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Influencing the crystallization behavior of binary mixtures of stearyl alcohol and stearic acid (SOSA) using ethylcellulose

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ABSTRACT

In the present study we have characterized the influence of the polymer gelator ethylcellulose (EC) on the crystallization behavior of mixtures of stearyl alcohol and stearic acid (SOSA). The presence of EC led to a more abrupt thermo-reversible crystallization process and an increase in the onset of crystallization temperature from 22.7 ± 0.35 °C to 26.5 ± 0.42 °C. X-ray analysis indicated that the polymorphism of the mixed SOSA crystals was maintained in the presence of EC; however, changes in the small angle region indicated the presence of the polymer network altered the higher-order organization of the crystal network. Significant changes in the microstructural organization were also observed by light microscopy. A random distribution of needle-like, oriented platelets were observed in SOSA gels, while branched, feather-like structures were apparent in the mixed EC/SOSA system. Temperature-sweep rheological experiments of the combined EC/SOSA system also indicated that prior to crystallizing, SOSA molecules plasticized the polymer chains, resulting in a decrease in the gelation point (cross-over point; $G' = G''$) from ~110 °C to 90 °C. This effect was corroborated by DSC experiments, in which it was observed that the glass transition temperature of EC decreased and broadened with increasing SOSA content. Back extrusion flow curves indicated that the addition of EC reduces the brittleness and increases the plasticity of the bulk material, as indicated by the brittleness factor quantified over the steady-state flow regime, even when the combined gelator system was substantially firmer. Although the presence of the EC network resulted in a stress overshoot during initial penetration, by incorporating EC below its critical gelation concentration eliminated the overshoot while still providing plasticity to the SOSA network, such that the flow behavior was shown to be comparable to several commercial margarines. This study has demonstrated the ability of EC to modify the crystallization behavior of a low molecular weight oleogelator, while increasing the plasticity of the polymer network, to form a synergistic oleogelator system.

1. Introduction

Fats are made up of a hierarchical three-dimensional network of crystalline triglycerides which immobilize the liquid oil component (Acevedo & Marangoni, 2010; Peyronel, Ilavsky, Pink, & Marangoni, 2014; Tang & Marangoni, 2006). These structures are responsible for many of the functional and desirable attributes of food products; however, such high melting point triglycerides are often rich in saturated and trans-fatty acids. Through recent decades, the over-consumption of saturated fats were thought to contribute to negative health effects, such as metabolic syndrome and pre- and type 2 diabetes (Bier, 2015). Recent research has indicated these fats may be more neutral in their impact on health (de Souza et al., 2014); however, the changing, and often contradictory information purveyed through public media has resulted in saturated fats having a negative stigma. Trans-fats, in particular, have come under heavy scrutiny in recent years, and are still universally believed to negatively impact human health (de Souza et al., 2014). As a result, the US FDA has recently imposed a ban on the use of partially hydrogenated oils, as these fats represent the main source of industrial trans-fats in the food chain. One common solution is to use palm oil or palm oil fractions with distinct melting ranges. However, the sustainable production of these fats and their high content of saturated fatty-acids may carry a negative consumer perception. For these reasons, food manufacturers are looking for new alternatives to replace traditional fats. Oleogels may provide one such alternative strategy to impart the desirable functional properties of such fats while eliminating trans-fats and greatly reducing the saturated fat content (Patel & Dewettinck, 2016; Wang, Gravelle, Blake, & Marangoni, 2016). Such

Abbreviations: CGC, critical gelation concentration; EC, ethylcellulose; SOSA, stearyl alcohol/stearic acid.

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systems benefits from the nutritional profile of the liquid oil which consist mostly of unsaturated fatty acids, with the solid texture arising from the formation of an oil-based gel.

The gelation mechanisms of edible oil gelators can generally be grouped into two broad categories. The first group describes the self-assembly of small molecules into a three-dimensional network. This can be achieved through the formation of a crystalline network akin to traditional fats, such as that observed in monoglycerides (Ojijo, Neeman, Eger, & Shimoni, 2004) and plant-based wax oleogels (Blake & Marangoni, 2015). Alternatively, some oleogelator molecules are able to structure oil via the formation of larger structures such as tubules, as seen in mixtures of phytosterols and oryzanol (Bot, den Adel, Roijers, & Regkos, 2009), or via one-dimensional fiber growth, which is observed in oleogels structured with 12-hydroxystearic acid (Co & Marangoni, 2012). The second category includes high molecular weight gelators, i.e. polymers. Polymers can form a gel network either via direct dispersion of the structurant in oil, or through a templating procedure to facilitate oil absorption. Ethylcellulose is the only known polymer which can be directly dispersed in oil (Dey, Kim, & Marangoni, 2011); however, it has recently been shown that certain hydrophilic polymers such as methylcellulose, or combinations of polymers including gelatin and xanthan gum, can been used to structure oil after employing a multistep templating procedure (Patel & Dewettinck, 2016). The major limitation in using oleogels in food systems has been in mimicking the functional properties of fats which are responsible for their unique texture and mouthfeel sensations. This process requires a level of understanding of the properties dictating these attributes which has perhaps only recently begun to be elucidated (Macias-Rodriguez & Marangoni, 2016; Peyronel et al., 2014). Additionally, the majority of known oleogelators have been discovered through serendipity, meaning researchers only have a limited set of tools available in terms of manipulating mechanical/textural properties to more accurately mimic the fats these gels are intended to replace.

One strategy which might be used to manipulate the structural arrangement, and thus the functional properties of oleogelator systems is by combining known gelators. In a recent study, it was demonstrated that the polar, surface-active molecules oleyl alcohol and oleic acid interact with the polymer gelator ethylcellulose (EC), enhancing the mechanical strength of the EC network (Gravelle, Davidovich-Pinhas, Zetzl, Barbut, & Marangoni, 2016). However, one of the first known oleogelator systems with potential food applications identified was mixtures of stearyl alcohol and stearic acid (SOSA; Gandolfo, Bot, & Flöter, 2004). Particularly, at a ratio of 7:3 SO:SA, these molecules were reported to produce a synergistic increase in gel strength associated with the formation of a network of needle-like mixed crystals (Gandolfo et al., 2004; Schaink, van Malssen, Morgado-Alves, Kalnin, & van der Linden, 2007). Therefore, the goal of the present work was to determine if introducing EC into the synergistic SOSA crystal network would influence the crystallization behavior of these small molecules, which may thus influence the physical properties of the resulting gel.

2. Materials and methods

2.1. Materials

Canola oil was purchased from a local supermarket (Costco Wholesale Canada, Ltd., Ottawa, ON, Canada). Ethylcellulose (45 cP; ETHOCEL™ STD. 45) was purchased from Dow Wolff Cellulosics (Dow Chemical Company, Midland, MI, USA). Stearyl alcohol (st-OH, or SO; 1-octadecanol; 95% purity) and stearic acid (st-acid or SA; 1-octadecanoic acid; 97% purity) were purchased from Acros Organics (Fisher Scientific, Ottawa, ON, Canada). Two commercial margarines were obtained from a local supermarket for comparison of flow behavior (see Section 2.7).

2.2. Preparation of oleogels

Oleogels were prepared with a total of 3 or 5 wt% SOSA (7:3 SO:SA) and each of these was prepared either with or without 6 wt% EC, for a total of 6 formulations. These formulations were selected to coincide with the minimum gelation concentration of each structurant (5 wt% and 6 wt% for SOSA and EC, respectively). With the exception of samples analyzed by small deformation rheology (see Section 2.6), the following preparation protocols were followed. Small samples (~15 g) were prepared in scintillation vials for X-ray and DSC analysis, as well as microscopy, while those intended for back extrusion were prepared in 100 g batches. Samples structured with only 7:3 SO:SA were prepared by combining the appropriate quantities of oil and structurant, and the mixture was heated in an incubator at 100 °C for 1 h to dissolve the SOSA and eliminate any effects of crystal memory. Samples intended for back extrusion were then mixed by hand with a glass stir rod and split between 3 polypropylene centrifuge tubes (Fisher Scientific), while those prepared in scintillation vials were then capped and inverted several times. Samples formulated with both EC and SOSA were prepared by first heating the oil/EC mixture on a benchtop hotplate under mixing until full dissolution of the polymer was achieved (sample temperature ~150 °C). At this point, the heat was reduced and the appropriate amount of SOSA was added. The sample was mixed for an additional 10 min, and subsequently poured into the appropriate vessel. With the exception of those tested by back extrusion, all samples were allowed to gel at room temperature overnight. Back extrusion samples were gelled at room temperature for ~2 h, and subsequently moved to a chilled incubator (~4 °C) for overnight storage. All samples were prepared in triplicate, and stored for a minimum of 1 day prior to analysis.

2.3. Differential scanning calorimetery (DSC)

Thermal behavior of the SOSA and EC/SOSA oleogels was evaluated using a Mettler-Toledo DSC 1 instrument (Mettler-Toledo, Mississauga, ON, Canada). A small sample of the previously prepared oleogels (~10 mg) was weighed into a 40 μl aluminum pan, which was then hermetically sealed. Experiments were performed using a 30–40 ml min^{-1} nitrogen flow rate and a 5 °C min^{-1} heating/cooling rate. Two heating/cooling cycles were performed on each gel: Samples were heated from 25 to 80 °C to melt the SOSA component of the composite gel, cooled to 0 °C, and this cycle was repeated from 0 to 80 °C and 80–0 °C. A 3 min isothermal equilibration step was used between each heating/cooling step. All measurements were repeated in triplicate.

An additional series of DSC measurements were conducted to investigate the effect of SOSA on the glass transition temperature (T_g) of EC. A series of samples were prepared containing ~6 mg of EC and increasing amounts of SOSA. A single stock of pre-made SOSA was prepared, melted, and re-crystallized to improve reproducibility. Samples were prepared with 0, 0.5, 1.0, 1.5, and 2.0 mg SOSA. Higher concentrations were not investigated, as the T_g was no longer detectible. A single heating/cooling cycle was performed on each gel, heating from 25 to 150 °C, and subsequently cooling to 0 °C after a 3 min isothermal equilibration step. A reference sample containing ~6 mg EC and 1.0 mg SOSA was run through three heating/cooling cycles to ensure reproducibility of the T_g.

2.4. X-ray diffraction (XRD)

Wide-angle X-ray diffraction patterns were collected using a Multiflex powder X-ray diffractometer (Rigaku MSC Inc., Toronto, ON, Canada). Oleogels were prepared prior to analysis on a benchtop hot plate, as described above. The molten gels were then poured directly onto a textured, square-welled glass sample holder and allowed to gel at room temperature. The X-ray source employed was a copper X-ray tube (CuKα1; $\lambda = 1.54$ Å) operating at 40 kV and 44 mA. Spectra