Advanced Powder Technology xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

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

Original Research Paper

On the properties and application of beeswax, carnauba wax and palm fat mixtures for hot melt coating in fluidized beds

M.G. Müller *, J.A. Lindner, H. Briesen, K. Sommer, P. Foerst

Technical University of Munich, Chair of Process Systems Engineering, Gregor-Mendel-Straße 4, 85354 Freising, Germany

ARTICLE INFO

Article history:
Received 14 August 2017
Accepted 21 December 2017
Available online xxxx

Keywords:
Hot melt coating
Crystallization
Wax and fat mixture properties
Wurster coater
Fluidized bed coating

ABSTRACT

Coating of particulate solids is a well-known process within the chemical, pharmaceutical and food industry. Most of these industries use it to achieve a defined product behavior. Melt-coatings, in this paper beeswax, carnauba wax and palm fat, are more difficult to apply compared to solvent-based coatings because of the complex solidification behavior.

This contribution focuses on the experimental investigation of the crystallization process. The thermal crystallization behavior of mixtures of beeswax, carnauba wax and palm fat is investigated to determine the processability and the achievable coating quality prior to lab trials. Mixing of the melts results in a broadening of the crystallization temperature range, making the process more challenging. The rheological behavior in the phase transition of different mixtures shows a rather sudden change in the flowability contrary to the extended thermal solidification. The sudden change is a consequence of the linking of the appearing crystals, which was visualized at different solidification temperatures by polarization microscopy. The Martens hardness of the solidified material was adjusted by blending between 2 and 17 N/mm^2. The coating was applied in a lab-scale fluidized bed based on parameters determined from the characteristics. A micro-computed tomography image shows a closed coating of varying thickness. It was possible to predict the coating process with these natural products out of the material properties, and adapt them by blending. Furthermore the results of this contribution show that there is a gap between the pure processabilty and the achievable coating quality.

1. Introduction

Fluidized bed based processing of particulate solids is an option for coating in the pharmaceutical, fine-chemical and food industry [1–3]. Film coating represents an essential processing step in the formulation of pharmaceutical, chemical and food applications [4–7]. One of the intentions of this processing is to alter the surface properties of the core material like taste masking, mouth-feel, color and texture or additional physical or chemical functionality [8,9]. Another target is the protection or controlled release [10,11]. For this purpose a thickness of 0.5–50 μm is necessary [12]. The processing steps can be done under favorable heat- and mass transfer conditions in a fluidized bed reactor batch-wise or continuously [13–15]. The coating-film, which is applied on the particle, is a solvent based polymer solution (aqueous or organic) or a solventless coating [16].

The parameters in the existing processes are often chosen based on experience. The operating conditions influence the growth rates and the mechanisms behind [17]. It is possible to monitor influencing factors in the process to control it [18]. Different parameters influence both solvent-based and hot melt coating processes like particle motion, atomization, drying, film formation, layering and inter-particle agglomeration [5,19]. The particle size does not change much in melt granulation, as long as agglomeration is avoided [20]. Critical for homogeneous coating is the achievable droplet size especially for small particles. The droplet size should be 5–10 μm [5]. The size of the sprayed droplets can be adjusted by the nozzle type and parameters [21], but is a challenge for high-viscosity media. Solvent-based coatings are dominant in industrial application over hot melt coatings. There are several disadvantages to solvent-based coatings though:

- In case of a non-water solvent, its removal from the exhaust gas might be necessary and its hazardous potential to the product might be an issue. In case of water-based solvent, the water vapor barrier of the water-soluble coating is less efficient compared to fat-based coatings.

* Corresponding author.
E-mail address: m.g.mueller@tum.de (M.G. Müller).

https://doi.org/10.1016/j.apt.2017.12.020

- Additionally, solventless processing needs only to transfer crystallization energy of the melt instead of a solvent in higher concentration, the processing times are hence shorter and energy consumption is lower compared to the solvent-based approach, making it interesting for low-cost applications [22]. Another advantage is the lack of a mass-transfer limitation.

For solvent-less coating processes there is a lack of knowledge of the process-influencing material properties, especially with food-grade materials. The process is more difficult to realize because of the need of a heated coating feed, the high agglomeration tendency [23] and the complex crystallization behavior of many hot melt coatings [24,25]. Instead of a single crystallization point, materials solidify over a temperature range. Because of the additional challenge, hot melt coatings are used rarely in industry. Up-scaling of hot-melt processes for pharmaceuticals to production scale similar to solvent-based coating is possible based on models, Kulah showed that a transfer from 20 to 200 kg product is possible easily for hot melt coatings [26].

Widely used materials are high-molecular-weight compounds such as polyethylene glycols, silicones, paraffins etc. [27]. Coating with lipid excipients requires understanding the physicochemical properties and effects on drug-release, which were investigated by [28].

An exemplary application of hot melt coating is the extension of shelf-life of egg-plant fruits by carnauba wax [29]. Another application of Carnaubawax coating is the improvement of flow and tabletability of mini-tablets [30]. The objective of this contribution is to link material specifications with the coating process. The materials used are beeswax, carnaubawax and palm fat for use as food-grade melt coatings. The presented data and approach may be used as a guideline for the characterization and use of melt coatings.

The estimation of the coating quality can be performed by micro-computed tomography. This was done e.g. by Perfetti to characterize morphology and thickness [31], Sondej analyzed as well the thickness distribution [32].

1.1. Biopolymers used for solventless coating

In solventless coating applications the hydrophobic coating material needs to meet several requirements [33]:

1. No physical or chemical degradation at temperatures below 200 °C;
2. Melting point in the 75–80 °C range for processing at common temperatures;
3. Melt transition over a narrow temperature range and no softening before melting for a defined crystallization;
4. Thermal behavior in the range of 30–200 °C independent of the preparation, storage conditions and thermal history;
5. No crystal modification when subjected to temperatures as high as 200 °C;
6. Stable without degradation when subjected to repeated-cooling cycles;
7. Available in varying hydrophilic-lipophilic balance (HLB) values to adapt to different core materials for homogeneous spreading;
8. Low melt viscosity for easy flow and spraying.

These requirements are fulfilled for most hydrophobic coating materials in the pharmaceutical and chemical industry. In the food industry, depending on special regulatory and lowcost requirements, the usable materials for solventless coating applications are restricted to natural, non-fossile waxes and fats/oils. Most of these materials do not meet the above requirements. Firstly, these natural materials represent a complex mixture of different substances from different chemical classes, and since they are a natural product their composition varies by geographical origin, source (animal/vegetable) and even seasonal variations [34–38]. Secondly, the established methods to characterize coating materials are mostly focused on solvent-based coatings and the solventless coatings meeting the requirements stated above [39–43]. Natural fats and waxes or biopolymers require a new approach to describe the material behavior for coating applications.

1.2. Micro scale effects of biopolymers

Marangoni, Acevedo and Narine [44–46] described the microscale effects depending on temperature changes. Most of the effects observed during the handling and processing of natural biopolymers are based on the microstructure of the different polymers.

- The macroscopic effects (size > 0.2 mm), which can be examined by rheology, mechanical testing and sensory impressions is based on the micro- and nanostructure.
- The microstructure (0.5 mm – 200 μm), which consists of the crystal clusters and the crystal network, can be classified by the solid fat content (SFC) and the mesocrystal size and shape.
- The nanostructure (0.4 nm – 500 nm) consisting of the Triacylglycerolmolecules and the Nanoplatelets is experimentally accessibly by investigating the molecular structure, polymorphism and nanocrystal size.

These three structural levels depend on each other. Depending on the molecular structure and the applied cooling rate, the other structural levels are influenced [47–49]. For coating applications the composition of the applied coating is defined, so the most crucial effect on the material is the applied temperature. As a consequence, in this work the crystals were visualized by polarization microscopy and and the observations are linked with the rheological and thermal behavior.

2. Materials and methods

The experiments were conducted at least three times. The statistical analysis was done with confidence intervals with $\alpha = 0.95$ based on the Student's t-distribution.

2.1. Thermal characterization by Differential-Scanning calorimetry (DSC)

The thermal characterization was done in a DSC 200 F3 Maia® (Netzsch, Selb, Germany) with liquid nitrogen cooling. For each measurement 11 mg ± 1 mg were weighted into aluminium crucibles with 6 mm diameter and 40 μl Volume. After sealing with an aluminium lid and pinching a hole in the lid, the samples were measured under nitrogen atmosphere to avoid oxidation.

The applied temperature program consists of two phases. In the first phase the sample preparation and elimination of the crystal memory takes place. In this segment the samples were heated to 106 °C at a heating rate of 10 K/min. The temperature was kept constant for 10 min and subsequently the samples were cooled to −60 °C at 10 K/min. After another 10 min isothermal relaxation the sample was heated again to 106 °C before the measurement phase started. In the measurement phase the temperature was cooled from 106 °C to 0 °C at a cooling rate of 10 K/min, then a 10 min isothermal relaxation took place before reheating at 10 K/min to 106 °C. The measurement procedure was repeated three times. The result is shown as solid fat content (SFC), i.e. iso-lines show the proportion of solidified material to the total amount of

Please cite this article in press as: M.G. Müller et al., On the properties and application of beeswax, carnauba wax and palm fat mixtures for hot melt coating in fluidized beds, Advanced Powder Technology (2018), https://doi.org/10.1016/j.apt.2017.12.020