VISCOELASTICITY

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CONTENTS

Summary

In this chapter, the fundamental theoretical and practical aspects of viscoelasticity are discussed with emphasis on concepts rather than on mathematics. This does not mean the subject is treated without equations, but that it is presented as a discussion in which mathematical complexity has been kept at the lowest possible level. Nevertheless, a basic knowledge of one variable calculus and first order ordinary differential equations is advisable for a better understanding of the theoretical principles discussed.

After the introductory remarks on the importance of viscoelasticity and its role in the behavior of materials, discussion continues on the main aspects from which the fundamental ideas of viscoelasticity evolved. Only the fundamental concepts of stress and strain are explicitly defined. Definitions of a good number of other concepts are included in the glossary. The following section introduces the notions of solid, liquid and solid-liquid behaviors as well as the criteria to distinguish them. Here, the idea of material behaviors, rather than material types is emphasized. The next two sections treat the fundamental aspects of linear viscoelastic behavior through the analysis of simple mathematical models describing rather ideal behaviors, which, although not necessarily found in practice, are useful for a basic understanding of the subject from a conceptual framework. A brief discussion on experimental techniques most commonly used to characterize the linear viscoelastic behavior of materials, including foods, is presented in the following section; emphasis is on the material properties that can be obtained rather than on the theoretical principles of rheometry involved.

The article ends with a discussion on the viscoelastic behavior of food biopolymers with special emphasis on polysaccharides. They were chosen because of their importance in the food industry as functional agents, also because their behavior in solution illustrates well the practical aspects of the theoretical principles discussed herein, and because in other areas of the encyclopedia, more detailed discussions on the viscoelastic properties of specific foods are presented. Full details about their chemical composition, structure and particular functional properties are not treated because the main purpose is to illustrate their characteristic rheological behaviors instead of their physicochemical properties. However, in order to understand the behaviors displayed, a brief discussion of some physical aspects is presented.

1. Introduction

Rheology is the science of deformation and flow of matter. It is a scientific discipline in its own right and has the reputation of being a complex subject because of the strong mathematical background normally needed in its study. Nevertheless, it is still possible to approach the subject from a conceptual framework by stressing the importance of fundamental concepts and ideas without delving into mathematical formulations. This approach is advantageous for beginners and for those who, while involved with materials from diverse industries (e.g., plastics, paints, oils, detergents, pharmaceuticals, foods, etc.), either do not have the background or are not interested in complex equations. Some knowledge of college mathematics is however advisable if a full understanding of

concepts is expected. The study of viscoelasticity is not the exception. Viscoelasticity is one of the most fascinating rheological behaviors known, which many materials can display. Its thorough understanding is useful, not only for allowing a better knowledge of a particular material, but also for providing a more rational approach to practical situations involving materials handling, processing and development.

In the case of foodstuffs, rheological behavior (of which viscoelasticity is certainly of utmost importance) plays a major role in quality control, consumer acceptance, process engineering and new product development. Therefore, knowledge of the subject is essential for people employed in industry. Viscoelasticity is also of interest to those in academia where intensive fundamental research in the past century has resulted in considerable progress in the field. A huge amount of research on the viscoelastic properties of foods exists, and in the past, efforts to gather the scattered information available in literature on solid, semisolid and fluid foods (includes agricultural, bakery, seafood and milk products together with emulsions and hydrocolloids), have produced authoritative state-of-the-art reviews (see Bibliography). Viscoelasticity has come of age in the twentieth century, yet many aspects involving the interrelation between viscoelastic properties and structural organization remain to be rationalized. This is true for both foods and food-related materials, whatever their origin, nature and degree of processing. Rationalism is becoming more important than empiricism and, with the advent of modern instruments, many of the currently available rheological techniques can be used on an almost routine basis; the rheological characterization of materials is easier than it was many years ago. The twenty-first century will see intensive research on the viscoelastic-structure relationship, as well as on the non-linear viscoelasticity of foods and food-related materials.

2. The Foundations of Viscoelasticity

2.1. Hooke's Postulate and Linear Elasticity

In 1678, British physicist Robert Hooke (1635-1703) in his work, De Potentia Restitutiva, proposed that Ut Pondus sic Tensia; "the weight is equal to the tension". Hooke spoke of the pondus, or weight, because at the time the tension was seen as the product of an increasing series of weights in pans suspended on coiled springs. However, the formulation of Hooke's proposal more familiar to us today is Ut Tensia, sic Vis; "the tension is equal to the force". The actual terminology simply means that an object stretches or compresses in proportion to the force acting upon it. If this is so, the object is said to be an elastic body, an elastic material, or a Hookean solid. Hooke's postulate forms the basis of the theory of elasticity and is considered his most important contribution to materials science. Hooke's postulate is formulated in terms of measurable quantities such as force, area and deformation. In order to understand their relationship, it is helpful to define two fundamental quantities: stress and strain.

2.1.1. Stress

When an external force is applied to a material, an internal reaction takes place, the intensity of which depends on both the magnitude of the force and the area upon which it acts. Such reaction is called the stress, σ, and is mathematically defined as the ratio of force, F, to area, A, when this approaches zero.

$$\sigma = \lim_{dA \to 0} \frac{dF}{dA}$$

(1)

Force is a vector quantity and has three space components. Stress is a second order tensor with the following nine components:

$$\begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix}$$

(2)
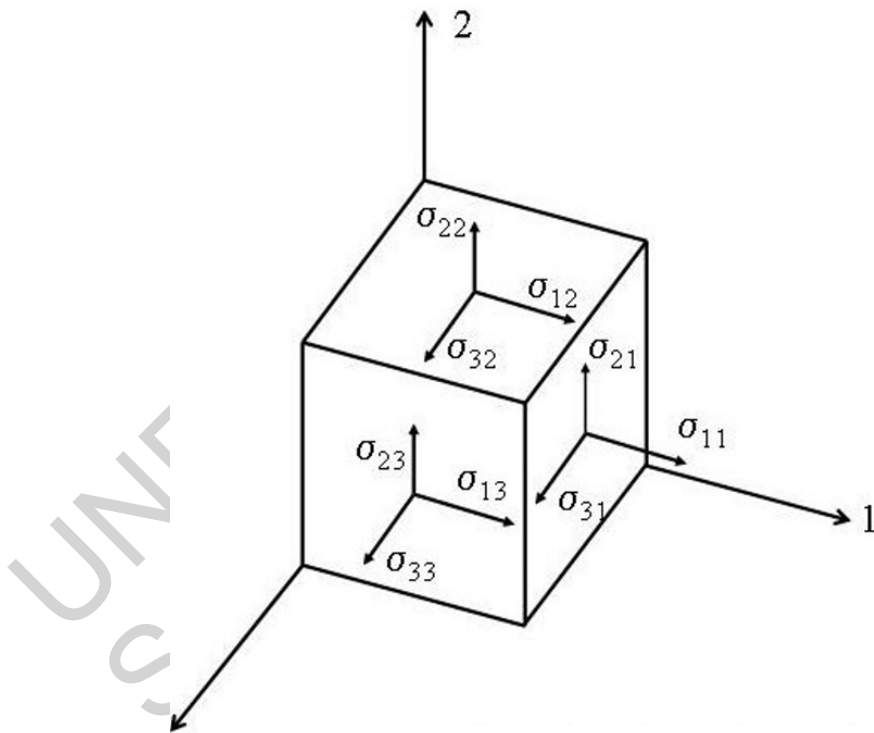
Figure 1. Components of stress in a general co-ordinate system of axes 1, 2, and 3. In rectangular co-ordinates, 1, 2 and 3 are replaced by x, y and z, respectively.

In the above array, the subscripts of the nine stresses have a special meaning: the first subscript indicates the direction of the force component, whereas the second one indicates the orientation of the area on which the force component is applied. This situation is illustrated in Figure 1 for a general reference system having axes 1, 2 and 3. Thus, for example, σ_{11} is the stress resulting from application of the force component,

having a direction parallel to axis 1 on the area perpendicular to this same axis. Force components parallel to axis 2 and axis 3 applied on this same area produce stresses $\sigma21$ and $\sigma31$, respectively (see Figure 1). A force perpendicular to the area produces a normal stress, which can be compressive or tensile, whereas a force parallel to the area yields a shear stress. In the array (2) shown above, all stresses with a repeated subscript, $\sigma11$, $\sigma22$ and $\sigma33$ are normal stresses, whereas the rest are shear stresses because they have different subscripts.

2.1.2. Deformation and Strain

Stress induces deformation, which is a change in shape, volume or both. Deformation is normally expressed in relative terms by a quantity called strain. Commonly, strain is the ratio of the actual change in length, ΔL, to the original length of the material, L0, but other similar definitions are possible. Tensile or compressive stresses produce tensile or compressive strains, ε, while shear stresses produce shear strains, γ. Strain is also a second order tensor and therefore has nine components. In fact, each stress has a corresponding strain bearing the same subscripts.

$$
\begin{bmatrix}
\varepsilon_{11} & \gamma_{12} & \gamma_{13} \\
\gamma_{21} & \varepsilon_{22} & \gamma_{23} \\
\gamma_{31} & \gamma_{32} & \varepsilon_{33}
\end{bmatrix}
\tag{3}
$$

2.1.3. Elastic Moduli

The ratio of stress to strain is called the elastic modulus, and depending upon the manner of force applied, three ratios or types of moduli can be computed for a Hookean solid:

When the force is perpendicular to the area, the resulting ratio is called the modulus of elasticity or Young's modulus, E, sometimes Y; it measures the stiffness of the material.
When the force is parallel to the area, the ratio is called the modulus of rigidity or shear modulus, G; it quantifies the resistance of the material to changes in shape.
When the same normal force is applied from all directions, isotropically, the ratio is called the bulk modulus, K, which measures the resistance of the material to a change in volume per original volume.

The respective definitions are as follows:

$$
E = \frac{\sigma_{ii}}{\varepsilon_{ii}}
\tag{4}
$$

Young's modulus

$$G = \frac{\sigma_{ij}}{\gamma_{ij}}$$

(5)

Shear modulus

$$K = \frac{\sigma_V}{\varepsilon_V}$$

(6)

Bulk modulus

In Equation (4), the subscripts ii indicate normal components of both stress and strain, such as 11, 22 and 33 in the arrays (2) and (3). In Equation (5) the subscripts ij indicate shear components of stress and strain and, finally, in Equation (6), the subscript V is used to indicate that both the stress and strain are volume quantities, that is, they refer to the change in volume of the material and the corresponding resistance to such change.

According to Hooke's observation, for many materials including foods, the stress is directly proportional to the strain only when the applied force is very small, infinitesimal. Therefore, Hooke´s postulate is the fundamental premise for the theory of infinitesimal strain elasticity. If the external force is too strong, the material can become permanently deformed and Hooke's postulate no longer applies. The maximum amount of stress a material can withstand before becoming permanently deformed is called the elastic limit. The elastic modulus and elastic limit of a material are influenced by its molecular structure. Hence, elasticity is considered as a property of a solid material that causes it to resume its original size and shape after having been compressed or stretched by an external force. Although in principle all solid materials are elastic, some are more elastic than others and can withstand larger forces before attaining their elastic limit. Beyond the elastic limit, when the strain is large, a situation of instability can occur that leads to fracture or total collapse of the material structure.

2.2. Newton's Postulate and Viscosity

A few years later, in 1687, Isaac Newton (1642-1727) published his book Philosophiae Naturalis Principia Mathematica, known as the Principia, in which his contributions to different fields of physics were discussed. Of particular interest to this section is his attention to liquids, which was summarized in the following proposition: "The resistance which arises from the lack of slipperiness of the parts of the liquid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another". In these terms, the postulate is perhaps unclear, but actually means that a viscous fluid deforms continuously, flows, in proportion to the shear stress acting upon it, and "the lack of slipperiness" is what is known as the fluid's viscosity, η. Viscosity is a measure of "resistance to flow" and the ratio of shear stress to shear rate $\dot{\gamma}$.

$$\eta = \frac{\sigma_{ij}}{\dfrac{d\gamma_{ij}}{dt}} = \frac{\sigma_{ij}}{\dot{\gamma}_{ij}}$$

(7)

Fluids obeying this simple behavior are called Newtonian (see Newtonian and Non-Newtonian Flow). A characteristic feature of Newtonian behavior is that viscosity is independent of shear strain or shear stress and remains constant as long as the temperature and pressure, in the case of gases, remain unchanged. Viscosity is therefore the property of a fluid that tends to prevent it from flowing when subjected to an applied force. High-viscosity fluids resist flow while low-viscosity fluids flow easily. The tenacity with which a moving layer of fluid drags adjacent layers of fluid along with it determines its viscosity. Newtonian behavior is normally observed in simple liquids such as water, organic solvents and diluted solutions. Deviations from this behavior occur frequently with more complex fluids, for example, with suspensions, emulsions, polymer solutions, and pastes (see Food Emulsions, and Food Suspensions). Nevertheless, such materials can exhibit Newtonian behavior at very low shear strains or shear stresses where proportionality between these two quantities exists (see Figure 10).

In the nineteenth century, more than one hundred years after Newton's reflection upon the flow of liquids, efforts to incorporate the effects of viscosity into the mathematical equations describing the flow of fluids were finally successful. First, in 1827 by the French engineer Claude Louis Marie Navier (1785-1836) and later, in 1831, independently by Siméon-Denis Poisson (1781-1840). Both were intrigued with the way in which molecules of a fluid were affected by stresses. Later, in 1834, Barré de Saint Venant (1797-1886) and in 1845, British mathematician Sir George Gabriel Stokes (1819-1903) derived and perfected the basic equations for viscous incompressible fluids, based on the linear relationship between stress and strain. These efforts gave rise to the well-known Navier-Stokes equations, which form the basis of fluid mechanics. Also, the first carefully documented friction experiments in low-speed pipe flow were carried out independently in 1839 by the French physiologist Jean Leonard Marie Poiseuille (1799-1869), who was interested in the characteristics of blood flow, and in 1840 by the German hydraulic engineer Gotthilf Heinrich Ludwig Hagen (1797-1884). They developed the well-known Hagen-Poiseuille equation, of fundamental importance in Newtonian fluid flow (see Newtonian and Non-Newtonian Flow).

2.3. Early Evidence of Deviation from Linear Behavior

Early evidence of deviation from linear behavior predicted by Hooke's and Newton's postulates dates back to 1835 when Wilhelm Eduard Weber (1804-1891), a German physicist specializing in electrodynamics, observed that when a certain longitudinal load was applied on a silk thread, a gradual stretching over time occurred after an initial immediate extension. On removal of the load, an immediate contraction took place, followed by a gradual shortening until the original length was recovered. This behavior showed that the silk thread, while considered a solid, clearly exhibited an associated liquid-like response and continuous deformation over time, and that neither Hooke's nor

Newton´s models alone could describe its behavior. In 1867, Scottish physicist James Clerk Maxwell (1831-1879) published a paper entitled "On the dynamical theory of gases", where he proposed a mathematical model, now called the Maxwell model, for a fluid possessing some elastic properties. This introduced, for the first time, the possibility of elastic and viscous characteristics existing in the same material; in other words, materials possessing fluid-like and solid-like behaviors.

Hooke's and Newton's postulates are two ideal cases of material behavior. As such, they are the opposite extremes of a very broad spectrum of the behavior of the materials. Very few structurally simple materials obey the behaviors described by these models under the rather narrow ranges of either stress or strain. However, these two relationships cannot describe the behavior of many real materials. Foodstuffs seldom behave according to such models under a wide range of stress or strain; their behavior lies somewhere between the two extremes. The observations of Weber and the formulations of Maxwell certainly called for a different approach to the study and quantitative description of the stress-strain relation for real materials. It was not, however, until the twentieth century that the discovery of new materials and the

development of manufacturing methods for new products gave a tremendous impulse to the science of materials.

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Biographical Sketch

Alberto Tecante is Professor of Food Engineering at the Universidad Nacional Autónoma de México (UNAM), Mexico City, Mexico. His teaching activities include graduate and undergraduate courses in Transport Phenomena, Fluid Mechanics, Mass Transfer Operations, Rheology, and Physical Chemistry of Macromolecules. One of his research areas is food macromolecules, where he concentrates on the relation between rheology and the structure of food polysaccharides. A second area is the texture and mechanical properties of food gels and polysaccharide mixtures. A third field of interest is gas-liquid mass transfer in rheologically complex fluids stirred with non-conventional agitators. He has worked as a technical adviser in food processing for the Mexican government, for the Ministry of Food and Agriculture of Guatemala, and as a consultant to different Mexican food industries, also as a visiting researcher at the Institut National de la Recherche Agronomique (INRA, Nantes, France). Professor Tecante is author and co-author of numerous papers, including book chapters, refereed publications, and proceedings at international congresses.