

**ASSESSMENT OF 3D PRINTING OF HEAT
DESICCATED MILK SEMI-SOLIDS (*KHOA*)**

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by

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*“Dedicated to my
family.”*

CERTIFICATE

This is to certify that the thesis entitled “**Assessment of 3D printing of heat desiccated milk semi-solids (*khoa*)**” being submitted by **Ms. Sukirti** to the **Indian Institute of Technology Delhi** for the award of “**Doctor of Philosophy**” is a record of bonafide research work carried out by her. She has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis. To the best of our knowledge, the results contained in this thesis have not been submitted in part or full to any other university or institute for the award of any degree or diploma.



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ABSTRACT

Heat desiccated milk semi solids (*Khoa*) which are characterized as heat induced milk protein network with loosely cemented fat globules are widely recognized base materials for the manufacturing of milk sweetmeats popular in the in the Southeast Asian countries. The present research assesses the possibility of 3D dairy derivatives as a method of creating discernible printed foods through design modelling for product profiles that tailored structure, texture, nutrition and functionality, which would reduce waste and energy consumption aligning with the sustainable development agenda. 3D food printing (3DFP) is a revolutionary technology which integrates the expertise in mechatronics, food engineering and 3D printing in the fields of ingredients, formulation, texture, and structure to create personalized food products in a single step. Pre-engineered standardized dairy ‘formulation’ employed with 3D printing offers a platform to develop diverse of milk products customized to individual dietary preferences and nutritional requirements automatically and could potentially replace the traditional manufacturing operations. However, the inadequate rheological characteristics of heat desiccated milk semi-solids (HDMS) restrict their application in 3D printing. Contemplating these observations, the present research entitled "*Assessment of 3D printing of heat desiccated milk semi-solids (Khoa)*" focusses primarily on inducing desired restructuring in HDMS for 3D printing dairy products with programmable structure, functionality, nutrition, and texture.

The study commenced by correlating printability with the rheological characterization of a multicomponent HDMS based formulation at pre-printing, extrusion, and post printing stages to mimic the conditions during pre-processing, processing, and post processing to address the challenges of variation in material characteristics of the formulation with temperature variation encountered during 3D printing. With this investigation, it was indicated the shear thinning behaviour, viscosity (η), yield stress (τ_0), storage modulus (G') and reduced the shear

recoverability were increased when the semi-skimmed milk powder (SSMP) was incorporated at a higher level and the proportion of heat desiccated milk powder (HDMP) decrease in the HDMS formulations. The gelation temperature of the HDMS formulations ranged between 28.1 to 29.4 °C. Due to the adequate τ_0 (1100.0 Pa) and G' (7026.4 Pa), the formulation SSMP (55): HDMP (5.0) exhibited the best dimensional stability, while the formulation SSMP (35): HDMP (25) brought about sagging in the printed constructs.

Furthermore, the study investigates the synergistic route of high intensity ultrasound (HIUS) and inulin incorporation to cause structural conformational changes, promote cross-linking and induce structural modification in HDMS. The mechanical, structural, colour and molecular interactions induced in HDMS at varied inulin concentrations (0, 2 & 4% w/w) and with and without HIUS pretreatment (0 W, 200 W, 400 W & 600 W) were examined. HIUS and inulin synergistically enhanced the non-Newtonian shear thinning behaviour, viscoelasticity, extrudability, which was validated from the fitted rheological parameters (k , n , τ_0) by Herschel-Bulkley model. The microstructural results corroborated the development of a robust cross-linked network between protein and inulin at the junction zone borders, suggestive of strong mechanical properties. The combined effect of inulin addition and HIUS induced exposure of hydrophilic groups and development of new hydrogen linkages, which improved elasticity as demonstrated by FTIR and Raman spectra. A profound effect on the secondary structure was linked to reduced α -helix and increased β -sheet in the formulations leading to improved structural integrity of the printed constructs. The HDMS formulation combined with 4% inulin and subjected to an HIUS intensity of 200 W, demonstrated the best 3D printability.

The research also broadened its scope to design fortified HDMS products by 3D printing. Different gel matrices (hydrogel, oleogel, and various compositions of bigels) were employed to encapsulate vitamin D₃. The gel systems were subsequently incorporated to HDMS in order

to enhance its flow behaviour and nutritional profile for 3D printing applications. The effect of various vitamin D₃ loaded gels on the structure, vitamin D₃ content and 3D printability of the HDMS formulations were explored. The microstructural investigation demonstrated that the 5:5 bigel was bicontinuous, while the 8:2 and 2:8 bigels showed a continuous network of oleogel and hydrogel, respectively. According to the differential scanning calorimetry studies, gels containing higher oleogel content exhibited greater peak temperatures and enthalpies, which were linked to increased melting temperatures. All the HDMS formulations revealed a viscoelastic solid behaviour ($G' > G''$), with frequency dependent G' values. The vitamin D₃ encapsulation and retention in the 3D printed HDMS structures was primarily governed by the oleogel fraction. The HDMS with oleogel exhibited the highest vitamin D₃ retention per printed construct (273.8 IU), while the HDMS with hydrogel showed the lowest vitamin D₃ in the 3D printed construct (132 IU). The hydrogel had a considerable dominance on the 3D printing behaviour, thereby the HDMS containing hydrogel exhibited the best 3D printability ($l=100%$, $b=100%$, $h=98.5%$).

Furthermore, the study aims to design vitamin D₃ nanoemulsion-based HDMS gels with two protein rich emulsifiers, namely sodium caseinate (NaCas) and whey protein isolate (WPI) and investigate the influence of emulsifier type and concentration on the milk protein matrices' rheological properties, crystalline pattern, structural characteristics, thermal behaviour, 3D printing behaviour and ability to encapsulate and retain vitamin D₃. The vitamin D₃-nanoemulsion-based dairy gels stabilised with NaCas and WPI exhibited superior viscoelasticity and 3D printability as compared to the control. The emulsifiers facilitated stronger inter and intra molecular crosslinking, which resulted in a robust gel, as seen from the FTIR spectra, SEM, and XRD patterns. NaCas further strengthened the protein-protein interactions as compared to WPI, hence vitamin D₃-nanoemulsion-based dairy gel stabilised with 1% NaCas exhibited the highest storage modulus (G') (19,580 Pa), maximum thermal

degradation temperature (376°C), and recorded the highest encapsulation efficiency (94.1%) and retention (377.2 IU/g) of vitamin D₃ attributed to the lowest droplet size (124.85 nm) and PDI (0.24), highest zeta potential (- 44.85 mV) and stability (TSI = 0.2) of nanoemulsion.

Additionally, consumer perception and sensory evaluation of the 3D printed HDMS constructs elucidated positive feedback from the population demographic concerning 3D food printing and 3D printed HDMS-based food products. There was a significant difference ($p < 0.05$) in the taste preferences 3D printed HDMS products; most respondents preferred the taste of nanoemulsion-based gel sample, while the control sample was the least preferred. The panelists' response towards purchase of 3D printed HDMS foods were largely positive with 60% of the respondents expressing that they “probably would purchase” the 3D printed foods upon commercialization.

Drawing from the accomplished outcomes, this research could be utilised to effectively fabricate and assess novel dairy-based food systems with customized nutritional profiles and personalized designs for additive manufacturing in dairy and food sectors.

Keywords: 3D printing; Heat desiccated milk semi-solids; Food structure; Vitamin D₃; Emulsion gels

सारांश

गर्मी से सुखाए गए दूध के अर्ध ठोस पदार्थ (खोआ) जिन्हें गर्मी से प्रेरित दूध प्रोटीन नेटवर्क के साथ वसा ढीले ग्लोब्यूलस के रूप में जाना जाता है, दक्षिण पूर्व एशियाई देशों में लोकप्रिय दूध मिठाइयों के निर्माण के लिए व्यापक रूप से मान्यता प्राप्त आधार सामग्री हैं। वर्तमान शोध संरचना, बनावट, पोषण और कार्यक्षमता को तैयार करने वाले उत्पाद प्रोफाइल के लिए डिज़ाइन मॉडलिंग के माध्यम से सुस्पष्ट मुद्रित खाद्य पदार्थ बनाने की एक विधि के रूप में 3डी डेयरी डेरिवेटिव की संभावना का आकलन करता है, जो टिकाऊ विकास एजेंडे के साथ अपशिष्ट और ऊर्जा की खपत को कम करेगा। 3डी फूड प्रिंटिंग (3डीएफपी) एक क्रांतिकारी तकनीक है जो एक ही चरण में वैयक्तिकृत खाद्य उत्पाद बनाने के लिए सामग्री, फॉर्मूलेशन, बनावट और संरचना के क्षेत्र में मेक्ट्रोनिक्स, खाद्य इंजीनियरिंग और 3डी प्रिंटिंग में विशेषज्ञता को एकीकृत करती है। 3डी प्रिंटिंग के साथ नियोजित पूर्व-इंजीनियर्ड मानकीकृत डेयरी 'फॉर्मूलेशन' व्यक्तिगत आहार प्राथमिकताओं और पोषण संबंधी आवश्यकताओं के लिए स्वचालित रूप से अनुकूलित विविध दुग्ध उत्पादों को विकसित करने के लिए एक मंच प्रदान करता है और संभावित रूप से पारंपरिक विनिर्माण कार्यों की जगह ले सकता है। हालाँकि, ऊष्मा शुष्कित दूध अर्ध-ठोस (एचडीएमएस) की अपर्याप्त रियोलॉजिकल विशेषताएँ 3डी प्रिंटिंग में उनके अनुप्रयोग को प्रतिबंधित करती हैं। इन टिप्पणियों पर विचार करते हुए, "हीट डेसिकेटेड मिल्क सेमी-सॉलिड्स (खोआ) की 3डी प्रिंटिंग का आकलन" शीर्षक वाला वर्तमान शोध मुख्य रूप से प्रोग्राम योग्य संरचना, कार्यक्षमता, पोषण और बनावट के साथ 3डी प्रिंटिंग डेयरी उत्पादों के लिए एचडीएमएस में वांछित पुनर्गठन को प्रेरित करने पर केंद्रित है।

सामग्री विशेषताओं में भिन्नता की चुनौतियों का समाधान करने के लिए प्री-प्रोसेसिंग, प्रोसेसिंग और पोस्ट प्रोसेसिंग के दौरान स्थितियों की नकल करने के लिए प्री-प्रिंटिंग, एक्सट्रूज़न और पोस्ट प्रिंटिंग चरणों में मल्टीकंपोनेंट एचडीएमएस आधारित फॉर्मूलेशन के रियोलॉजिकल लक्षण वर्णन के साथ प्रिंटिबिलिटी को सहसंबंधित करके अध्ययन शुरू किया गया। 3डी प्रिंटिंग के दौरान तापमान भिन्नता के साथ फॉर्मूलेशन का सामना करना पड़ा। इस जांच के साथ, यह संकेत दिया गया कि जब अर्ध-स्किमड दूध पाउडर (एसएसएमपी) को शामिल किया गया तो कतरनी पतला व्यवहार, चिपचिपाहट (η), उपज तनाव (τ_0), भंडारण मापांक (G') और कतरनी वसूली क्षमता में वृद्धि हुई थी। उच्च स्तर और एचडीएमएस फॉर्मूलेशन में ताप शुष्कित दूध पाउडर (एचडीएमपी) का अनुपात कम हो जाता है। एचडीएमएस फॉर्मूलेशन का जेलेशन तापमान 28.1

से 29.4 डिग्री सेल्सियस के बीच था। पर्याप्त τ_0 (1100.0 पास्कल) और G' (7026.4 पास्कल) के कारण, फॉर्मूलेशन एसएसएमपी (55): एचडीएमपी (5.0) ने सर्वोत्तम आयामी स्थिरता प्रदर्शित की, जबकि फॉर्मूलेशन एसएसएमपी (35): एचडीएमपी (25) ने शिथिलता ला दी।

इसके अलावा, अध्ययन उच्च तीव्रता वाले अल्ट्रासाउंड (एचआईयूएस) और इनुलिन निगमन के सहक्रियात्मक मार्ग की जांच करता है ताकि संरचनात्मक गठनात्मक परिवर्तन हो, क्रॉस-लिंकिंग को बढ़ावा दिया जा सके और एचडीएमएस में संरचनात्मक संशोधन को प्रेरित किया जा सके। एचडीएमएस में विभिन्न इनुलिन सांद्रता (0, 2 और 4% w/w) पर और HIUS प्रीट्रीटमेंट (0 W, 200 W, 400 W और 600 W) के साथ और उसके बिना प्रेरित यांत्रिक, संरचनात्मक, रंग और आणविक इंटरैक्शन की जांच की गई। एचआईयूएस और इनुलिन ने सहक्रियात्मक रूप से गैर-न्यूटोनियन स्यूडोप्लास्टिक कतरनी पतलेपन के व्यवहार, विस्कोइलास्टिसिटी, एक्सट्रुडेबिलिटी को बढ़ाया, जिसे हर्शेल-बकले मॉडल द्वारा फिट किए गए रियोलॉजिकल मापदंडों (k , n , τ_0) से मान्य किया गया था। सूक्ष्म संरचनात्मक परिणामों ने जंक्शन क्षेत्र की सीमाओं पर प्रोटीन और इनुलिन के बीच एक मजबूत क्रॉस-लिंक्ड नेटवर्क के विकास की पुष्टि की, जो मजबूत यांत्रिक गुणों का संकेत देता है। इनुलिन जोड़ और एचआईयूएस के संयुक्त प्रभाव ने हाइड्रोफिलिक समूहों के संपर्क और नए हाइड्रोजन लिंकेज के विकास को प्रेरित किया, जिससे लोच में सुधार हुआ जैसा कि एफटीआईआर और रमन स्पेक्ट्रा द्वारा प्रदर्शित किया गया है। द्वितीयक संरचना पर गहरा प्रभाव फॉर्मूलेशन में कम α -हेलिक्स और बढ़ी हुई β -शीट से जुड़ा था, जिससे मुद्रित संरचनाओं की संरचनात्मक अखंडता में सुधार हुआ। एचडीएमएस फॉर्मूलेशन को 4% इनुलिन के साथ मिलाकर और 200 W की एचआईयूएस तीव्रता के अधीन, सर्वोत्तम 3डी प्रिंटिबिलिटी का प्रदर्शन किया गया।

अनुसंधान ने 3डी प्रिंटिंग द्वारा फोर्टिफाइड एचडीएमएस उत्पादों को डिजाइन करने के लिए अपना दायरा भी बढ़ाया। विटामिन डी3 को समाहित करने के लिए विभिन्न जेल मैट्रिसेस (हाइड्रोजेल, ओलेजेल और बीईजेल की विभिन्न संरचनाएं) का उपयोग किया गया था। 3डी प्रिंटिंग अनुप्रयोगों के लिए इसके प्रवाह व्यवहार और पोषण प्रोफ़ाइल को बढ़ाने के लिए जेल सिस्टम को बाद में एचडीएमएस में शामिल किया गया। एचडीएमएस फॉर्मूलेशन की संरचना, विटामिन डी3 सामग्री और 3डी प्रिंटिबिलिटी पर विभिन्न विटामिन डी3 से भरपूर जैल के प्रभाव का पता लगाया गया। माइक्रोस्ट्रक्चरल जांच से पता चला कि 5:5 बीईजेल द्वि-निरंतर था, जबकि 8:2 और 2:8 बीईजेल ने क्रमशः ओलेओजेल और हाइड्रोजेल का एक निरंतर नेटवर्क दिखाया। विभेदक स्कैनिंग कैलोरीमेट्री अध्ययनों के अनुसार, उच्च ओलेजेल सामग्री वाले जैल ने उच्च

शिखर तापमान और एन्थैल्पी का प्रदर्शन किया, जो बढ़े हुए पिघलने वाले तापमान से जुड़े थे। सभी एचडीएमएस फॉर्मूलेशन ने आवृत्ति पर निर्भर G' मूल्यों के साथ एक विस्कोइलास्टिक ठोस व्यवहार ($G' > G''$) का खुलासा किया। 3डी प्रिंटेड एचडीएमएस संरचनाओं में विटामिन डी3 एनकैप्सुलेशन और प्रतिधारण मुख्य रूप से ओलेओगेल अंश द्वारा नियंत्रित किया गया था। ओलेगेल वाले एचडीएमएस ने प्रति मुद्रित निर्माण (273.8 आईयू) में उच्चतम विटामिन डी3 प्रतिधारण प्रदर्शित किया, जबकि हाइड्रोजेल वाले एचडीएमएस ने 3डी मुद्रित निर्माण (132 आईयू) में सबसे कम विटामिन डी3 दिखाया। 3डी प्रिंटिंग व्यवहार पर हाइड्रोजेल का काफी प्रभुत्व था, जिससे हाइड्रोजेल युक्त एचडीएमएस ने सर्वोत्तम 3डी प्रिंटेबिलिटी (एल = 100%, बी = 100%, एच = 98.5%) प्रदर्शित की।

इसके अलावा, अध्ययन का उद्देश्य दो प्रोटीन युक्त इमल्सीफायरों, अर्थात् सोडियम कैसिनेट और व्हे प्रोटीन आइसोलेट के साथ विटामिन डी3 नैनोइमल्शन-आधारित एचडीएमएस जेल को डिजाइन करना और दूध प्रोटीन मैट्रिस के रियोलॉजिकल गुणों पर इमल्सीफायर प्रकार और एकाग्रता के प्रभाव की जांच करना है। क्रिस्टलीय पैटर्न, संरचनात्मक विशेषताएं, थर्मल व्यवहार, 3डी प्रिंटिंग व्यवहार और विटामिन डी3 को समाहित करने और बनाए रखने की क्षमता। सोडियम कैसिनेट और व्हे प्रोटीन आइसोलेट के साथ स्थिर विटामिन डी3-नैनोइमल्शन-आधारित डेयरी जेल ने नियंत्रण की तुलना में बेहतर विस्कोइलास्टिसिटी और 3डी प्रिंटेबिलिटी प्रदर्शित की। इमल्सीफायर्स ने मजबूत अंतर और इंटर आणविक क्रॉसलिंकिंग की सुविधा प्रदान की, जिसके परिणामस्वरूप एक मजबूत जेल प्राप्त हुआ, जैसा कि एफटीआईआर स्पेक्ट्रा, एसईएम और एक्सआरडी पैटर्न से देखा गया है। सोडियम कैसिनेट ने व्हे प्रोटीन आइसोलेट की तुलना में प्रोटीन-प्रोटीन इंटरैक्शन को और मजबूत किया, इसलिए विटामिन डी3-नैनोइमल्शन-आधारित डेयरी जेल को 1% सोडियम कैसिनेट के साथ स्थिर करके उच्चतम भंडारण मापांक (G') (19,580 पास्कल), अधिकतम थर्मल गिरावट तापमान (376 डिग्री सेल्सियस) प्रदर्शित किया गया, और उच्चतम एनकैप्सुलेशन दक्षता (94.1%) और विटामिन डी3 की अवधारण (377.2 आईयू/जी) दर्ज की गई, जिसका श्रेय सबसे कम बूंद के आकार (124.85 नैनो मीटर) और पीडीआई (0.24), उच्चतम जीटा क्षमता (- 44.85 मिली वोल्ट) और स्थिरता (टीएसआई = 0.2) नैनोइमल्शन को जाता है।

इसके अतिरिक्त, 3डी मुद्रित एचडीएमएस की उपभोक्ता धारणा और संवेदी मूल्यांकन से 3डी खाद्य मुद्रण और 3डी मुद्रित एचडीएमएस-आधारित खाद्य उत्पादों के संबंध में जनसंख्या

जनसांख्यिकीय से सकारात्मक प्रतिक्रिया प्राप्त होती है। 3डी मुद्रित एचडीएमएस उत्पादों की स्वाद प्राथमिकताओं में एक महत्वपूर्ण अंतर ($P < 0.05$) था; अधिकांश उत्तरदाताओं ने नैनोइमल्शन-आधारित जेल नमूने के स्वाद को प्राथमिकता दी, जबकि नियंत्रण नमूने को सबसे कम पसंद किया गया। 3डी मुद्रित एचडीएमएस खाद्य पदार्थों की खरीद के प्रति पैनलिस्टों की प्रतिक्रिया काफी हद तक सकारात्मक थी, 60% उत्तरदाताओं ने व्यक्त किया कि वे व्यावसायीकरण पर 3डी मुद्रित खाद्य पदार्थों को "संभवतः खरीदेंगे"।

कीवर्ड: 3डी प्रिंटिंग; सूखे दूध को अर्ध-ठोस गर्म करें; खाद्य संरचना; विटामिन डी3; इमल्शन जैल

TABLE OF CONTENT

	Page no
Certificate	<i>i</i>
Acknowledgements	<i>ii-iii</i>
Abstract	<i>iv-x</i>
List of Figures	<i>xix-xxii</i>
List of Tables	<i>xxiii-xxiv</i>
Abbreviations	<i>xxv-xxvi</i>
Chapter I Introduction	1-10
1.1. Background of Research	2
1.2. Identified Research Gaps & Motivation	6
1.3. Research Objectives	8
1.4. Thesis Structure	8
Chapter II Literature Review	11-57
2.1. Indian Milk Products	12
2.1.1. Milk Sweetmeats	14
2.1.2. Heat Desiccated Milk Semi-solids	17
2.2. 3D Printing in Food Processing	18
2.2.1. Background	18
2.2.2. Techniques Associated with the 3DP Process	21
2.2.3. Factors Affecting 3D Printing Precision	24
2.2.3.1. Parameters Concerning Food Matrix	24
2.2.3.1.1. Formulation	26
2.2.3.1.2. Rheological Properties	30
2.2.3.1.3. Textural Properties	31
2.2.3.1.4. Sensory Attributes	31
2.2.3.2. Parameters Governing Printing Machine	32
2.2.3.2.1. Print Speed and Extrusion Rate	32
2.2.3.2.2. Infill Level	32

2.2.3.2.3.	Layer Height and Nozzle Size	33
2.2.3.2.4.	Extrusion Rate	33
2.2.4.	Approaches to Predict the 3D Food Printing Precision of Food Formulations	34
2.2.4.1.	Determining the dimensional stability of the 3D printed constructs.	34
2.2.4.2.	Novel Screening Through Rheological Evaluation	35
2.2.4.3.	Flow Analysis During 3DFP Computational Fluid Dynamics	35
2.2.4.4.	Non-destructive Techniques: Low Field Nuclear Magnetic Resonance (LFNMR) and Near-infrared (NIR)	37
2.2.4.5.	Numerical Techniques for 3D Printed Construct Analysis	37
2.2.4.6.	Assessment of 3D Printability Based on Alternative Reference Material.	38
2.2.4.7.	Morphological Evaluation	39
2.2.5.	3D Printing in Food Sector	39
2.3.	Strategies for Modifications of Food Materials for 3D Printing Applications	46
2.3.1.	Physical Modification	46
2.3.1.1.	Thermal Treatment	46
2.3.1.2.	High Pressure Treatment	47
2.3.1.3.	Microwave Treatment	48
2.3.1.4.	Addition of Hydrocolloids	49
2.3.1.5.	Ultrasound Treatment	49
2.3.1.6.	pH Shifting	50
2.3.1.7.	Addition of Salt	51
2.3.2.	Chemical Modification	51
2.3.2.1.	Reaction with Sugars	51
2.3.2.2.	Complexation with Polyphenol	52
2.3.2.3.	Complexation with Polysaccharides	53
2.3.2.4.	Addition of Di or Trivalent Cations	53
2.3.2.5.	Biosurfactants	54
2.3.3.	Enzymatic Modification	54
2.4.	3D Printing for Health Improvement and Personalized Nutrition	55
Chapter III Assessment of the 3D Printability of Heat Desiccated Milk-semisolids as a Food Formulation by Correlating with its Rheological Properties		58-94
3.1.	Background	59
3.2.	Materials and Methods	62

3.2.1.	Raw materials	62
3.2.2.	Preparation of Formulations	62
3.2.3.	Rheological Analysis	63
3.2.3.1.	Shear Viscosity Test	63
3.2.3.2.	Amplitude and Frequency Sweep Tests	63
3.2.3.3.	Temperature Ramp Test	64
3.2.3.4.	Rotational Recoverability Test	64
3.2.4.	3D Printing Process	64
3.2.5.	Assessment of Printability	65
3.2.6.	Statistical Analysis	66
3.3.	Results and Discussion	66
3.3.1.	Rheological Behaviour of Formulations During the Pre-printing Stage (25 °C)	66
3.3.1.1.	Shear Thinning Behaviour	66
3.3.1.2.	Viscoelastic Behaviour	69
3.3.1.3.	Yield Stress	73
3.3.1.4.	Thermo-responsive Behaviour	74
3.3.1.5.	Initial Screening of Printability of the Formulations	76
3.3.2.	Rheological Behaviour of Formulations During Printing (Extrusion Stage at 40 °C)	78
3.3.2.1.	Shear Thinning Behaviour	78
3.3.2.2.	Investigation of the Yield Stress of the Formulation at Printing Temperature (40 °C)	81
3.3.2.3.	Viscoelastic Behaviour	83
3.3.3.	Rheological Behaviour of Formulations During the Recovery Stage (25 °C)	86
3.3.4.	Correlating Rheological Behaviour of the Formulations with 3D Printability	88
3.4.	Conclusion	93
Chapter IV Study of the Effect of High Intensity Ultrasound Pretreatment and Incorporation of Inulin on Restructuring of Heat Desiccated Milk-Semisolids with 3D Printing		95-125
4.1.	Background	96
4.2.	Materials and Methods	99
4.2.1.	Raw Materials and Sample Preparation	99
4.2.2.	Preparation of 3D Printing Material Supply	99

4.2.3.	Rheological Characterization	100
4.2.4.	Fourier Transform Infrared (FTIR) Spectroscopy	101
4.2.5.	Microstructural Properties	101
4.2.6.	Colorimetric Analysis	101
4.2.7.	Raman Spectroscopy	102
4.2.8.	3D Printing Process and Assessment of Printability	102
4.2.9.	Statistical Analysis	103
4.3.	Results and Discussion	103
4.3.1.	Steady and Dynamic Oscillatory Rheological Attributes	103
4.3.2.	FTIR Spectra Analysis	109
4.3.3.	Microstructure	112
4.3.4.	Instrumental Colour Attributes of 3D Printed Constructs	114
4.3.5.	Raman Spectroscopy	116
4.3.6.	3D Printing Behaviour	118
4.3.7.	Correlation	122
4.4.	Conclusion	124

Chapter V Investigation on the Effect of Food Grade Vitamin D₃ Gels as Additives on the 3D Printing Behaviour of Heat Desiccated Milk Semi-Solids 126-152

5.1.	Background	127
5.2.	Materials and Methods	129
5.2.1.	Raw Materials	129
5.2.2.	Preparation of Gel Systems	129
5.2.2.1.	Oleogel	129
5.2.2.2.	Hydrogel	130
5.2.2.3.	Bigels	130
5.2.3.	Swelling Capacity of Gels	130
5.2.4.	Rheological Characterization of Gel Systems	131
5.2.5.	Microstructure of Gels	131
5.2.6.	Thermal Properties of the Gel Systems	132
5.2.7.	Encapsulation Properties of the Gel Systems	132
5.2.8.	Development of Personalised Micronutrient Delivery System via 3D Printing Technology	133
5.2.8.1.	Preparation of the Material Supply for 3D Printing	133

5.2.8.2.	Rheological Characterization of the 3D Printing Feed Material	133
5.2.8.3.	3D Printing Performance of the HDMS Formulations	134
5.2.8.4.	Quantification of Vitamin D ₃ in the 3D printed HDMS Constructs	134
5.2.9.	Statistical Analysis	135
5.3.	Results and Discussion	135
5.3.1.	Appearance and Physical Stability of Different Gel Systems	135
5.3.2.	Swelling Capacity of Gels	136
5.3.3.	Rheological Characterization of Gel Systems	137
5.3.4.	Microstructure of Gels	138
5.3.5.	Thermal Properties of Gel Systems	141
5.3.6.	Encapsulation Properties of the Gel Systems	144
5.3.7.	Development of Personalised Micronutrient Delivery System via 3D Printing Technology	145
5.3.7.1.	Rheological Characterization of the 3D Printing Material Supply	145
5.3.7.2.	3D Printing Behaviour of Vitamin D ₃ gel Incorporated HDMS Formulations	148
5.3.7.3.	Evaluation of Vitamin D ₃ in the 3D Printed Vitamin D ₃ Gel Incorporated HDMS Formulations	150
5.4.	Conclusion	151
Chapter VI	Modulation of the 3D Printability of Vitamin D₃-nanoemulsion-based Heat Desiccated Milk-Semisolids Gels	153-190
6.1.	Background	154
6.2.	Materials and Methods	156
6.2.1.	Raw Materials	156
6.2.2.	Preparation of Vitamin D ₃ Nanoemulsions	156
6.2.3.	Physical Stability of Nanoemulsions	157
6.2.3.1.	Multiple Light Backscattering	157
6.2.3.2.	Measurement of Mean Droplet Size, Polydispersity Index and Zeta Potential	157
6.2.4.	Development of Vitamin D ₃ -Nanoemulsion-Based Dairy Gels	157
6.2.5.	Characterization of Vitamin D ₃ -Nanoemulsion-Based Dairy Gels	159
6.2.5.1.	Rheological Properties	159
6.2.5.2.	Thermogravimetric Analysis	159
6.2.5.3.	Fourier Transform Infrared Spectroscopy	160
6.2.5.4.	X-ray Diffraction	160

6.2.5.5.	Scanning Electron Microscopy	160
6.2.6.	Vitamin D ₃ (Cholecalciferol) Encapsulation Efficiency of Nanoemulsion-Based Dairy Matrices	161
6.2.7.	3D Printing Behaviour of Vitamin D ₃ -Nanoemulsion-Based Dairy Gels.	161
6.2.8.	Estimation of Vitamin D ₃ (Cholecalciferol) in the 3D printed Nanoemulsion-Based Dairy Constructs	161
6.2.9.	Statistical Analysis	162
6.3.	Results and Discussion	163
6.3.1.	Physical Stability Analyses of Vitamin D ₃ Nanoemulsions	163
6.3.1.1.	Multiple Light Backscattering	163
6.3.1.2.	Mean Droplet Size, Polydispersity Index and Zeta Potential of the Nanoemulsions	165
6.3.2.	Rheological Properties of Vitamin D ₃ -Nanoemulsion-Based Dairy Gels as Affected by Emulsifier Type and Concentration	166
6.3.3.	Thermal Gravimetric Analyses of Vitamin D ₃ -nanoemulsion-based Dairy Protein Gels	174
6.3.4.	Chemical Structural Characterization of Vitamin D ₃ -nanoemulsion-Based Dairy Protein Matrices	175
6.3.5.	XRD Pattern of Different Vitamin D ₃ -nanoemulsion-Based Dairy Gels	178
6.3.6.	Microstructure of Different Vitamin D ₃ -Nanoemulsions-Based Dairy Matrices	182
6.3.7.	Vitamin D ₃ Encapsulation Efficiency of vitamin D ₃ -nanoemulsion-Based HDMS Gels as Affected by Emulsifier Type and Concentration.	183
6.3.8.	Assessment of 3D Printability of Vitamin D ₃ -Nanoemulsion-Based HDMS Gels	184
6.3.9.	Vitamin D ₃ in the 3D printed Nanoemulsions-Based Dairy Constructs.	188
6.4.	Conclusion	188

Chapter VII Consumer Perception of 3D Printed Heat Desiccated Milk Semi-Solids Based Products 191-198

7.1.	Background	192
7.2.	Materials and Methods	193
7.2.1.	3D Printing Formulation	193
7.2.2.	3D Printing Process	193
7.2.3.	Consumer Acceptance Study	194
7.2.4.	Design of Questionnaire	195

7.3.	Results and Discussion	195
Chapter VIII Summary, Conclusion, and Future Perspectives		199-207
8.1.	Conclusion	200
8.1.1.	Interplay of Formulation Engineering and Systematic Rheological Approach to Develop HDMS Formulations for Application in Extrusion-Based 3D Printing	200
8.1.2.	Formulation Engineering Employing a Synergistic Approach to create HDMS Formulations for Extrusion-Based 3D Printing Applications	201
8.1.3.	Fortification by Design to Develop vitamin D ₃ Fortified HDMS-Based Formulations for Extrusion-Based 3D Printing	202
8.2.	Applications of research Outcomes	204
8.3.	Recommendations for Future Work	205
	References	208
	Appendix	235
	Biodata	241

LIST OF FIGURES

Figure No.	Title	Page No.
Fig. 2.1	Classification of Indian dairy sweetmeats	14
Fig. 2.2	Structure of Indian dairy industry	14
Fig. 2.3	A schematic diagram of the 3D food printing	20
Fig. 2.4	A schematic illustration of types of 3D printing technologies	22
Fig. 2.5	A schematic representation of integration of 3D printing and encapsulation	56
Fig. 3.1	Pictorial view of the piston type extrusion 3D printer	65
Fig. 3.2	Steady shear rheological properties of formulations at pre-printing stage (25 °C) (a) flow curves of formulations, (b) shear rate and dynamic viscosity relationship	68
Fig. 3.3	Variation of storage modulus G' and loss modulus G'' with shear strain at 6.28 rad s ⁻¹	71
Fig. 3.4	Frequency sweep test showing variation in G' and loss modulus G'' during pre-printing (25 °C)	72
Fig. 3.5	Thermo-responsive behaviour of formulations with a heating rate of 3 °C min ⁻¹	74
Fig. 3.6	Initial screening of printability of composite dairy based formulations; (a) 1D printability by observing the consistency of lines, (b) 2D printability by measuring the area of the lattice scaffolds, and (c) schema of area formation of formulations from 2D printability	77
Fig. 3.7	Flow curves of formulations during extrusion stage at 40 °C	78
Fig. 3.8	Shear rate and dynamic viscosity relationship during extrusion stage at 40 °C	79
Fig. 3.9	Yield stress (τ_0) values of the formulations determined at printing temperature (40 °C) by oscillatory analysis	82
Fig. 3.10	Dynamic oscillatory shear rheological properties of formulations during extrusion stage at 40 °C, (a) variation of storage modulus G' and loss modulus G'' with shear strain at 6.28 rad s ⁻¹ , and (b) frequency sweep test showing variation in G' and loss modulus G''	85

Fig. 3.11	Shear recoverability of inks during recovery stage (25 °C) (a) recovery tests of formulations under alteration of high and low shear rates, and (b) shear recoverability of formulations obtained during the test	87
Fig. 3.12	Images of constructs printed at 40 °C using different formulations	89
Fig. 3.13	Surface interaction plot of dimensional stability factor (DSF) in terms of (a) length, (b) breadth, and (c) height as a function of storage modulus and yield stress	90
Fig. 3.14	Surface interaction plot of dimensional stability factor (DSF) in terms of (a) length, (b) breadth, and (c) height as a function of viscosity and yield stress	91
Fig. 3.15	Surface interaction plot of dimensional stability factor (DSF) in terms of (a) length, (b) breadth, and (c) height as a function of phase angle and gelation temperature	92
Fig. 4.1	Images of HDMS and inulin for formulation of 3D printing material supply	100
Fig. 4.2	Viscosity profiles of HDMS formulations as affected by HIUS treatment and inulin addition, (a) HIUS treatment (0, 200, 400 & 600 W), (b) Inulin (2 % w/w) with HIUS treatment (0, 200, 400 & 600 W), and (c) Inulin (4 % w/w) with HIUS treatment (0, 200, 400 & 600 W)	104
Fig. 4.3	Effect of HIUS treatment and inulin addition on the amplitude sweep profiles of HDMS formulations, (a) HIUS treatment (0, 200, 400 & 600 W), (b) Inulin (2 % w/w) with HIUS treatment (0, 200, 400 & 600 W), and (c) Inulin (4 % w/w) with HIUS treatment (0, 200, 400 & 600 W)	107
Fig. 4.4	Effect of HIUS treatment and inulin addition on the frequency sweep profiles of HDMS formulations, (a) HIUS treatment (0, 200, 400 & 600 W), (b) Inulin (2 % w/w) with HIUS treatment (0, 200, 400 & 600 W), and (c) Inulin (4 % w/w) with HIUS treatment (0, 200, 400 & 600 W)	109

Fig. 4.5	FTIR spectra of HDMS formulations influenced by synergistic effect of inulin addition and HIUS treatment	112
Fig. 4.6	Microstructure (x200) of HDMS formulations influenced by combined HIUS treatment and inulin addition	114
Fig. 4.7	Raman spectra (500-2500 cm^{-1}) as affected by combined HIUS treatment and inulin addition	118
Fig. 4.8	Images of 3D constructs printed from HDMS formulations with varied inulin concentration and HIUS intensities	120
Fig. 5.1	Appearance and physical stability of various structured gels (hydrogel, oleogel, and bigels)	136
Fig. 5.2	Swelling capacity of different structured gel systems (hydrogel, oleogel, and bigels)	137
Fig. 5.3	Storage moduli of various structured gels at varying temperature (25-85 $^{\circ}\text{C}$) at heating rate of $5^{\circ}\text{C min}^{-1}$	138
Fig. 5.4	Microstructure of different structured gels as obtained from CLSM and cryo-SEM	141
Fig. 5.5	Thermographs of various structured gels (hydrogel, oleogel, and bigels)	142
Fig. 5.6	Storage and loss moduli of HDMS incorporated with different vitamin D_3 loaded gels (a) amplitude sweep (0.01-100%), and (b) frequency sweep (0.1-100 rad s^{-1})	147
Fig. 5.7	3D printing behaviour of vitamin D_3 gel incorporated HDMS formulations, (a) 3D printed constructs of various vitamin D_3 fortified HDMS gels, and (b) dimensional stability (%) in linear dimensions	149
Fig. 5.8	Vitamin D_3 content (IU) in the 3D printed fortified HDMS construct incorporated with different vitamin D_3 loaded gels	151
Fig. 6.1	A schematic representation of molecular structure of vitamin D_3 -nanoemulsion-based HDMS gels stabilized with NaCas and WPI	158
Fig. 6.2	Visual appearance of (a) vitamin D_3 nanoemulsions and (b) vitamin D_3 -nanoemulsion-based HDMS gels prepared with different emulsifier types and concentrations	164

Fig. 6.3	Turbiscan stability index (TSI) of vitamin D ₃ nanoemulsions stabilised by whey protein isolate and sodium caseinate	164
Fig. 6.4	Rheological behaviour: (a) viscosity profile, (b) amplitude sweep, (c) frequency sweep, (d) temperature sweep, and (e) shear recovery profile of vitamin D ₃ -nanoemulsion-based HDMS gels with emulsifier variants	173
Fig. 6.5	Thermal gravimetric analysis of (a) HDMS, NaCas, WPI, vitamin D ₃ , and (b) vitamin D ₃ -nanoemulsion-based HDMS gels prepared with different emulsifier types and concentrations	175
Fig. 6.6	FTIR spectra of vitamin D ₃ -nanoemulsion-based HDMS gels formulated with varied emulsifier type and concentration	178
Fig. 6.7	Effect of emulsifier type and concentration on the XRD patterns of (a) HDMS, NaCas, WPI, vitamin D ₃ , and (b) vitamin D ₃ -nanoemulsion-based HDMS gels	181
Fig. 6.8	Microstructure of vitamin D ₃ -nanoemulsion-based HDMS gels formulated with varied emulsifier type and concentration	183
Fig. 6.9	3D printed constructs of vitamin D ₃ -nanoemulsion-based HDMS gels produced with different emulsifier variants	186
Fig. 7.1	Representative images of 3D printed HDMS products used for consumer perception study	194
Fig. 7.2	Familiarity of the respondents' (N=25) towards 3D printing or 3D printed foods	196
Fig. 7.3	Just about right (JAR) scales for (a) sweetness, and (b) texture	196
Fig. 7.4	Consumer preferences' distribution for the sensory attributes of the 3D printed HDMS food products	197
Fig. 7.5	Willingness of the participants (N=25) to purchase the 3D printed HDMS food products	198

LIST OF TABLES

Table No.	Title	Page No.
Table 2.1	Market size of traditional dairy products	13
Table 2.2	Popular milk sweetmeats consumed worldwide	16
Table 2.3	Comparative assessment of various categories of 3D printing technologies	23
Table 2.4	Application of 3D printing in food formulations	43
Table 3.1	Concentration levels of ingredients used for preparation of formulations	63
Table 3.2	Estimated rheological parameters of formulations during pre-printing (25 °C)	69
Table 3.3	Viscoelastic properties of formulations at pre-printing stage (25 °C)	71
Table 3.4	Thermo-responsive behaviour of formulations	76
Table 3.5	Estimated rheological parameters of formulations during printing stage (40 °C)	81
Table 3.6	Yield stress values at printing temperature (40 °C) by dynamic oscillatory analysis	83
Table 4.1	Steady and dynamic oscillatory rheological parameters influenced by the combined effect of HIUS treatment and inulin addition	106
Table 4.2	Colour parameters of 3D printed constructs with different intensities of HIUS treatment and inulin levels	116
Table 4.3	3D printability of HDMS formulations as affected by varying intensities of HIUS treatment and inulin concentration	121
Table 4.4	Colour coded Pearson correlation map for the relationship among rheological attributes, structure, and 3D printability of HDMS formulations	123
Table 5.1	Peak temperature (T_p), enthalpy (ΔH), onset and endset points of different vitamin D ₃ encapsulated gels	143

Table 5.2	Vitamin D ₃ encapsulation efficiency in different gel systems	144
Table 6.1	Effect of type and concentration of emulsifier on mean droplet size, polydispersity index (PDI) and zeta - potential of vitamin D ₃ nanoemulsions	166
Table 6.2	Steady and dynamic rheological attributes of vitamin D ₃ -nanoemulsion-based dairy gels influenced by the type and concentration of emulsifier	168
Table 6.3	Vitamin D ₃ encapsulation efficiency and retention in the nanoemulsion-based dairy gels as affected by emulsifier type and concentration	184
Table 6.4	Assessment of 3D printability of different vitamin D ₃ -nanoemulsion-based HDMS gels	187

LIST OF SYMBOLS AND ABBREVIATIONS

°C	Degree centigrade
3D	Three dimensional
ANOVA	Analysis of variance
b	Breadth
cm	Centimetre
Eq.	Equation
FAO	Food and Agriculture Organization
Fig.	Figure
FT-IR	Fourier transform infrared spectroscopy
g	Gram
h	Hour
h	Height
HPLC	High performance Liquid Chromatography
IU	International unit
K	Kelvin
Kg	Kilogram
kJ	Kilo joule
kV	Kilo volt
l	Length
LVR	Linear viscoelastic range
mg	Milligram
min	Minute
mM	Milli molar
mm	Millimetre
mol	Mole
nm	Nanometer
Pa	Pascal
PDI	Polydispersity index
rpm	Revolutions per minute
s	Second
SD	Standard deviation
SEM	Scanning Electron Microscopy

XRD	X-ray diffraction
μg	Microgram
μL	Microlitre
μm	Micrometre
