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The emulsion crystallization of hydrogenated castor oil into long thin fibers

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ABSTRACT

The present study discusses the optimal crystal growth conditions required for the emulsion crystallization of hydrogenated castor oil (HCO) into several crystal morphologies. The best possible crystal shape is furthermore identified in case high rheology modifying performance is required. HCO was crystallized in a meso- and micro-continuous process which allowed for a controlled and fast screening of several crystal morphologies at different crystallization conditions. Applying high isothermal temperatures (above 55 °C) resulted in a combination of rosettes, thick fibers and thin fibers. At lower isothermal temperatures (below 55 °C) the shape gradually evolved to a combination of short needles, spherically shaped and/or irregularly shaped crystals. Crystals with the highest aspect ratio were obtained when crystals were grown between 30 °C and 45 °C and were subsequently reheated above 63 °C, forming high amounts of large thin fibrous crystals. When diluted to 0.25 wt% these fibrous crystals increased the low shear viscosity far better compared to the other crystal shapes.

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1. Introduction

The crystallized form of hydrogenated castor oil (HCO), a triacylglycerol (TAG) [1], plays a crucial role as a rheology modifier in many household products and cosmetics. These TAG crystals are appealing because they provide a pseudoplastic behavior, increase the low shear viscosity and act as a stabilizer, thereby preventing physical separation, at relatively low concentrations. The ability of fats to structure and stabilize is also frequently applied in the food industry [2]. When a TAG or any other material is used as a structurant, parameters such as the aspect ratio of the molecules, crystal shape, molecular forces, volume fraction, size- and shape distribution, and the bulk flow field will play a crucial role in obtaining the best structuring characteristics. An example of this can be found in the literature for 12-hydroxystearic acid where the crystalline network significantly impacts the oil binding capacity and elasticity [3–5]. The present paper will focus on identifying the different crystal shapes and the optimal process conditions when crystallizing HCO in oil in water (O/W) emulsion, the polymorphism of each shape is determined and the low shear

viscosity increase at low concentrations is presented for each shape.

Triacylglycerols tend to crystallize in typically three different configurations or polymorphs, depending on the positioning of the three acyl groups. The three most common polymorphs are α , β' and β , although more polymorphisms are known to exist [6–8]. Each polymorph crystallizes in a preferred morphology (or shape) and these shapes are determined by the relative growth rate of the different crystal surfaces. In most cases, TAG's crystallize as spherulites which consist of a sphere from where needle like crystals form from the center [9]. Other known morphologies are needle shaped in the β configuration and an amorphous mass of very tiny crystals in the α configuration. According to [10,11], HCO has typically one of the 3 morphologies: fibers, rosettes and irregularly shaped crystals. A rosette, similarly to a spherulite, consists of a sphere where fiber crystals form from one central point or interface. A combination of rosettes and fibers was obtained when the O/W emulsion was cooled slowly or at high isothermal conditions. More irregularly shaped crystals were formed when the cooling rate was increased or at relatively low isothermal temperatures. These crystal shapes were only obtained when a high amount of surfactant was added to the aqueous phase. The reason for this is not yet clear but numerous effects of surfactant on the crystallization of TAG's have already been reported extensively [12,13].

In the present work the emulsion crystallization was carried out in a micro- and meso-scaled continuous process enabling

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small emulsion sizes, a fast temperature response, and uniform temperature profiles. A micromixer was used to emulsify 4 wt% HCO with an aqueous solution containing an ionic surfactant. Coils provided the necessary residence time for the crystallization. This allowed for the identification of more precise temperature ranges in which the different morphologies are favored. The crystal shapes obtained after each crystallization protocol were characterized by light microscopy and atomic force microscopy (AFM). The crystal polymorphs were studied by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Last the low shear-viscosity increase obtained for a typical example of these morphologies was compared.

2. Materials and methods

2.1. Hydrogenated castor oil (HCO) and monoethanolamine linear alkylbenzene sulfonate

The hydrogenated castor oil used in these experiments was a standard factory product supplied by Brasil Olea de Mamona Ltda, BOM (Bahia, Brazil). Monoethanolamine linear alkylbenzene sulfonate (MEALAS) solution was manufactured by Procter and Gamble, P&G (Strombeek-bever, Belgium), containing 16.7 wt% HLAS (linear alkylbenzene sulfonic acid), 3.34 wt% MEA (monoethanolamine) and 79.96 wt% water.

2.2. Meso- and micro-scale continuous process for the production of HCO crystals

Hydrogenated castor oil (HCO) was crystallized with a meso- and micro-scale continuous process. This continuous process contained 2 steps: a mixing step and a crystallization step. In the first step 96 wt% of a MEALAS solution was mixed with 4 wt% hydrogenated castor oil above 86 °C, this is to allow melting of HCO and to avoid clogging. To generate sufficiently small oil droplets, a continuous meso- and micro-setup with an 11 step split and recombine mixer with an inner diameter of 0.6 mm was used (Ehrfeld, Wendelsheim, Germany). To provide sufficient residence time for the crystallization step, metal hoses from Swagelock (Ohio, USA) were used as residence time units, which were held at the crystallization temperature by immersing them in warm water baths (Fig. 1). Fast cooling was possible with 1/8 in. coils. For relatively large residence times, 3/8 in. coils were used to avoid reaching the upper limit of the pumps (30 bar). The crystallization kinetics of non-isothermal crystallization conditions was studied by differential scanning calorimetry (DSC), similar as in [10]. The residence time of the crystallization was based on the obtained residence time through DSC. The total flow rate during the emulsification and the crystallization was respectively 10 kg/h and 1.2 kg/h. This setup was chosen because of the need for fast

cooling and heating. To eliminate further re-crystallization or post crystallization phenomena, the crystallized HCO was immediately cooled down to room temperature and stored at 20 °C. The stability of the crystals was followed by measuring the viscosity over time.

2.3. Polarized light microscope (PLM) and atomic force microscopy (AFM)

The crystal microstructure was imaged by a polarized light microscope. The microscope was equipped with a digital camera controlled by an imaging control software. The objective had a magnification of 100 or 50 times and the ocular had a magnification of 10 times. For AFM a single side polished Si wafer (<100>, 381 μm thick, 2 nm native oxide, sourced from IDB Technologies, UK) was first cracked or cut into a piece of approximate dimensions 20 × 20 mm². The aqueous structuring premix was applied to the Si wafer, using a cotton bud (Johnson & Johnson, UK). The paste-coated wafer was placed into a lidded poly(styrene) Petri dish (40 mm diameter, 10 mm height, Fisher Scientific, UK) and left for 5 min in air under ambient conditions (18 °C, 40–50% RH). The Petri dish was then filled with H₂O (HPLC grade, Sigma-Aldrich, UK) and the sample was left in the immersed conditions for approximately 1 h. Following this, a cotton bud was used to remove the paste which has floated up away from the Si wafer surface, whilst the Si wafer was still immersed under HPLC grade H₂O. The Si wafer was then removed from the Petridish and rinsed with HPLC grade H₂O. Subsequently, the Si wafer was dried in a fan oven at 35 °C for 10 min. The wafer surface was then imaged as follows: the Si wafer was mounted in an AFM (NanoWizard II, JPK Instruments) and imaged in air under ambient conditions (18 °C, 40–50% RH) using a rectangular Si cantilever with pyramidal tip (PPP-NCL, Windsor Scientific, UK) in intermittent contact mode. The image dimensions were 20 μm × 20 μm, the pixel density was set to 1024 × 1024, and the scan rate was set to 0.3 Hz, which corresponds to a tip velocity of 12 μm/s.

2.4. Rheometer

The viscosity of the crystallized hydrogenated castor samples was measured on an Anton Paar MCR 302 rheometer (Anton Paar, Graz, Austria) using a cone and plate geometry with a gap of 206 μm and an angle of 2°. Because of the shear thinning behavior of crystallized hydrogenated castor oil the viscosity was measured at different shear rates varying between 0.01 s⁻¹ and 70.00 s⁻¹, in order from low to high shear rates because high shear rates can cause damage to the crystals. For the lower shear rates a constant shear rate was held until a steady state viscosity was reached, above 0.1 s⁻¹ the viscosity was measured with one measurement of 10 s. All measurements were done at 20 °C. The stability of the HCO crystals was assessed by measuring the viscosity over a period of 2 months.

2.5. Differential scanning calorimetry (DSC)

A TA Q2000 differential scanning calorimeter (TA Instrument, New Castle, DE) was used to characterize the thermal behavior during the melting process of HCO crystals. An empty hermetically anodized aluminum pan covered with a lid was used for baseline calibration. Approximately 5 mg samples were introduced into the DSC hermetically sealed anodized aluminum pans. The melting curve was obtained by heating a crystallized sample to 95 °C at a rate of 3 °C/min. Measurements were done on crystallized HCO samples obtained from the crystallization carried out in the meso- and micro-scaled continuous process. These samples were stored

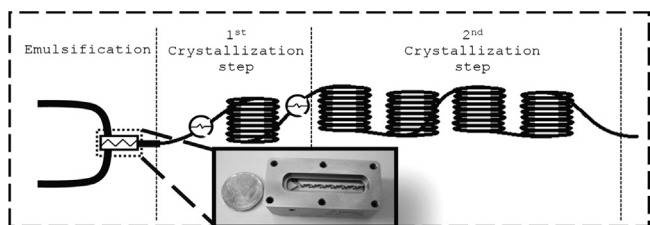


Fig. 1. Schematic presentation of the meso- and micro-scaled continuous process. An oil phase is emulsified with an aqueous phase by an 11 steps split and recombine mixer with an inner diameter of 0.6 mm. The O/W emulsion is then cooled down as fast as possible and held for a period of time at a fixed temperature to induce the necessary nucleation/growth. The third step is optional. This step enables the crystallization to continue at a much higher temperature as that applied during the second step.

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