



Rheological characterization and simulation of chitosan-TiO₂ edible ink for screen-printing

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ABSTRACT

Traditional ink owning harmful components has caused many problems, so this paper developed chitosan-TiO₂ edible inks and used it as the model to study the relationship between rheology and printing, for better development of edible inks. Rheological properties and the corresponding fitting were investigated. The developed ink exhibited non-Newtonian behavior, shear-thinning behavior, and temperature-dependent properties. Shear strain, frequency and temperature had great impact on modulus of inks. Low $J(t)$ (compliance) values reflected strong material structure and the related final recovery ratio attained 65.9%. Based on the fitting results, the screen-printing simulation were further researched for closer practical application. The recovery rate reached 55% with high initial recovery coefficient ($K_3 = 10.7$), indicating that the ink recovered sooner to the high viscosity after the shear was released and was suitable for printing. The ink was also printed on coated paper. Fastness was up to 91% and scratch resistance achieved H. The print effect on black cardboard and PET film was also excellent. The prepared edible ink provides a novel alternative to traditional ink and holds great potential in printing industry, especially on food.

1. Introduction

Edible-ink printing on edible products, including food and medicine, draws attention from many industries [1–5]. It can greatly reduce the pollution of the traditional ink for edible products and promote the products to be more distinctive and attractive. But the application of edible ink on the market at present is small. The main reason is that the corresponding edible-ink technology is not very mature now. Resin and colorant need to be expanded and the application research needs to be deepened.

To ensure the dispersion of pigment in ink, the resin is of vital importance. Chitosan, a linear polysaccharide with amino-group and hydroxyl-group, has been widely used in food [6–8]. It can be dissolved in dilute acid solutions and form solutions with certain viscosity. It can act as resin of edible inks because of its compatibility, edibility, film-forming ability, wide source and biodegradation [9–13]. It can also adjust the chitosan-based ink to different printing ways. In this study, a composite ink with chitosan and TiO₂ was developed. Edible pigment TiO₂, with non-toxicity, excellent whiteness and great brightness, is one of the best white pigments. TiO₂ has been used in many consumer daily products, including not only cosmetics (e.g., sun block), but also food and various medical products [14–19].

In our previous work, we have researched and prepared edible inks

based on chitosan and edible pigments [20,21]. However, the rheology characterization did not involve in linear and non-linear fitting that could make the obtained ink closer to industrial production. Herein, a chitosan-TiO₂ composite ink was developed and used as model to study the rheological properties and simulation. Though there are studies about chitosan-TiO₂ nanocomposite [22,23], the composite ink made from chitosan and edible pigment TiO₂ is rarely researched. The stabilizer is an indispensable part for sustaining stability of ink. Tween 80 and methylcellulose, common stabilizer used in food, have advantages like low cost and easy access. Thus, this paper prepared chitosan-TiO₂ composite edible inks with Tween 80 and methylcellulose separately, explored the properties, and then screen-printed the ink on the substrates (in Scheme 1). The obtained inks were characterized in terms of rheological properties, SST, and screen-printing quality. The relationship built between rheology and printing would be promising in significantly promoting the development of ink industry and printing field.

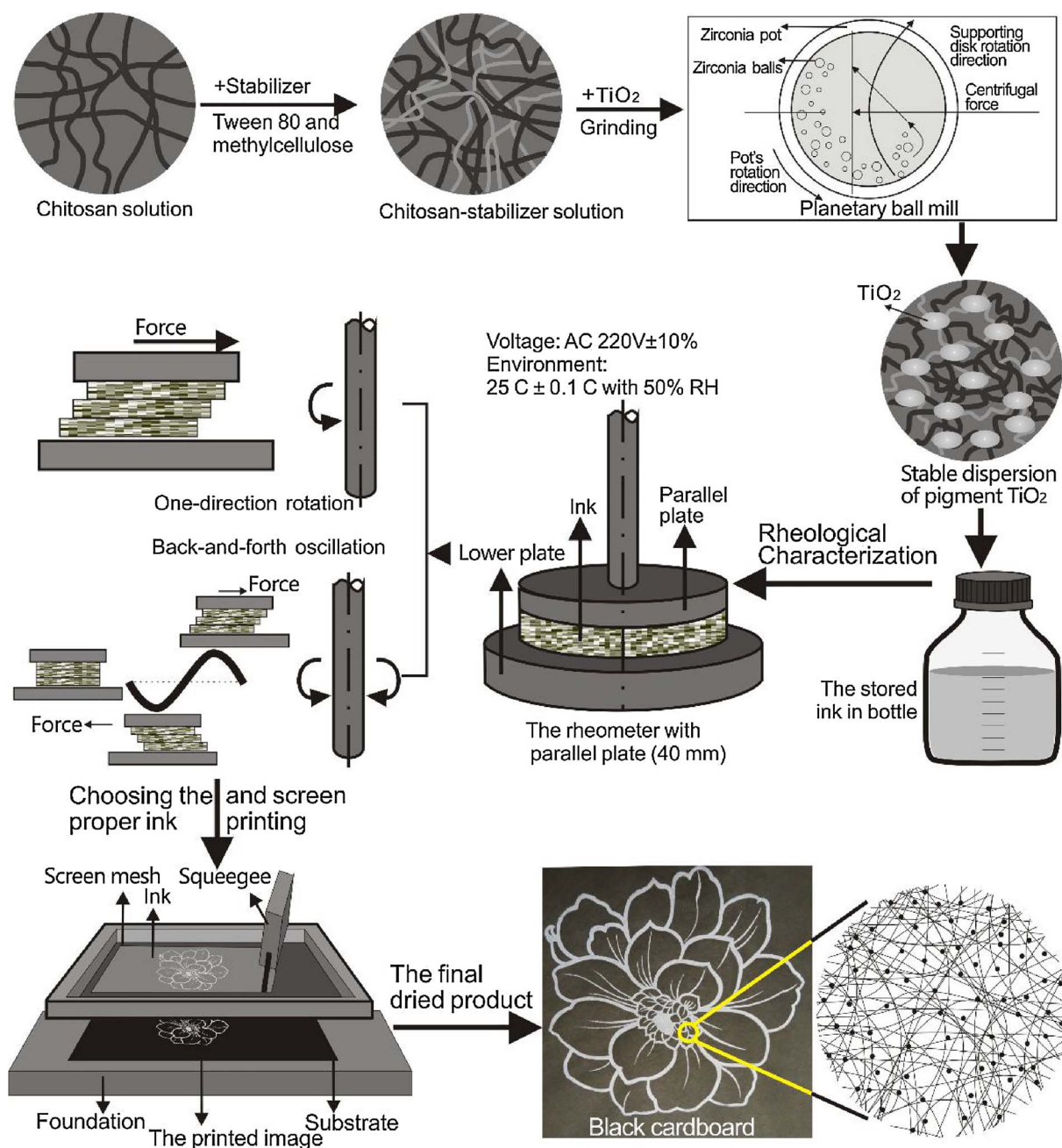
2. Experimental

2.1. Materials

Chitosan, with M_w 750 kDa and degree of deacetylation 85%, was considered according to previous research [20,21]. It was purchased

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Scheme 1. Preparation, characterization and application of composite ink.

from Shanghai Ruji Biotechnology Development Corporation. Edible pigment TiO₂ was purchased from Wuhan Keyihua S & T Co., Ltd. Tween 80 ($M_W = 1.310$ kDa) and methylcellulose ($M_W = 100$ kDa) were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD.

2.2. Preparation of chitosan-TiO₂ composite edible inks

Chitosan was added into acetic acid solution (2%, v/v), with the final chitosan concentration being 2% (w/w). The quantitative amount of Tween 80 and methylcellulose were respectively added into the chitosan-acetic acid solution, and stirred unceasingly for 5 min. Edible pigment TiO₂ with distilled water went through ultrasonic treatment for 1 h. Then the processed TiO₂ was placed into chitosan solution and agitated for 1 h at the speed of 1600 r/min. The phenomenon of Weissenberg effect could occur, i.e., the ink was drawn towards the rod and rose up around it instead of being thrown outward, which should

be considered seriously. Finally, the planetary ball mill was used to grind the preliminary chitosan-TiO₂ composite ink for 6 h. The composite ink made from chitosan and pigment TiO₂ with the mass ratio 3: 4.1 was coded as CT. The inks made up of chitosan, pigment TiO₂ and Tween 80 (mass ratio 3: 4.1: 0.5 and 3: 4.1: 1) were coded as CTT-1 and CTT-2 respectively. The inks composed of chitosan, pigment TiO₂ and methylcellulose (mass ratio 3: 4.1: 0.5 and 3: 4.1: 1) were coded as CTM-1 and CTM-2 separately. The formulations were shown in Table 1.

2.3. Rheology test

Rheological tests were performed for the developed inks at 25 °C ± 0.1 °C with 50% RH (relative humidity) by rheometer (KINEXUS PRO : Malvern, United Kingdom). Geometry serial number of parallel plate is PU40 SR2281SS.

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