

Modeling the Rheological Properties of Plant-based Foods: Soft Matter

Principles

David Julian McClements*

Department of Food Science, University of Massachusetts, Amherst, MA 01003

**Corresponding author:* David Julian McClements. Department of Food Science, University of Massachusetts, Amherst, MA 01003, USA. Tel: 413 545 2275; email: mcclemen@umass.edu

Abstract

There is growing interest in the design and fabrication of next-generation plant-based (NG-PB) foods that have physicochemical and functional properties that simulate those of traditional animal-based foods, like meat, seafood, egg, and dairy products. Many of these products can be considered as colloidal materials containing particles or polymers that determine their properties, which means that these properties can be understood using soft matter physics concepts. The rheological properties of NG-PB foods may vary widely, including low viscosity fluids (like milk), high viscosity fluids (creams), soft solids (like yogurt), and hard solids (like some cheeses). For manufacturers of NG-PB foods to mimic this broad range of products it is important to have theoretical models to identify, predict, and control the key parameters impacting their textural attributes. In this article, the theoretical models developed to describe the properties of fluid, semi-solid, and solid colloidal dispersions are described, and their potential for improving the design and fabrication of NG-PB foods is highlighted. In the future, it will be important to establish the most appropriate models for different categories of NG-PB foods and to determine their range of applications.

Keywords: soft matter physics; rheology; plant-based foods; colloidal dispersions; nanoparticles; biopolymers

1. Introduction

In this article, the term “next-generation plant-based (NG-PB) foods” is used to refer to foods formulated from plant-derived ingredients, such as lipids, proteins, and polysaccharides, that are specifically designed to mimic the properties of animal sourced foods like meat, seafood, eggs, and dairy products¹. The focus of this article is on understanding, predicting, and controlling the rheological characteristics of NG-PB foods, like the flowability of milk and cream analogs or the hardness of meat, egg, and cheese analogs². Rheological attributes like shear viscosity (for fluids) and elastic modulus and fracture properties (for solids) influence the processing, quality, shelf life, and sensory attributes of NG-PB foods^{1,3}. It is therefore important to understand the factors that contribute to the rheology of this category of foods, as this enables food designers and manufacturers to create products with the rheological attributes required for their intended

application. The rheological properties of materials depend on how they flow or deform when a particular type of stress is applied to them, such as a normal, shear, and/or extensional stress ⁴. NG-PB foods exhibit a wide range of rheological characteristics depending on their compositions and processing. For instance, NG-PB milks are typically low viscosity liquids, NG-PB sauces and dressings are viscous fluids, NG-PB yogurts and eggs are soft gels, and NG-PB cheddar cheese and cooked meat are hard gels ¹. Even within a particular rheological category, the properties of NG-PB foods can vary considerably. For instance, the fracture properties of solid NG-PB foods may range from hard and brittle to soft and malleable, which is important for determining their mouthfeel and other sensory qualities.

NG-PB foods span the whole range of materials normally covered by soft matter physics, and so the principles of this discipline can be employed to better understand and control their properties ⁵⁻⁷. The majority of NG-PB foods are primarily comprised of colloidal particles and polymers, which play a critical role in determining their overall rheological attributes. These colloidal particles include oil bodies, oil droplets, protein particles, starch granules, and plant tissue fragments, while the polymers include polysaccharide and protein molecules, as well as their assemblies ¹. The main focus of this article is to outline the current understanding of colloidal and polymer dispersions, with an emphasis on providing physical concepts and theoretical models describing their properties. These concepts and models should improve our understanding of the factors that impact the rheology of NG-PB foods, which should facilitate the design and fabrication of better-quality products.

2. Plant-based Foods as Colloidal Dispersions

As mentioned in the introduction, the majority of NG-PB foods can be considered to be colloidal dispersions consisting of small particles and/or polymer molecules suspended in an aqueous matrix (**Figure 1**). In this section, we provide a brief overview of the different kinds of these products.

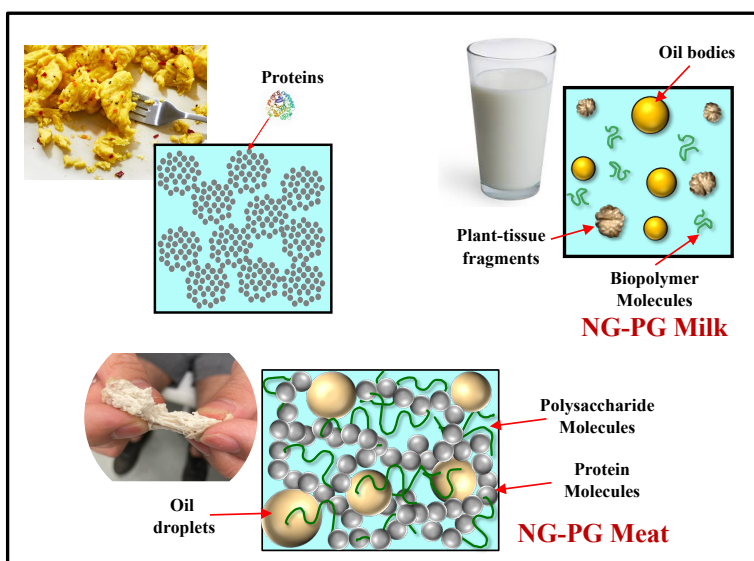


Figure 1. Schematic diagram of the importance of colloids and polymers in selected NG-PB food products. Proteins, polysaccharides, oil bodies, and oil droplets are all examples of colloidal materials found in these soft-matter foods.

2.1. NG-PB dairy products: Milk, cream, yogurt, and cheese

NG-PB milks are complex colloidal dispersions containing several kinds of particles or polymers suspended in an aqueous solution, which may also contain dissolved substances like sugars and salts^{8,9}. For instance, they may contain oil bodies, oil droplets, plant cell fragments, protein aggregates, and/or polysaccharides dispersed in water (**Figure 1**). These products typically have a relatively low viscosity that is designed to simulate the low viscosity of cow's milk⁹. However, in some cases, thickening agents (such as gums) are added to inhibit the creaming or sedimentation of the colloidal particles they contain, which leads to a pronounced increase in their viscosity^{10,11}. Structurally, NG-PB creams are similar to NG-PB milks, but the fat content is higher, which leads to a higher viscosity (see later). NG-PB yogurts are soft gels whose rheological properties are dominated by the present of a 3D network of aggregated biopolymers, usually formed from added proteins, starches, and/or gums, or by polymers secreted during microbial fermentation¹². NG-PB cheeses are semi-solid materials that may vary from relatively soft gels (like Brie) to hard gels (like cheddar)^{13,14}. The rheological properties of these materials are also dominated by a 3D network of biopolymer molecules, but the presence of fat droplets and/or a fat crystal network may also contribute to their texture and mouthfeel.

2.2. NG-PB meat and seafood products

NG-PB meat and seafood products are often designed to have a fibrous microstructure that mimics those found in the equivalent animal products¹⁵. Food manufacturers aim to simulate this kind of microstructure because it influences the desirable textural and mouthfeel attributes of the end product. Often this kind of fibrous structure is created by using an appropriate blend of proteins and polysaccharides (**Figure 1**). Some of the most common proteins used to formulate commercial NG-PB meat and seafood products include those isolated from soybeans, peas, rice, mung beans, faba beans, and wheat proteins, while some of the most common polysaccharides include starch, methylcellulose, and various gums. Fibrous structures are typically formed using mechanical methods, such as extrusion or shear cell technology^{3,16}, but it can also be created using soft matter physics approaches, such as phase separation-shearing-gelation methods¹. Fibrous structures are usually formed using proteins and/or polysaccharides as structure-forming elements¹⁶. There has also been interest in creating NG-PB adipose tissue to simulate the adipose tissue found in real meat and seafood products. For instance, highly concentrated oil-in-water emulsions fabricated from plant or microbial fats, proteins, and polysaccharides have been developed as NG-PB adipose tissue analogs to mimic the whitish appearance and solid-like texture of real adipose tissue¹⁷⁻¹⁹. Some of the plant-based versions have even been designed to simulate the melting and crystallization of real adipose tissue. In an alternative approach, liquid plant-derived oils have been converted into solid fats using enzyme glycerolysis, which led to products that exhibited similar characteristics as high-melting animal fats²⁰. Oleogels and emulsion gels formulated from plant-derived ingredients have also been developed recently to replace the fats in meat and seafood products²¹.

Typically, NG-PB meat and seafood products are semi-solid materials whose hardness and fracture properties are designed to simulate those found in the real animal sourced products they are intended to replace. From a rheological point of view, they can be considered to consist of filled polymer gels that contain fibers and particles (**Figure 1**).

2.3. NG-PB egg and egg products

NG-PB egg analogs are typically colloidal dispersions containing particles (like oil droplets) and polymers (like proteins and/or polysaccharides) (**Figure 1**)^{1,22}. Commercially, they may be sold in a fluid or solid form. In the fluid form, they are usually viscous fluids that form gels when they are heated during cooking, such as frying or baking. The initial viscosity of fluid NG-

PB eggs needs to be relatively high to prevent creaming or sedimentation of any particulate matter during storage, such as fat droplets, starch granules, or protein aggregates. During heating, gelation usually occurs as a result of the unfolding and aggregation of globular plant proteins, which leads to the formation of a 3D protein network that provides elastic properties²³. Ideally, gelation should begin at the same temperature as for real eggs (around 65 to 70 °C) and the gels formed should have similar textural attributes to real eggs. In the solid form, NG-PB egg products may be sold in a pre-gelled state that mimics the properties of cooked egg, like egg slices that can be cooked in a microwave, toaster, or frying pan.

Egg analogs may also be used to create other products that real eggs are typically used for, such as plant-based salad dressings or mayonnaises²⁴. These products are concentrated oil-in-water emulsions that typically have a yield stress and a high viscosity. These semi-solid characteristics may arise for several reasons, including the fact that the oil droplets are closely packed together in concentrated systems, the oil droplets may be aggregated with each other, or thickening or gelling agents (like gums or starches) are added.

3. Colloidal Dispersions

In this section, we highlight the main characteristics of the particles and polymers present in the colloidal dispersions that might be found in NG-PB foods that may influence their rheological properties. Typically, it is important to identify the different kinds of particles and polymers present, as well as to have knowledge of their molecular and physicochemical properties, as this influences the processing, shelf life, quality attributes, and sensory properties of these foods.

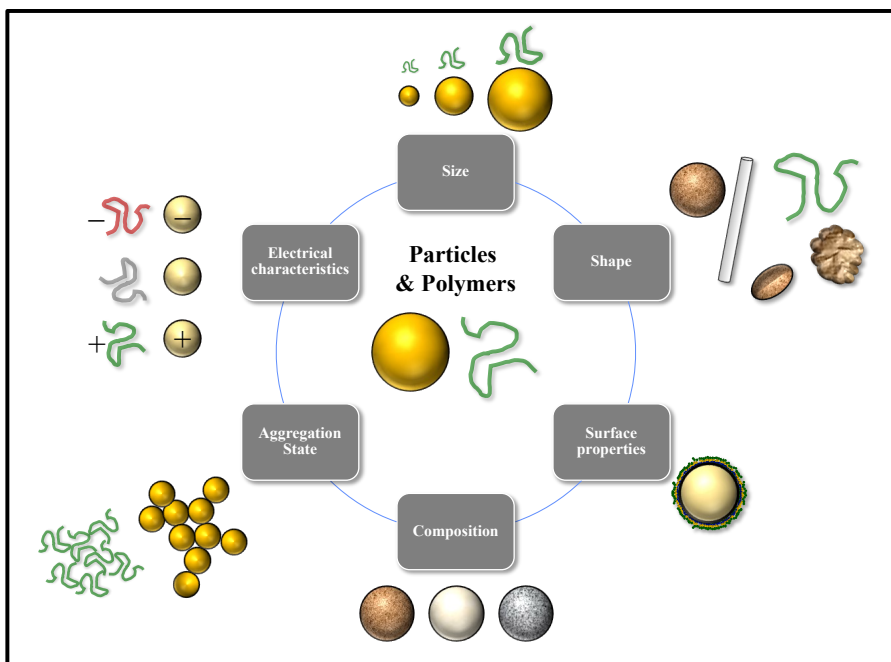


Figure 2. The properties of the particles and polymers in NG-PB foods varies, which alters their rheological properties.

3.1. Particles

Colloidal particles vary in their compositions, sizes, shapes, polarities, charges, interactions, and aggregation states (**Figure 2**), which determines their impact on the rheology of NG-PB foods. In general, the properties of colloidal particles impact the rheology of both fluid and solid foods, which can often be described by theoretical equations or computational models ⁴.

Composition: The particles in NG-PB foods may be comprised of different edible substances depending on their origin and processing, including proteins, polysaccharides, lipids, phospholipids, minerals, and their combinations ^{1, 15}. For instance, the oil bodies present in many oil-rich plant materials (such as nuts and beans) consist of a triacylglycerol core surrounded by a layer of phospholipids with proteins embedded in it ^{25, 26}. These oil bodies may be present in NG-PB milks created using top-down methods that utilize size-reduction operations to disrupt plant tissues and release the oil bodies ⁹. The oil droplets in NG-PB milks formulated using bottom-up methods, like homogenization of oil, water, and emulsifier, typically consist of a triacylglycerol core surrounded by a layer of emulsifier molecules (often proteins, polysaccharides, phospholipids, and/or saponins) ⁹. In their natural state, raw starch granules consist of a mixture of amylose and amylopectin molecules organized into amorphous and

crystalline regions²⁷. During processing and cooking, the raw starch granules absorb water and swell (gelatinize), which changes their composition and functional attributes. Some NG-PB foods, such as milk and cheese analogs, are created from comminuted plant materials (such as nuts or seeds), and therefore contain plant tissue fragments, including cell wall materials rich in dietary fibers²⁸. NG-PB meat, seafood, and egg products often contain protein assemblies, such as fibers or particulates, that vary considerably in their length scales (**Figure 2, Table 1**). These assemblies can be formed from many different kinds of plant proteins, including those isolated from soy, corn, wheat, pea, mung bean, and potato. Identification of the various kinds of colloidal particles in a NG-PB food is important because they influence its rheological properties.

Particle size and shape: The particles in NG-PB foods may vary considerably in their sizes and shapes (**Figure 2**). For instance, their dimensions may range from a few nanometers (small protein aggregates) to a few millimeters (texturized vegetable proteins), which covers around six orders of magnitude in length scale. The oil bodies or oil droplets in NG-PB milks and creams typically vary from around 100 to 5000 nm⁹. The protein particles formed when globular plant proteins are heated above their thermal denaturation temperature may also vary from around 100 to 5000 nm depending on protein type, protein concentration, solution conditions, and processing conditions^{29,30}. Raw starch granules may vary in size from below a micrometer to above 100 micrometers depending on the species and maturity of the plant source, as well as the growing conditions³¹. Gelatinized starch granules are considerably larger than raw ones because they absorb water from their surroundings when they are heated and swell³². Plant tissue fragments may vary considerably in dimensions (from micrometers to millimeters) depending on the method used to breakdown the original plant materials, such as mechanical, chemical, or enzymatic methods²⁸. Texturized vegetable proteins are typically designed to be a few millimeters in size to mimic the dimensions of the pieces found in comminuted meat products³³. Mechanical size-reduction methods like milling, grinding, and homogenization may be used to reduce the particle size of plant tissues to inhibit gravitational separation in products like plant-based eggs and milk, or to improve the mouthfeel by removing large particles that would give a gritty or rough feeling like in plant-based milks and creamers. Enzyme treatments using proteases, amylases, cellulases, hemicellulases, or pectinases are sometimes used to reduce the size of starch granules, protein particles, or plant-tissue fragments for similar reasons.

The shape of the particles in NG-PB foods may also vary considerably (**Figure 2**). Oil bodies, oil droplets, starch granules, and colloidal protein aggregates are often spherical or spheroidal. However, protein aggregates and plant tissue fragments may have fibrous or irregular shapes. For instance, NG-PB meat or seafood products often contain protein or polysaccharide aggregates or domains that have fibrous structures, because this better simulates the textural attributes and mouthfeel of real products ^{2,3}. These fibrous structures can be produced using processing methods (like extrusion or shear cells) or physicochemical methods (like phase separation, shearing, and gelling).

In general, the size and shape of the colloidal particles within NG-PB foods have a large impact on their textural attributes. For instance, particles larger than about 50 µm can be detected as discrete objects within the human mouth, which may be undesirable in products where a smooth mouthfeel is required (like plant-based milks and creams) but desirable in products where a more textured mouthfeel is desirable (like plant-based burgers or sausages). The size and shape of food particles also influence their ability to form 3D networks, which influences the textural attributes of semi-solid and solid NG-PB foods, like meat, seafood, and egg analogs. Consequently, it is important to know and control these attributes.

Interfacial properties: The interfacial properties of the particles in NG-PB foods may also impact their rheological properties, mainly because they influence the colloidal interactions between them, which determines their aggregation state. Some of the most important interfacial properties are their polarity, charge, and thickness ³⁴. Some particles found in NG-PB foods are predominantly polar because they have a preponderance of hydrophilic groups on their surfaces, including oil bodies, oil droplets, and plant-tissue fragments. Other particles are predominantly non-polar because they have numerous hydrophobic groups on their surfaces, including protein assemblies formed by zein or gliadin ³⁵. It should be noted that the polarity of particles may change depending on the processing conditions used. For instance, the surfaces of oil droplets coated with globular proteins may go from polar to non-polar when they are heated because the adsorbed proteins unfold and expose hydrophobic groups ³⁶.

The electrical characteristics of the particles in NG-PB foods are also important because they influence their interactions with each other, as well as with other charged substances in the system. Under neutral pH conditions, most kinds of particles found in NG-PB foods are negatively charged or neutral. However, the charge on particles containing appreciable amounts

of proteins on their surfaces, such as oil bodies, oil droplets, or protein aggregates, may go from negative to positive as the pH is reduced from above to below their isoelectric point³⁷⁻³⁹. This is because the amino and carboxyl groups on the proteins become progressively protonated as the pH is reduced ($-\text{NH}_2 \rightarrow -\text{NH}_3^+$ and $-\text{COO}^- \rightarrow -\text{COOH}$), which leads to an increase in positive charge and decrease in negative charge. At the isoelectric point of the proteins, the number of negative and positive charges are balanced, leading to a zero net charge. A reduction in the net charge on the particles in a NG-PB food can promote their aggregation, which usually leads to an increase in viscosity or gel strength^{40,41}. The controlled aggregation of proteins and protein-coated oil droplets is important for the creation of NG-PB cheeses, which often rely on isoelectric precipitation to form semi-solid structures.

For particles that are coated by polymeric materials, like proteins or polysaccharides, their resistance to aggregation also depends on the thickness of the adsorbed layer⁴². Typically, the strength of the steric repulsion between particles increases as the thickness of the adsorbed polymer layer increases. Consequently, it may be important to control the thickness of an adsorbed layer to manipulate the stability and rheology of these colloidal dispersions.

Table 1: Examples of the variations in the characteristics of particulate matter found in NG-PB foods. The charge is given under neutral conditions. Under acidic conditions, proteins may become positively charged (as in dressings or soft drinks). Key: TVP = texturized vegetable protein.

Type	Composition	Diameter	Shape	Charge	Polarity
<i>Oil bodies</i>	Fat, protein, and phospholipids	100 to 5000 nm	Spherical	Negative	Polar coating
<i>Oil droplets</i>	Fat and emulsifier	100 to 5000 nm	Spherical	Negative	Polar coating
<i>Colloidal protein</i>	Protein	100 to 5000 nm	Spheroid	Negative	Polar to non-polar*
<i>Protein fibrils</i>	Proteins	Several nm	Fibrous	Negative	Polar to non-polar*
<i>Starch granules</i>	Starch	2 to 40 μm	Spheroid	Negative to neutral	Polar exterior
<i>Plant tissue fragments</i>	Dietary fiber	100 nm to 100 μm		Negative	Polar exterior

<i>TVP</i>	Protein	2 to 30 mm	Irregular chunks	Negative	Polar to non-polar exterior*
------------	---------	------------	---------------------	----------	---------------------------------

* The polarity of protein particles depends on the type used. Zein and gliadin are non-polar, whereas most other plant proteins are polar (at room temperature).

In summary, when considering the rheological properties of a NG-PB food containing colloidal particles it is important to have knowledge of their composition, size, shape, and interfacial properties. This usually depends on having a range of suitable analytical tools to provide information about these properties ¹.

3.2. Polymers

The most important polymers in NG-PB foods are usually proteins and polysaccharides from plant (or sometimes microbial) sources ^{1, 16}. These biopolymers vary in the number, type, and sequence of monomers present, as well as the nature of the bonds between them. Proteins are assembled from amino acids held together by peptide bonds, whereas polysaccharides are assembled from monosaccharides held together by glycosidic bonds. In this section, we highlight some of the most important attributes of the polymers present in NG-PB foods that may influence their rheological properties.

Composition: The monomers that make up plant proteins and polysaccharides vary considerably depending on their origin, which has a major impact on their physicochemical, functional, and nutritional properties. For instance, the type of monomers present influences the polarity and electrical characteristics of proteins and polysaccharides, which influences their conformation, interactions, and ability to form gels. For proteins, the amino acid composition also influences their nutritional attributes, such as the fraction of essential and non-essential amino acids present, as well as their digestibility and bioavailability. For polysaccharides, the type and bonding of monosaccharides influences their digestibility within the gastrointestinal tract, which impacts their health benefits. For this reason, there is interest in utilizing dietary fibers to create structures in NG-PB foods, rather than rapidly digestible starches. Consequently, it is often important to establish the nature of the polymers used to formulate NG-PB foods, and their impact on the texture.

Molecular characteristics: The molecular characteristics of polymers determine their impact on the physicochemical, functional, sensory, and nutritional properties of NG-PB foods. Several

molecular characteristics are especially important, including the molecular weight, conformation, branching, flexibility, polarity, and charge of the polymer chains^{43,44}. For instance, the ability of polymers to thicken solutions or form gels is often influenced by their molecular weight⁴⁵. Larger polymers are typically more effective at thickening and gelling than smaller ones. The polarity and charge of polymers influences their interactions with other molecules^{46,47}. For instance, the number of non-polar, polar, and charged groups impacts the hydrophobic, hydrogen bonding, and electrostatic interactions between the polymer chains, which influences their structuring and gelling properties. In turn, this influences the methods that can be utilized to form gels from different kinds of polymers. As an example, polymers that can form strong hydrogen bonds with each other (such as agar) can be gelled by cooling them to a temperature where the polymer chains adopt helical structures that crosslink with each other through hydrogen bonding. Polymers with a strong negative charge (like alginate, carrageenan, or pectin) can be gelled by adding appropriate cations (like calcium or potassium) to form electrostatic bridges. Polymers with a high surface hydrophobicity (like globular proteins above their thermal denaturation temperature) can be gelled by heating them to promote their unfolding and aggregation through hydrophobic attraction. Consequently, knowledge of the molecular characteristics of the polymers used to formulate NG-PB foods is important for understanding and controlling their formation and rheological properties.

4. Modelling of Rheological Properties of Fluid-like Plant-based Foods

Many NG-PB foods exhibit predominantly fluid-like characteristics, including milk, cream, and fluid egg analogs. These systems are basically colloidal dispersions containing particles (like oil bodies or fat droplets) and polymers (like hydrocolloids) dispersed in water (**Figure 1**). Consequently, the theoretical models used to relate the rheological properties of these colloidal dispersions to their composition and structure can be utilized to understand, predict, and control the properties of fluid-like plant-based foods.

4.1. Types of fluid-like behavior

In general, fluids can be described as either ideal or non-ideal depending on how their rheology changes with applied shear stress.

4.1.1. Ideal fluid behavior

The rheological properties of ideal fluids are described by their shear viscosity (η), which is

the slope of the shear stress *versus* shear rate. For this type of fluid, the shear stress (τ) is directly proportional to the shear rate ($\dot{\gamma}$) and so their rheology can be described by the following simple expression:

$$\tau = \eta \dot{\gamma} \quad (1)$$

The units of the shear stress are Pascals (Pa), whereas those of the shear rate are reciprocal seconds (s^{-1}), and so the units of the apparent shear viscosity are Pa s. For ideal fluids, the shear viscosity is independent of the applied shear rate.

4.1.2. Non-ideal fluid behavior

Several NG-PB foods exhibit non-ideal fluid behavior, which means the applied shear stress is no longer proportional to the shear rate. The most common type of non-ideal behavior observed in these products is shear-thinning, which refers to a decrease in shear viscosity with increasing shear rate (or stress). For instance, the apparent shear viscosity of some milk or fluid egg analogs decreases with increasing shear rate because they contain particles or polymers held together by weak forces, which are disrupted when the applied shear stress is raised. In principle, the apparent shear viscosity can also increase as the applied shear rate is raised, which is known to as shear thickening, but this kind of behavior is less common in foods. One potential cause of shear thickening is a greater tendency for polymers or particles to aggregate with each other when the shear rate is raised because this increases the collision frequency between them.

The change in the apparent viscosity of non-ideal fluids with shear rate can be modeled using the Cross model ⁴⁸:

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (K\dot{\gamma})^{1-n}} \quad (2)$$

In this equation, η_0 is the plateau apparent shear viscosity at very low shear rates, η_{∞} is the plateau apparent shear viscosity at very high shear rates, K is the Cross constant, and n is the power index. The value of the power index provides information about the kind of non-ideal behavior exhibited by the fluid: $n = 1$ for an ideal fluid; $n < 1$ for a shear thinning fluid; and $n > 1$ for a shear thickening fluid. The rheological behavior of this kind of non-ideal fluid can therefore be described by finding the η_0 , η_{∞} , K , and n parameters that give the best fit between the model and experimental measurements of apparent shear viscosity *versus* shear rate. In

colloidal dispersions containing aggregated polymers or particles, the magnitude of K is governed by the strength of the bonds holding the structures together⁴⁹. An example of the dependence of the apparent viscosity on shear rate predicted by the Cross model is shown in **Figure 3** for a shear thinning fluid.

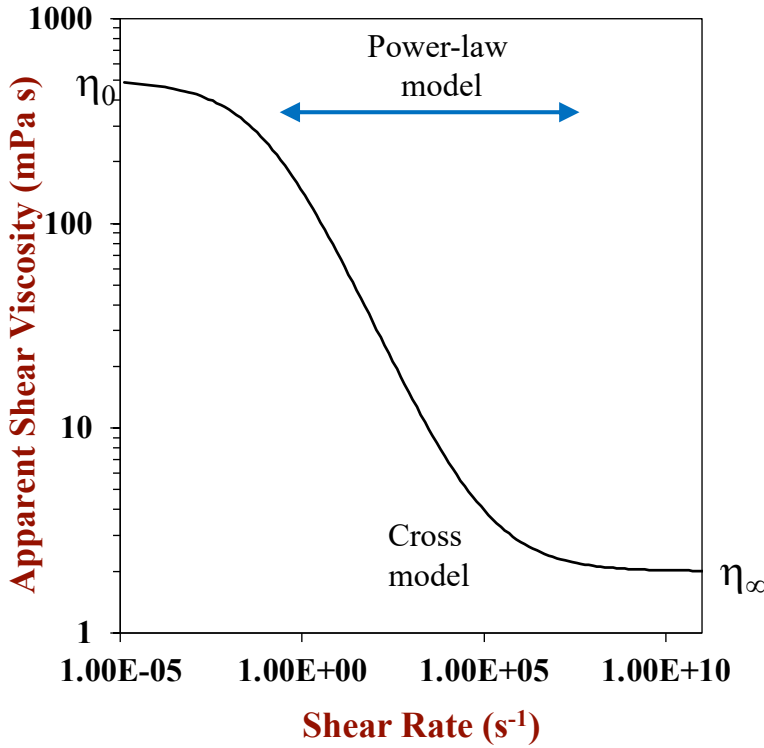


Figure 3. The change in viscosity of non-ideal fluid NG-PB foods can often be described by the Cross model. The power-law model is only applicable in the region where $\log(\text{viscosity})$ is proportional to $\log(\text{shear rate})$.

In practice, it may only be possible to measure the apparent shear viscosity over intermediate shear rates rather than the entire shear rate range, which extends many orders of magnitudes, due to the limitation of existing rheometers. In this case, the apparent shear viscosity can sometimes be described using a simple power law model⁵⁰:

$$\eta = K(\dot{\gamma})^{n-1} \quad (3)$$

Here, K is the consistency index and n is the power index. In this situation, the rheology of a fluid can be described by finding the K and n values that give the best fit between the model and experimental measurements of apparent shear viscosity *versus* shear rate.

In some cases, the viscosity of non-ideal fluids depends on how long the shear stress is

applied to the sample. For example, the apparent shear viscosity may decrease (shear thinning) or increase (shear thickening) over time depending on the nature of the sample. This kind of shear thinning behavior may occur because structures within a sample (such as aggregated polymers or particles) become increasingly disrupted the longer the shear stress is applied. Conversely, this kind of shear thickening may occur if the applied shear stress induces particle or polymer aggregation during the measurement.

4.2. Theoretical models relating the rheology of colloidal fluids to their properties

The theoretical models developed to describe the rheology of colloidal fluids are usually based on calculations of the frictional losses that occur when a fluid flows around the particles or polymers dispersed in a liquid during the application of a stress. Many fluid NG-PB foods can be considered to be colloidal suspensions consisting of polymers or particles (like polysaccharides, protein aggregates, oil bodies, oil droplets, or plant cell fragments) dispersed in an aqueous solution. Their rheological properties can therefore be related to their composition and structure using theoretical models developed to describe colloidal dispersions^{48, 51}. In general, the viscosity of a colloidal suspension increases as the concentration of polymers or particles it contains is raised, with the magnitude of the rise being governed by the types of polymers or particles present.

For dilute colloidal suspensions containing non-interacting rigid spherical particles, the shear viscosity (η) can be related to the disperse phase volume fraction (ϕ) of the particles using an equation first derived by Albert Einstein:

$$\eta = \eta_1(1 + 2.5\phi) \quad (4)$$

Here, η_1 is the shear viscosity of the aqueous phase surrounding the particles. This equation can usually be employed when the disperse phase volume fraction is below around 0.05 (5%), providing that other assumptions are met, *i.e.*, the particles are hard, rigid, and separate. When the concentration of particles within a colloidal suspension increases the fluid flow around one particle influences that around the neighboring particles, thereby leading to increased energy dissipation. As a result, there is an increase in the viscosity over that predicted by the Einstein equation. The viscosity of more concentrated colloidal suspensions can be modeled using a semi-empirical equation derived using effective medium theory^{48, 51}:

$$\eta = \eta_1 \left(1 - \frac{\phi}{\phi_c}\right)^{-2} \quad (5)$$

Here, ϕ_c is a critical packing parameter (≈ 0.65), which is assumed to be the volume fraction where the colloidal particles become jammed together, leading to elastic-like properties.

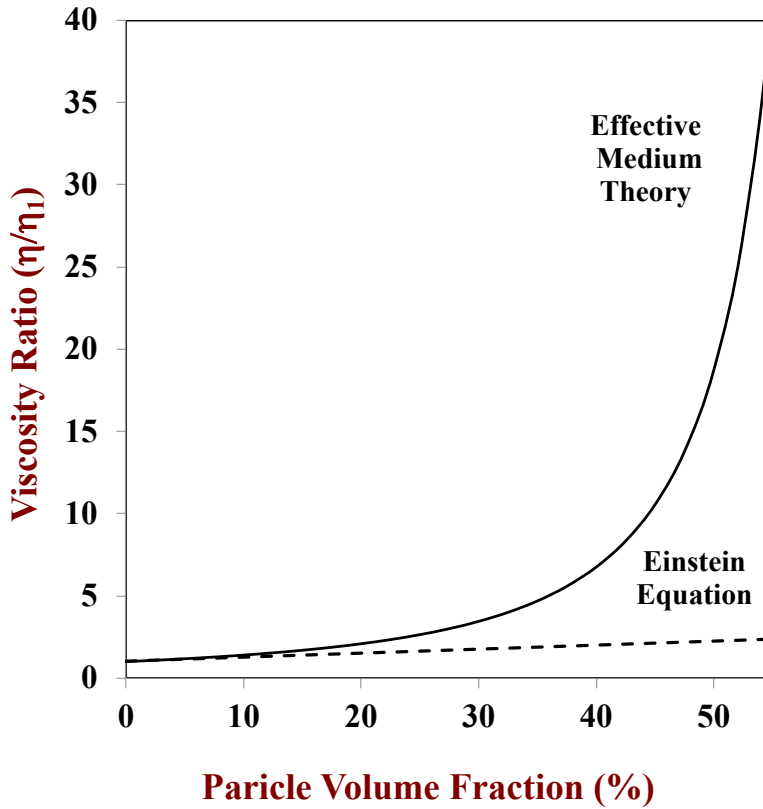


Figure 4. The increase in shear viscosity with increasing particle concentration for colloidal particle dispersions can be described by the Einstein equation for dilute systems and by the effective medium theory for concentrated systems

The increase in viscosity with increasing particle volume fraction predicted by these two equations is plotted in **Figure 4**. At low volume fractions ($< 5\%$), both equations give fairly similar values, but at higher volume fractions the effective medium theory predicts a much higher viscosity than the Einstein equation. The effective medium theory predicts that the viscosity should increase steeply when the particle volume fraction exceeds about 45% , which is because the particles start to strongly interact with each other. The impact of particle concentration on the viscosity of colloidal suspensions is the reason why milk ($\phi < 5\%$ fat) has a low viscosity, heavy cream ($\phi \approx 40\%$ fat) has a high viscosity, and mayonnaise ($\phi \approx 70\%$ fat) is a semi-solid material.

Similar equations can be used to describe the rheological properties of colloidal suspensions containing polymers. However, in this case the volume fraction of the particles (ϕ) should be replaced by the effective volume fraction of the polymers (ϕ_{eff}):

$$\phi_{\text{eff}} = R_V \phi \quad (6)$$

Here, R_V is the volume ratio of the polymer molecules, which is the total volume occupied by an individual polymer molecule in solution (polymer chain plus entrained water) divided by the volume occupied by the polymer chain alone: $R_V = V_T/V_P$. This equation assumes that a polymer molecule can be assumed to act like an effective sphere that perturbs the fluid flow within the colloidal suspension. In this case, the effective sphere contains both polymer molecules and solvent. The volume ratio of a polymer can be related to its molecular characteristics using the following approximate equation:

$$R_V = \frac{4\pi r_H^3 \rho N_A}{3M} \quad (7)$$

Here, r_H is the hydrodynamic radius of the polymer molecules, ρ is the density of the polymer chain, N_A is Avogadro's number, and M is the molecular weight of the polymer. Taken together, these expressions indicate that the viscosity of a polymer solution should rise as the polymer concentration is raised and the hydrodynamic radius of the polymer is increased (for a fixed molecular weight). Thus, polymers with open extended structures (high r_H) should be more effective thickening agents than ones with tight compact structures (low r_H). This explains why polysaccharides like xanthan or gellan gum are highly effective at increasing the viscosity of a solution, whereas globular proteins like soy or pea protein are not. For polymers of the same conformation (*e.g.*, random coil), the volume ratio, and therefore viscosity, increases with increasing molecular weight (even though M is in the denominator of the equation). This phenomenon is a result of the fact that r_H and M are dependent variables, with the radius of hydration increasing as the molecular weight increases. The relationship between the hydrodynamic radius and molecular weight of polymers depends on their conformation: $r_H \propto M$ for rigid rods; $r_H \propto M^{1/2}$ for random coils; and $r_H \propto M^{1/3}$ for globular structures. Thus, R_V is proportional to M^2 , $M^{3/2}$, and M for rods, coils, and globules, respectively⁵².

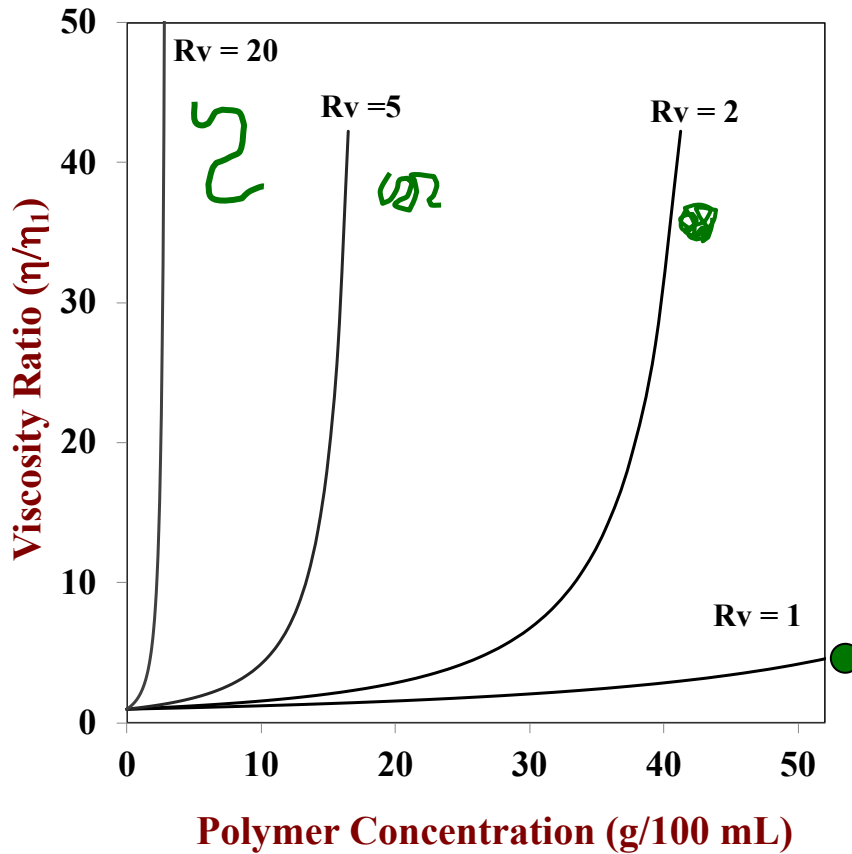


Figure 5. The increase in shear viscosity with increasing polymer concentration for polymer solutions depends strongly on the conformation of the polymers.

The predicted concentration-dependence of the viscosity of polymer solutions with different R_v values is shown in **Figure 5**. These predictions suggest that adding globular proteins ($R_v \approx 1$) to an aqueous solution will only cause a pronounced rise in viscosity when the concentration exceeds about 30-40 g/100 mL. In contrast, adding polysaccharides with highly extended structures ($R_v \gg 1$) to aqueous solutions results in a pronounced rise in viscosity when the concentration exceeds a much lower value (< 1 g/100 mL). Knowledge of this effect is useful when selecting plant-based ingredients for application in some types of NG-PB food products. For instance, it may be important that a milk analog contains a high amount of protein but that it also has a low viscosity. In this case, it would be advantageous to select a protein source that has a compact globular structure, such as soy or pea protein. In contrast, a PB dressing product may need to be highly viscous to inhibit gravitational separation and to provide desirable textural attributes. However, it may be important that the ingredient costs and calorie content are not too

high. In this case, the viscosity of the product can be increased by adding a relatively low concentration of a polysaccharide with a highly extended structure, such as xanthan, locust bean, or gellan gum.

4.3. Major factors impacting the rheology of colloidal fluids

The theoretical models discussed in the previous section provide some important insights into the major factors impacting the rheological properties of colloidal fluids containing polymers or particles. Some of the most important factors are highlighted below:

Continuous phase rheology: The theoretical equations derived to describe the rheology of colloidal fluids show that their viscosity is proportional to the viscosity of the continuous phase. Consequently, increasing the viscosity of the continuous phase by adding thickening agents will increase the overall viscosity of the system.

Particle or polymer concentration: The theoretical equations show that increasing the concentration of the particles or polymers in a colloidal fluid increases the overall viscosity. Typically, the viscosity increases relatively slowly with increasing concentration for dilute systems, but then increases steeply when particle-particle or polymer-polymer interactions become more important (**Figure 4**). Consequently, a critical concentration has to be exceeded before the viscosity increases dramatically.

Polymer conformation: For polymers, their ability to increase the viscosity of a colloidal fluid depends on their conformation. The greater the effective volume they occupy in solution (higher R_V), the greater their thickening power (**Figure 5**). Consequently, larger stiffer linear polymers tend to be the most effective at increasing the viscosity of colloidal dispersions, like xanthan gum.

Aggregation state: The viscosity of colloidal fluids tends to increase when the particles or polymers are aggregated because there is then an increase in the effective volume fraction occupied by them. In other words, the disturbance in the fluid flow profile is greater, which leads to greater energy dissipation due to friction, leading to a higher viscosity.

Particle size: Particle size does not have a major direct impact on the viscosity of colloidal dispersions, as seen in the Einstein and effective medium theory equations shown earlier. However, it may have an indirect effect by affecting the aggregation state and interactions between the particles.

In general, the rheological properties of fluid foods can therefore be altered by changing the

type, concentration, and interactions of the polymers or particles they contain.

4.4. Examples of rheological properties of fluid NG-PB foods

In this section, several examples of the rheological behavior of fluid NG-PB foods, such as plant-based milk or egg analogs is given. The shear viscosity, consistency index, and flow index (determined from the power-law model) of selected NG-PB foods are summarized in **Table 3**. At a constant shear rate (10 s^{-1}), the shear viscosity of these foods varies widely, from relatively low for milk analogs to relatively high for plant-based salad dressings. The flow index of several of the milk analogs is close to one ($n \approx 1$), which means they behave like ideal liquids, where the shear viscosity does not depend strongly on shear rate. This is probably because they are relatively dilute colloidal dispersions that contain particles or polymers that are not strongly aggregated with each other. Several of the more viscous products, especially the dressings, have flow indices much lower than unity ($n \ll 1$), which indicates that they are highly shear thinning fluids. The pronounced decrease in the viscosity of these products with increasing shear rate can be attributed to the presence of aggregated or entangled polymers or particles, like polysaccharides, protein aggregates, oil bodies, oil droplets, or plant-tissue fragments. As the shear rate increases, the structures in these fluids become aligned, deformed, or disrupted, thereby leading to a decrease in viscosity. The rheology of NG-PB foods that are highly concentrated or contain aggregated polymers or particles, like some plant-based salad dressings and mayonnaises, can be treated as plastic materials, which behave like a solid below a critical yield stress but a fluid above this value. The equations used to describe these kinds of semi-solid foods are discussed in section 5.1.2.

Table 3. Shear viscosities and rheological parameters of some NG-PB foods and animal-based ones whose properties have been modeled by the power-law theory. Modified from McClements and Grossmann ¹.

Product type	Viscosity at 10 s^{-1} (mPa·s)	Consistency index K (Pa s ⁿ)	Flow index (n)	Reference
Cow's milk	2.2-2.6	-	1.00	8
Almond milk	4.6-26.3	-	0.82-0.56	8
Oat milk	6.8	-	0.89	8
Soy milk	2.6-7.6	-	1.00-0.90	8
Hen's whole egg	28	-	1.00	53

Hens' egg white	26	0.140	0.33	54
NG-PB egg white	16	0.089	0.28	54
NG-PB whole egg	8.2			
Salad dressing	2400	15	0.21	55

499

500 **5. Modelling of Rheological Properties of Solid-like Plant-based Foods**

501 Several kinds of NG-PB foods exhibit predominantly solid-like properties, including meat,
502 seafood, cooked egg, and cheese analogs (**Figure 6**). Nevertheless, they also exhibit some fluid-
503 like properties, like viscoelasticity or plasticity, which means they should more strictly be
504 considered to be soft solids. The rheology of colloidal soft solids is strongly influenced by the
505 type, concentration, and interactions of the polymers and/or particles they contain. The elastic
506 properties of many conventional animal sourced products are a result of the presence of a three-
507 dimensional network of crosslinked polymers (commonly proteins). For instance, the solidity of
508 meat and seafood products is a result of the complex hierarchical structures formed by various
509 proteins (such as actin, myosin, and collagen) in the muscle and connective tissues, the solidity
510 of cheeses and yogurts is a result of networks formed by aggregated casein molecules, whereas
511 the solidity of cooked eggs is a result of networks of aggregated globular proteins from egg white
512 and egg yolk. NG-PB foods designed to mimic the textural attributes of animal sourced foods
513 therefore often use food polymers, like proteins, starches, and/or gums, to create network
514 structures that provide similar textural attributes to the animal-based products they are designed
515 to replace ².

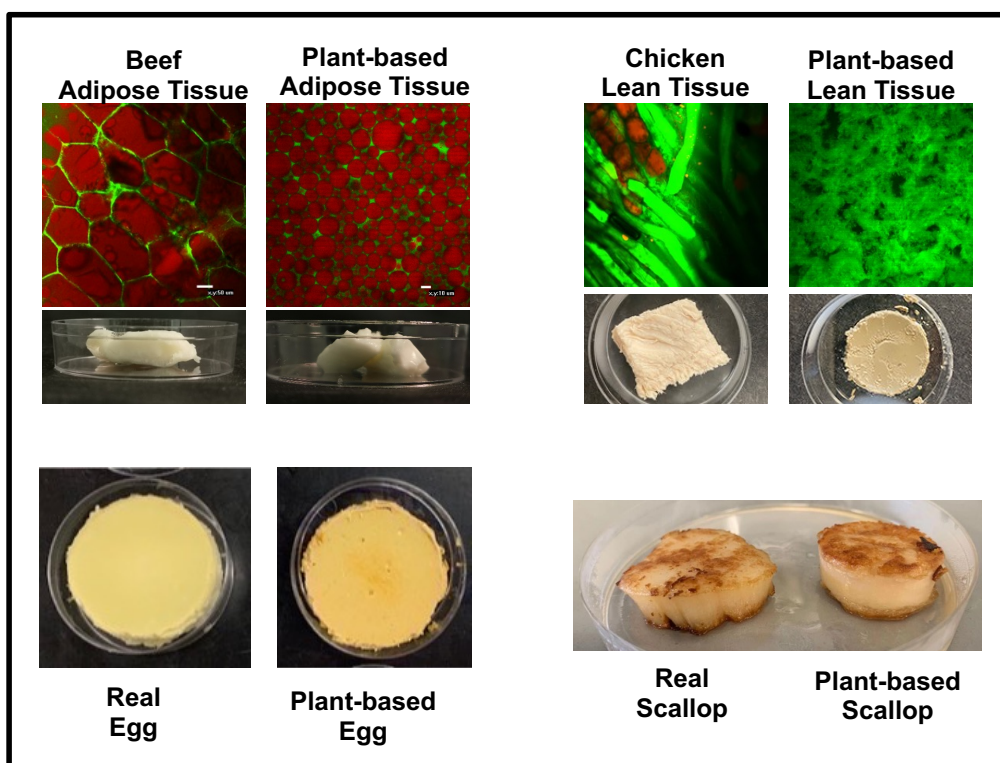


Figure 6. Examples of solid-like plant-based analogs of animal sourced foods like meat, seafood, and eggs. These products were all prepared in the authors laboratory from plant-based proteins, polysaccharides, and lipids.

It should be noted, however, that there are other components in animal sourced foods that also impact their overall textural attributes, including adipose cells in meat and seafood, milk fat globules in dairy products, lipoproteins in egg yolk, ice crystals and air bubbles in ice cream, and fat crystals in cheese and butter. As a result, food formulators often employ analogous plant-based ingredients to simulate the textural attributes normally provided by these structural elements in NG-PB foods, including oil droplets, air bubbles, and fat crystals.

The rheology of soft solids is also dependent on the type of non-covalent and/or covalent bonds acting between the various structural elements they contain, such as van der Waals, hydrogen bonding, hydrophobic, electrostatic, and chemical interactions⁴⁸. The sign (attractive or repulsive), magnitude (weak to strong), and range (short to long) of non-covalent interactions is often influenced by solution and environmental conditions, such as pH, ionic strength, and temperature. As a result, the rheological properties of solid-like NG-PB foods can be manipulated by controlling these parameters during their manufacturing and preparation.

Covalent bonds are typically stronger and more robust than non-covalent ones. They may be established between the structural elements within a NG-PB food through chemical reactions, such as the Maillard reaction or disulfide bond formation, or through enzymatic crosslinking reactions, such as those promoted by transglutaminase or laccase. The textural attributes of these foods can therefore be manipulated by controlling the reaction conditions to alter the type and number of crosslinks formed between the structural elements in a NG-PB food, such as proteins and polysaccharides. It is therefore important to understand the chemical reactivity of the different structural elements in these foods, so that solution and environmental conditions can be altered to induce the network formation required for specific applications.

In general, the textural attributes of solid and semi-solid foods are often characterized in terms of their elastic modulus and fracture properties⁵⁶. The elastic modulus provides an indication of the ability of the material to resist deformation when a force is applied: the higher the elastic modulus, the harder the material. The fracture properties provide an indication of the ability of a material to resist rupture when a force is applied. They can be represented by the minimum stress needed to promote disruption (fracture stress), as well as the relative change in the dimensions of the material before it first becomes disrupted (fracture strain). These parameters are related to the brittleness and malleability of materials (Section 5.1.2). Several kinds of NG-PB foods exhibit plastic-like behavior, where they act as a solid below a critical yield stress, but a fluid above this value, including PB meat, seafood, cheese, yogurt, and spreads. It is important to control the rheology of these foods because they impact their physicochemical, functional, and sensory properties, such as hardness, softness, brittleness, malleability, spoonability, spreadability, cutting, and eating attributes. Even though solid-like NG-PB foods display a wide variety of textural attributes, their rheology can often be characterized using only a small number of mathematical models⁵⁷. Some of these models are simply descriptive models developed to describe the rheological properties of a material in terms of a few key parameters, whereas others are based on a mathematical analysis of the physics of colloidal suspensions containing interacting polymers or particles. These models can be used to relate the composition, structure, and interactions of colloidal suspensions to their rheological properties in a more rigorous fashion and provide important information about the key parameters that influence their rheology.

5.1. Types of solid-like behavior

Like fluids, the rheological properties of solid-like foods can be described as ideal or non-ideal depending on how they respond to an applied stress.

5.1.1. Ideal solid behavior

The rheological properties of ideal solids are usually characterized by plotting the applied stress (τ) versus the resulting strain (γ), with the slope of this line being equal to the elastic modulus (E) of the material (**Figure 7**). This relationship is described by Hooke's law: $\tau = E \times \gamma$. Methods for measuring the elastic modulus of solid-like materials using compression or shear tests have been described elsewhere¹. For compression tests, Young's modulus (Y) is usually used, whereas for shear tests, the shear modulus (G) is usually used.

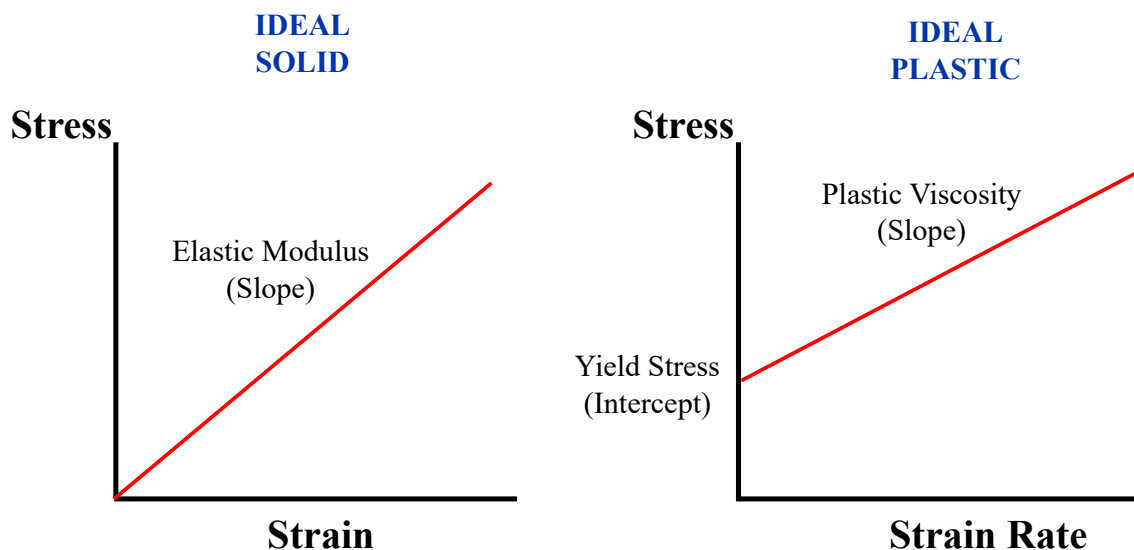


Figure 7. The rheology of ideal solids can be described by their elastic modulus, while the rheology of ideal plastics can be described by their yield stress and plastic viscosity.

In general, the mechanical properties of solid colloidal materials are governed by the types and concentrations of particles and/or polymers they contain, as well as the number, orientation, and strength of the forces acting between them⁵⁸. Theories developed to describe their properties are based on an analysis of the number of bonds present between the particles, as well as the strength of each bond, which depends on the change in interaction potential with distance (**Figure 8**).

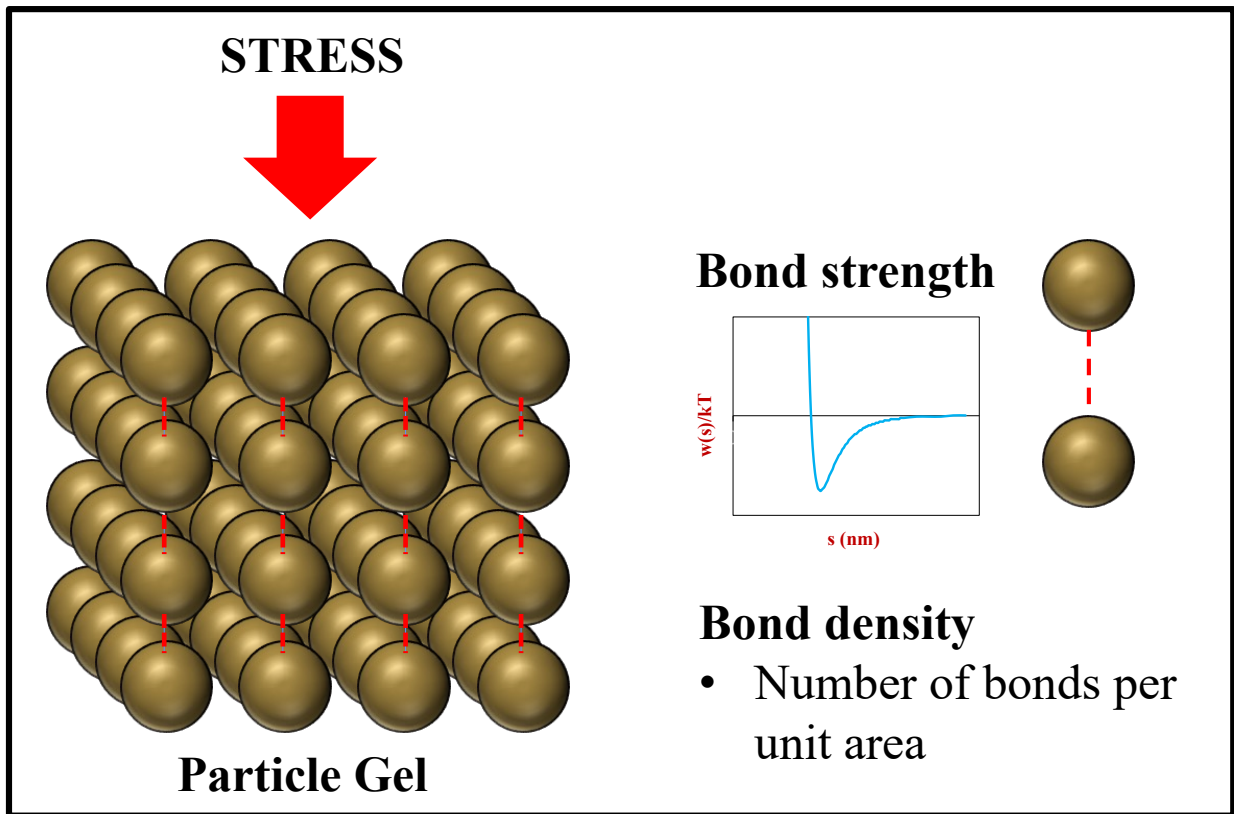


Figure 8. Highly schematic representation of a particle gel. The rheology of this type of gel depends on the strength and density of the bonds between the different particles. The stronger and more numerous the bonds, the greater the modulus.

Applying a stress to the surface of a colloidal solid causes the bonds between the structural elements to become deformed, which causes the material to become compressed, with the extent of compression depending on the number and strength of the bonds. For an ideal solid, all of the energy applied to the material is stored within these bonds while the stress is applied but is released when the stress is removed, and the material returns to its initial state. The elastic modulus of a colloidal solid tends to increase as the number and strength of the bonds between the structural elements rises. Researchers have developed several mathematical models to relate the structure, composition, and interactions of colloidal solids to their rheological attributes. These models are usually based on a theoretical analysis of the forces acting between the particles or polymers in a colloidal material (see Section 5.2).

5.1.2. Non-ideal solid behavior

A linear relationship between stress and strain is typically only observed at low strains for most solid or semi-solid NG-PB foods. At somewhat higher strains, this relationship becomes non-linear, and at still higher strains, the material may become ruptured, and a break occurs in the stress-strain curve. Moreover, many NG-PB foods exhibit both solid-like and liquid-like behavior, either simultaneously (viscoelastic materials) or sequentially (plastic materials). More sophisticated mathematical models are required to describe the rheology of these kinds of non-ideal solids.

Fracture properties: At relatively low strains ($< 1\%$), solid NG-PB foods often act as ideal solids where the stress is linearly related to the strain. However, at higher strains they may become temporarily or permanently disrupted because the bonds holding the different structural elements together are broken. In some cases, the bonds may repair themselves once the stress is removed (self-healing systems), whereas in other cases the bonds do not recover, and so the fracture is permanent. Knowledge of the behavior of NG-PB foods at large strains is practically important because it influences their resistance to mechanical forces during storage and transport, as well as their behavior during food preparation (cutting, slicing, or spreading), and consumption (chewing) ^{56, 58, 59}.

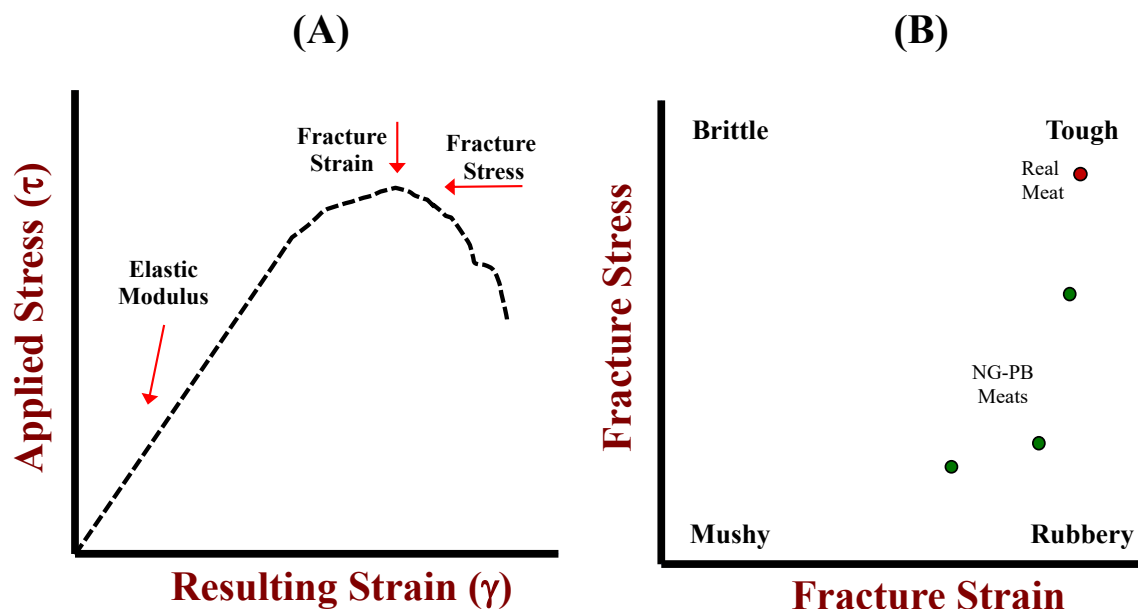


Figure 9. (A) The fracture properties of solid or semi-solid NG-PB foods can be characterized by measuring the relative deformation (strain) of the material as the magnitude of the applied force per unit area (stress) is increased. The elastic modulus, fracture stress and fracture strain can be determined from this stress-strain profile. (B) A 2D Texture Map can be used to

characterize the fracture properties of NG-PB foods and compare them to real ones.

When the applied stress is no longer proportional to the resulting strain, an *apparent* elastic modulus can be defined, which is equal to the slope of the stress *versus* strain plot at a particular strain value. In this region, the food may still return back to its original shape once the applied stress is removed. However, after a particular stress is exceeded, the food may flow or fracture and so not return back. The *fracture stress* (τ_{Fr}) and *fracture strain* (γ_{Fr}) of a food can be determined from a plot of the applied stress *versus* the resulting strain (**Figure 9**). These parameters can then be represented on a 2-D map, which is useful for comparing the behavior of NG-PB foods with the animal-based ones these are designed to replace. Foods that fracture at low strains/low stresses are referred to as *mushy*, those that fracture at low strains/high stresses are referred to as *brittle*, those that fracture at high strains/low stresses are referred to as *rubbery*, and those that fracture at high strains/high stresses are referred to as *tough*. Foods tend to fracture when the forces holding their structural elements together, such as proteins, polysaccharides, or colloidal particles are exceeded⁵⁸. Fracture often starts at locations within a material where the bonds are relatively weak, such as cracks or dislocations. For this reason, controlling the number and location of these discontinuities within a food may be important to obtain the required fracture properties.

Ideal plastics: NG-PB foods like cream cheese, butter, and mayonnaise analogs have rheological characteristics that can be described as plastic. These materials act like elastic solids below a critical applied stress, known as the yield stress, but they act like liquids when the yield stress is exceeded. When a shear stress is applied to an ideal plastic, its rheological properties can be modelled using the following expressions:

$$\tau = G\gamma \quad \text{when } \tau < \tau_Y \quad (8)$$

$$\tau - \tau_Y = \eta\dot{\gamma} \quad \text{when } \tau \geq \tau_Y \quad (9)$$

Here, G , τ_Y , and η are the shear modulus, yield stress, and plastic viscosity of the material. Thus, the applied stress is proportional to the strain below the yield stress (like an ideal elastic solid) but it is proportional to the rate of strain above the yield stress (like an ideal viscous liquid). The stress-strain rate relationship for an ideal plastic material is shown in **Figure 7**. When developing a NG-PB food that exhibits this kind of rheological behavior it is important to

match the elastic modulus, yield stress, and plastic viscosity to that of the animal sourced food it is intended to substitute. The rheology of plastic materials is usually characterized by measuring the stress *versus* strain or stress *versus* rate of strain profile using compression or shear testing instruments ¹.

At the structural level, NG-PB foods with plastic properties typically consist of 3D networks of particles or polymers that interact with each other through relatively weak attractive forces. For instance, cream cheese or yogurt analogs usually consist of a network of protein or polysaccharide molecules dispersed in a liquid aqueous phase, whereas butter analogs consist of a network of solid fat crystals dispersed in a liquid oil phase. When the stresses applied to this kind of material are less than the yield stress, the bonds holding the particles or polymers together within the 3D network are deformed but not disrupted. Once, the stresses are removed the bonds give up the energy stored within them and return to their original shape, thereby exhibiting elastic-like behavior. In contrast, when the applied stresses are greater than the yield stress of the material, the bonds between the particles or polymers are disrupted and the material starts to flow, which leads to liquid-like behavior. The ability of some foods to exhibit plastic behavior is essential for their commercial applications. For instance, the spreadability of cream cheese or butter analogs, the pourability of mayonnaise analogs, and the spoonability of yogurt analogs all depend on these kinds of material properties. Examples of the rheological parameters of selected NG-PB foods that can be considered to be non-ideal plastic materials are compared to those of animal-sourced foods in **Table 4**.

Table 4. Examples of the rheological parameters of selected animal-sourced foods and NG-PB foods that can be characterized as non-ideal plastics. Their rheological properties were described by fitting the Herschel-Bulkley model to the shear stress *versus* shear strain curves. Adopted from McClements and Grossmann ¹.

	Yield Stress (Pa)	Consistency index K (Pa s ⁿ)	Flow index (n)	Ref.
Dairy yogurt	11.7	2.50	0.55	60
Almond yogurt	28.4	6.45	0.37	60
Soy yogurt	27.2	3.52	0.45	60
Whole hen's egg	0.20	0.030	0.97	53
Whole NG-PB egg	9.7	0.11	0.95	Our laboratory

Salad dressing	47	16.3	0.52	61
Mayonnaise analog	81.4	82.6	0.21	Our laboratory

Non-ideal plastics: Many NG-PB foods have predominantly solid-like properties below a critical yield stress but have liquid-like properties at higher stresses and can therefore be considered to be plastic-like materials. However, they do not behave like ideal elastic materials below the yield stress and/or ideal viscous materials above the yield stress, and so they can be considered to be non-ideal plastics. As an example, these foods may undergo some flow when a stress is applied below the yield stress, and they may exhibit shear thinning or shear thickening behavior about the yield stress. For these kinds of material, it may be difficult to accurately determine the yield stress because some flow occurs even at low applied stresses. This kind of behavior may be exhibited by NG-PB foods whose structures are gradually disrupted over a range of applied stresses, rather than due to an abrupt disruption of the structures at a specific applied stress.

The rheological behavior of non-ideal plastics that behave like ideal solids below the yield stress but like non-ideal liquids above the yield stress can be described by the Herschel-Bulkley (HB) equation:

$$\tau = \tau_Y + K\dot{\gamma}^n \quad \text{for } \tau \geq \tau_Y \quad (10)$$

Here, K is the plastic consistency index and n is the plastic flow index. The values of these parameters can be found by fitting the HB equation to the experimental data. Several representative values of the τ_Y , K and n parameters obtained by fitting this model to experiments on NG-PB food products or animal-source products are shown in **Table 4**. When designing NG-PB foods it is usually desirable to ensure that their yield stress, consistency index, and flow index match those of the animal sourced food they are intended to replace.

Viscoelastic materials: NG-PB foods such as meat, seafood, and egg analogs are viscoelastic materials that exhibit both viscous- and elastic-like properties simultaneously^{56, 58, 59}. When a fixed shear stress is applied to an ideal viscous material it flows at a fixed shear rate as long as the stress is applied. The shear rate increases linearly as the applied shear stress is increased, with the slope being the shear viscosity. The viscous flow leads to energy dissipation due to frictional losses. In contrast, when a fixed shear stress is applied to an ideal elastic material it

deforms to a fixed strain as long as the stress is applied, but then returns back to its original shape when the stress is removed. The relative deformation (strain) of the material increases linearly as the applied shear stress is increased, with the slope being the elastic modulus. In this case, all of the energy that was originally stored in the bonds during compression, is released during deformation, so the material returns back to its original shape and there is no energy dissipation associated with frictional losses. When a stress is applied to a viscoelastic material it behaves like both an elastic solid and a viscous fluid at the same time because it is both deforms and flows. As a result, part of the energy is stored in the material and part of it is lost as heat due to friction. Consequently, a *viscoelastic* material does not instantaneously deform to a new shape when a stress is applied and does not instantaneously return to its original shape after the stress is removed (**Figure 10**). Viscoelastic materials can be characterized as viscoelastic solids or liquids depending on how they respond to an applied stress. When a stress is applied to a viscoelastic solid it deforms at a finite rate (rather than instantaneously) until it reaches a fixed deformation but once the stress is removed its dimensions return to their original values at a finite rate. Many NG-PB meat, seafood, and cheese analogs exhibit this kind of behavior, provided the stress is not too large to cause fracture. When a stress is applied to a viscoelastic liquid it continues to flow as long as the stress is applied but when the stress is removed it only partially recovers its original shape. NG-PB mayonnaise and cheese spreads exhibit this kind of behavior.

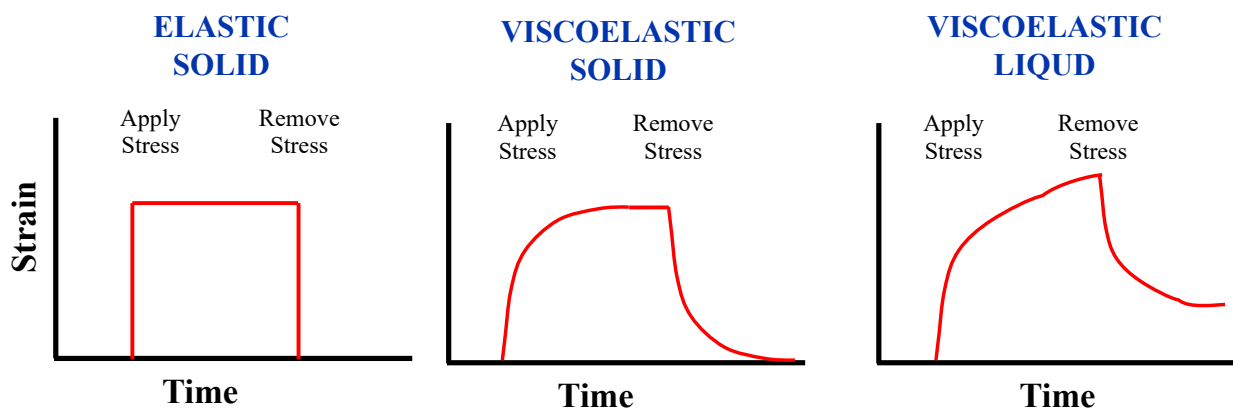


Figure 10. Many solid or semi-solid NG-PB foods demonstrate viscoelastic behavior because they act as solids and liquids simultaneously.

The rheology of viscoelastic materials is usually characterized by measuring their dynamic

shear rheology (G) as a function of time, frequency, strain, or temperature. A sample is placed in the measurement cell of the rheometer and then an oscillating shear stress is applied and the magnitude and phase of the resulting oscillating shear strain is measured^{56, 59}. The storage (G') and loss (G'') modulus or the complex shear modulus (G^*) and phase angle (δ) are then plotted *versus* the parameter of interest.

5.2. Theoretical models relating the rheology of colloidal solids to their properties

The most suitable theoretical model for describing the rheological properties of a particular NG-PB food depends on the type of structural elements it contains, as well as their spatial organization and interactions. An egg analog made from globular proteins (like soy, pea, or mung bean protein) may be treated as a colloidal solid containing monodisperse spheres that interact with each other. A cheese analog comprised of fat droplets embedded in a protein network may be treated as a complex composite material containing spheres embedded in a polymer matrix. A meat analog composed of phase separated protein-rich and polysaccharide-rich regions organized into fibrous structures may be treated as an anisotropic two-phase material. Consequently, it is important to identify the main structural elements in a NG-PB food, and to establish their structural organization, when trying to identify a suitable theory to describe their properties. Once an appropriate theoretical model has been identified then it can be used to give useful insights into the main factors influencing the rheology of the material, such as particle size, concentration, arrangement, or interaction strength⁶². In the remainder of this section, mathematical models that have been developed to describe the rheology of different kinds of solid colloidal dispersions that may be representative of NG-PB foods are considered.

5.2.1. Polymer matrices

Some types of NG-PB foods can be considered to be polymer matrices consisting of a network of entangled or crosslinked polymer molecules. Consequently, theories developed to describe the properties of polymer matrices can be utilized to understand, predict, and control their behavior. For example, the following mathematical model has been derived to predict the rheological properties of polymer materials containing a network of semi-flexible filaments⁶³:

$$G \approx \frac{6\rho\kappa^2}{k_B T l_C^3} \quad (11)$$

In this equation, G is the shear modulus, ρ is the filament length density, κ is the bending

rigidity of the filaments, l_c is the average distance between the crosslinks, k_B is Boltzmann's constant, and T is the absolute temperature. Analysis of this equation provides some useful insights into the importance of the major factors impacting the shear modulus of this kind of polymer material. For instance, the equation predicts that the shear modulus increases as the concentration of filaments rises (through ρ), as the stiffness of the filaments rises (through κ), and as the crosslinking density of the filaments rises (through l_c). This model is based on an analysis of the entropy and enthalpy effects occurring within the polymer network when it is deformed. These effects depend on the number of configurations the filaments can adopt, as well as their resistance to being deformed. This equation may be useful for modeling the rheological properties of meat and seafood analogs containing fibrous networks of semi-flexible polymers. Atomic force microscopy analysis has shown that gellan gum forms this kind of polymer network ⁶⁴, which is a commonly used ingredient in some plant-based foods.

5.2.2. Particle gels

Some NG-PB foods are formed by inducing the aggregation of globular proteins, such as meat, seafood, and egg analogs ¹. In this case, it is often possible to use theoretical models developed to describe the properties of colloidal particle gels consisting of a network of aggregated spheres that extend throughout the volume of a system (**Figure 11**). Several theoretical approaches have been utilized to develop relationships between the composition, structure, and interactions of particle suspensions and the rheological properties of the gels they form, which have been reviewed in detail elsewhere ^{51, 65, 66}.

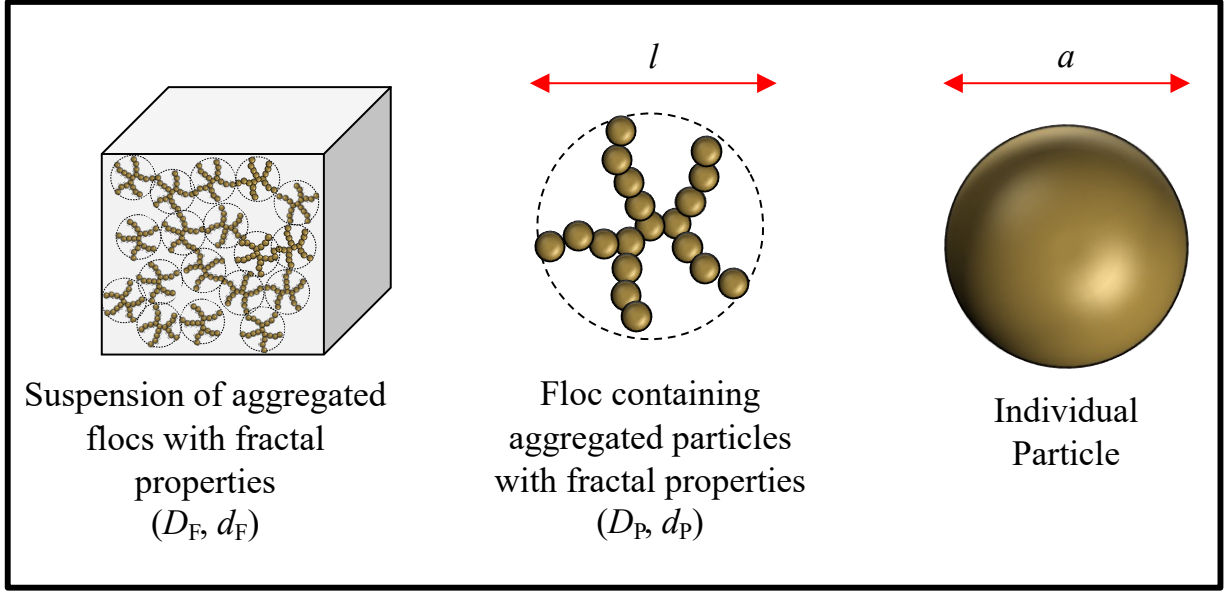


Figure 11. Many solid or semi-solid NG-PB foods can be considered to be particle gels, made up of networks of aggregated particles. These networks can have a fractal structure.

In this section, a theoretical model recently developed to describe the rheology of colloidal suspensions containing aggregated spherical particles assembled into fractal structures is considered⁶⁷. This model assumes that the rheological properties of the colloidal suspensions can be related to their microstructure by assuming that the individual particles are assembled into flocs with a fractal structure, and that these flocs then aggregate with each other to form a network with another fractal structure (**Figure 11**). It also assumes that the bonds between the particles and flocs can be considered to act like springs that can bend or stretch. The elastic component (G') of the shear modulus can then be related to the composition, microstructure, and interactions of the system using the following expression:

$$G' = \frac{U}{a\delta^2} \phi^{\frac{2+f(d_F)}{3-D_F}} \left(\frac{l}{a}\right)^{\frac{3-D_P}{3-D_F}(2+f(d_F))-(2+f(d_P))} \quad (12)$$

Here, U is the interaction potential between a pair of aggregated particles, a is the diameter of the individual particles, δ is the distance between a pair of aggregated particles, ϕ is the volume fraction of the particles present in the overall system, l is the diameter of the flocs, D_P is the fractal dimension of the particles inside the flocs, d_P is the fractal dimension (from 1.1 to 1.4) of the elastic backbone inside the flocs (*i.e.*, the load bearing particles), D_F is the fractal dimension of the aggregated flocs in the overall system, and d_F is the fractal dimension (from 1.1 to 1.4) of

the elastic backbone of the aggregated flocs in the overall system (*i.e.*, the load bearing flocs). The function in this equation, $f(x)$, is related to the relative strength of the interactions between the particles compared to the flocs, as well as to the degree of bending or stretching experienced by the load bearing units ⁶⁷:

$$f(x) = \alpha(2\varepsilon+x)^{-1} \quad (13)$$

Here, α is a parameter that varies between 0 (weak-link regime) to 1 (strong-link regime), and ε is a parameter that varies from 0 for pure stretching to 1 for pure bending. In the weak-link regime, the overall rheological properties of the system are dominated by the strength of the interactions between the individual particles inside the flocs, whereas in the strong-link regime they are dominated by the strength of the interactions between the flocs. The fractal dimension (D) of a system is determined by the nature of the interactions between the particles ⁶⁶. In diffusion-limited cluster aggregation (DLA), the particles are strongly attracted to each other and tend to stick to each other at the place they first make contact as they move around due to Brownian motion, leading to a more open structure being formed. The fractal dimension of pure DLA behavior has been estimated to be 1.78. In reaction-limited aggregation (RLA), the particles are only weakly attracted to each other and so do not always stick together when they first come into contact. Consequently, the particles in aggregates can undergo rearrangements leading to more compact structures being formed. The fractal dimension of pure RLA behavior has been estimated to be 1.99. In practice, other values can be obtained depending on the nature of the aggregation mechanism with extreme values ranging from around 1 for a highly open structure to around 3 for a highly compact structure.

The same theoretical approach has also been used to derive mathematical equations to describe the plastic behavior of colloidal fractal gels ⁶⁷. These equations are typically based on an analysis of the force required to disrupt the bonds between the structural elements in the gel ⁴. The double fractal model has been used to relate the yield stress (τ_Y) and yield strain (γ_Y) to the concentration, structural organization, and interactions of the spherical particles in a gel:

$$\gamma_Y = \frac{\delta}{a} \Phi^{\frac{-f(d_F)}{3-D_F}} \left(\frac{l}{a} \right)^{-\frac{3-D_P}{3-D_F} f(d_F) + f(d_P)} \quad (14)$$

$$\tau_Y = \frac{U}{a\delta^2} \phi^{\frac{2}{3-D_F}} \left(\frac{l}{a}\right)^{\frac{2(D_F-D_P)}{3-D_F}} \quad (15)$$

826

827 The equations for G' , γ_Y , and τ_Y can be simplified considerably if assumptions are made about
 828 the nature of the system. For example, if it is assumed that the fractal properties of the particles
 829 and flocs are similar ($D_F = D_P$, and $d_F = d_P$) and that particle-particle interactions dominate
 830 (weak-link regime: $\alpha=0$), then these equations become:

$$G' = \frac{U}{a\delta^2} \phi^{\frac{1}{3-D_P}} \quad (16)$$

$$\gamma_Y = \frac{\delta}{a} \phi^{\frac{1}{3-D_P}} \quad (17)$$

$$\tau_Y = \frac{U}{a\delta^2} \phi^{\frac{2}{3-D_P}} \quad (18)$$

834 These equations suggest that the shear modulus and yield stress should increase as the strength of
 835 the interactions between the particles increases, the particles become smaller, the distance
 836 between the particles decreases, or the fractal dimension decreases. They also predict that the
 837 yield strain should increase as the particle size or fractal dimension decrease, or as the distance
 838 between the particles increases. This kind of knowledge can be used to design NG-PB foods
 839 with enhanced rheological properties. For instance, the pH, ionic strength, or temperature may
 840 be altered to increase the strength of the attractive forces between the individual proteins, which
 841 will increase the interaction potential (U) and decrease the fractal dimension (D), thereby
 842 increasing the overall strength of the protein gel. Alternatively, the size or concentration of
 843 protein molecules used to formulate the gel can also be altered to modulate its properties.

844 The above equations will only be valid when the flocs form a network that occupies the entire
 845 volume of the system, which will occur when the percolation threshold is exceeded. To a first
 846 approximation, this concentration can be obtained from the following equation: $\phi_{\text{eff}} = \phi_F(l/a)^{3-D_F}$
 847 $= 1$, where ϕ_{eff} and ϕ_F are the effective volume fraction and actual volume fraction of the flocs in
 848 the system⁶⁷. By accounting for the fact that the flocs are occupied by particles, a critical
 849 particle volume fraction (ϕ_{crit}) for percolation can be obtained:

$$\phi_{\text{crit}} = (a/l)^{6-D_F-D_P} \quad (19)$$

This expression predicts that the volume fraction of particles required to form a 3D network that extends throughout the system, and therefore gives elasticity, should decrease as the floc dimensions increase (l) and the fractal dimensions (D_F and D_F) decrease.

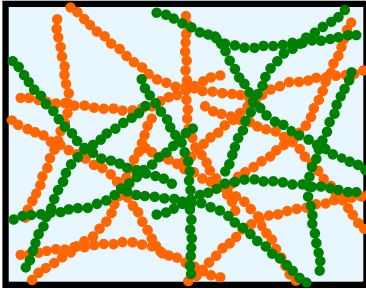
Computer simulations have proven to be a powerful tool for understanding the microstructure and rheological properties of colloidal particle gels⁶⁸. These simulations show how the structural organization and rheology of particle gels depend on the size, concentration, and interactions of the particles they contain. This knowledge can then be used to guide the ingredients and processing conditions used to create particle gels with the required properties.

It is important to note that the models used to describe the rheological properties of colloidal particle gels are often too simplistic for understanding the properties of real protein gels. These models often assume that the particles are homogeneous spheres, whereas protein ingredients often contain a mixture of different proteins that have different sizes, shapes, and heterogeneous surface chemistries, which alters the nature of the structures formed when they aggregate. For instance, they may have hydrophobic patches at some locations on their surfaces, which limit the places where they can form bonds with their neighbors, thereby altering their structural organization within aggregates.

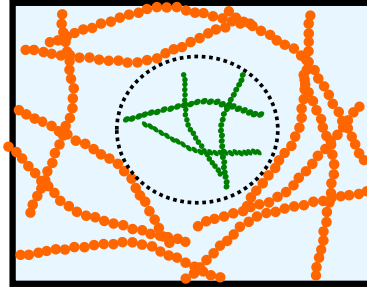
5.2.3 Composite polymer gels

The rheological properties of the gels that can be produced using a single biopolymer, such as a protein or polysaccharide, are often unsuitable for mimicking the properties of solid animal sourced foods, like meat, seafood, cheese, or cooked egg. This problem can often be overcome by using combinations of different biopolymers. Different kinds of structures can be formed in composite materials formed when two gelling biopolymers are used, depending on the nature of the interactions between them, including interpenetrating, phase-separated, and co-gelling systems (**Figure 12**). Each of these gel types has different physicochemical and functional properties, which provides flexibility in using biopolymers to simulate the rheological properties of solid animal sourced foods.

Interpenetrating Network



Phase Separated Networks



Co-Gelling Networks

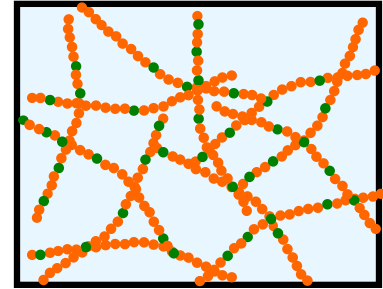


Figure 12: Different kinds of gels can be formed from two biopolymers depending on the interactions involved, including interpenetrating network, phase separated network, and co-gelling networks.

Interpenetrating (IP) networks, which contain two types of biopolymers crosslinked by different gelling mechanisms, may be particularly suitable as meat and seafood analogs. Because they contain two biopolymers that behave differently, they can be designed to have properties that are different from the hydrogels formed using single biopolymers. Studies have shown that hydrogels consisting of interpenetrating networks can be designed to be both strong and ductile (flexible), which are important attributes for simulating the properties of meat and seafood products and is difficult to achieve using single network hydrogels^{69, 70}. These kinds of hydrogels contain two biopolymer networks with different attributes: a rigid (strong and brittle) one formed by strongly crosslinked biopolymers and a flexible (soft and ductile) one formed by weakly crosslinked biopolymers⁶⁹. When an external force is applied to this type of IP hydrogel, the crosslinks in the rigid biopolymer network act as sacrificial bonds that are disrupted first, which causes the mechanical energy to be dissipated throughout the system, thereby improving the resistance to crack propagation and fracture. In contrast, the crosslinks in the flexible biopolymer network remain intact, thereby maintaining the overall integrity of the hydrogel. The rigid bonds can then reform when the external force is removed, leading to a strong and resilient hydrogel.

Combinations of two biopolymer networks can also be used to mimic the thermal behavior of meat and seafood products during cooking. When these products are heated, they often undergo an initial softening due to unfolding of the collagen in the connective tissue and then a hardening

due to unfolding and aggregation of the muscle proteins. This kind of complex thermal behavior could be mimicked using a combination of cold-set and heat-set biopolymers in IP hydrogels. However, it is important to select the most appropriate types and concentration of biopolymers to obtain an appropriate elastic modulus-temperature profile.

5.2.4. Filled gels

Solid and semi-solid NG-PB foods, like meat, seafood, and egg analogs, often contain inclusions such as fat droplets, protein particles, or starch granules embedded in a biopolymer matrix¹. The presence of these inclusions impacts the rheological properties of the material by an amount that depends on their size, shape, mechanical properties, aggregation state, and interactions with the surrounding biopolymer matrix⁷¹. The inclusions may act as active or inactive fillers depending on whether they have strong attractive interactions with the biopolymer matrix or not, respectively (**Figure 13**). Typically, active fillers tend to increase the gel strength whereas inactive ones tend to decrease it⁷². The size of the inclusions relative to the pore size of the biopolymer matrix also impact the overall gel strength⁷³. For inactive fillers, inclusions that are smaller than the pore size may not have a major impact on the gel strength because the structure of the biopolymer matrix is not disrupted. In contrast, inclusions larger than the pore size may decrease the gel strength because they disrupt the biopolymer matrix. The shape of the inclusions may also be important because it influences the stress distribution throughout the material. The concentration of the inclusions within a biopolymer matrix also impacts the rheological properties of composite materials. For active fillers, it has been shown that incorporating inclusions up to a certain concentration increases the gel strength but above this concentration it reduces it, which has been attributed to the tendency of high levels of inclusions to disrupt the biopolymer network. Consequently, it is possible to modulate the properties of NG-PB foods by controlling the types and amounts of inclusions present.

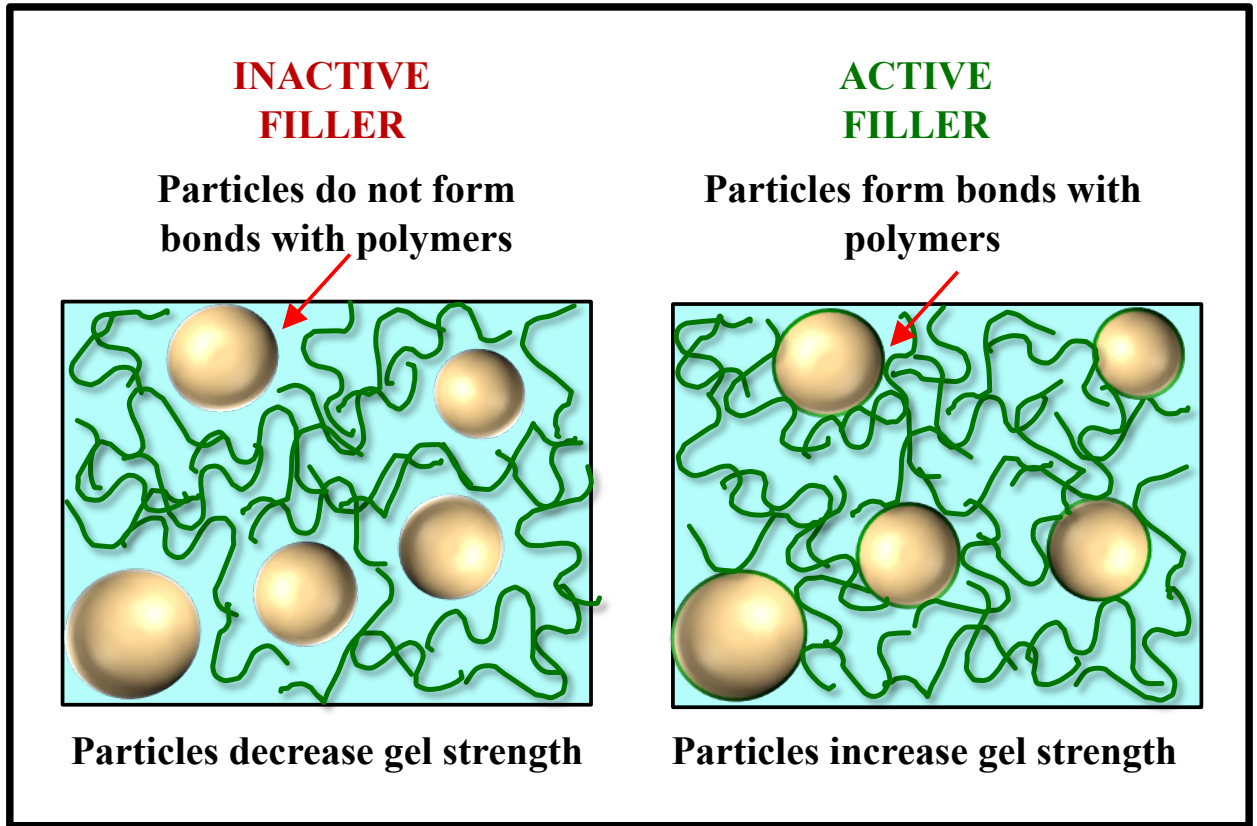


Figure 13. Schematic diagram of the structure and interactions of filled gels that contain inactive fillers that do not interact strongly with the polymer network, or active fillers that do..

Mathematical models have been developed to describe the impact of inclusions on the properties of gels⁷⁴⁻⁷⁷. For instance, the equation below models the impact of active rigid spherical inclusions on the elastic modulus of a polymer matrix⁷⁷:

$$E_C = E_m \left(1 + \frac{15(1-\nu_m)(M-1)\phi_f}{(8-10\nu_m)M+7-5\nu_m-(8-10\nu_m)(M-1)\phi_f} \right) \quad (20)$$

Here, $M = E_f/E_m$, and E_C , E_f , and E_m are the elastic moduli of the composite material, the filler particles, and the surrounding matrix, respectively. In addition, ν_m is the Poisson ratio (assumed to be 0.5 for gels) and ϕ_f is the volume fraction of particles embedded within the matrix. This model was derived assuming that the particles are active fillers that strongly interact with the polymer matrix. Other models are more appropriate for inactive fillers⁷¹.

In general, the mathematical theories developed to model the mechanical properties of filled gels indicate that the impact of the inclusions depends on their concentration, size, shape, mechanical properties, surface properties, and interactions with the surrounding polymer matrix.

This knowledge can be utilized by the manufacturers of NG-PB foods to create products that better simulate those of animal sourced ones.

5.3. Major factors impacting the rheology of colloidal solids

In general, many different factors can impact the rheological behavior of colloidal gels depending on their composition, structure, and interactions. The relative importance of these factors depends on the types and amounts of polymers or particles present, as well as the environmental and solution conditions used. In this section, the power of using theoretical equations to model the properties of colloidal gels is highlighted by showing their ability to identify and quantify the main factors impacting the rheology of these systems. The main focus will be on particle gels since these are often used to formulate meat, seafood, egg, and cheese analogs through controlled assembly of globular plant proteins. The equations developed to model double fractal colloidal particle gels discussed above indicate that their rheology depends on various factors:

Interaction strength (U): The strength of the attractive interactions between protein molecules may be controlled by altering solution or environmental conditions during gel preparation. Heating proteins above their thermal denaturation temperature promotes unfolding, which exposes non-polar groups, thereby increasing the hydrophobic attraction between them. Conversely, cooling a protein gel formed at a high temperature increases the attractive interactions between the protein molecules due to an increase in the strength of the hydrogen bonding, thereby leading to an increase in gel strength. Most proteins have an electrical charge, which alters the electrostatic interactions with their neighbors. Adding salts or adjusting the pH towards the isoelectric point reduces the magnitude of the electrostatic repulsive interactions between them, which can promote stronger bonds being formed, leading to an increase in gel strength.

Particle concentration (ϕ): The elastic modulus, yield stress, and yield strain of a colloidal particle gel can also be modulated by altering the particle concentration. The equations based on the double-fractal model predict that the elastic modulus and yield stress increase with increasing particle concentration. Thus, the strength of gels formed from proteins can usually be increased by raising the protein concentration. The full versions of the above equations predict that the yield strain should decrease with increasing particle concentration in the strong-link limit ($\alpha = 1$) but should increase in the weak-link limit ($\alpha = 0$), which was also predicted in earlier models of

fractal particle gels⁷⁸. Consequently, measurements of the impact of particle concentration on the yield strain may be a useful method of determining which is the dominant interaction (particle-particle or floc-floc) in the system. This knowledge can then be used to select the most appropriate version of the model to use (e.g., $\alpha = 0$ or 1).

Particle size (a and l): The theoretical equations also provide valuable insights about how the size of the particles (a) or flocs (l) influence the rheological properties of colloidal particle gels. Typically, the elastic modulus, yield stress, and yield strain all increase as the size of the particles in the system decrease.

Fractal dimensions (D and d): The fractal dimensions of a colloidal particle gel depend on the structural organization of the particles within the flocs, as well as the flocs within the overall system⁶⁷. Typically, the percolation threshold (the minimum particle concentration required to form a gel) decreases as the fractal dimensions decrease., i.e., as the structure becomes more open. Colloidal particle gels where the particle-particle interactions dominate ($\alpha=0$) and the fractal properties of the particles and flocs are similar are used to demonstrate the impact of fractal dimensions on the rheological properties. The shear modulus, yield stress, and yield strain all increase with decreasing fractal dimensions (D_p) for this kind of system. Thus, it may be possible to increase the gel strength by creating structures with a lower fractal dimension. This can be achieved by increasing the strength of the attractive interactions between the particles in the system: the stronger the attraction, the lower the fractal dimension because the particles tend to stick together tightly after contacting each other, thereby leading to a more open structure. In contrast, when the interactions are relatively weak, the particles can reorganize themselves after coming into contact, leading to a more compact structure and higher fractal dimension.

Experimentally, it is possible to manipulate many of the properties of particle gels by altering solution or environmental conditions, such as biopolymer concentration, biopolymer type, pH, ionic strength, or temperature. Consequently, it is possible to create plant-based gels with different properties that may be suitable for different applications.

5.4. Examples of rheological properties of solid NG-PB foods

In this section, selected examples of the rheological characterization of solid and semi-solid NG-PB foods from the author's and other researchers' laboratories are provided to demonstrate the application of these methods.

5.4.1. Temperature-sweep experiments

Temperature-sweep experiments are commonly used to characterize the rheological properties of solid and semi-solid foods, including those assembled from plant-based ingredients¹. They provide valuable insights into the key events that occur during the heating or cooling of foods, such as thermal denaturation of proteins, helix-coil transitions of polysaccharides, and melting-crystallization of fats. These experiments are usually carried out using a dynamic shear rheometer operating in oscillation mode at a fixed frequency and strain (below the linear viscoelastic region). The test sample is placed in the measurement cell of the rheometer, allowed to reach the starting temperature, and then heated and/or cooled in a controlled manner. The dynamic shear modulus is then measured as a function of temperature and the data is plotted as either the storage (G') and loss (G'') moduli or the complex shear modulus (G^*) and phase angle (δ) *versus* temperature.

As an example, the thermal gelation of globular proteins is considered because they are often used to formulate NG-PB meat, seafood, egg, and cheese products. In these applications, an aqueous protein solution is first prepared by dissolving native globular proteins in water under appropriate pH and salt conditions. These conditions are selected to ensure the proteins are initially soluble before heating but will form an irreversible heat-set gel during heating. Typically, the electrostatic interactions in the protein solution are modulated by controlling the pH and ionic strength. The solution is then heated to a temperature above the thermal denaturation temperature of the proteins, which causes them to unfold and aggregate with their neighbors, which is mainly driven by the increased hydrophobic attraction that arises when non-polar groups are exposed at the surfaces of the denatured protein molecules. If the protein concentration is sufficiently high, then the aggregated proteins form a 3D network that occupies the entire volume of the sample, leading to elastic-like properties. To accurately simulate their quality attributes and cooking properties, the gelation temperature and final gel strength of NG-PB foods should be as similar as possible to those of the animal sourced foods they are intended to replace (such as egg or meat).

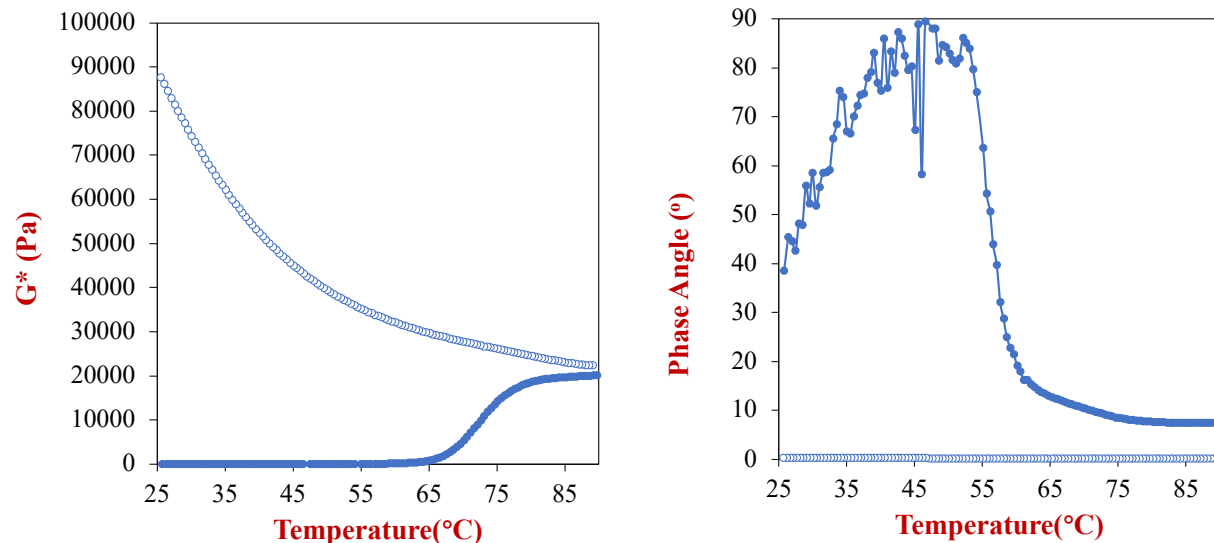


Figure 14: Dynamic shear rheology measurements versus temperature can be used to characterize the textural attributes of NG-PB foods. In this study, the complex shear modulus and phase angle of 20 wt% potato protein (pH 7) solutions were measured as a function of temperature at a fixed frequency (1 Hz) and strain (1%), which was in the LVR (Data kindly supplied by Hualu Zhou).

An example of the rheological behavior of a 20 wt% potato protein solution (pH 7) during heating and cooling is shown in **Figure 14**. The rheology was characterized by measuring the dynamic shear modulus *versus* temperature at a fixed frequency (1 Hz) and strain (1%), which was in the linear viscoelastic region. The complex shear modulus (G^*) and phase angle (δ) are plotted versus temperature during heating and cooling. Initially, the shear modulus was relatively low because the protein molecules were in their native state and did not associate strongly with each other because of the relatively strong electrostatic repulsion between them (**Figure 14a**). However, when they were heated above about 65°C, the shear modulus increased steeply, which can be attributed to protein unfolding and aggregation around the thermal denaturation temperature of the potato proteins, thereby leading to a 3D elastic network being formed. The shear modulus then increased slightly when the system was heated further, which was probably because more protein molecules unfolded and participated in network formation. When the protein gels were cooled, there was a pronounced increase in the shear modulus, which can be attributed to strengthening of the hydrogen bonding between the protein molecules in the gel network.

The phase angle was initially around 40°, which suggested that the protein dispersions exhibited a small amount of elasticity, perhaps due to some weak attractive interactions between

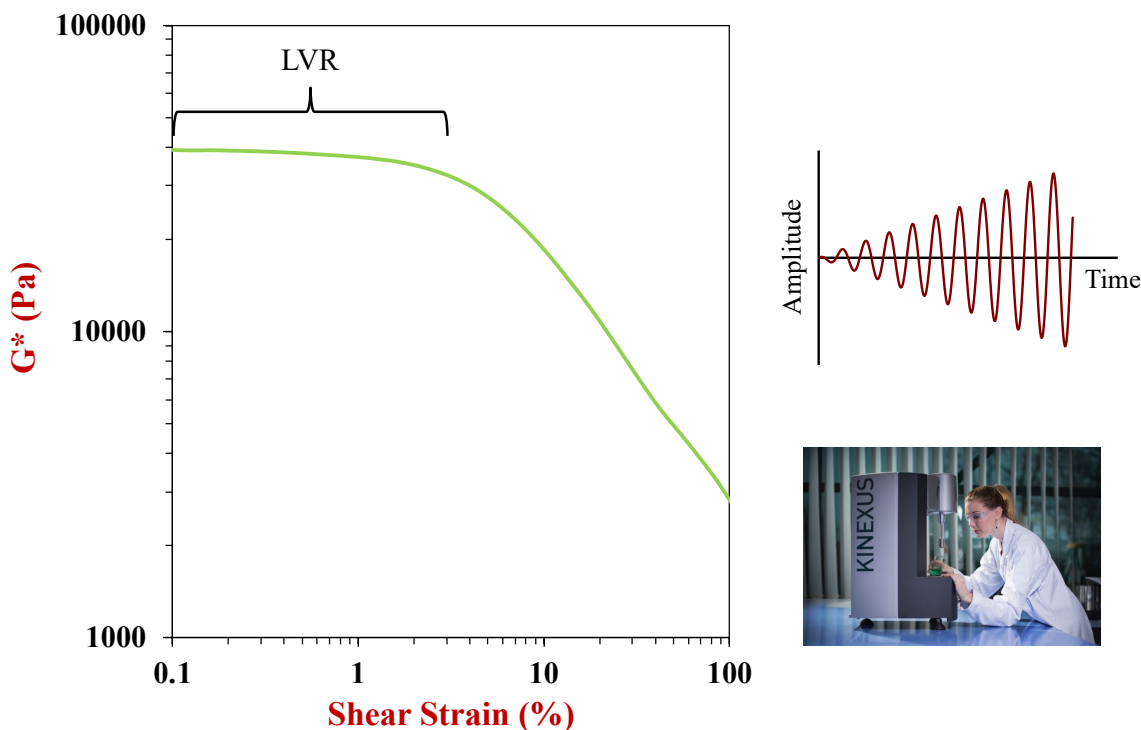
the proteins (**Figure 14b**). During heating, the phase angle first increased above 45°, which suggested that this weak network dissociated so the proteins became more mobile, thereby leading to a more fluid-like behavior. However, once the temperature exceeded about 65 °C, there was a steep decrease in the phase angle, which can be attributed to the formation of a 3D network of aggregated protein molecules that provide some elasticity. The phase angle remained low during further heating and cooling, which indicates that the protein gels formed retained their strongly elastic properties. As mentioned earlier, it is often important to mimic the gelling temperature and final gel strength of animal-sourced products.

In general, these kinds of measurements can be used to determine the impact of different additives and other variables on the gelation temperature and gel strength of plant-based foods, including protein type, protein concentration, salt content, pH, polysaccharide type, and polysaccharide concentration. In addition, they can be used to compare the thermal behavior of NG-PB foods to that of animal sourced foods, which may be useful for simulating their cooking behavior. As an example, temperature sweep measurements of the shear modulus *versus* temperature have been used to assess the suitability of a globular plant protein derived from duckweed (Rubisco) for simulating the cooking and textural attributes of globular egg white proteins from hen's egg ⁵⁴. In another study, these measurements were used to characterize changes in the texture of salmon during heating, with the aim of providing information that could be used to formulate better plant-based seafood analogs ⁷⁹. They have also been used to characterize the textural properties of plant-based adipose tissue formulated from high internal phase oil-in-water emulsions during heating and cooling ¹⁷. Other researchers have used this approach to characterize the properties of gels made from quinoa flour, which were produced for potential application in formulating NG-PB meat analogs ⁸⁰.

5.4.2. Strain-sweep experiments

Strain-sweep experiments are also commonly used to characterize the rheological properties of solid or semi-solid colloidal foods. These experiments are usually carried out using a dynamic shear rheometer operating in oscillation mode at a fixed frequency. In these experiments, the test sample is placed in the measurement cell of the rheometer and allowed to equilibrate to the measurement temperature. An oscillating stress is then applied whose magnitude is incrementally increased over time (**Figure 15**), and then the magnitude and phase of the resulting oscillating strain is recorded. The dynamic shear modulus (G'/G'' or G^*/δ) is then plotted as a

1085 function of increasing stress or strain.



1086
1087 **Figure 15.** The complex shear modulus of a material measured using dynamic shear rheometry
1088 is often linear up to a critical strain and then decreases steeply. The region where the modulus
1089 remains constant is known as the linear viscoelastic regime (LVR). This is a curve for a plant-
1090 based chicken sample made in our laboratory. Figure of rheometer kindly supplied by Netsch.
1091

1092 As an example, the change in shear modulus with applied strain for heat-set potato protein
1093 gels is shown in **Figure 15**. The elastic modulus remains relatively constant at low shear strains
1094 but then decreases substantially when a particular strain is exceeded, which may be taken to
1095 indicate yielding. The yield stress and yield strain can then be obtained from this point. Upon a
1096 further increase in applied stress, there may be a further steep decrease in the elastic modulus,
1097 which is indicative of fracturing of the gel. The fracture stress and strain can then be obtained
1098 from this point.

1099 The impact of the magnitude of the applied strain on the dynamic shear rheology of peanut
1100 protein gels has been characterized using this method⁸¹. This study found that the shear
1101 modulus remained relatively constant at low applied strains (< LVR) but decreased appreciably
1102 once the strain exceeded about 1%. They also found that the storage modulus was greater than
1103 the shear modulus ($G' > G''$) across the entire strain range studied (0.01 to 10%). Strain sweeps

have also been used to compare the rheological properties of plant protein gels (zein or gluten) with those of animal sourced foods (like real cheese and chicken)⁸². Again, the shear modulus of all samples remained relatively constant at low strains but decreased steeply when a particular strain was exceeded. However, there were appreciable differences between the samples. For instance, the yield strain of the zein gels was appreciably lower than that of chicken but fairly similar to that of cheese, which impacts the kinds of NG-PB foods zein gels can be applied in. Strain sweep experiments have also been used to characterize the rheology of plant protein doughs, such as those formulated from potato, pea, or soy protein, which may form a basis for formulating some NG-PB foods⁸³.

5.4.3. Frequency-sweep experiments

Useful information about the textural attributes of solid or semi-solid foods can often be obtained by measuring changes in their rheological properties when the frequency of the oscillating shear stress applied to them is increased. Again, these experiments are typically carried out using a dynamic shear rheometer. The test sample is placed in the measurement cell of the instrument, allowed to reach the target temperature, and then an oscillating stress of progressively increasing frequency is applied at a fixed strain (within the LVR). The dynamic shear modulus (G' / G'' or G^*/δ) is then plotted as a function of increasing frequency. This kind of experiment can provide valuable insights into the dynamic processes occurring within materials under stress, such as changes in the structural organization of the polymers or particles they contain, which can be characterized by relaxation times or frequencies. For instance, the time for polymers or particles within a gel network to rearrange themselves when a stress is applied can be determined, which provides insights into the characteristics of these structural elements. The relaxation frequency (f_R) is taken to be the point where the elastic and storage modulus crossover each other ($G'=G''$) when the frequency is increased, which can then be converted to a relaxation time ($t_R = 1/f_R$).

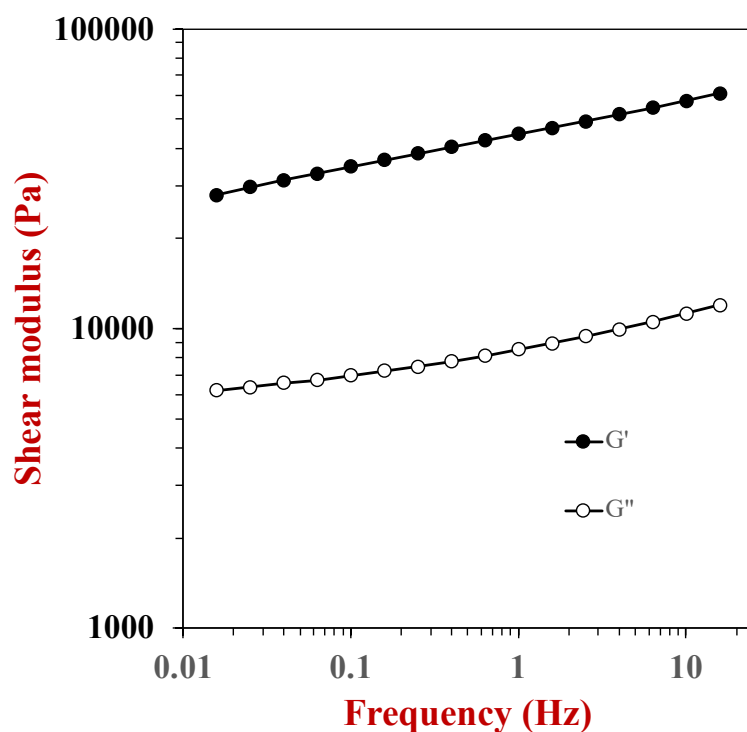


Figure 16. Influence of applied frequency on the storage (G') and loss (G'') moduli of 10 wt% potato protein gels (pH 7) measured at a strain of 1% (in linear viscoelastic regime) at 25 °C. (Data kindly supplied by Hualu Zhou).

Measurements of the shear modulus *versus* frequency profile for a heat-set plant-protein gel is shown in **Figure 16**. In this case, the storage modulus was greater than the loss modulus across the entire frequency range studied, which indicated that the gels were always predominantly elastic. There was a slight increase in both the storage and loss moduli as the frequency was raised, which may be because the structural entities formed by the proteins in the gels had less time to respond to the applied oscillating stress at higher frequencies, so there was more resistance to deformation. Other researchers have characterized the dynamic shear rheology of peanut protein gels using this approach⁸¹. They also reported an increase in shear modulus when the frequency was raised, and that the storage modulus was always higher than the loss modulus over the frequency range studied (0.1 to 10 Hz). The frequency dependence of plant polysaccharide (fenugreek gum) gels has also been characterized using this approach⁸⁴. At low frequencies, $G'' > G'$, which indicated that the polysaccharide solutions were predominantly fluid-like. When the frequency was raised, both G' and G'' increased but there was a crossover

point ($G' = G''$) at an intermediate frequency, after which $G' > G''$, indicating that the gels became more solid-like at higher frequencies. These gels could therefore be characterized by a relaxation time. At low frequencies, there was sufficient time for the polysaccharide molecules to rearrange when an oscillating stress was applied, leading to fluid-like behavior. In contrast, at high frequencies, there was insufficient time for these molecules to rearrange, leading to more resistance to deformation and solid-like behavior. The relaxation frequency was found to decrease with increasing polysaccharide concentration, which can be attributed to the fact that the greater entanglements and interactions of the polysaccharide molecules in more concentrated systems inhibits their movement. These kinds of frequency sweep tests can therefore provide valuable information about the dynamic properties of the biopolymer gels used to formulate some NG-PB foods.

5.4.4. Large deformation experiments

In many practical applications, it is important to understand how NG-PB foods behave when they undergo large deformations. For instance, the cutting of meat, the slicing of cheese, the scrambling of eggs, or the mastication of solid foods all involve large deformations of the material, which cause the food structure to become disrupted. Consequently, it is important to characterize the rheological behavior of NG-PB foods exposed to large stresses and strains. In this section, we provide examples of some of the most common experimental approaches used to obtain this kind of information for these foods.

Large amplitude oscillatory shear (LAOS): LAOS experiments are typically carried out using a dynamic shear rheometer^{85, 86}. The test sample is placed in the measurement cell and then an oscillating shear stress that progressively increases in amplitude is applied. This test is therefore similar to the strain-sweep tests described earlier (Section 6.2.4.2). However, LAOS experiments focus on the behavior of the material within the larger deformation regime, rather than the transition from the linear to non-linear viscoelastic regimes. Because the stress-strain and stress-strain rate relationships are non-linear at high deformations specialized mathematical approaches are needed to interpret and represent the data^{85, 86}. This is mainly because second and higher order harmonics contribute to the rheological properties of the material in the non-linear regime, whereas only first-order harmonics contribute in the linear regime^{86, 87}. Information about the transient behavior of a material under large deformation can be obtained by plotting Lissajous curves, which show the stress *versus* strain relationship for the elastic

component and the stress *versus* strain rate profile for the viscous component of the shear modulus (**Figure 17**). The shape of these curves provides insights into the nature of the material being tested, such as viscous, elastic, viscoelastic, or plastic. The energy dissipation per unit volume of material per oscillation cycle can be calculated from the area under the Lissajous curves, which provides useful insights into the impact of deformation on structural and textural changes^{88, 89}.

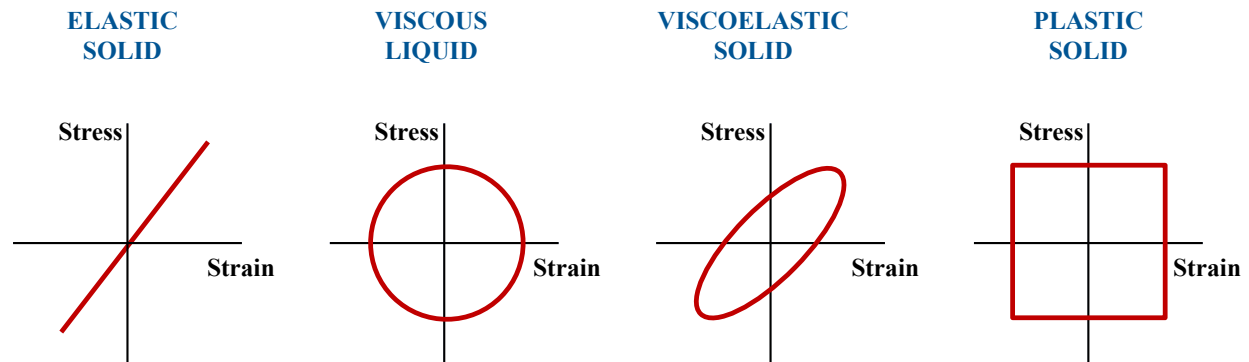


Figure 17. Highly schematic representation of the different kinds of Lissajous plots that can be obtained for different materials. In practice, other shapes can be seen for more complex materials, especially during large deformation measurements.

The LAOS method has been used to test several model plant-based foods. For instance, it was used to quantify the impact of gum concentration on the rheology of soy protein isolate - carboxymethyl flaxseed gum (SPI-CMFG) mixtures⁹⁰. The authors reported that the storage modulus, loss modulus, and apparent shear viscosity of the SPI-CMFG mixtures increased with increasing CMFG concentration. Other researchers utilized both small and large amplitude oscillatory shear (SAOS and LAOS) tests to characterize the impact of composition on the rheology of konjac glucomannan solutions at low and high deformations⁹¹. The storage modulus, loss modulus, and apparent viscosity of the konjac glucomannan solutions increased with increasing polymer concentration but decreasing NaCl concentration. The LAOS tests showed that increasing the konjac glucomannan concentration changed the shape of the Lissajous plots, which provided insights into changes in the conformation and interactions of the polysaccharides. In another study, researchers used LAOS to study the suitability of blends of plant proteins (soy or pea proteins) and polysaccharides (cellulose or pectin) for formulating meat analogs⁸⁸. The polysaccharide-protein composites had more fibrous structures than protein alone, which could be useful for mimicking the structural and textural attributes of real meat.

LAOS testing was used to provide information about changes in the rheology of the protein-polysaccharide composites when their compositions were changed. The same authors used this method to test the impact of thermal processing on the properties of plant protein gels formed from pea, soy, or wheat gluten proteins⁸⁹. SAOS and LAOS tests have also been used to characterize the rheological properties of plant-based edible inks suitable for 3D food printing applications⁹². These edible inks were prepared by blending soy protein with either guar gum or xanthan gum to achieve the required printing characteristics.

Large-deformation compression tests: The mechanical properties of materials at large deformations are often assessed using compression tests. Typically, a test material of fixed shape and dimensions, such as a cylinder of known height and diameter, is placed on the measurement cell of the instrument. The force acting on a probe as it compresses the test material at a fixed speed is then measured over time. This information is used to calculate the relationship between the applied stress and the resulting strain of the material (**Figure 9**). At low deformations, the stress is proportional to the strain and the elastic modulus can be calculated from the initial slope. However, at higher deformations the material may exhibit some flow or disruption, and so the stress is no longer proportional to the strain. In the case of fracturing, the fracture stress and fracture strain can be determined as the point where there is an obvious break in the stress-strain relationship. These parameters can then be plotted on a 2D plot of critical stress *versus* critical strain to provide insights into the textural attributes of the test material (**Figure 9**). Typically, the material can be classified as brittle, tough, mushy, or rubbery depending on where it falls on the texture map⁸⁸.

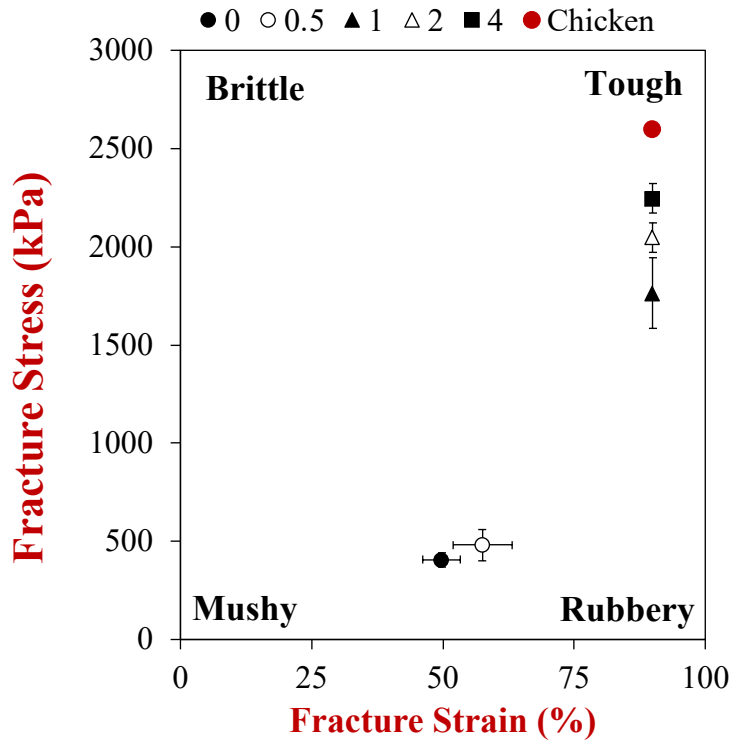


Figure 18. A 2D Texture map can be used to characterize the fracture properties of NG-PB foods and compare them to real ones. In this case, the fracture stress and strain of several plant-based chicken formulations (which consisted of 10% potato protein and 0, 0.5, 1, 2, or 4% gellan gum) are compared to those of real chicken. Data kindly provided by Hualu Zhou.

As an example, our laboratory has used this approach to compare the properties of plant-based chicken analogs to real chicken (**Figure 18**). The chicken analogs were prepared by preparing a series of potato protein-gellan gum composite gels with different compositions. The textural attributes of the chicken analogs could be manipulated to be somewhat similar to those of real chicken by using sufficiently high concentrations of plant protein and polysaccharide. These kinds of texture maps can also be developed by measuring the stress and strain of plant-based composites using a dynamic shear rheometer, where the critical stress and strain at the end of the linear viscoelastic region are used ⁸⁸.

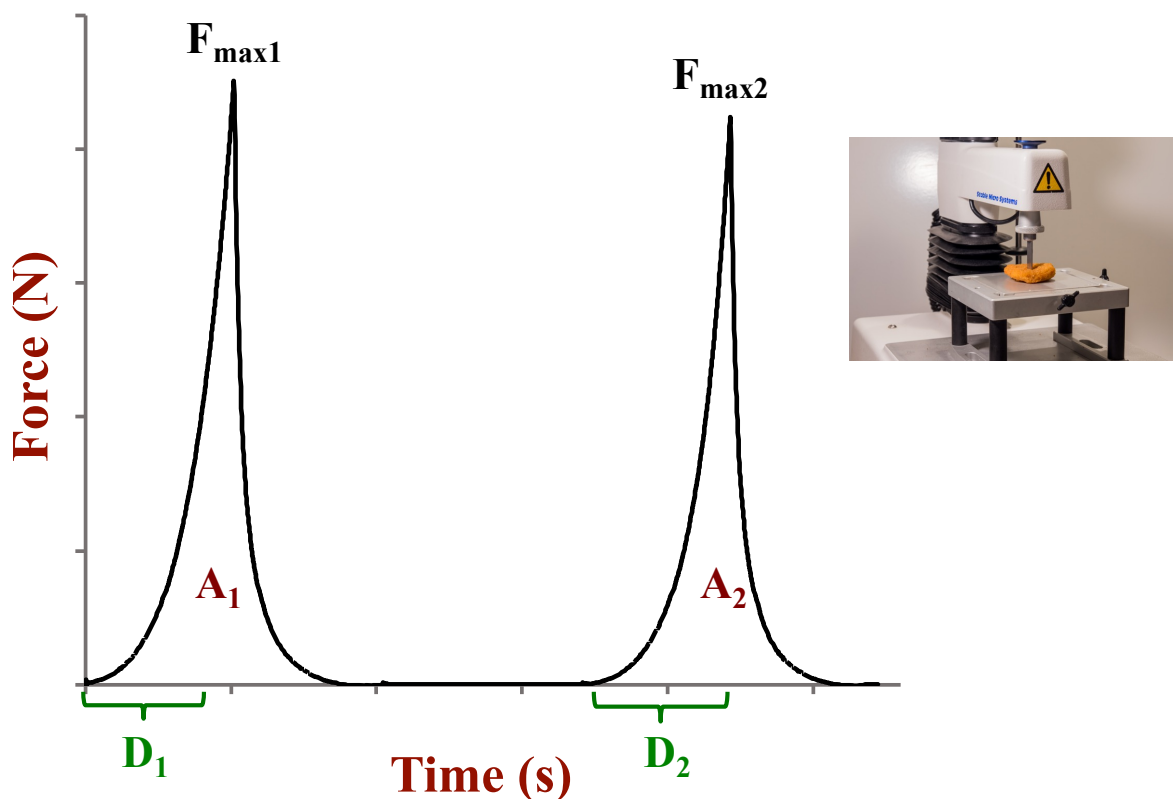


Figure 19. The rheology of solid or semi-solid NG-PG foods is often characterized by texture profile analysis (TPA), which involves compressing/decompressing the sample twice and measuring the force versus time or distance. Measurement probes with different sizes and shapes can be used to mimic practical situations. Representative measurements are shown that are used to determine TPA parameters, such as forces, areas, and distances. Image of instrument kindly supplied by Texture Technologies Corporation.

Texture profile analysis: The TPA method is probably the most common approach for characterizing the large deformation behavior of solid and semi-solid foods, including NG-PB foods¹. As mentioned earlier, a test sample with a well-defined size and shape (such as a cylinder) is placed on the measurement cell and then the sample is compressed-decompressed twice (Section 5.2.1.1). The change in the force with time (or deformation) is then recorded and analyzed (**Figure 19**). Various textural parameters can then be calculated from the height, position, and area of the two peaks obtained during the double compression-decompression cycle, such as the hardness, fracturability, cohesiveness, springiness, resilience, gumminess, and chewiness (**Table 2**). Ideally, the parameters measured for a NG-PB food should match those of the animal sourced food it is designed to replace. This method can therefore be used to determine the impact of different parameters on the textural attributes of NG-PB foods such as

their composition or preparation method, as well as to compare the properties of NG-PB foods to those of animal sourced foods.

The TPA method has been used in our laboratory to compare the properties of real beefburgers with several plant-based ones^{93,94}. The TPA parameters determined using a double compression-decompression test are summarized in **Table 5**. Radar plots of selected PB burgers are shown in **Figure 20**, which compare the percentage of each TPA parameter to that found for real beefburgers (100%). Notably, there were large differences between the textural attributes of the NG-PB burgers and the real beefburgers, which would be expected to lead to sensory differences. These results highlight the need for further research to better simulate the textural attributes of real meat using plant-based meat analogs.

Table 5. Comparison of the TPA parameters of several commercial plant-based (PB) burgers with those of real beef burgers. Data taken from experiments in our laboratory⁹⁴.

	PB1	PB2	PB3	PB4	PB5	Beef
Hardness (g)	440 ± 80	1300 ± 250	1500 ± 180	240 ± 29	270 ± 21	2400 ± 450
Adhesiveness (g.sec)	-0.91 ± 0.77	-0.34 ± 0.27	-1.2 ± 0.65	-1.2 ± 0.60	-1.6 ± 0.65	-0.47 ± 0.19
Resilience (%)	14 ± 3.4	20 ± 1.6	16 ± 1.0	7.2 ± 0.87	5.8 ± 0.68	24 ± 1.3
Cohesion	0.41 ± 0.07	0.52 ± 0.03	0.46 ± 0.02	0.24 ± 0.02	0.21 ± 0.02	0.61 ± 0.02
Springiness (%)	61 ± 11	79 ± 5.0	64 ± 3.2	34 ± 3.5	32 ± 3.8	88 ± 2.8
Gumminess	190 ± 64	660 ± 120	700 ± 94	59 ± 7.1	57 ± 8.0	1400 ± 270
Chewiness	120 ± 58	530 ± 120	450 ± 62	20 ± 3.6	18 ± 4.0	1300 ± 250

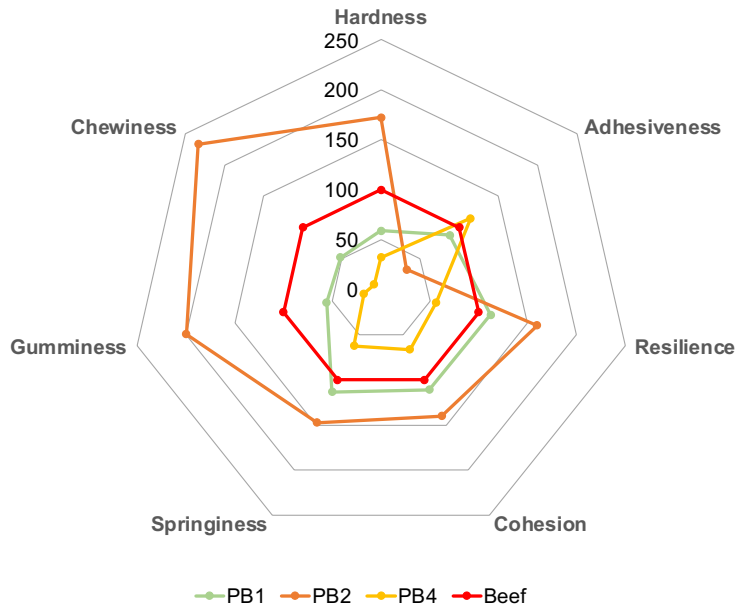


Figure 20. Comparison of the TPA parameters of several commercial plant-based (PB) burgers with those of real beef burgers. Data taken from experiments in our laboratory (Zhou, et al., 2022a).

Many other researchers have also used TPA to characterize the rheological properties of model or commercial plant-based foods. For instance, this method has been used to establish the impact of a dietary fiber (psyllium) on the textural attributes of plant-based sausages⁹⁵. The researchers found that the addition of the dietary fiber increased the firmness, hardness, springiness, cohesiveness, resilience, and chewiness of the plant-based sausages, which altered their sensory attributes. In another study, TPA was used to characterize the effects of sweet potato starch and konjac glucomannan on the textural attributes of plant-based pork rinds formulated from emulsion gels composed of soy protein and soy oil⁹⁶. The hardness, cohesiveness, and chewiness of the pork rind analogs could be optimized by controlling the amounts of starch and glucomannan added. TPA has also been used to characterize the impact of formulation and processing parameters on the creation of various other plant-based foods, including the addition of methylcellulose on beefburger analogs⁹⁷, the addition of apricot seed extract on kefir analogs⁹⁸, and the impact of heating and cooling on pork back fat analogs⁹⁹.

6. Conclusions

There has been a surge of interest in the creation of NG-PB foods that accurately simulate the properties of traditional animal-based products, like meat, seafood, egg, and dairy products.

These products exhibit a broad diversity of rheological characteristics, including low viscosity fluids (like milk), high viscosity fluids (creams), soft solids (like yogurt), and hard solids (like some cheeses). Moreover, solid or semi-solid products may be expected to be brittle, rubbery, mushy, or tough depending on their nature. Consequently, it is important for the manufacturers of NG-PB foods to be able to mimic this broad range of products. This requires the availability of analytical methods to quantify and compare the properties of foods, as well as mathematical models to identify the key factors that impact their textural attributes.

In this article, it was shown that most NG-PB foods can be considered to be fluid, semi-solid, or solid colloidal dispersions consisting of polymers and/or particles dispersed in an aqueous medium. Consequently, their rheological properties can be measured and modelled using the analytical techniques and theoretical equations that have been developed to describe colloidal dispersions. It has been demonstrated that identifying an appropriate theoretical model can provide valuable insights into the relative importance of different parameters that impact the rheological attributes of NG-PB foods. These models can therefore be used to optimize the design of products with improved textural properties. In the future, it will be important to establish the most appropriate models for different categories of NG-PB foods and to determine their range of applications. Moreover, it will be useful to tabulate the characteristics of a wide range of NG-PB foods using standardized methods so that useful comparisons can be made with other products.

Acknowledgements

This material was partly based upon work supported by the National Institute of Food and Agriculture, USDA, Massachusetts Agricultural Experiment Station (MAS00559) and USDA, AFRI (2020-03921 and 2022-09185) grants, as well as the Good Food Institute.

References

1. D. J. McClements and L. Grossmann, *Next-generation Plant-based Foods: Design, Production, and Properties*, Springer, New York, NY, 2022.
2. D. J. McClements and L. Grossmann, *Comprehensive Reviews in Food Science and Food Safety*, 2021, **20**, 4049-4100.
3. K. Kyriakopoulou, B. Dekkers and A. J. van der Goot, *Plant-Based Meat Analogues*, 2019.
4. J. Mewis and N. J. Wagner, *Colloidal Suspension Rheology*, Cambridge University Press, New York, 2012.
5. T. A. Vilgis, *Reports on Progress in Physics*, 2015, **78**.

6. A. Boire, D. Renard, A. Bouchoux, S. Pezenec, T. Croguennec, V. Lechevalier, C. Le Floch-Fouere, S. Bouhallab and P. Menut, in *Annual Review of Food Science and Technology*, Vol 10, eds. M. P. Doyle and D. J. McClements, 2019, vol. 10, pp. 521-539.
7. R. G. M. van der Sman, *Advances in Colloid and Interface Science*, 2012, **176**, 18-30.
8. S. Jeske, E. Zannini and E. K. Arendt, *Plant Foods for Human Nutrition*, 2017, **72**, 26-33.
9. D. J. McClements, E. Newman and I. F. McClements, *Comprehensive Reviews in Food Science and Food Safety*, 2019, **18**, 2047-2067.
10. X. Kong, Z. Q. Xiao, M. D. Du, K. T. Wang, W. Yu, Y. H. Chen, Z. L. Liu, Y. Q. Cheng and J. Gan, *Gels*, 2022, **8**.
11. L. Sen and S. Okur, *Food Chemistry*, 2023, **402**.
12. M. Montemurro, E. Pontonio, R. Coda and C. G. Rizzello, *Foods*, 2021, **10**.
13. L. Grossmann and D. J. McClements, *Trends in Food Science & Technology*, 2021, **118**, 207-229.
14. E. C. Short, A. J. Kinchla and A. A. Nolden, *Foods*, 2021, **10**.
15. K. Kyriakopoulou, J. K. Keppler, A. J. van der Goot and R. M. Boom, in *Annual Review of Food Science and Technology*, Vol 12, 2021, eds. M. Doyle and D. J. McClements, 2021, vol. 12, pp. 29-50.
16. K. Younis, A. Ashfaq, A. Ahmad, Z. Anjum and O. Yousuf, *Journal of Texture Studies*, 2023, DOI: 10.1111/jtxs.12704.
17. X. Y. Hu and D. J. McClements, *Journal of the American Oil Chemists Society*, 2022, **99**, 78-78.
18. X. Y. Hu and D. J. McClements, *Innovative Food Science & Emerging Technologies*, 2022, **78**.
19. X. Y. Hu, H. L. Zhou and D. J. McClements, *Food Structure-Netherlands*, 2022, **33**.
20. R. A. Nicholson and A. G. Marangoni, *Current Opinion in Food Science*, 2022, **43**, 1-6.
21. J. X. Guo, L. J. Cui and Z. Meng, *Food Hydrocolloids*, 2023, **137**.
22. Z. Lu, Y. Liu, Y. E. J. Lee, A. Chan, P. R. Lee and H. S. Yang, *Food Chemistry*, 2023, **403**.
23. G. Vu, X. Xiang, H. Zhou and D. J. McClements, *Foods*, 2023, **12**, 2.
24. R. C. F. de Menezes, Q. C. D. Gomes, B. S. de Almeida, M. F. R. de Matos and L. C. Pinto, *International Journal of Gastronomy and Food Science*, 2022, **30**.
25. J. Hao, X. Y. Li, Q. Y. Wang, W. W. Lv, W. G. Zhang and D. X. Xu, *Journal of the American Oil Chemists Society*, 2022, **99**, 635-653.
26. F. Zaaboul, Q. L. Zhao, Y. J. Xu and Y. F. Liu, *Food Hydrocolloids*, 2022, **124**.
27. E. Bertoft, *Agronomy-Basel*, 2017, **7**.
28. F. Flach, L. Fries, J. Kammerhofer, J. Hesselbach, B. Finke, C. Schilde, G. Niederreiter, S. Palzer, S. Heinrich and A. Kwade, *Advanced Powder Technology*, 2019, **30**, 2823-2831.
29. O. G. Jones and D. J. McClements, *Comprehensive Reviews in Food Science and Food Safety*, 2010, **9**, 374-397.
30. D. Saglam, P. Venema, E. van der Linden and R. de Vries, *Current Opinion in Colloid & Interface Science*, 2014, **19**, 428-437.
31. M. Li, V. D. Daygon, V. Solah and S. Dhital, *Critical Reviews in Food Science and Nutrition*, 2022, DOI: 10.1080/10408398.2021.1992607.
32. Y. Ai and J. L. Jane, *Starch-Starke*, 2015, **67**, 213-+.
33. S. Samard and G. H. Ryu, *Journal of the Science of Food and Agriculture*, 2019, **99**, 2708-2715.
34. I. J. Joye and D. J. McClements, *Current Opinion in Colloid & Interface Science*, 2014, **19**,

- 1374 417-427.
- 1375 35. N. Reddy and M. Rapisarda, *Materials*, 2021, **14**.
- 1376 36. M. Miriani, M. Keerati-u-rai, M. Corredig, S. Iametti and F. Bonomi, *Food Hydrocolloids*,
1377 2011, **25**, 620-626.
- 1378 37. T. G. Burger and Y. Zhang, *Trends in Food Science & Technology*, 2019, **86**, 25-33.
- 1379 38. D. Iwanaga, D. A. Gray, I. D. Fisk, E. A. Decker, J. Weiss and D. J. McClements, *Journal of*
1380 *Agricultural and Food Chemistry*, 2007, **55**, 8711-8716.
- 1381 39. K. Hu and D. J. McClements, *Food Hydrocolloids*, 2015, **44**, 101-108.
- 1382 40. E. ten Grotenhuis, M. Paques and G. A. van Aken, *Journal of Colloid and Interface Science*,
1383 2000, **227**, 495-504.
- 1384 41. Y. R. Tang and S. Ghosh, *Food Hydrocolloids*, 2021, **113**.
- 1385 42. T. Tran and D. Rousseau, *Food Hydrocolloids*, 2013, **30**, 382-392.
- 1386 43. B. Du, S. P. Nie, F. Peng, Y. D. Yang and B. J. Xu, *Food Frontiers*, 2022, **3**, 631-640.
- 1387 44. L. Sha and Y. L. L. Xiong, *Trends in Food Science & Technology*, 2020, **102**, 51-61.
- 1388 45. X. Yang, A. Q. Li, X. X. Li, L. J. Sun and Y. R. Guo, *Trends in Food Science &*
1389 *Technology*, 2020, **102**, 1-15.
- 1390 46. A. J. Stephen, G. O. Phillips and P. A. Williams, *Food Polysaccharides and Their*
1391 *Applications*, CRC Press, Boca Raton, FL., Second Edition edn., 2017.
- 1392 47. M. Q. Guo, X. Hu, C. Wang and L. Ai, in *Solubility of Polysaccharides*, ed. Z. Xu,
1393 IntechOpen, On-line, 2017, DOI: [https://www.intechopen.com/books/solubility-of-](https://www.intechopen.com/books/solubility-of-polysaccharides)
1394 [polysaccharides](https://www.intechopen.com/books/solubility-of-polysaccharides), ch. Chapter 2, pp. 1-17.
- 1395 48. D. J. McClements, *Food Emulsions: Principles, Practice, and Techniques*, CRC Press, Boca
1396 Raton, 2nd edn., 2015.
- 1397 49. D. Quemada and C. Berli, *Advances in Colloid and Interface Science*, 2002, **98**, 51-85.
- 1398 50. R. J. Hunter, *Introduction to Modern Colloid Science*, Oxford University Press, Oxford,
1399 U.K., 1994.
- 1400 51. D. B. Genovese, J. E. Lozano and M. A. Rao, *Journal of Food Science*, 2007, **72**, R11-R20.
- 1401 52. D. J. McClements, *Food Hydrocolloids*, 2000, **14**, 173-177.
- 1402 53. T. D. Panaite, S. Mironeasa, M. Iuga and P. A. Vlaicu, *Emirates Journal of Food and*
1403 *Agriculture*, 2019, **31**, 304-314.
- 1404 54. H. L. Zhou, G. Vu and D. J. McClements, *Journal of the American Oil Chemists Society*,
1405 2022, **99**, 169-169.
- 1406 55. J. L. Briggs and J. F. Steffe, *Journal of Texture Studies*, 1997, **28**, 517-522.
- 1407 56. M. A. Rao, *Rheology of Fluid, Semisolid, and Solid Foods: Principles and Applications*,
1408 Springer Science, New York, N.Y., Third Edition edn., 2013.
- 1409 57. T. F. Tadros, *Rheology of Dispersions: Principles and Applications*, Wiley-VCH,
1410 Weinheim, Germany, 2010.
- 1411 58. P. Walstra, *Physical Chemistry of Foods*, Marcel Decker, New York, NY., 2003.
- 1412 59. T. van Vliet, *Rheology and Fracture Mechanics of Foods*, CRC Press, Boca Raton, FL,
1413 2013.
- 1414 60. N. Grasso, L. Alonso-Miravalles and J. A. O'Mahony, *Foods*, 2020, **9**.
- 1415 61. M. J. Hernandez, J. Dolz, J. Delegido, C. Cabeza and M. Dolz, *Journal of Dispersion*
1416 *Science and Technology*, 2008, **29**, 213-219.
- 1417 62. Y. P. Cao and R. Mezzenga, *Nature Food*, 2020, **1**, 106-118.
- 1418 63. C. P. Broedersz and F. C. MacKintosh, *Reviews of Modern Physics*, 2014, **86**, 995-1036.
- 1419 64. T. Funami, S. Noda, M. Nakauma, S. Ishihara, R. Takahashi, S. Al-Assaf, S. Ikeda, K.

- 1420 Nishinari and G. O. Phillips, *Journal of Agricultural and Food Chemistry*, 2008, **56**,
1421 8609-8618.
- 1422 65. P. J. Lu and D. A. Weitz, in *Annual Review of Condensed Matter Physics, Vol 4*, ed. J. S.
1423 Langer, 2013, vol. 4, pp. 217-233.
- 1424 66. A. D. Dinsmore, in *Experimental and computational techniques in soft condensed matter*
1425 *physics*, ed. J. Olafsen, Cambridge University Press, Cambridge, UK, 2010, ch. Chapter
1426 3, pp. 62-96.
- 1427 67. L.-V. Bouthier, R. Castellani, E. Hachem and R. Valette, *Physics of Fluids*, 2022, **34**,
1428 083105.
- 1429 68. E. Dickinson, *Advances in Colloid and Interface Science*, 2013, **199**, 114-127.
- 1430 69. S. Bi, J. Pang, L. Huang, M. Sun, X. Cheng and X. Chen, *International journal of biological*
1431 *macromolecules*, 2020, **146**, 99-109.
- 1432 70. P. P. Zhu and Z. Zhong, *Mechanics of Materials*, 2021, **152**.
- 1433 71. E. Dickinson, *Food Hydrocolloids*, 2012, **28**, 224-241.
- 1434 72. H. Koc, M. Drake, C. J. Vinyard, G. Essick, F. van de Velde and E. A. Foegeding, *Food*
1435 *Hydrocolloids*, 2019, **94**, 311-325.
- 1436 73. D. J. McClements, F. J. Monahan and J. E. Kinsella, *Journal of Texture Studies*, 1993, **24**,
1437 411-422.
- 1438 74. A. J. Gravelle, S. Barbut and A. G. Marangoni, *Rsc Advances*, 2015, **5**, 60723-60735.
- 1439 75. A. J. Gravelle, R. A. Nicholson, S. Barbut and A. G. Marangoni, *Food Research*
1440 *International*, 2019, **122**, 209-221.
- 1441 76. H. Khalesi, W. Lu, K. Nishinari and Y. P. Fang, *Food Chemistry*, 2021, **364**.
- 1442 77. A. J. Gravelle and A. G. Marangoni, *Food Hydrocolloids*, 2021, **119**.
- 1443 78. W. H. Shih, W. Y. Shih, S. I. Kim, J. Liu and I. A. Aksay, *Physical Review A*, 1990, **42**,
1444 4772-4779.
- 1445 79. Z. Y. Zhang, H. Pham, Y. B. Tan, H. L. Zhou and D. J. McClements, *Food Biophysics*,
1446 2021, **16**, 512-519.
- 1447 80. M. Felix, Z. Camacho-Ocana, M. L. Lopez-Castejon and M. Ruiz-Dominguez, *Food*
1448 *Hydrocolloids*, 2021, **120**.
- 1449 81. Y. D. Zhu, D. Li and L. J. Wang, *Powder Technology*, 2019, **358**, 95-102.
- 1450 82. K. D. Mattice and A. G. Marangoni, *Current Research in Food Science*, 2020, **3**, 59-66.
- 1451 83. R. G. M. van der Sman, P. Chakraborty, N. P. Hua and N. Kollmann, *Food Hydrocolloids*,
1452 2023, **135**.
- 1453 84. P. V. Gadkari, M. J. T. Reaney and S. Ghosh, *International Journal of Biological*
1454 *Macromolecules*, 2019, **126**, 337-344.
- 1455 85. K. M. Kamani, G. J. Donley, R. K. Rao, A. M. Grillet, C. Roberts, A. Shetty and S. A.
1456 Rogers, *Journal of Rheology*, 2023, **67**, 331-352.
- 1457 86. H. S. Joyner, in *Annual Review of Food Science and Technology, Vol 12, 2021*, eds. M.
1458 Doyle and D. J. McClements, 2021, vol. 12, pp. 591-609.
- 1459 87. H. S. Melito, C. R. Daubert and E. A. Foegeding, *Journal of Food Engineering*, 2012, **113**,
1460 124-135.
- 1461 88. F. K. G. Schreuders, M. Schlangen, I. Bodnar, P. Erni, R. M. Boom and A. J. van der Goot,
1462 *Food Hydrocolloids*, 2022, **124**.
- 1463 89. F. K. G. Schreuders, L. M. C. Sagis, I. Bodnar, P. Erni, R. M. Boom and A. J. van der Goot,
1464 *Food Hydrocolloids*, 2021, **110**.
- 1465 90. Y. X. Ma, J. L. Niu, D. Li and L. J. Wang, *International Journal of Food Engineering*, 2020,

- 1466 **16.**
1467 91. Y. X. Ma, D. B. Su, Y. Wang, D. Li and L. J. Wang, *Lwt-Food Science and Technology*,
1468 2020, **128**.
1469 92. J. Yu, X. Y. Wang, D. Li, L. J. Wang and Y. Wang, *Food Hydrocolloids*, 2022, **131**.
1470 93. G. Vu, H. L. Zhou and D. J. McClements, *Journal of Agriculture and Food Research*, 2022,
1471 **9**.
1472 94. H. L. Zhou, G. Vu, X. P. Gong and D. J. McClements, *Acs Food Science & Technology*,
1473 2022, **2**, 844-851.
1474 95. A. T. Noguerol, V. Larrea and M. J. Pagan, *European Food Research and Technology*,
1475 2022, **248**, 2483-2496.
1476 96. Q. B. Zhang, L. Huang, H. Li, D. Zhao, J. N. Cao, Y. Song and X. Q. Liu, *Molecules*, 2022,
1477 **27**.
1478 97. A. Bakhsh, S. J. Lee, E. Y. Lee, N. Sabikun, Y. H. Hwang and S. T. Joo, *Foods*, 2021, **10**.
1479 98. K. Uruc, A. Tekin, D. Sahingil and A. A. Hayaloglu, *Innovative Food Science & Emerging*
1480 *Technologies*, 2022, **82**.
1481 99. B. Cui, Y. Y. Mao, H. S. Liang, Y. Li, J. Li, S. X. Ye, W. X. Chen and B. Li, *International*
1482 *Journal of Biological Macromolecules*, 2022, **206**, 481-488.
1483