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Preparation and Properties of Blue Edible Inkjet Ink Based on Chitosan Oligochitosan

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Different formulations of blue edible inkjet inks were prepared in this study using chitosan oligochitosan as a binder. The properties of different formulations of the ink were analysed by measuring conductivity, surface tension, viscosity, and antimicrobial properties. Chromaticity and density experiments were also conducted on the blue inkjet inks. Results show that the quality of the printed matter was improved considerably, including enhanced resolution, antimicrobial resistance, and reduced graphic burrs, after the addition of chitosan oligosaccharide.

1. Introduction

Traditional ink is comprised of a dispersed colloidal slurry mixture that includes pigments, binders, solvents, and additives (Ding et al., 2011; Robert, 2015). Each component of traditional ink shows insecurity due to limitations in technology and materials, particularly pigments and additives. Heavy metals, specifically, in pigments and additives pose a significant threat to human health. Drying agents added to ink include aromatic solvents such as benzene, xylene, polycyclic aromatic hydrocarbons, and their derivatives, which pollute the air and threaten the health of print workers as they evaporate (Ink, 2015). Volatile organic compounds (VOC), also used as drying agents, cause similar problems (Volatile, 2015). Edible ink, a relatively new alternative to traditional ink, is comprised of materials such as coloring agents, solvents, binders (usually edible, natural polymers,) and surfactants that are safe for human consumption (Chrysavgi et al., 2011; GeorgeSavvidis et al., 2013). Chitosan oligochitosan (COS) is nontoxic, biodegradable, and antimicrobial, and has been studied for numerous applications in food, pharmaceuticals, and cosmetics (Yin et al., 2013; Wang et al., 2008; Yin et al., 2010); its low viscosity, high solubility, and good film-forming and metal ion chelating properties make COS an effective ink binder. In this study, different formulations of blue edible inkjet inks were prepared using COS. The properties of these different ink formulations were analysed by measuring their conductivity, surface tension, viscosity, and antimicrobial properties. Chromaticity, density, and bacteriostatic experiments were also conducted on the ink samples. The results are compared and discussed below.

2. Testing methods

2.1 Materials

Inkjet ink consists of colouring agent, solvent, binder and surfactant. The colouring agent, naturally, determines the colour of the ink, the solvents disperses pigments, the binder promotes film formation, and the surfactant adjusts the surface tension of the ink.

Natural gardenia blue pigment is commonly used as a colorant. It has been included in Chinese GB2760-2011 national food safety standards, “Standards of Using Food Additives” (QB/T, 2013,). It features bright colour, high pigmentation, and light and heat resisting properties, with tones in the pH 4~8 range at favourable stability without precipitation. In addition, it is very soluble in water and aqueous ethanol and does not fade after heating in 120 ℃ for 60min.

The solvent used in this study to dissolve the natural gardenia blue pigment was deionized water. COS was used as a binder to assist imprinted film formation. Surfactant with ethanol, which was used here, increase ink

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stability and regulate the surface tension and viscosity of the ink as well as maintaining clear and dry ink impression.

2.2 Ink preparation

The ink configuration process was as follows: deionized water, edible alcohol, gardenia blue pigment and COS were selected according to the ink formulations listed in Table 1. Edible alcohol was added to deionized water, and then mixed with edible alcohol solvent to generate mixed solution “A”. COS was then added to mixed solution A until completely dissolved to form mixed solution “B”; gardenia blue pigment was then added to mixed solution B until completely dissolved to form mixed solution “C”. Mixed solution C was stirred for 30 min using a DF-101S Heat collection-Constant temperature type magnetic stirrer at 10000 rpm and room temperature. Mixed solution C was then passed through a Pin-type filter (.45um membrane pore size, 25mm diameter), the filtrate was the needed ink.

Fifteen different edible inkjet ink formulations were prepared in this study, as listed in Table 1. The amount of COS was varied for inks 1-5 while other components remained constant, the amount of edible alcohol varied for inks 6-10 while other components remained constant and the amount of gardenia blue pigment for inks 10-15 while other components remained constant.

Table 1: Ink formulations

No.	H_2O(g)	Alcohol(g)	Gardenia blue pigment (g)	Chitosan oligosaccharide (g)
1	15	8	1	0
2	15	8	1	0.5
3	15	8	1	1
4	15	8	1	1.5
5	15	8	1	2
6	15	4	1	1
7	15	6	1	1
8	15	8	1	1
9	15	10	1	1
10	15	12	1	1
11	15	8	0.2	1
12	15	8	0.4	1
13	15	8	0.6	1
14	15	8	0.8	1
15	15	8	1	1

2.3 Conductivity, surface tension, and viscosity measurements

Conductivity measurements were performed using a DDS-11C Conductivity Meter (Shanghai, China). Surface tension measurements were conducted with an A10 Automatic Surface Tensiometer (Shanghai, China) fitted with a De Nouy platinum ring. Viscosity measurements were performed using an NDJ-1 Rotational Viscometer (Shanghai, China) with a No. 0 rotor. The above properties were all measured at room temperature and atmospheric pressure.

2.4 Inkjet printing and color measurement

Inkjet printing was performed using an Epson K100 Black-White Inkjet Printer (Shenzhen, China) at 25℃ with A4 printing papers as substrates. A syringe and syringe-driven filter (0.45um membrane pore size, 25mm diameter) were used in this step to filter the ink and fill the ink cartridge.

The CIE 1976 L*, a*, b*, and solid density values of the prints were measured using an X-Rite spectroeye spectrophotometer (USA) under D65 illumination; the 10° ultraviolet (UV) standard observer and specular component were excluded.

2.5 Bacteriostatic ring experiment

Bacteriostatic ring experiments were conducted to determine the antibacterial activity of the ink in this study. Small, round pieces of paper (5mm diameter) stained with ink were placed on a solid medium that had been vaccinated with Escherichia coli. The ink on the paper then spread outward by absorbing the moisture in the solid medium to form a bacteriostatic ring.

3. Results and discussion

In this study, the surface tension, viscosity, conductivity of the above fifteen different formulations were as listed in Tables 2-4. A graph detailing the results of the bacteriostatic ring experiment is shown in Fig. 10. The CIE 1976 L*, a*, b*, and solid density values are provided in Table 5, and a CIE 1976 a*b* color planer diagram is shown in Fig. 13.

3.1 Surface tension

Inks suitable for inkjet printing have a surface tension in the range of 25–60 mN/m [10]. The surface tension values of all inks prepared are shown in Table 2. Inks 1, 5-7, and 10-12 had surface tension value within the range of 22-35 mN/m.

Figure 1 shows where the surface tension values of the inks decreased at first, then increased as COS concentration increased. The concentration of COS in ink 1 was 0%, and 7.7% in ink 5.

Figure 2 shows where the surface tension values of the inks decreased at first, then increased as alcohol concentration increased. Inks 6, 7, and 10 had surface tension between 25 and 60 mN/m. The alcohol concentration of inks 6, 7, and 10 were 19.0%, 26.1%, and 41.4% respectively.

Similarly, Figure 3 shows where the surface tension values of the inks decreased at first then increased as gardenia blue ink concentration increased approximately to 3.2%.

Table 2: Ink surface tension

No.	Surface tension(mN/m)	No.	Surface tension(mN/m)	No.	Surface tension(mN/m)
1	30.2	6	35.87	11	30.21
2	24.4	7	27.27	12	30.16
3	24.92	8	24.92	13	22.78
4	23.55	9	23.42	14	23.12
5	30.86	10	28.52	15	24.92

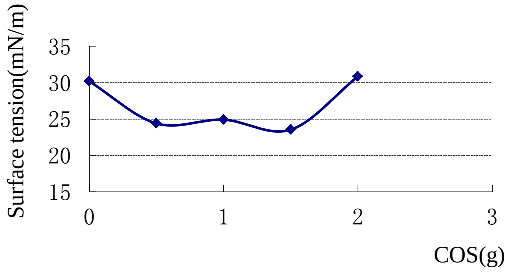


Figure 1: Surface tension with varying COS concentration

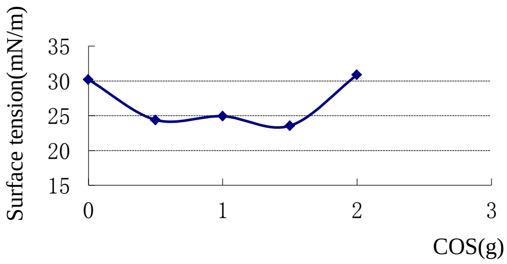


Figure 2: Surface tension with varying alcohol concentration

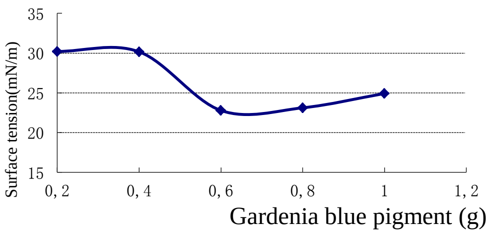


Figure 3: Surface tension with varying gardenia blue ink concentration

3.2 Conductivity

Inks suitable for inkjet printing have conductivity below 10 ms/cm [10]. As shown in Table 3, the range of the conductivity values of the inks in this study was 1-12 ms/cm – all inks showed acceptable conductivity except inks 6 and 7. The concentration of alcohol in ink 6 was only 19.0%, suggesting that low alcohol concentration has a negative impact the conductivity of edible inkjet ink.

Table 3: Conductivity of edible inkjet ink

No.	Conductivity(ms/cm)	No.	Conductivity(ms/cm)	No.	Conductivity(ms/cm)
1	6.96	6	11.42	11	1.17
2	6.12	7	10.33	12	2.24
3	5.06	8	7.45	13	2.47
4	4.76	9	5.21	14	3.58
5	4.36	10	4.36	15	4.36

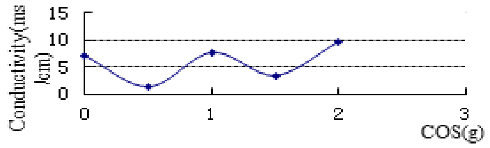


Figure 4: Ink conductivity with varying COS concentration

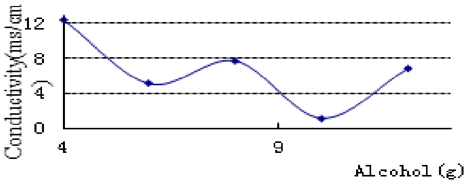


Figure 5: Ink conductivity with varying alcohol concentration

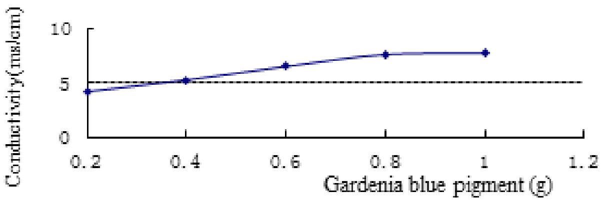


Figure 6: Ink conductivity with varying gardenia blue ink concentration

3.3 Viscosity

Inks suitable for inkjet printing have viscosity in the range of 1-15mpa.s [10]. The viscosity values of all inks prepared, which ranged from 1-3 mpa.s, are shown in Table 4.

Figure 7 shows the viscosity values of the inks increase at first then decrease with the increasing of COS. Figure 8 shows the viscosity values of the inks increase at first then decrease with the increasing of Alcohol. Figure 9 shows the viscosity values of the inks increase with the increasing of gardenia blue ink.

Table 4: Ink viscosity

No.	Viscosity (mpa.s)	No.	Viscosity (mpa.s)	No.	Viscosity (mpa.s)
1	1.83	6	1.95	11	2.09
2	2.01	7	2.04	12	2.1
3	2.21	8	2.18	13	2.12
4	2.39	9	2.3	14	2.17
5	2.3	10	2.3	15	2.3

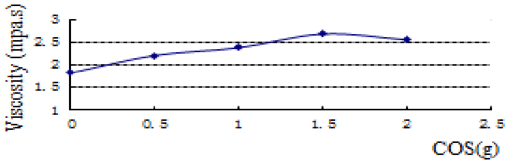


Figure 7: Ink viscosity with varying COS concentration

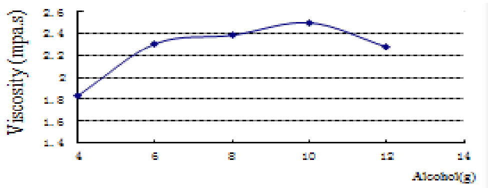


Figure 8: Ink viscosity with varying alcohol concentration

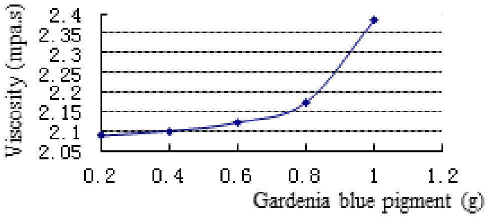


Figure 9: Ink viscosity with varying gardenia blue ink concentration

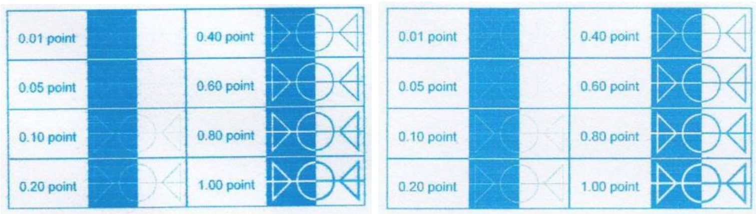
The ink formulations within acceptable ranges of conductivity, surface tension, and viscosity parameters were inks 1, 5, and 10-12; the color of inks 11 and 12 was too light.

3.4 Inkjet printing

3.4.1. Inkjet effects: As shown in Figure 10, the printing line of ink 1 (0% COS concentration) was not sufficiently smooth, but the printing line of ink 5 (which did contain COS). Figure 11 shows where the resolution and image details of the ink 5 printing sample were clearer than those of ink 1, demonstrating that COS binder plays an important role in colorant film.

No. 1 *No. 5*

Figure 10: The diagram of printing line



No. 1 *No. 5*

Figure 11: The diagram of print resolution

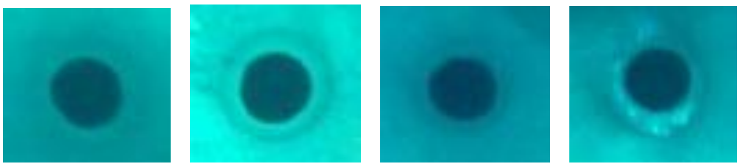
3.4.2. Density and colorimetric analysis: Table 5 shows the density and colorimetric values of printed samples. Density must be equal to or greater than 0.8 to meet China Light Industry Standard QB/T 2730.1-2013. [10]

Table 5: Ink density and chromaticity values

No.	Colorimetric value			Density
	L*	a*	b*	
1	68.36	-31.04	-45.37	1.08
5	67.75	-30.44	-45.43	1.12
7	66.66	-30.49	-45.3	1.16
10	70.81	-31.58	-42.24	0.95

3.5 Bacteriostatic ring experiment

Inks 1, 5, 7, and 10 were absorbed into round paper samples, which were then were put into solid medium inoculated with Escherichia coli. The inks in the papers spread and restrained the development of Escherichia coli at varying levels by absorbing water from the solid medium. Figure 12 shows the resultant ink antibacterial circles – inks 5, 7, and 10 showed bigger circles than ink 1, implying that COS addition effectively restrained the growth of Escherichia coli.



No. 1 No. 5 No. 7 No. 10

Figure 12: Ink antibacterial circle diagram

4. Conclusion

Fifteen formulations of blue edible inkjet inks were investigated in this study. The conductivity, surface tension, and viscosity of ink samples 5 and 10 fell within acceptable ranges; these inks contained chitosan oligo chitosan (COS), which was shown to improve ink quality as well as antibacterial properties.

Ink formulations 5, 7, and 10 met China's light industry standards QB/T 2730.1-2013 at viscosity of 1~15mpa.s, surface tension of 25~60 mN/m, conductivity <10ms/cm, and imprint colour density ⩾ 0.8. The results of this study altogether confirm that adding COS to edible inkjet ink improves the resolution and antimicrobial resistance of the ink and prevents graphic burr phenomena.

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