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Rheological characterization of tuna myofibrillar protein in linear and nonlinear viscoelastic regions

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ABSTRACT

The gelation characteristics of myofibrillar proteins are indicative of the ultimate texture of fish products. This study investigated the impact of pH (5.6–7.0) on viscoelastic properties of tuna myofibrillar proteins using dynamic oscillatory rheometer under both small-amplitude oscillatory shear (SAOS) and large-amplitude oscillatory shear (LAOS). Using small-strain oscillatory tests, the rheological properties during gelling were quantified. Results indicated that protein denaturation and gel formation were pH dependent. LAOS tests indicated that pH strongly affected the structure of the myofibrillar proteins system as shown by deformation of the nonlinear stress response curve. Increasing pH produced an increasingly strong, more stable network. All non-linear behaviors increased with increasing strain in a similar manner, suggesting a general mechanism responsible for strain effects that was similar for non-linear and fracture behavior. Furthermore, pH also appeared to influence the water-holding capacity and surface hydrophobicity.

1. Introduction

Tuna and tuna-like species are very important because of their high global economic value and their frequent use in international trade for canning and sashimi production. Tuna meat is highly perishable, so many different methods are used to determine its quality and thus its optimal handling. Because the gelation characteristics of myofibrillar proteins are indicative of the texture of the meat product, gaining an understanding of myofibrillar protein is beneficial for the development of processed tuna or tuna waste products, as well as for maintaining the quality of these products.

In particular, rheological techniques can be used to determine subtle changes in muscular tissue (Westphalen et al., 2006), and thus they have many applications in the fields of food acceptability, food processing, and food handing (Barbosa-Cánovas et al., 1996). For example, rheological measurements are used to physically characterize raw materials prior to processing, intermediate products during manufacturing, and the final food products (Tabilo-Munizaga and Barbosa-Cánovas, 2005). Food products are both structurally and rheologically complex, and in many cases they consist of mixtures of solids and fluid. Because rheology concerns the flow and deformation of substances and especially their behavior in the transient range between solids and fluids, it is a very useful tool.

The rheological characteristics of fish muscle are thought to be governed by both the myofibrillar and connective tissue proteins, while the sarcoplasmic proteins contribute very little to texture (Barroso et al., 1998). A number of studies on myofibrillar protein gels have used large-deformation testing, including one-cycle compression, tension, or puncturing, to measure the final gel strength. However, these tests do not allow the dynamic gelation process to be assessed. Xiong (2005) used texture profile analysis (TPA) to examine the role of myofibrillar protein in water-binding in brine-enhanced meat by measuring the gel strength of different mixtures of myofibrillar and soy proteins. Large-deformation testing can destroy tissue quite rapidly, while small-amplitude oscillatory testing is a nondestructive technique that can be applied without causing structural damage to the sample. Small-amplitude oscillatory shear (SAOS) testing is extremely sensitive to the physical structure and chemical composition of the sample, which makes it useful for evaluating gelation kinetics (Romero et al., 2011). Recently, large-amplitude oscillatory shear (LAOS) testing has been extensively employed in rheological analyses of many complex systems (Fuongfuchat et al., 2012; Wang et al., 2012, 2011). The storage modulus G' and loss modulus G'' are defined only in the linear viscoelastic regime, and therefore their values at large strain amplitude may have ambiguous physical meaning. However, provided that sufficient care is taken, LAOS testing can provide abundant additional information, including data on the structure and energy consumption. Still, studies on the physicochemical and gelation characteristics of myofibrillar proteins from tuna in general have been rather limited.

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The objective of this work was to evaluate the extent to which pH influences the rheological properties of tuna myofibrillar protein and to examine the relationships between the measured viscoelastic properties and the water-binding and surface hydrophobicity of myofibrillar protein.

2. Materials and methods

2.1. Materials

Skinned, finely chopped, and frozen big-eye tuna (*Thunnus obesus*) was supplied by Zhongshui Fisheries General Corporation (Shanghai, China). The tuna was cut into blocks of approximately 50 g. All samples were wrapped with polyethylene film, packed individually in zip-lock packets, and stored at −60 °C until use. All chemicals used in this study were of analytical grade.

2.2. Myofibril isolation

Extraction of myofibrillar proteins at 4 °C was carried out essentially as described by Katoh et al. (1977), with slight modification. The muscle was trimmed, homogenized, and washed 8 times with 40 mM tris-maleate buffer (0.16 M KCl, 1% Triton X-100, pH 7.5). Samples were centrifuged for 20 min at 1500*g*, and the pellet was resuspended and washed three times with 40 mM tris-maleate buffer (0.16 M KCl, pH 7.5) until the supernatant became clear. The pellet was collected following centrifugation between each wash. After this process, the pellet was again washed with four volumes of cold 0.1 M NaCl in order to remove the buffer and was then centrifuged for 20 min at 1000*g*. After drying, eight volumes of cold 0.1 M NaCl was added to the pellet, which was then homogenized in a blender for 10 min at 1000*g* and subsequently filtered through a nylon net (#16) to remove the connective tissue. The washed myofibril pellet was stored at 4 °C until use.

2.3. Sample preparation

The protein content was determined for each sample using the Lowry method (Gornall et al., 1949). Samples were suspended and adjusted to 3% (w/v) protein using 0.6 M NaCl, 50 mM sodium phosphate buffer. The protein samples were adjusted to pH 5.6, 6.0, 6.5, and 7.0 using 100 mM Na_2HPO_4 (pH 9.15) and 100 mM NaH_2PO_4 (pH 4.7) and were stored at 4 °C prior to measurement.

2.4. Dynamic rheological measurement

2.4.1. Small-amplitude oscillatory shear test

The oscillatory rheological experiments were conducted in a controlled-stress/strain rheometer (Physica MCR 301; Anton Paar, Ostfildern, Germany) using a plate/plate geometry with a 1.0 mm gap. We selected a sandblasted surface to avoid any risk that the gel system studied was prone to slip effects. The temperature of the bottom plate (50 mm diameter) was controlled with a Peltier system (Viscotherm VT2, Phar Physica, Ostfildern, Germany) for fast and precise temperature control. A glass solvent trap was used to prevent evaporation.

Temperature sweep analysis from 20 °C to 60 °C was performed at a rate of 1 °C/min. In this experiment, the changes in the dynamic rheological parameters including the storage moduli (G') and loss moduli (G'') are measured during heating. A constant frequency of 1 rad/s and an amplitude stress of 1 Pa were used, which were within the linear viscoelastic region for the samples.

Dynamic strain sweep experiments were conducted to determine the linear viscoelastic region (LVER) at different temperatures using a strain range of 0.01–1000% at a constant frequency of 1 rad/s. At least three repetitions of each measurement were made.

2.4.2. Large-amplitude oscillatory shear test

As the strain amplitude increases, the rheological properties remain constant up to a critical strain amplitude, after which they change. The region below the critical strain amplitude is defined as the linear region, whereas the region above the critical strain amplitude is nonlinear. Dynamic testing in the nonlinear region is termed LAOS testing (Sim et al., 2003). LVER was also defined as the strain for which G' corresponded to 95% of the maximum storage modulus (G'_{max}) obtained during the sweep tests (Ferris et al., 2009). Ewoldt et al. (2008) proposed a new framework to describe the complex nonlinear response in LAOS experiments using Lissajous plots. In this framework, the area within a Lissajous plot of the shear stress versus strain represents the dissipated energy, whereas that in a plot of the shear stress versus the strain rate is related to the stored energy.

In the linear range, a Lissajous plot of the shear stress versus strain will have an elliptical shape for a general viscoelastic material. However, any nonlinearity will distort this shape. A linear viscoelastic response appears as an ellipse that contains two mirror planes (the major and minor axes of the ellipse), but if there is a steady nonlinear viscoelastic response, the mirror planes are lost. However, this framework requires only that the response is periodic, $\sigma(t) = \sigma(t + T)$, where T is the period of oscillation, and it allows both odd and even harmonics in the Fourier series of the stress response. For a typical simple fluid, in which the material behaves the same in both shear directions, only odd harmonics are allowed. With this mathematical description, rheological properties can be obtained directly from Lissajous figures. The full framework for characterizing nonlinear viscoelasticity was summarized by Ewoldt (2009) as

$$G'_M = \left.\frac{d\sigma}{d\gamma}\right|_{\gamma=0} = \sum_{n:\text{odd}} nG'_n \tag{1}$$

$$G'_L = \left.\frac{\sigma}{\gamma}\right|_{\gamma=\gamma_0} = \sum_{n:\text{odd}} G'_n(-1)^{\frac{n-1}{2}} \tag{2}$$

$$\eta'_M = \left.\frac{d\sigma}{d\dot{\gamma}}\right|_{\dot{\gamma}=0} = \frac{1}{\omega}\sum_{n:\text{odd}} nG''_n(-1)^{\frac{n-1}{2}} \tag{3}$$

$$\eta'_L = \left.\frac{\sigma}{\dot{\gamma}}\right|_{\dot{\gamma}=\dot{\gamma}_0} = \frac{1}{\omega}\sum_{n:\text{odd}} G''_n \tag{4}$$

Here, G'_M is the minimum-strain modulus (shear modulus at zero strain) or tangent modulus at $\gamma = 0$ and G'_L is the large-strain modulus (shear modulus at maximum strain) or secant modulus representing the slope of a straight line from the origin $[\sigma:\gamma] = [0:0]$ to$[\sigma:\gamma] = [\sigma(\gamma_1):\gamma_1]$. Similarly, η'_M is the minimum-rate dynamic viscosity and η'_L is the large-rate dynamic viscosity.

The strain stiffening ratio is defined as

$$S = \frac{G'_L - G'_M}{G'_L} \tag{5}$$

$S > 0$ indicates a type of intercycle stiffening, and $S < 0$ indicates that the material is undergoing strain softening. At $S = 0$, the linear elastic range is retained.

Similarly, the shear-thickening ratio is defined as

$$T = \frac{\eta'_L - \eta'_M}{\eta'_L} \tag{6}$$

$T > 0$ indicates a type of intercycle shear thickening, whereas $T < 0$ indicates that the material is undergoing shear thinning during an oscillation cycle. $T = 0$ holds in the linear elastic range.