Food Hydrocolloids 46 (2015) 19–27

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Reversible thermal behaviour of vegetable oil cellulose ether emulsions as fat replacers. Influence of glycerol

Teresa Sanz*, Marina Falomir, Ana Salvador

Instituto de Agroquímica y Tecnología de Alimentos (IATA-CSIC), Agustín Escardino, 7, 46980 Paterna, Valencia, Spain

ARTICLE INFO

Article history:
Received 22 July 2014
Received in revised form
27 October 2014
Accepted 10 November 2014
Available online 15 December 2014

Keywords:
Cellulose ether emulsions
Glycerol
Fat replacer
Rheology
Methylcellulose
Hydroxypropylmethylcellulose

ABSTRACT

Thermal reversibility properties of vegetable oil cellulose ether emulsions with and without glycerol incorporation were studied by small amplitude oscillatory shear, optical microscopy and particle size analysis. Differences in the viscoelastic properties were observed among the different cellulose emulsions at 20 °C and 80 °C after thermal gelation. At 20 °C the highest viscoelasticity was shown by the MX emulsion. The emulsion gelation temperature decreased with cellulose ether methoxyl content and with the presence of glycerol. Emulsion MX showed the lowest thermal stability. Heating the MX cellulose emulsion caused syneresis, fat flocculation and the appearance of particle size polydispersity, indicating lower thermal stability and lower thermal reversibility. The different viscoelastic properties and thermal stabilities obtained by varying the type of cellulose, both with and without glycerol incorporation, increase the number of possible food applications where the emulsions could be employed as suitable fat replacers. Whether higher or lower emulsion thermal stability is more or less convenient for a specific food application is a future topic of study.

1. Introduction

The development of new foodstuffs is mainly driven by consumer demand for healthy products. On the topic of fat containing products the interest is focused on fat reduction, but more importantly on improving the quality of the employed fat, which implies trans-fatty acid elimination and saturated fat reduction.

Trans-fatty acids have been shown to increase levels of "bad cholesterol" low-density lipoprotein (LDL) and decrease levels of "good cholesterol" high-density lipoprotein (HDL). Trans-fatty acids also interact with proper metabolism development. Saturated fatty acids have been shown to increase LDL levels without changing HDL levels. While the debate regarding the exact health effects of these fatty acids (particularly saturated fatty acids) is unsolved, what is clear is that food manufacturers have initiated a trend of moving away from ingredients containing saturated fatty acids and trans-fatty acids on the basis of consumer demand (Co & Marangoni, 2012).

The reduction and/or elimination of saturated and trans-fatty acids from diets constitutes a difficult task for food manufacturers. A lot of functionality is only possible due to the presence of the aforementioned fatty acids. In bakery products, one example is the shortening power (prevention of gluten network formation) of hardstock fats such as commercial shortenings, butter and lard. The shortening power of such hardstock fats is attributable to their physical properties, particularly their plasticity and elasticity (Ghotra, Dyal, & Narine, 2002). The plasticity of such fats allows them to coat gluten particles and prevent the cross-linking of gluten proteins, thus resulting in a short and crumbly texture. Another function of the solid-like elasticity and oil-binding capacity of the fat is to prevent the liquid triacylglyceride phase of the fat from "seeping" into the dough. Also, the solidity of the fat allows it to form a barrier between dough sheets. This laminating action makes products such as croissants and Danish pastries possible.

Fats with low percentages of saturated fatty acid, such as olive oil or sunflower oil are liquid at ambient temperature and cannot accomplish the structural functions associated to solid fats.

One way to confer semi solid structure to liquid oils without generating trans-fatty acids or increasing the saturated fatty acids is to incorporate them in a cellulose ether emulsion. Emulsions composed of vegetable oil, water and a cellulose ether, (methylcellulose (MC) or hydroxypropylmethylcellulose (HPMC)), possess a semisolid consistency and have been found suitable to completely replace traditional shortening in biscuits while obtaining good

* Corresponding author.
E-mail address: tesanz@iata.csic.es (T. Sanz).

http://dx.doi.org/10.1016/j.foodhyd.2014.11.030
0268-005X/

sensory acceptability (Tarancón, Fiszman, Salvador, & Tárrega, 2013; Tarancón, Sanz, Fiszman & Tárrega, 2014; Tarancón, Sanz, Salvador & Tárrega, 2014). The emulsion confers appropriate texture and rheological properties to the dough, thus allowing biscuit manufacture and the obtention of suitable sensory properties. The gelation thermal properties of the cellulose ethers may explain their better performance as fat replacers in comparison to other approaches.

The use of cellulose emulsion could be extended to other food products. According to Dow manufacturers the use of Methocel MX emulsions as replacers of solid saturated fats in meat products, confer the expected juicy, succulent and firm bite.

In general, its suitability as fat replacer will depend on the emulsion performance at different stages during the food manufacture process, as well as, on the interactions with the other ingredients in the food items.

Cellulose is a hydrophilic compound, but cellulose fibres contain crystalline ordered regions formed by intra- and intermolecular hydrogen bonds, which make cellulose not soluble or swellable in water. Introducing hydroxypropyl or methoxyl substituents along the anhydroglucose backbone help break down its crystallinity. Despite the fact that methyl and hydroxypropyl moieties are hydrophobic groups, the polymer retains enough hydrophilicity to be highly water soluble. Introduction of these hydrophobic groups gives the polymer surface activity and unique hydration-dehydration characteristics (Sarkar, 1979).

Methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) ethers possess the unique property of reversible thermogelation. In solution form these polymers are completely hydrated and there is little polymer−polymer interaction other than simple entanglement. As the temperature is increased, an initial drop in viscosity is observed due to the decrease in hydration water. When critical temperature is reached, sufficient dehydration occurs to promote polymer−polymer interactions instead of polymer−solvent interactions. As a consequence, these cellulose ether solutions start to gel. Upon cooling, the gelation process is completely reversed and the gel formed will revert to sol state, recovering its original consistency. The temperature at which the gelation process starts and the strength of the gel formed depends on the type and degree of substitution of the cellulose, molecular weight and concentration and presence of electrolytes (Nishinari, Hofmann, Moritaka, Kohyama, & Nishinari, 1997; Sarkar, 1979).

Glycerol (also known as glycerin) is a polyol (1,2,3-propanetriol), naturally present in the structure of triglycerides, which are fatty acid esters of this alcohol. Three hydroxyl groups in glycerol are responsible for its solubility in water and its hygroscopic nature. In the food industry it is mainly employed as humectant, thickener, lubricant, sweetener or anti-freezer, among other uses. It is used in commercially prepared low-fat foods such as cookies, where it acts as a humectant, keeping cookies fresh, and as a thickening agent in liqueurs. As used in foods, glycerol is categorized by the American Dietetic Association as a carbohydrate. Glycerol has a caloric density similar to table sugar, but a lower glycemic index and different metabolic pathway within the body, so some dietary advocates accept glycerol as a sweetener compatible with low carbohydrate diets (Pagliaro & Rossi, 2008).

The objective of this work was to evaluate the thermorheological properties, microstructure and droplet size distribution of emulsions prepared with cellulose ethers with different chemical substitution and molecular weight and to evaluate the influence of the addition of glycerol, as a texture modifier. Emulsion properties were researched at ambient temperature, during heating and during heating and cooling (evaluation of thermo reversibility). The final aim of the research is to increase knowledge about emulsion thermal behaviour and to increase knowledge of the different textures that can be achieved with cellulose emulsions as a first step to better understanding their functionality and to increase their number of food applications as fat replacers.

2. Materials and methods

2.1. Emulsion preparation

The influence of glycerol was evaluated in emulsions prepared with three different cellulose types (F4M, A4M and MX).

Oil-water-cellulose ether emulsions were prepared with three different cellulose ethers with thermogelling ability supplied by The Dow Chemical Co. (F4M, A4M and MX). F4M and A4M have approximately the same molecular weight and differ in their chemical substitution, F4M is a hydroxypropyl methylcellulose and A4M is a methylcellulose. Cellulose MX is a methylcellulose with greater methoxyl substitution than A4M and higher molecular weight. Their specifications, as supplied by the manufacturer are as followed: F4M is a hydroxypropylmethylcellulose (29.0% methoxyl, 6.8% hydroxypropyl, viscosity of 4000 mPa s at 2% aqueous solution at 20 °C measured by The Dow Chemical Company following reference methods ASTM D1347 and ASTM D2363). A4M is a methylcellulose (30.0% methoxyl, viscosity of 4000 mPa s at 2% aqueous solution at 20 °C measured by The Dow Chemical Company following reference methods ASTM D1347 and ASTM D2363), and MX is a methylcellulose with lower gelation temperature than A4M (viscosity of 50,000 mPa s at 2% aqueous solution at 20 °C measured by The Dow Chemical Company following reference methods ASTM D1347 and ASTM D2363). 200 g of emulsion were prepared in each batch. The ingredients of the emulsion were sunflower oil with high levels of oleic acid (Carrefour, Madrid, Spain), water and the different cellulose ethers. Emulsions without and with glycerol were prepared. The proportions employed were sunflower oil 51%, cellulose ether 2% and water 47% for the emulsions without glycerol and sunflower oil 47.4%, cellulose ether 1.9%, water 43.7% and glycerol 7.0% for the emulsions with glycerol. The cellulose ether was first dispersed in the oil or oil/glycerol mixture using a Heidolph stirrer at the lowest speed for 5 min. The mixture was then hydrated by gradually adding the water at 1 °C while continuing to stir. A water temperature of 1 °C was selected according to the specific hydration requirement of cellulose MX ethers, and was also employed for celluloses A4M and F4M. The 200 g mixture contained in a 600 ml baker (10 cm diameter) was then homogeneized with an IKA T18 basic (Ultra-Turrax) with the dispersion tool S18N-19G (stator diameter 19 mm and rotor diameter 12.7 mm) at 6500 (1/min) during 15 s and subsequently at 24,000 (1/min) during 30 s.

2.2. Rheological behaviour

Small amplitude oscillatory tests were performed in a controlled stress rheometer (AR-G2, TA Instruments, Crawley, England) with the temperature controlled by a Peltier system. The rheometer was equipped with a 40 mm roughened parallel plate with a gap of 1 mm. The samples were allowed to rest in the measurement position for 10 min equilibration time. Each measurement was carried out 2 times with emulsions of different batches. To protect against dehydration, vaseline oil (Panreac, Spain) was applied to the exposed surfaces of all the samples.

Stress sweeps were carried out at a frequency of 1 Hz to measure the extent of the linear viscoelastic response.

To simulate the effect of heating in the emulsion structure, temperature sweeps were performed from 20 °C to 80 °C at a heating rate of 1 °C/min using the control strain mode of the rheometer. Besides, to study the thermo reversibility properties, a