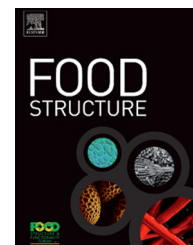


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# Plant wax crystals display platelet-like morphology



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## ABSTRACT

Cryogenic scanning electron microscopy was used to image de-oiled 2% rice bran wax, sunflower wax, and candelilla wax oleogels. Contrary to previous reports on the morphology of plant-based waxes, all three species appear as platelets. These findings contest previous theories about the dependency of oil gelation on a needle-like morphology and development of an entangled network, and suggest that surface effects such as surface area and surface roughness may contribute to oil binding capacity.

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## 1. Introduction

The physiochemical properties of plant-based waxes and their respective oleogels have been studied by several groups in recent years. Early work conducted by Dassanayake et al. established that the minimal wax concentration required for oil gelation, i.e., the critical concentration, of rice bran wax (RBX) was 1% (w/w), while that of candelilla wax (CLX) and carnauba wax (CRX) were 2% and 4% (w/w), respectively (Dassanayake, Kodali, Ueno, & Sato, 2009). They attributed these differences to the morphology of each wax, concluding that RBX's needle-like crystals, observable using optical light microscopy, formed an entangled gel network that is capable of entrapping large amounts of liquid oil. Thus, less wax was required to gel oil compared to a wax of with a non-needle-like morphology.

Additional findings obtained by X-ray diffraction studies indicated that the chemical homogeneity of RBX crystals allows for efficient molecular packing in an  $O_{\perp}$  subcell

arrangement, and results in singular and narrow endothermic and exothermic peaks when analyzed by differential scanning calorimetry. In comparison, CLX and CRX display multiple broad peaks due to the presence of a variety of non-ester components with different melting and crystallization temperatures.

Work by Toro-Vazquez et al. provided further insight on the effects of minor components on the crystal morphology of CLX (Toro-Vazquez et al., 2007). During cooling, these minor components, predominantly comprised of n-alkanes nonacosane and tritriacontane, form mixed molecular structures with the major alkane component, hentriacontane. This interaction affects molecular packing, resulting in the formation of smaller crystals described as spherulitic and worm-like (Blake, Co, & Marangoni, 2014; Dassanayake et al., 2009). Unlike RBX, these crystals are not capable of forming an entangled crystalline network in oil, and thus were previously regarded as less efficient gelator species.

To ascertain the effect of wax crystal morphology on oleogel functionality, we compared the oil binding capacity of

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RBX, CLX, and CRX oleogels in a previous study (Blake et al., 2014). We found that CLX oleogels exhibited higher oil binding capacities compared to RBX, despite their spherical morphology (Blake et al., 2014). We believe that this is due to the high surface area of CLX crystals, which may allow for greater quantities of oil to adsorb onto wax surfaces. In addition, CLX crystals were highly dispersed throughout the oil phase, reducing pore area and increasing the tortuosity of the network compared to a network comprised of larger pores and less homogeneously dispersed RBX crystals. The latter network would have less wax surface area and larger pore areas, allowing oil to escape the network more easily.

The focus of more recent studies has shifted to the crystal habits of these waxes when exposed to external factors such as shear and cooling rate. Morales-Rueda et al. found that faster cooling rates resulted in the development of less organized rotator phase species with poorly structured junction zones (Morales-Rueda, Dibildox-Alvarado, Charó-Alonso, Weiss, & Toro-Vazquez, 2009). Faster cooling also resulted in the formation of smaller crystals. This caused an increase in the elastic modulus of CLX gels. Similarly, Hwang et al. reported that an increase in cooling rate yielded smaller SFX crystals, producing a firmer gel (Hwang, Kim, Singh, Winkler-Moser, & Liu, 2011). These works demonstrate how cooling rate can be used to tailor the network microstructure, and in turn, the mechanical properties of a gel.

In other studies by Alvarez-Mitre et al. and Chopin-Doreto et al., they found that shearing CLX gels to pre-nucleation metastable conditions promotes the formation of flow-induced mixed molecular packing structures (Alvarez-Mitre, Morales-Rueda, Dibildox-Alvarado, Charó-Alonso, & Toro-Vazquez, 2012; Chopin-Doroteo et al., 2011). These structures influence the nucleation and crystallization kinetics during subsequent cooling stages, significantly altering the microstructure. The authors concluded that shearing not only increases crystal size, but also encourages meshing between plates, altering the ratio between transient junction zones and permanent junction zones compared to statically cooled samples. However, this was dependent on the extent of shearing. Shearing to metastable conditions, defined by the authors as 10 °C above the crystallization temperature of CLX, prevented crystal breakage and allowed for the development of permanent junction zones, while shearing to nucleation may have imparted some damage to a developing network that began forming during the nucleation stage.

From a review of this body of work, it is clear that the morphology of the wax crystal network is a significant contributor to the physiochemical properties of wax oleogels. Thus, it is essential that a sound understanding of the crystal habits of these gelators (and the effect of these habits on gel functionality) is acquired. The most common means of studying wax morphology is optical light microscopy. However, the resolution and length scale of this technique are limited. This is a particular concern for CLX crystals since their dimensions are below 10  $\mu\text{m}$  and therefore difficult to clearly image using optical light microscopy. The abundance of liquid oil surrounding the network also diminishes the quality of the image, further obscuring the microstructural features of the solid phase and making it difficult to distinguish them from the solvent (oil) phase.

In short, optical light microscopy cannot provide a comprehensive depiction of wax crystal morphology. This represents a challenge, since such fundamental knowledge is a prerequisite for understanding the relationship between network microstructure and gel functionality. For this reason, cryogenic scanning electron microscopy (cryo-SEM) was used to image RBX, SFX, and CLX gels. The goal was to determine the shape of wax crystals that comprise gel networks, and to compare these findings to those previously obtained using optical light microscopy (Blake et al., 2014).

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## 2. Materials and methods

### 2.1. Gel preparation

Wax oleogels were prepared by depositing solid wax into a 15 mL glass vial containing peanut oil so that the wax comprised 2% of the total mix (w/w). The wax-oil mix was placed in a 90 °C oven for 30 min, allowing the wax to completely melt. The molten gels were then cooled at room temperature (23 °C) for 24 h.

### 2.2. Solvent removal

SEM samples were prepared by placing a known amount of gel (less than 100 mg) on a 1 cm  $\times$  1 cm sheet of polycarbonate paper containing 0.4  $\mu\text{m}$  pores (Poretics, AMD Manufacturing Inc., Mississauga, Canada). This paper was stacked on top of a piece of Whatman 1 filter paper cut to the same dimensions. The papers were weighed before and after gel deposition so that the weight of the gel and the amount of oil present in the sample could be calculated. Isobutanol was then used to remove the oil phase (Rogers, Smith, Wright, & Marangoni, 2007) by dripping it over the sample gradually. The oil:solvent ratio used was 1:25 (w/w). The de-oiled gel was allowed to dry for 48 h before imaging to ensure that all of the solvent had evaporated.

### 2.3. Cryogenic scanning electron microscopy sample preparation

The gel-loaded filter papers were glued to the surface of a copper holder using Tissue-Tek O.C.T. Compound (Canemco Supplies, St. Laurent, Quebec, Canada). The copper holder was designed for use for the Emitech K1250X Cryo-preparation unit (Ashford, Kent, UK). The copper holder was then plunged into liquid nitrogen (–210 °C), immobilizing the wax crystals in the residual oil phase. Following the freezing procedure, the copper holder was returned to a sample preparation chamber, placed under vacuum, and manually fractured. The sample was then sputter coated with 30 nm of gold and transferred to the SEM unit (Hitachi S-570, Tokyo, Japan), which was also under vacuum. Samples were imaged using an acceleration voltage of 10 kV. Quartz PCI imaging software version 8 (Quartz Imaging Corp., Vancouver, BC) was used to capture digital images of the samples.

2% CLX gels that did not undergo the solvent removal process were first imaged to determine the necessity of the solvent removal, sublimation, and the freeze-fracture

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