Food Research 8 (2) : 16 - 21 (April 2024)
Journal homepage: https://www.myfoodresearch.com

FOOD RESEARCH

RESEARCH PAPER

Development of cellulose based food-ink from cellulose powder

[1]Azman, N.Y., [1,*]Fuzi, S.F.Z.M. and [2,3]Abdul Manas, N.H.

[1]*Department of Technology and Natural Resources, Faculty of Applied Sciences and Technology, Universiti Tun Hussein Onn Malaysia, Pagoh Edu Hub, 84600, Johor, Malaysia*
[2]*Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia*
[3]*Institute of Bioproduct Development, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia*

Article history:
Received: 21 February 2022
Received in revised form: 30 March 2022
Accepted: 3 July 2022
Available Online: 3 March 2024

Keywords:
Cellulose,
CMC,
3D printing,
Food ink,
Additive manufacturing,
Shear thinning behaviour

DOI:
https://doi.org/10.26656/fr.2017.8(2).104

Abstract

Three-dimensional or 3D printing studies utilizing biopolymer, a digital manufacturing technology acting as additive manufacturing, have gained global attention, particularly in the food industries. However, the utilization of cellulose powder to create food ink for 3D printing is relatively recent. Therefore, this study aimed to prepare cellulose-based food ink, analysed using carboxymethyl cellulose powder (CMC) through rheology and thermal analysis. The formulated cellulose-based food ink from carboxymethyl cellulose powder underwent examination through rheology, thermogravimetric analysis (TGA), and Fourier -transformed infrared spectroscopy (FTIR). The results showed shear-thinning behaviour for rheology properties and the presence of the hydroxyl group (–OH stretching), C–H stretching vibration and ether groups (–O– stretching), which was excellent for 3D printing. The amount of CMC powder used in the food ink formulation was increased due to the higher thermal stability of the food ink as determined by the TGA. This discovery is applicable to 3D printing in the food industry since CMC powder exhibits shear thinning behaviour at low concentrations and has stable thermal characteristics comparable to printable and edible materials.

1. Introduction

Additive manufacturing (AM) is a digital manufacturing process that uses a layer-by-layer approach to create highly customisable three-dimensional (3D) printed models. This is perfected using data from computer-aided design (CAD) software, with the finished product being printed precisely as the software has designed or drawn it (Puppi and Chiellini. 2020). Metals, pharmaceuticals, ceramics and bioprinting medical applications all benefit from manufacturing these items made from various materials such as metals, composites and polymers. This versatile and flexible production primarily focuses on the rapid production of low-volume, high-value products (Tofail *et al.,* 2018). However, AM has a limited variety of safe materials for humans and the environment, biodegradable, biocompatible, chemically versatile and fundamentally useful.

In keeping with the current trend of a sustainable economy, renewable or naturally derived biopolymers have gotten much attention as they are regarded as the most abundant renewable feedstocks on the planet and have shown potential as a substitute for fossil oil-based plastic polymer. Natural-derived polymers or biocomposites are large complex macromolecules produced by living organisms. They can be used in many industries such as food, medical and environmental applications because they are easy to handle, green chemistry and reliable (Udayakumar *et al*., 2021). Biopolymers with good processability and printer friendliness, such as shear-thinning behaviour and high zero shear viscosity, allow for the precise and simple 3D charting of constructions with high resolution, shape accuracy and structural stability (Liu *et al*., 2019). Examples of naturally derived polymers are cellulose, hemicellulose, lignin, starch, alginate, chitosan and their derivatives. Furthermore, the variety of cellulose derivatives available expands the range of potential uses. In medical engineering, biological devices, electronics, food packaging and textiles, there have been many recent studies on 3D printing utilising cellulose and its derivatives. Due to their matrix-forming capacity, cell compatibility, and cross-linking feasibility, cellulose ethers, notably CMC, have recently been identified as effective structural components of bioinks for wound

*Corresponding author.
Email: *fatimahz@uthm.edu.my*

eISSN: 2550-2166
Published by Rynnye Lyan Resources

healing (Mallakpour *et al.,* 2021). The high swelling and transparency of cellulose ether hydrogels may also provide significant benefits in terms of maintaining an optimal moist environment, nutrient exchange, and visual assessment (Habib *et al.,* 2018).

Research has also been done on the use of cellulose in food ink for 3D printing. The printability of food ink is determined by its composition. The food sector can apply 3D printing using cellulose-based ink as a prototyping tool to plan and prototype new products. The food industry may be interested in amorphization and restructuring cellulose into new architectures, especially since cellulose is a low-cost, readily available material. With more research being done to improve the rheology of food ink for better printability and form retention, bioprinters with multi-nozzles have opened new opportunities for 3D printing for food applications. Most of the research that utilises cellulose was extracted, and one study was printed onto the cellulose powder rather than the food ink itself. Holland *et al*. (2018) conducted research in which xanthan gum food ink was printed on cellulose powder in 10 layers to investigate ink viscosity and heating conditions.

Thus, the objective of this study was to develop food ink for potential 3D printing using cellulose powder and to investigate the ink's rheological and thermal properties. Food ink made from cellulose powder is a relatively new field of study, and this study will investigate the potential use of cellulose powder in food ink. CMC-based inks have been shown to provide insufficient mechanical stability to printed structures, necessitating the use of a range of additives (Zennifer *et al.,* 2021). The food ink used in this study was primarily composed of carboxymethyl cellulose (CMC) powder, with some formulations also containing semi-skimmed milk powder (SSMP). Lille *et al*. (2017) claimed that skimmed milk powder is an excellent additive since it demonstrated the high yield stress required for good shape stability following 3D printing.

2. Materials and methods

2.1 Sample collection

The CMC powder was purchased from the brand Emory and SSMP was purchased from Nestle Milano, Portugal. The SSMP consisted of 29.9% protein, 44% carbohydrates and 15.5% fat (manufacturer's data).

2.2 Food ink formulation preparation

The formulations of all four food inks (F1, F2, F3, and F4) were prepared as shown in Table 1. After trial and error, the formulations were finalised by adding the CMC powder to water, followed by SSMP. Firstly, CMC and SSM powders were weighed using an analytical balance (HR-AZ/HR-A Series, Tokyo). Secondly, CMC and SSM powders were added to water and mixed with continuous stirring using a glass rod or spatula. The mixture was then homogenised using a homogeniser (PRO Scientific Inc, USA) at 5000 rpm for 10 mins. Formulations containing more CMC powder will require additional time (10–30 mins) or a greater increase in rpm (800–5000 rpm) to accomplish homogenisation. The addition of SSMP powder helped CMC powder to dissolve or homogenise in water better. The final homogenisation step was carried out by extruding the paste once through a 5 mL disposable syringe (Muzamal Industries and Medical Manufacturing, Malaysia). Figure 1 illustrates an example of food ink being extruded onto a petri dish using Formulation 1 (F1), comprising 7% CMC and 1% SSMP. The food ink was stored at room temperature for a minimum of 2 hrs prior to rheological characterisation and thermal analysis, which were carried out on the same day.

Table 1. Measurement of food ink formulations.

Ingredients (% w/v)	F1	F2	F3	F4
CMC powder	7	10	10	11
SSMP	1	1	-	-

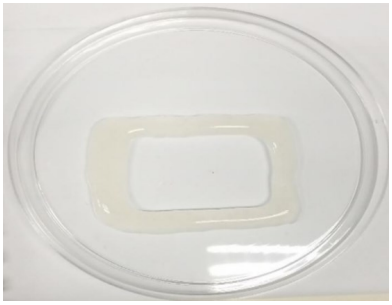

Figure 1. Example of potential food ink being extruded onto a petri dish using F1.

2.3 Preparation of dried food ink sample

Samples were dried in an oven drying (Memmert UNB 100, Germany) at 50°C for 24 hrs. The dried samples were broken into smaller pieces for TGA analysis.

2.4 Rheological analysis of food ink

The viscoelastic properties of the food ink sample prepared were analysed by flow sweep measurements with a Discovery HR 10 rheometer (TA Instruments, UK). Stainless steel parallel plates with a diameter of 20 mm and a gap of 1 mm. Measurements were carried out at 22°C. The samples were loaded, and the edges were trimmed. The shear rate was varied logarithmically from 0.01 to 1000 s^{-1} with 5 measuring points per decade. Each food ink sample was measured in triplicate.

https://doi.org/10.26656/fr.2017.8(2).104

2.5 Fourier Transform Infrared Spectroscopy analysis

The Fourier Transform Infrared Spectroscopy (FTIR) analysis was an FTIR-ATR with the equipment used in the study was Agilent Cary 630 FTIR spectrometer, USA. Each of the infrared spectra is in the range of 4000–400 cm^{-1}. Oven-dried samples were used for this analysis.

2.6 Thermogravimetric analysis

The thermal stability of the materials was evaluated with thermogravimetric analysis (TGA) (TA Instruments, UK) performed at a heating rate of 20°C/ min from 30-800°C with a flow rate of 20 mL/min in nitrogen atmosphere (El-Sakhawy *et al*., 2019). The samples of about (10±3) mg were used for each food ink sample.

3. Results and discussion

3.1 Rheological analysis of food ink

Rheology is a scientific field that studies the flow and deformation of matter (solid, liquid and gas) under the influence of stress (Benchabane and Bekkour, 2008). As shown in Figure 2, the viscosity increases as CMC powder increases in the formulation. This is due to the increase in the intermolecular interactions between the CMC molecules. The viscosity of food inks shows shear-thinning behaviour, which decreases as the shear rate increases. Disentanglement of the polymer coils in solution or increased orientation of the polymer coils in the flow direction produces shear-thinning behaviour. The viscosity shows a fall dramatically from 129.013 to 8.00172 Pa.s and 767.232 to 2.99544 Pa.s for F1 (Figure 2a) and F2 (Figure 2b), respectively.

Two formulations with a high amount of CMC powder in Figure 3 exhibited initial shear-thickening behaviour, in which the apparent viscosity increases as the shear rate increases, followed by shear-thinning behaviour. In Figure 3a, the viscosity of 779.310 to 907.272 and falls in viscosity to 17.5314 Pa.s, while in Figure 3b, the viscosity increases 354.276 to 928.088 and falls in viscosity 3.35894 Pa.s. This was already observed in other studies on the rheological properties of CMC stress (Benchabane and Bekkour, 2008). Liu *et al*. (2019) reported that one of the theories on the shear-thickening behaviour is the "flow-induced formation of macromolecular associations". This is interpreted as the increase in viscosity because of the stiff inner structure due to the formation of webs of polymer coils and the increase in the intermolecular interactions as the shear rate increases. Furthermore, shear-thinning behaviour is observed when the shear rate is increased further. In practice, this means that the flow encounters less resistance at higher shear rates. This shear-thinning behaviour is thought to be induced by the disentanglement of polymer coils in solution or enhanced orientation of polymer coils in the flow direction.

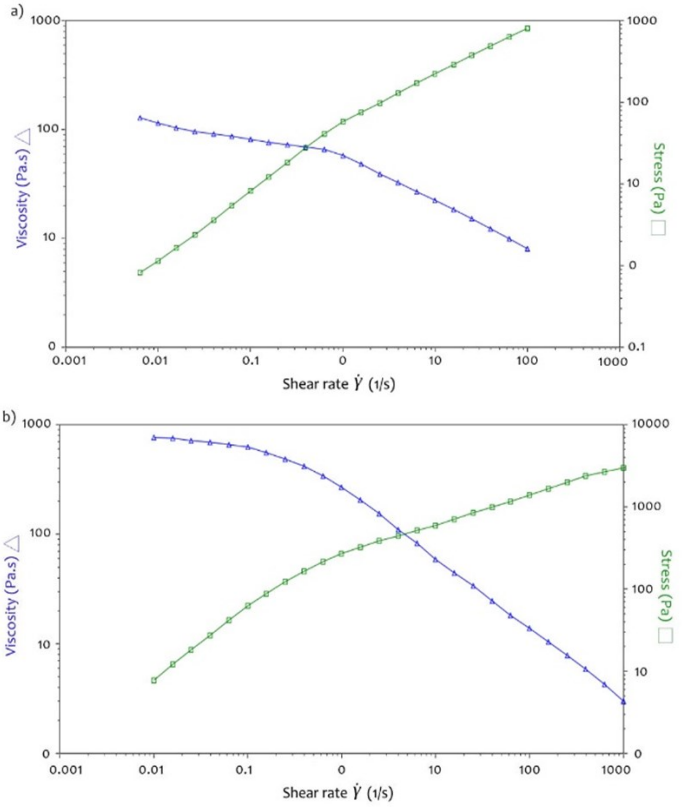

Figure 2. The increase in viscosity in a) F1 when compared with b) F2.

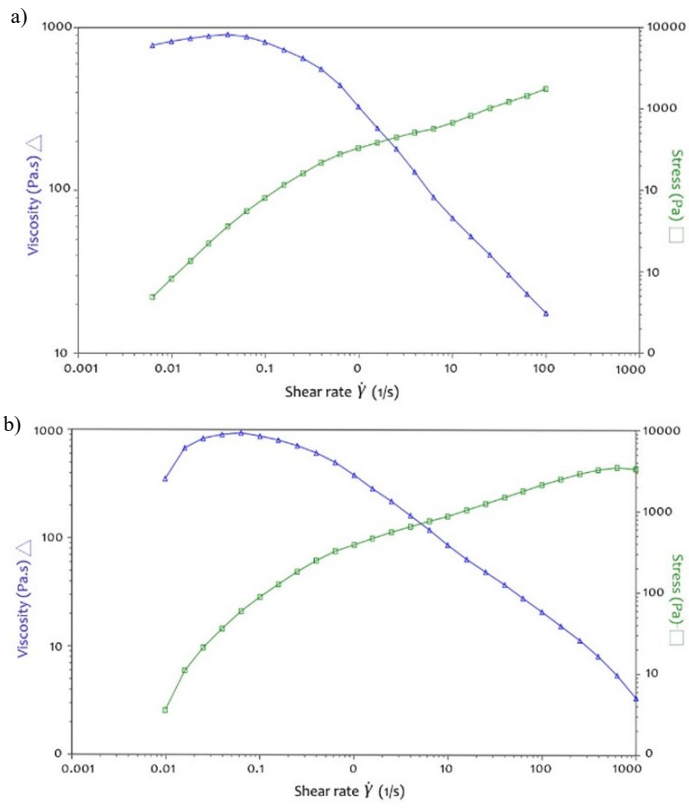

Figure 3. The slight increase in viscosity at the beginning in a) F3 when compared with b) F4.

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3.2 Fourier transform infrared spectroscopy analysis

Figure 4 depicts that the characteristic band of CMC appear at 3200 - 3600, 2800 - 3000 and 1000 - 1300 cm^{-1} belong to a hydroxyl group (–OH stretching), C–H stretching vibration and ether groups (–O– stretching) (Klunklin *et al*., 2020). A comparison between Figure 4, Figure 5 for F1 (7% CMC + 1% SSMP) and Figure 6 for F4 (11% CMC) signifies the change in intensity. The peak intensity for the hydroxyl group and ether group notably increases in Figure 5 and Figure 6. Evidently, the 3200 – 3600 cm^{-1} band is commonly associated with OH stretching vibrations and hydroxyl group hydrogen bonds

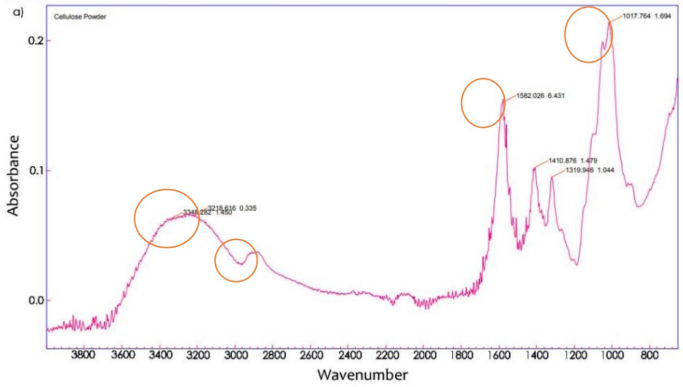

Figure 4. FTIR analysis of CMC powder.

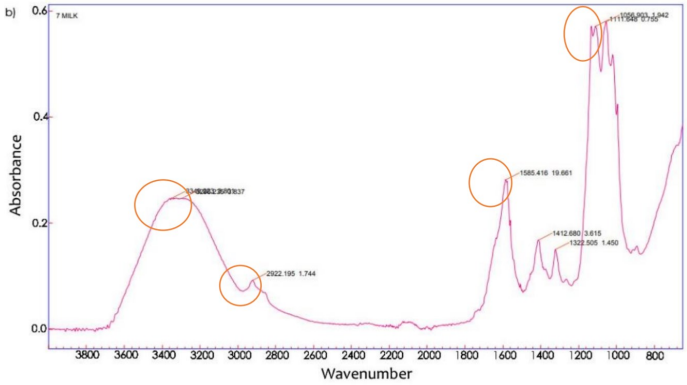

Figure 5. FTIR analysis of F1 (7% CMC + 1% SSMP).

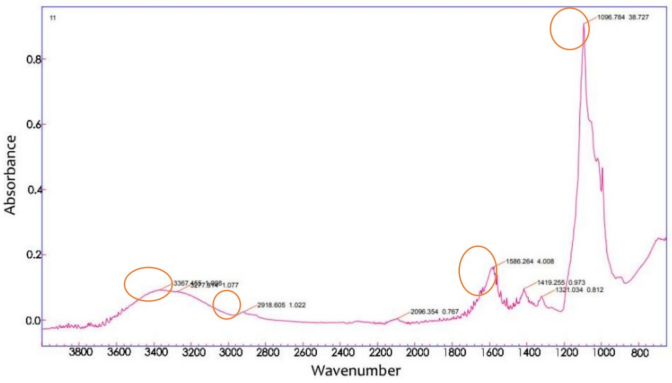

Figure 6. FTIR analysis of F4 (11% CMC).

Table 2. Wavenumber and the functional groups in food ink formulations.

Wavenumber (cm^{-1})	Functional group
3200 - 3600	hydroxyl group (–OH stretching)
2800 - 3000	C–H stretching vibration
1580 - 1600	C-C=C symmetric stretch
1000 - 1300	ether groups (–O– stretching)

found in cellulosic materials. The water absorption or the bound water linked to the substrate on cellulosic material increases because of CMC's high water tendency (Célino *et al*., 2013). The summary of wavenumber and functional groups in food ink formulations is shown in Table 2.

3.3 Thermogravimetric analysis

Table 3 summarises the TGA data of CMC and the four food ink formulations. All TGA graphs showed three temperature steps, as shown in Table 3. The first weight loss is mainly attributed to the evaporation of physically bound water in the cellulosic structure. The initial slope becomes less steep as the CMC powder increases in the food ink formulation. This is possible because of the high water-binding capacity of cellulose.

The first weight loss was followed by the main decomposition. This is because of pyrolytic decomposition, leading to the formation of aromatized units and the decomposition of the carbonaceous residues. El-Sakhawy *et al*. (2019) stated that the weight loss of the CMC sample was due to the decarboxylation of carboxylic groups in CMC and the loss of CO_2.

The third weight loss was because the damaged molecules were thermally unstable, they were subjected to further degradation, which continued until the polymer chains' ends, resulting in aromatized units and, eventually, a cross-linked carbon skeleton. As the amount of CMC powder in the food ink composition rises, the slope becomes more gradual (Figures 7 and 8). The residual weight percentage is stated in Table 3. All food ink showed stable thermal stability at high temperatures.

4. Conclusion

The food ink was made with cellulose powder, which is CMC and the rheology and thermal analysis show the potential use for food ink. The rheological properties of the food ink revealed that the viscosity of CMC/SSMP solutions increases as the CMC concentration increases; at a 7:1 ratio, the food ink solutions exhibit nearly Newtonian behaviour. However, at a little higher 10:1 ratio, the food ink solution exhibits pseudoplastic behaviour; the shear-thinning is generated by polymer chains unravelling under the influence of flow, and the molecular chains are oriented in the direction of the flow, which is excellent for 3D printing. Therefore, in this investigation, the inclusion of SSMP was found to be significant. All food ink has stable thermal stability, with F4 having the best thermal stability of food ink increasing as the amount of CMC powder in the formulation increases.

https://doi.org/10.26656/fr.2017.8(2).104

Table 3. TGA data of CMC, F1, F2, F3 and F4.

Sample	Weight loss at 800°C (%)	Residual weight (%)	Temperature of steps in TGA (°C)		
			Step 1	Step 2	Step 3
CMC powder	74.5	25.5	30.45	293.81	441.44
F1	77.6	22.4	41.92	241.96	529.16
F2	74.6	25.4	40.59	241.41	685.95
F3	74.7	25.3	28.75	244.73	456.33
F4	79.5	20.5	36.50	247.95	700.00

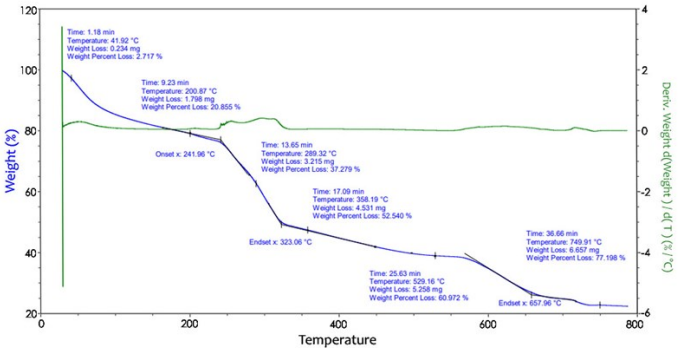

Figure 7. Thermogravimetric analysis (TGA) curves of F1 (7% CMC + 1% SSMP).

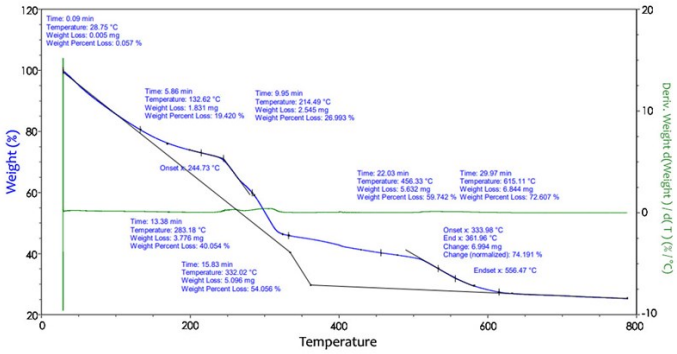

Figure 8. Thermogravimetric analysis (TGA) curves of F3 (10% CMC).

Conflict of interest

The authors declare no conflict of interest.

Acknowledgements

The research has been sponsored by Ministry of Higher Education Malaysia and Universiti Tun Hussein Onn Malaysia under Malaysian Technical University Network (MTUN) Research Grant (Grant No. Q620), Additionally, support was provided by Universiti Teknologi Malaysia under the Fundamental Research Grant Scheme (FRGS) (Grant No.FRGS/1/2020/TK0/UTM/02/6.

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