 125].

viscosity range of 10 to 10,000 mPa·s using model systems thickened by xanthan, guar, and starch. These results indicate that η^* measured at a frequency of 50 rad/s can be considered a suitable criterion for predicting perceived thickness in widely differing systems [125]. Skriver *et al.* [126] also reported relationships between oral (and non-oral) viscosity and dynamic rheological test parameters.

The relationship between taste and flavor and rheological properties seems to depend on the structure of the solution and the concentration. It is well established that the intensity of perceived taste and flavor decreases as the product thickness increases [127]. In model solutions containing random coil polysaccharides, suppression of taste and flavor starts when the polysaccharide concentration exceeds the critical concentration where the polymer coil starts to entangle. The exception to this is xanthan gum where good flavor release is achieved at a concentration in excess of the critical concentration [123,124,128,129]. At comparable viscosities, cornstarch suppresses sweetness far less than random coil polysaccharide, which is suggested to be a consequence of a weak gel structure [125].

Other textural properties have been related to dynamic viscoelastic data [118, 130, 131]. For example, Toufeili *et al.* [130] determined that the progress of textural changes responsible for the generation of the sensory stale response in Arabic bread was marked by the transition of the bread pastes from viscoelastic solids ($G' > G''$) to elastoviscous liquids ($G'' > G'$) [130]. Ramana *et al.* [131] established a linear relationship between sensory texture determined by taste panel and G' of cooked carrots.

Summary

The theory of dynamic viscoelastic tests has been known for long and have been in use in the polymer industry. However, the application of dynamic tests for studying food materials have been delayed until recently due to either lack of proper instrumentation and/or high cost. The advances in computer and instrumentation technology have led to improved rheometer design at an affordable cost. This has promoted widespread use of dynamic rheological testing of foods. The ability of dynamic rheometers to perform tests at a wide range of frequencies provides information not easily obtainable by other methods. In the case of high speed processing of foods, for example, viscoelastic characterization at a high frequency is very critical.

Determining the fundamental structural characteristics of foods is still the main focus of linear viscoelastic tests. Nevertheless, new research efforts have been afoot in correlating transient and dynamic rheological parameters to various sensory quality attributes and some relevant functional properties. We expect such efforts to continue. But success in such attempts will come only if

the methods and the properties are well rooted in the fundamental structural aspects of both the food materials and the targeted properties. In this regard, we hope more researchers will use the linear viscoelastic data to elucidate the structure–function relationships of foods rather than to report trends and/or to obtain simple statistical correlations with some end-use properties.

In as much as the linear viscoelastic methods are useful, they suffer from the fact that they employ very small strains to be relevant to study material properties during real processes that often employ large and rapid deformations (e.g. food mixing and extrusion). Though the Cox–Merz rule is helpful in some situations, new rheometers have been developed to address specifically these issues that are nonlinear [132,133]. These new rheometers have expanded the ability of rheologists to obtain information heretofore unavailable but critical for successful food process design and/or product development [3]. We expect that further research in the nonlinear viscoelasticity in conjunction with the results obtained via linear viscoelastic tests will move the food rheologists closer to characterizing food material properties and quality attributes more completely than what is possible at present.

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