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Extensional properties of macromolecules

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There is increasing interest in the food industry in the development of new or improved commercially available food products. New methods to test the characteristics of raw materials and products are necessary. The viscosity (consistency or texture) of foods is an important rheological variable during processing because it influences the equipment design necessary for food production. Additionally, viscosity determines functionality and consumer acceptance of foods. This review focuses on extensional viscosity characterization as a tool to aim the development of novel and improved food products and processes. Extensional deformation is involved in processes as extrusion, film blowing, and fiber spinning, but it is also important in determining and understanding interactions among food components (e.g., proteins, polysaccharides, and lipids) in food products (e.g., bread, pasta, syrups, snacks, and salad dressings).

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Introduction

In recent decades, studies on the physical properties of many food systems have increased because the components and ingredients of food systems are directly related to the quality, nutrition and energy source that they can provide consumers [1–3], particularly lipid-based foods, proteins and carbohydrates. Food quality is defined by texture, color and sensory properties, which promote acceptance and preference by consumers. Food science has devoted several years of research to the study of individual ingredients in food systems, particularly stabilizing agents.

Diverse research projects have attempted to elucidate the effects and changes that stabilizing agents in foods produce through the formation of physical and chemical interactions between macromolecules in the food matrix. Additionally, researchers have focused on the influence of the chemical characteristics of stabilizers on changes in viscous and elastic properties [1,4–17]. Studies on food systems and their ingredients have used several techniques, including differential scanning calorimetry, rheology shear and extensional flow, to determine physical parameters [1,7–17]. This work is a review of research related to rheological studies focused on the extensional flow applied to solid and liquids foods containing polymeric and non-polymeric food components.

Extensional properties of foods

Since the middle of the last century, rheology had many applications in different fields related to the production, handling and quality control of foods [1–3,13,17,18]; rheological studies include determining the deformation and shear rate of food systems produced by external forces [1,3,18]. Determination of the rheological properties of different ingredients and foods is useful because it can elucidate the composition, texture, and structural changes observed during agitation, processing, packaging, storage and consumption [1,3,13,18]. During those processes, foods are subjected to a combination of shear and extensional flow; therefore, it is important to know the structural changes on the food components that are produced by both flows [1,18]. Extensional flow is a deformation that involves elongation of the fluid molecules along the streamlines; according to the resulting deformation, the extensional flow may be classified as uniaxial or biaxial [2,15,17,19]. Uniaxial extensional flow is the most studied and developed from a theoretical and experimental standpoint [20••,21–23].

Several studies on extensional flow in dilute, semi-dilute and concentrated polymer solutions have been performed using theoretical, experimental and numerical simulations [2,4,5,10–16,20••,21–25]. Trouton proposed a relationship between extensional and shear viscosity for Newtonian fluids that states that: $\eta_E = 3\eta_0$, where η_E is the extensional viscosity in the steady-state and η_0 is the shear viscosity in zero-shear; at a low shear rate, $Tr = \eta_E/\eta_0 = 3$ [4,15].

Despite the need to know the extensional flow properties of fluids, it was not until the 1970s and 1980s that the work in this field was conducted because of advances in theory development and new equipment technology. That work focused on determining the η_E of high viscosity shear fluids ($\eta > 1000$ Pa s) as polymer melts [2,4]. Moreover, with the advent of technology and the development of electronic components, the first measurements of the extensional properties of low viscosity shear fluids ($\eta \sim 0.01$–10 Pa s) were performed in the 1990s [2]. Recent research has discussed that the determination of the extensional properties of low viscosity fluids is influenced by effects of inertia, surface tension, and gravity because the magnitude of these effects are of the same order than viscoelastic responses [4,10,12,13,15].

The development of products (new or improved) with specific functionalities is a daily activity of the food industry. The specific functionalities of foods are necessary because consumers require products with sensory characteristics. Foods are formulated with diverse ingredients, such as hydrocolloids (gums), proteins, sugars, lipids, etc., and they influence the functionality (e.g., texture) and acceptability by consumers. One of the most important functionalities of foods is the viscosity. The addition of hydrocolloids to food formulation produces a 'stringy' appearance, meaning the product does not cleanly break when the container is tilted upward. Extensional viscosity measurement was proposed as a method to determine this sensory characteristic property [26••]. Methods used to test high viscosity liquids include fiber wind-up and entrance pressure drop, whereas the opposed jets method was used to test low viscosity liquids. Liquid foods were the first materials used to determine η_E, an important variable that gives information on the structural features of a liquid; also, η_E is used in process design calculations, control processes, food process modeling and for determining the overall and sensory quality of liquid foods. It is well recognized that η_E is sensitive to the molecular makeup of macromolecules, such as the chain-length distribution (in branching polymers) and arrangement of macromolecules (mainly proteins and polysaccharides) in the food matrix [27••,28,29•]. The diverse type of flow occurring during food consumption and processing such as swallowing, atomization, flow through porous media, turbulent flow reduction, etc., involves extensional flow. Solid materials are found in wide variety foods; wheat doughs are some of the most complex solids systems because of their elastic behavior due to the protein fraction and imbibed starch granules in their network. Food systems are categorized as liquid and solid foods (including semi-solids).

Methods to determine extensional properties of foods

From an experimental point of view, some of the largest challenges for determining the extensional properties of fluids are equipment designed to generate a homogeneous extensional shear free flow under steady strain rate conditions [2,20••,30••]. Despite of the measurement challenges, recently novel instruments to characterize extensional properties of a wide range of polymeric materials has been developed. They include measurement of pressure drops through a contraction in the capillaries and channels [31], using capillary rheometers [2,32], and the use of special rheometers for extensional flow, such as filament-stretching extensional rheometer (FiSER) [4] and capillary break-up extensional rheometer (CaBER) [15,16,20••,24]. Therefore, studies on the extensional flow of viscoelastic fluids and diluted low viscosity fluids in shear free conditions have been increasing [2,13,15,16,20••,21]. However, few researchers have related the study and determination of the extensional properties of biopolymers in solution [1,4,5,8,10,12,13,15,16,21,24].

Table 1 summarizes the characteristics of the different instruments that have been used to study the extensional properties of biopolymers in solution and their application ranges. The studies indicate several drawbacks to obtaining information on the analyzed systems that should be considered during experiments.

Physics of extensional properties

During a study on the extensional flow of polymer solutions, it is common to establish a dimensionless number for dynamic measurements and material functions, for example the Trouton ratio ($Tr = \eta_E/\eta_0$). This expression is a function of the Hencky strain ($\varepsilon_H = \dot{\varepsilon}_0 t$) and Deborah number ($De = \lambda\dot{\varepsilon}_0$), where λ is the longest relaxation of the molecules constituting the polymer solution, which can be obtained from small strain oscillatory flow dynamic tests. Furthermore, methodologies established

Table 1

Summary of extensional rheometer designs and application to biopolymers in solution.

Instrument type	Flow	Shear viscosity range (s^{-1})	Limitations	References
Entrance flow	Uniaxial extension	>1	Variable strain rate, mixed with shear	[31]
Opposed jet	Uniaxial extension	0.01–1	Variable strain rates and strain histories	[19]
Geometries with a hyperbolic contraction	Uniaxial extension	0.01–500	Variable strain rate, mixed with shear	[2,32]
Filament stretching, constant volume, medium viscosity	Uniaxial extension, constant strain rate	1–1000	Sample gripping limited to medium and high viscosity	[4]
Capillary breakup rheometry	Uniaxial extension	0.01–10	Inertial and surface tension dominate at low viscosity, variable strain rates	[4,5,8,10,12,13,15–17]