Food Hydrocolloids 79 (2018) 282–290

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Flow behavior studies of kefiran systems

Stylianos Exarhopoulos [a, b], Stylianos N. Raphaelides [a, *], Michael G. Kontominas [b]

[a] Central Research Laboratory for the Physical and Chemical Testing of Foods, Department of Food Technology, ATEI of Thessaloniki, P.O. Box 141, 57400 Thessaloniki, Greece
[b] Department of Chemistry, University of Ioannina 45110, Ioannina, Greece

ARTICLE INFO

Article history:
Available online 28 December 2017

Keywords:
Kefiran
Shear flow properties
Lubricated squeeze flow

ABSTRACT

The flow properties of a series of kefiran aqueous solutions with concentrations ranging from 0.25 to 4.0% (w/v) were examined at 4, 25 or 40 °C under controlled shear rate mode and over six orders of magnitude.The results indicated that the flow behavior of kefiran systems in solution is that of a pseudoplastic fluid at low shear rates whereas at high shear rates is that of a Newtonian one. Freeze-thaw treatment of kefiran solutions affected their structure, forming quasi-like cryogels whose consistency is concentration depended whereas their network integrity depended, possibly, on hydrogen bonding. Thermal treatment of kefiran solutions in two consecutive freeze-thaw cycles indicated that the texture of the systems remained virtually unchanged. Lubricated squeeze flow studies of kefiran quasi cryogels showed that their elongational viscosity was concentration dependent and they exhibited pseudoplasticity.

1. Introduction

Kefiran, an extracellular polysaccharide is the product of the action of certain lactic acid bacteria on milk during kefir production and comprises 50% of the mass (dry basis) of kefir grains. It is a heteropolysaccharide with roughly equal amounts of galactose and glucose molecules (Kooiman, 1968). Kefiran, as a hydrocolloid, has been considered as a potential texture modifier although its effectiveness as such is still under investigation. Thus, it has been reported (Rimada & Abraham, 2006) that the addition of kefiran to skim milk to produce gels by acidification with glucono-δ-lactone increases the apparent viscosity of the gels up to a certain kefiran concentration. However, the addition of kefiran in quantities beyond that concentration not only did not improve the consistency of the mixture gel but instead caused the collapse of its network. The researchers attributed this behavior to a depletion phenomenon induced by kefiran. Piermaria, de la Canal, and Abraham (2008) reported that kefiran solutions at 25 °C and concentrations up to 1 g/L exhibited Newtonian behavior in the range of shear rates from 55 to 500 s^{-1} whereas at higher concentrations (2, 4 and 8 g/L) they exhibited a pseudoplastic behavior. They performed their experiments using a rheometer with a geometry of serrated parallel plates employing a gap of 1 mm. Interesting enough was the fact that they recorded unusually high shear stress values (from 100 to over 7000 Pa) for the samples examined. The stresses were proportional to kefiran concentration whereas the viscosities recorded were too low (from 4 to 22 mPa*s at 100 s^{-1} shear rate) to justify such high shear stress values measured over the above mentioned range of shear rates. On the other hand, Ghasemlou, Khodaiyan, and Oromiehie (2011) reported for a kefiran solution (2% w/w) at 25 °C a viscosity value of 412 mPa*s at 100 s^{-1} shear rate whereas Esnaashari et al. (2014) reported that a kefiran solution of 3% w/w concentration at 25 °C exhibited a viscosity value of 558 mPa*s at 100 s^{-1}. They employed a rheometer equipped with a measuring unit of a cone and plate geometry. Moreover, a kefiran solution of 4% w/w concentration at the same temperature and shear rate as the previous one, exhibited a viscosity value slightly higher than that of the former one. Recently, Piermaría, Bengoechea, Abraham, and Guerrero (2016) reported shear viscosity values for kefiran solutions of concentrations 0.25, 1.0 and 2.0% w/w, at a shear rate of 100 s^{-1}, of approximately 13, 22 and 84 mPa*s respectively. They employed a rheometer with a parallel plate geometry having a gap of 0.5 mm. The same researchers also performed extensional viscosity experiments for the 2% kefiran sample and reported that it exhibited near Newtonian behavior.

Based on these observations which appear to be in conflict with each other, the present work was initiated in a effort to elucidate

* Corresponding author.
E-mail address: rafael@food.teithe.gr (S.N. Raphaelides).

https://doi.org/10.1016/j.foodhyd.2017.12.030
0268-005X/

how kefiran concentration and temperature affect the flow properties of kefiran samples when they are measured under shearing for over six decades of shear rate values and to assess whether the kefiran can be utilized as a thickener or not. Moreover, it was also aimed to assess the flow behavior of kefiran cryo-gels and how their freeze-thaw stability is affected.

2. Materials and methods

2.1. Kefiran production

Kefiran was isolated from kefir grains produced on an industrial scale using Ultra High Temperature (UHT) treated skimmed bovine milk as a raw material purchased from a local dairy. The isolation and purification of kefiran was achieved employing a combination of processing steps as described by Rimada and Abraham (2003) and Ruas-Madiedo and de los Reyes-Gavilan (2005). In brief, the method involved heating of kefir grains at 80 °C, treatment with trichloroacetic acid followed by three successive ethanol precipitation steps. The purified kefiran was then freeze dried and stored for future use.

2.2. Chemical analysis and characterization

The purity of the kefiran was evaluated by determining its moisture content (4.54%), gravimetrically, i.e. drying at 102 ± 1 °C to a constant weight (AOAC, 1990), its protein content (0.1% d.b.) by the Kjeldahl method (AOAC, 1990), and its total carbohydrate content (99.5%, d.b.), employing the phenol-sulphuric acid method (AOAC, 1990). Intrinsic viscosity measurements using an Ubbelohde capillary viscometer revealed that the critical concentration (C*) of kefiran in aqueous solution was 0.55% w/v; the molecular weight (M_w) of kefiran was found to be 6.7×10^5 Da, using static light scattering, whereas zeta potential measurements showed that kefiran in aqueous solution was negatively charged (- 7.26 mV) (Exarhopoulos, Raphaelides, & Kontominas, 2017).

2.3. Shear viscosity experiments

The measurements were performed using a DMA rheometer, Bohlin C-VOR 150 (Malvern Instruments Ltd, Worcestershire, UK). The geometry of the sample holder was that of cone (angle 4°) and plate and the instrument was operated in the controlled shear rate mode.

2.4. Lubricated squeeze flow experiments

The samples were prepared in the form of cryogels. That is, sample solutions of kefiran of various concentrations were poured into cylindrical molds of dimensions 0.016 m in diameter and 0.0155 m in height and frozen at −18 °C for 24 h. Then they were stored refrigerated at 4 °C for 24 h, prior to their measurement at ambient temperature.

The sample mold was placed on a glass plate of dimensions 0.1 × 0.1 m whose surface at the point of placing the mold was covered with a thin layer of paraffin oil. After the removal of the sample from the mold its upper surface was also covered with a thin layer of paraffin oil in order to achieve conditions of lubricated flow on both surfaces of the sample. The sample was uniaxially compressed to 50% of its initial height using a Texture Analyser TA.XT.plus (Stable Micro Systems Ltd., Godalming, U.K.), equipped with a 30 kg maximum load force cell. The sample was squeezed by a flat metal plunger attached to the cell whose diameter was 0.05 m. The surface of the plunger in contact with the sample was also lubricated with a thin layer of liquid paraffin to avoid artifacts due to friction. Replicates of each sample were measured under constant strain rate set to one of four different values i.e. nominal values of 1.0, 4.0, 7.0 or 10.0%, whereas the compression speed employed was 0.01 mm/s. All replicates of the samples were tested in triplicates. The measurements were carried out at ambient temperature (24.0 ± 1.0 °C).

The calculation of elongational viscosity was based on the assumption that homogeneous deformation pertained i.e. perfect slip of the sample at the boundary was achieved.

Thus, the average normal (vertical) stress difference $\sigma = T_{rr} - T_{zz}$ was calculated as the momentary compressive force F (t) divided by the cross-sectional area of the specimen i.e.

$$\sigma = \frac{F(t)}{\pi R^2} \tag{1}$$

the biaxial flow components were derived from

$$Vz = \dot{\varepsilon}_T H(t) \tag{2}$$

$$Vr = -\dot{\varepsilon}_T \frac{r}{2} \tag{3}$$

Where, V_z and V_r are the normal and radial velocity components respectively, H (t) the momentary sample height at time t and r the radial distance. The momentary strain rate $\dot{\varepsilon}_T$ is defined as

$$\dot{\varepsilon}_T = \left[-\frac{dH_{(t)}}{dt}\right] \frac{1}{H_{(t)}} \tag{4}$$

The biaxial strain rate $\dot{\varepsilon}_b$ is defined as (Chatraei, Macosko, & Winter 1981)

$$\dot{\varepsilon}_b = \frac{1}{2}\dot{\varepsilon}_T \tag{5}$$

when steady flow is achieved, i.e. stress and strain rate reach constant values then the elongational viscosity $\eta_B(\dot{\varepsilon}_b)$ derives from equation (6) (Dealy, 1984)

$$\eta_B(\dot{\varepsilon}_b) = \lim_{t \to \infty} \left[\eta_B^+(t, \dot{\varepsilon}_b)\right] \tag{6}$$

2.5. Confocal laser scanning microscopy

The morphology of thermally treated kefiran systems was examined using a Confocal Laser Scanning Microscope (CLSM) model LSM 700, Carl Zeiss Microscopy GmbH, Jena, Germany. The kefiran solutions of various concentrations were dyed using an aqueous solution (0.1% w/v) of the dye Acridine Orange. The samples were prepared as described in section 2.4. That is, an aliquot (2 mL) of sample solution was transferred into test tubes and a drop of the dye solution was added using a pipette. After swirl mixing it was left to rest for 5 min. Then, a small amount of the sample was transferred on a glass slide and covered by a glass cover. The specimen was placed in a freezer at −18 °C for 24 h and then stored under refrigeration at 4 °C for 24 h, prior to its examination at ambient temperature. Certain samples were subjected to two consecutive freeze-thaw cycles prior to their examination.

3. Results and discussion

3.1. Shear viscosity measurements

The viscosity measurements, covered a range of shear rates from