Broadband Viscoelastic Spectroscopy: A New Technique for Characterizing Rheological Behavior of Solid Foods

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BROADBAND VISCOELASTIC SPECTROSCOPY: A NEW TECHNIQUE FOR CHARACTERIZING RHEOLOGICAL BEHAVIOR OF SOLID FOODS

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The broadband viscoelastic spectroscopy (BVS) is a new technique for characterizing rheological behavior of solid foods. Conventional methods to obtain rheological behavior of materials over a broad range of frequencies are time-temperature superposition (TTS) technique and direct method using specific instruments. TTS technique works only for materials that are **thermorheologically simple** *and over a limited range of about three decades of time or frequency. Materials for which the measured curves do not overlap by making a horizontal shift on the frequency axis are* **thermorheologically complex**. *Food systems are inherently complex with multiple constituents rendering them thermorheologically complex. Thus, it is necessary to acquire data directly over a wide frequency range in a single test to truly characterize such complex materials. The problems associated with TTS can be circumvented by using the BVS, which is capable of directly measuring viscoelastic properties over an extended frequency range. Applications of the BVS are introduced for characterizing viscoelastic behavior of food materials. Some advantages of the BVS technique over the TTS and other available instruments are also discussed.*

Keywords: *Creep test, Mozzarella cheese, Time-temperature Superposition, Viscoelasticity, Whey protein gel.*

INTRODUCTION

Texture is an important attribute of food products. It encompasses qualities associated with eating and processing efficiency.[1] A number of factors affect food texture leading to various characteristics. Understanding influence of factors that affect texture is a key step in improving quality of food products. Foods generally consist of various components forming up complex systems. Each of the components contributes to certain characteristics of the foods. Studying the effects of different components on food characteristics using simple model systems would help us better understand the contribution of each component.

Determination of fundamental mechanical properties of food is of important to understand the molecular mechanisms.[2]

Like for all other materials, the relationship between stress and strain of food materials depends on time or frequency. It is due to the materials generally consisting of both viscous and elastic parts. This is known as viscoelastic behavior. In rheological study, viscoelastic properties of materials are commonly presented in a wide range of frequency or time domain. The information about these properties over many decades is generally preferable since the applications of interest may be in different regions ranging from creep to ultrasonic region. However, most of the commercially available instruments are capable of testing only a limited range of frequencies.

TIME-TEMPERATURE SUPERPOSITION

In addition to time, viscoelastic behavior of most materials is generally a function of temperature as well. It was not until Leaderman[3] made the observation about creep behavior of polymeric materials that the principle of time-temperature superposition (TTS) was discovered. He reported that creep compliance curves obtained for polymeric material at different temperatures had the same shape but their positions on a logarithmic scale were different. The time scale could be contracted by increasing the temperature.[4] The TTS principle was first implemented by Tobolsky and Andrews.[5] They constructed a combined curve, generally called master curve, over an extended time scale from individual stress relaxation curves. This was achieved by shifting the curves along the axis of logarithmic time scale on either sides of a selected reference temperature. The TTS is also known as the "reduced parameters technique."

For materials which can be represented by a smooth master curve by applying the TTS technique, change of temperature is equivalent to a shift of logarithmic time/ frequency scale; they are classified as thermorheologically simple.[6] All the processes contributing to viscoelasticity of these materials are expected to have the same temperature dependence.[4,7] Amorphous polymers which contain no crystallites and no pronounced polar groups are classic examples in this category[6,7,8]. In contrast, obtaining a smooth master curve for some materials needs not only a horizontal shift but also a vertical shift. These materials are classified as thermorheologically complex.[10]

Suppose the property of interest is creep compliance, which may be written as $J(t,T)$ where t is time and T is temperature. From the logarithmic plots of $J(t,T)$ vs. time, the plots may be horizontally shifted so that parts of them coincide yielding a single plot which covers many decades of a logarithmic time scale. The compliance function is now in the following form:

$$J(t,T) = J(\zeta, T_{ref}), \tag{1}$$

where ζ is the reduced time defined as $\dfrac{t}{a_T(T)}$ with $a_T(T)$ as the shift factor; and T_{ref} is the selected reference temperature.[11] This is the TTS technique. The shift factor depends on temperature and type of materials as well. Temperature-dependent creep behavior for many materials follows the Arrhenius relation as in the following form:

$$\ln a_T = \frac{U}{k}\left(\frac{1}{T_2} - \frac{1}{T_1}\right), \tag{2}$$

with U as the activation energy; k as the Boltzmann's constant; and T_1 and T_2 represent different levels of absolute temperatures. For polymers, the shift factor tends to follow the empirical WLF (Williams-Landel-Ferry) equation:

$$\log a_T = -\frac{C_1(T - T_{ref})}{C_2 + (T - T_{ref})},$$ (3)

where C_1 and C_2 are the constants depending on particular type of polymers.[7] The WLF equation is however restricted to materials in the state above the glass transition tempera-ture. It should be noted that obeying the TTS principle does not definitely indicate whether the material in question behaves linearly or not.[11]

The TTS technique is also very useful tool to obtain stress-rupture data for structural materials at the low level as used in practical situation within a relatively short time. Instead of running a long time conventional creep testing, the failure of material could be reached within a few hours by accelerating with a thermally activated process. Then the stress-rupture data covering an extended range of time scale could be obtained using the TTS.[10]

Problems Associated with the TTS Technique

Though the TTS technique has been used for many decades especially for polymeric materials, it is generally difficult to obtain a smooth master curve. A small error at the overlap region may accumulate when many data sets are combined. There are also no firm rules that have been developed for constructing a master curve. In addition, the accuracy of the master depends on various factors, for example, variation of the shift factors with temperature, variation of environmental conditions during the tests, initial preparation of the specimens, types of the experimental systems, and rate of application of heat to reach the required isothermal temperature level.[10] Even for the thermorhelogically simple material like polystyrene, nearly perfect superimposed creep compliance data could be obtained only in a very limited range of time scale.[4, 12]

BROADBAND VISCOELASTIC SPECTROSCOPY (BVS)

The BVS is technique for characterizing viscoelastic behavior of solid materials over an extend frequency scale in a single measurement. The BVS rheometer was first developed by Chen and Lakes.[13] The apparatus offered significant advantages over many earlier approaches while incorporating some desirable features of those. It was capable of creep, subresonant dynamic and resonant dynamic experiments in both torsion and bend-ing modes. Bending test can be very useful to explore viscoelastic phenomena due to stress-induced flow in high moisture foods. The BVS technique was particularly suited to materials of high mechanical damping. Several viscoelastic elasotmers and poly(methyl)methacrylate were selected for the tests to illustrate its capability. The equiv-alent frequency for torsion ranged from less than 10^{-6} to 10^4 Hz.

Some limitations of the BVS were later discovered which included effect of instru-mental compliance on experimental results for thick specimens and insufficient phase resolution for materials of tan δ less than 0.1. Brodt et al.[8] performed a series of

refinements and successfully overcame these problems. In addition, isothermally direct measurements over many decades of time/frequency scale is required if the master curve needs to be verified.[13] This could also avoid a cumbersome process of implementing the TTS technique. The ability of the BVS to permit measurements over a wide range of time or frequency scale under isothermal conditions is extremely useful for materials that are thermorheologically complex, for example, composites and food materials.

BVS Rheometer Construction

By applying torque electromagnetically, the displacement of the specimen free end can be optically observed with the light detector. This is how the BVS works. The whole system of the BVS consists of many parts including a cylindrical chamber, a support rod, the Helmholtz coil, a laser, and a light detector. The chamber is made from 1-cm thick brass material. Inside there is a layer of permeable magnetic shield aimed to isolate magnetic field from the system. A support rod has a diameter of approximately 2.5 cm. and made from stainless steel. Different sizes of the Helmholtz coil sets are used depending on the range of the required load. In the same set, there are two groups of coil in the orientations 90° apart enabling the applications of either torsion or bending load. The light detector is of the split-diode type.

A schematic diagram of the BVS is presented in Fig. 1. Electrical current is fed to the Helmholtz coil which is located around a specimen. For torsion, sinusoidal torque for dynamic studies and step function torque for creep studies are generated by the Helmholtz coil acting on a small, high intensity neodymium iron boron magnet attached at the free end of a specimen.[8, 13] Some more details of the refinements can be found elsewhere.[8]
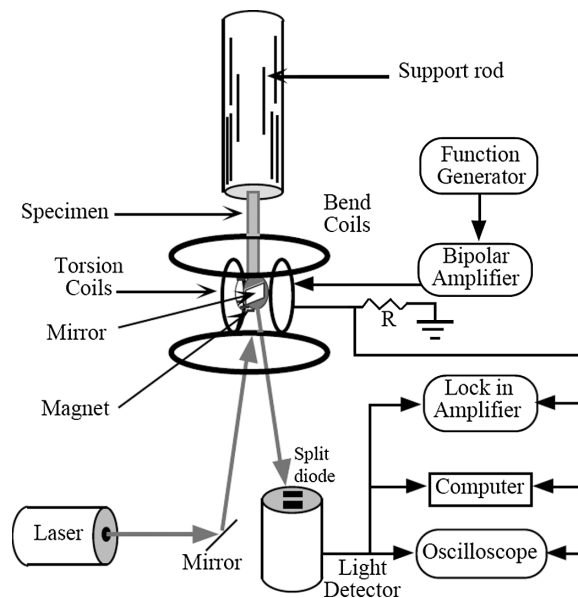

Figure 1 Schematic diagram of the BVS (after[22]).

Specimen Mounting

The appropriate size and shape of a specimen in question depend on its properties. The specimen is mounted at one end of the support rod, fitted on a rigid frame, by cementing material. A magnet is attached to the free end of the specimen. Cyanoacrylate glue is normally used for this purpose. Under the same electromagnetic field, the bigger the magnet, the more torque it offers. However, the size of a magnet is restricted by its inertia which limits the ability of measurement at a high frequency range. For inexperienced experimenter, in general, the expected deformation should be pre-determined based on specimen dimensions and the estimated stiffness, strength of the magnet, sensitivity of the light detector to guide the appropriate size of the magnet. A small piece of mirror is attached to the magnet for reflecting the laser beam from a laser source to the light detector. For many hygroscopic materials like foods, paraffin oil may be used for coating the specimen surface to restrict moisture loss during extended periods of experiment. Controlled temperature and humidity chamber can also be created to surrounding the specimen.

Calibrations

Light detector. Sensitivity and linear range of the response of the split-diode silicon light detector are needed to be calibrated before starting an experiment. The sensitivity should be obtained under the loading condition that covers the entire range of the application. In general, a wide linear range corresponds to less sensitivity. Range of linearity of the light detector is necessary for selecting the appropriate detector with the specific experiment. The light detector is mounted on the top a small stage driven by a micrometer. Calibration is carried out by turning the micrometer and recording the output voltage from a digital multimeter. From a plot between the displacement and the output voltage, the sensitivity (K in μm/V) and the linear range can be identified.

Magnet. Torque produced by each set of permanent magnet and the Helmholtz coil may be different. Since torque is inferred from the current flowing through the Helmholtz coil, the calibration value for inferring torque is needed to be determined before using any magnet with a specific coil. The current is indirectly determined from the voltage across a non-inductive resistor. The 6061 aluminum alloy, which has been well characterized is normally used as a test specimen for this purpose.[14] At the frequencies significantly below that of the aluminum specimen's first torsional resonance, the magnet strength Mag (N m/A) is inferred from the following quasistatic relation based on known parameters for the aluminum alloy specimen.

$$\left|G^*\right| = \frac{M \times L}{\phi \times \left(\frac{1}{2}\pi r^4\right)}, \text{ and} \tag{4}$$

$$\left|G^*\right| = \frac{Mag \times V_T \times \dfrac{L}{R_{feedb}}}{\tan^{-1}\left(\dfrac{V_{ang}}{1000 \times 2 \times K \times dist}\right)\left(\dfrac{1}{2}\pi r^4\right)}, \tag{5}$$

where G^* is the complex shear modulus (GPa or N/mm^2); M is torque (N m); L is a length of the specimen (m); r is a diameter of the specimen (m); ϕ is the twist angle at the free end of specimen (rad); V_T is the applied voltage for the Helmholtz coil (V); R_{feedb} is the feedback resistance (Ω); V_{ang} is the output voltage from the light detector (V); K is the sensitivity of the light detector (μm/V); and *dist* is the distance between a mirror attached on the magnet and the light detector (mm).

CREEP AND DYNAMIC EXPERIMENTS

The capability to perform creep test is another advantage of the BVS over some instruments that have been developed for viscoelastic studies. Applying constant torque to the free end of specimen over time is made possible by feeding a step function input signal to the amplifier which drives the Helmholtz coil. Then the angular displacement of the specimen end is recorded as a function of time. Knowing torque and specimen geometry, shear stress can be calculated. Calculation for the value of shear strain can be made from the angular displacement and specimen geometry.

Sinusoidal torque is generated by applying an ac signal as an input for the amplifier to drive the Helmholtz coil. Angular displacement of the specimen end is then recorded. The absolute dynamic modulus and the loss tangent can be inferred via an inversion of the exact analytical solution which is valid for both resonant conditions and through resonances for the loss tangent of any magnitude. In case of dynamic torsional experiments, the exact solution is available for the problem of a solid rod specimen with circular cross section. Details of the data reduction procedure for dynamic tests can be found in Brodt et al.,[8] Edwards et al.[15] and Lakes.[7]

APPLICATIONS OF BVS FOR FOOD RHEOLOGY

We have conducted experiments[16] to compare the viscoelastic behavior over an extended frequency range of some selected food materials using a commercially available instrument (Bohlin rheometer) and the BVS. Since the Bohlin rheometer is capable of maximum testing frequency of only 150 Hz, the TTS technique was employed to obtain rheological data over a wide range of frequency. It was revealed that cooked ham and gummy candy could be classified as thermorheologically simple materials in the frequency range of 10^{-4} to 10^3 Hz and 10^{-6} to 10^4 Hz, respectively. The G′ (shear modulus in phase) master curves obtained for these materials are shown in Figs. 2 and 3. For ham under the test frequency range lower than 10^{-2} Hz, the values of G′ obtained with the TTS technique were slightly less than those results obtained using the BVS. At the frequency range higher than 10^{-1} Hz, in contrast, the values of G′ are higher when the TSS was applied. It could also be observed that the variation of G′ values obtained with the BVS at a particular frequency was noticeable. This may be due to heterogeneous nature of the ham itself. A smoother G′ master curve was obtained from the tests of gummy candy. The master curve was also in good agreement with the results from the BVS test. In addition, less variation of G′ values was observed since the texture of gummy candy was quite homogeneous.

Subramanian and Gunasekaran[17] reported that the rheological behavior of one-week-old low-moisture-part-skim Mozzarella cheese in the frequency range of less than three decades obeyed the TTS principle. However, we have reported[16] that obtaining a smooth master curve for the rheological behavior of Mozzarella cheese in the frequency
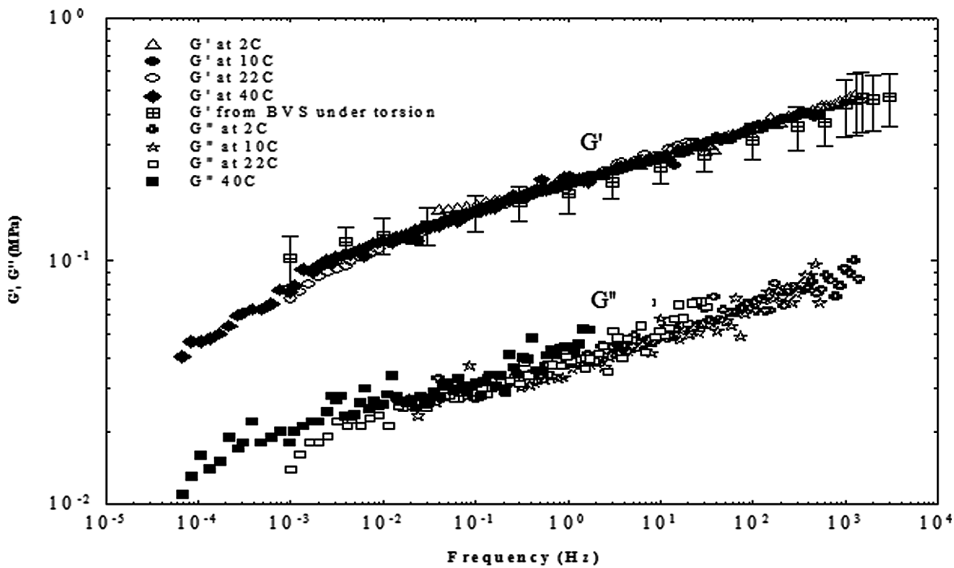
Figure 2 Rheological behavior inferred from dynamic data obtained with the BVS and the master curve constructed using data from the Bohlin rheometer at the reference temperature of 22°C for cooked ham (after[16]).
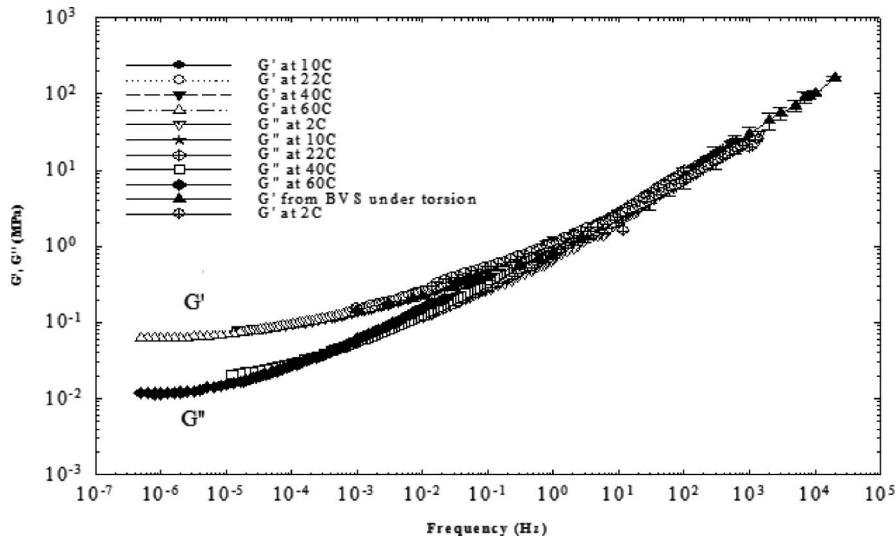

Figure 3 Rheological behavior inferred from dynamic data obtained with the BVS and the master curve of the results from the Bohlin rheometer at the reference temperature of 22°C for gummy candy (after[16]).

range of about 4.5 decades was not possible (Fig. 4). The difference of temperature dependence of each component in the cheese could be the reason for this thermorheologically complex behavior.

There were some limitations in the range of frequency of rheological data for food materials obtained with the TTS technique. The lower end of a master curve was limited
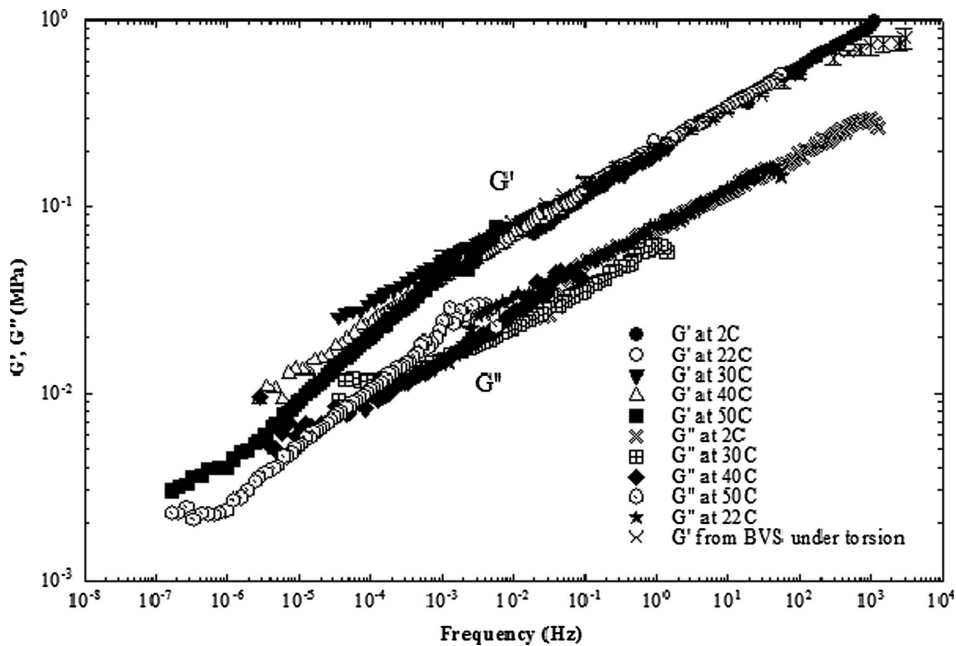
Figure 4 Rheological behavior inferred from dynamic data obtained with the BVS and the master curve of the results from the Bohlin rheometer at the reference temperature of 22°C for Mozzarella cheese (after[16]).

by the maximum appropriate temperature that the food sample could be subjected. The freezing point of water restricted the upper frequency end since water in food specimen would freeze at the temperature lower than this point. On the other hand, the rheological data with broader range of frequency could be obtained with the BVS isothermally. A specimen and a magnet that is attached to the specimen could be prepared in small sizes to obtain rheological behavior of the sample at high frequency using the BVS. As long as environmental conditions in the BVS testing chamber are maintained such that the food sample does not dry out, the behavior at much lower frequency might be inferred from the result of long-time creep test.

Investigations of fundamental properties of solid food texture have been widely carried out using food gels. Based on the properties and amount of the filler particle in gel matrix and the presence or absence of interactions between the filler particle and the gel network, the rheological properties of filled gels can to be predicted.[18] Upon heating, globular protein molecules undergo irreversible changes in their structure by partial unfolding which results in the exposure of some reactive groups buried in their native structure. These unfolded or denatured molecules may aggregate due to interactions of the exposed active groups. When the aggregates grow until they can eventually build up a 3-dimensional structure and entrapped some water inside, the gel is formed. Manipulation of pH, type and amount of salt allows one to alter mechanical properties, microstructure and water-holding properties of the gel without changing protein concentration.[2, 19] In solution with 25–30 mM NaCl, WPI gels formed has very high maximum shear strain values and are translucent and gelatin-like in appearance, called the stranded gels. The gel formed in the presence of 7.5 mM $CaCl_2$ has very low maximum shear strain values and

are opaque and curd-like, resembling coagula rather than gels, called particulate gels. The differing effect of NaCl and $CaCl_2$ on shear strain was shown to be general monovalent (Na, Li, K, Rb, Cs) or divalent (Ca, Mg, Ba) cation effects.[20] Particulate gels release much water from their structure while the stranded gels basically do not. It has been reported that nonlinear relationship between shear stress and shear strain were found in the stranded gels.[2] For 10% protein suspension, increasing the concentration of either salt caused a sharp increase in shear stress values of gel to a maximum with 50–75 mM NaCl.[20] However, Schmidt et al.[21] reported the maximum hardness of WPI gels with 200 mM NaCl.

In our study, the protein suspension was prepared by dissolving 20 g of WPI powder (98% protein) in the 200 mM NaCl solution prepared from distilled water and stirred using a magnetic stirrer for 1 h. The suspension was adjusted to total volume of 100 mL so that the 20% WPI suspension is obtained. The pH of the suspension was kept at native state of 6.8. The suspension was again stirred for 30 min and transferred to stainless steel molding cylinders of 10-mm inner diameter. The inner surface of these molds was coated with paraffin oil prior to filling with protein suspension. The molds were heated in a water bath at the temperature set to 90°C for 30 min then cooled down in water. After cooling, the samples were removed from the molding cylinders and kept in small plastic containers. The plastic containers were then put in airtight plastic bags (Food Saver®), vacuum packed and heat sealed. The solid gel samples were stored overnight at 4°C for subsequent testing with the BVS.

Prior to the test, the gel sample was carefully cut to a length of 5 mm. Thin brass plates with diameter approximately the same as that of the gel specimen were attached onto both ends of the specimen using cyanoacrylate glue. This was to equally distribute torque over the cross section of specimen. One end was attached to the support rod. Another was attached with a magnet having a small mirror on its face as shown in Fig. 5. The outer surface of gel specimen was then coated with paraffin oil to prevent moisture loss. The support and specimen were then placed inside the testing chamber of the BVS setup for 2 h to allow the glue to cure. A small glass beaker containing water was also placed inside the chamber. Air was blown into the water through a flexible plastic tube in order to maintain the atmosphere inside the chamber at high humidity level. This was to assist in preventing moisture loss from the gel specimen. The humidity level inside the chamber was monitored throughout the experiment using the Multifunctional Enviromental Instrument (Solomat, MPM500e). In this experiment, the relative humidity was in the range of 89–90% relative humidity. It should be noted that the glue curing time in this experiment was selected as that for the case of other engineering materials, for example
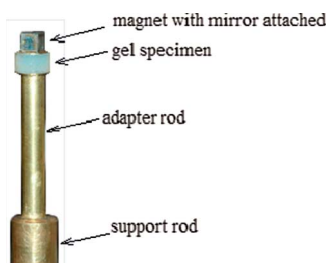

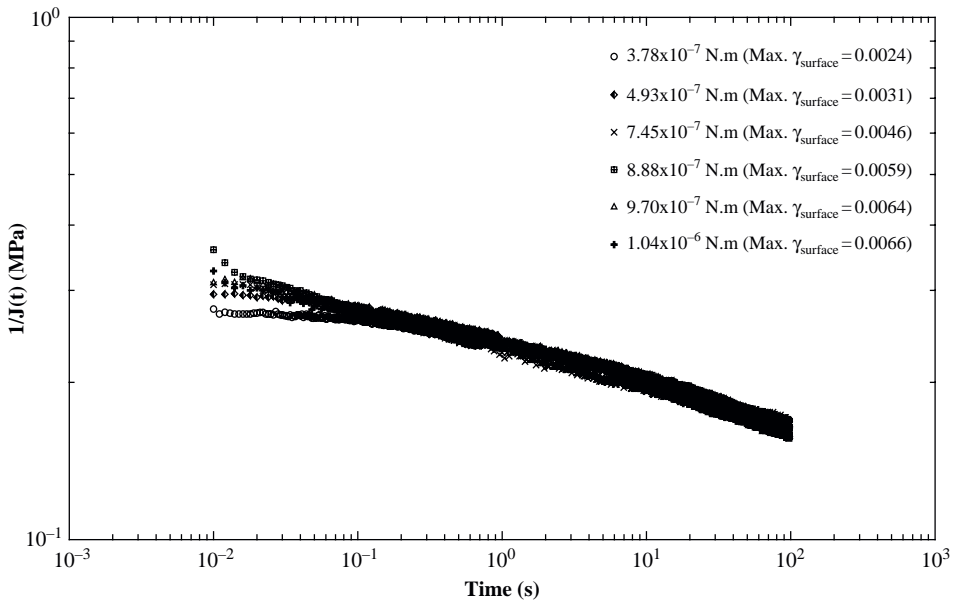**Figure 5** Whey protein isolate gel specimen mounting.

Figure 6 Creep behavior of whey protein isolate gel at different levels of applied torque.

metal alloys, aluminum, polymethyl methacrylate (PMMA), which have been studied using the BVS. Food materials generally have much lower stiffness as compared to engineering materials mentioned above. For creating the same level of strain, the torque needed for food materials would be much lower than that for those engineering materials. Accordingly, the cure time for the experiment with food materials would be shorter.

Creep test was then performed at six levels of torque ranging from 3.78×10^{-7} to 1.04×10^{-6} N m. The specimen was allowed to recover for 10 times the test period. Creep compliances were calculated via Eq. (5) and the results are shown in Fig. 6. Creep compliances were obtained for four decades of time. Maximum shear strain at specimen surface ranged from 0.0024 to 0.006. The highest creep compliance was about 6.25 MPa^{-1} at the beginning of the test and gradually decreased to about 3.33 MPa^{-1} as the test progressed to 100 s. It could be seen that the gel sample under the test conditions was still in a linear range since creep compliances from different levels of torque were of nearly the same at any point over the test period.

CONCLUSION

Commercially available rheometers generally have an upper limit of test frequency much lower than what is available in the BVS. With the implementation of TTS technique, the frequency range of the master curve of food materials largely depends on nature of the food in question. The lower frequency could be dictated by the maximum temperature the food sample can be subjected to without any change, e.g., drying out. For those solid foods in which the main component is water, the upper frequency is limited by the freezing point of water. In the case of foods containing of several components, such as cheese, the master curve can be obtained within only a few decades of frequency. Also,

many tests are needed when one wants to construct a master curve of materials using the TTS technique. This generally requires several hours of tedious work and patience of the experimenter. On the other hands, the BVS provides a quick way to isothermally obtain rheological data over the same range of frequency as compared to using the TTS. In a torsion test with commercially available rheometers, food specimen is held by either under compression or glued to test platens. This would create certain level of undesirable normal force along with shear during the test. However, in the BVS the specimen is loaded magnetically without direct contact. The normal force due to the small weight of the specimen and magnet is fairly small and is negligible compared to the applied torque. In addition, exploring some viscoelastic phenomena due to stress-induced flow in high moisture content materials is possible in bending mode using the BVS.

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