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EFFECT OF HYDROCOLLOIDS ON MOLECULAR STRUCTURE, RHEOLOGY, AND PRINTABILITY IN 3D FOOD PRINTING TECHNOLOGY

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ABSTRACT

Three-dimensional food printing (3DFP), particularly extrusion-based direct ink writing, depends on the ability of a food formulation to move through a narrow nozzle and then rapidly recover a mechanically stable structure after deposition. Native purées, starch pastes, protein dispersions, and mixed food systems seldom occupy this complete processing space because flowability and post-deposition stability are coupled to composition, water distribution, molecular association, particle packing, and temperature. Hydrocolloids are therefore not simply viscosity modifiers; they are molecular design tools that alter hydration, chain conformation, interpolymer association, phase behaviour, gelation, and the balance between viscous dissipation and elastic recovery.

This review expands on hydrocolloid structure, food rheology, extrusion printing, protein-polysaccharide interactions, and post-processing. Hydrational properties establish the effective hydrodynamic volume; those structures determine zero- and finite-shear viscosity, yield stress, viscoelasticity, and structural recovery; and these rheological properties finally govern extrusion pressure, filament continuity, dimensional fidelity, interlayer stability, and post-processing behaviour. Evidence from starch, vegetable, fruit, protein, meat-analogue, and emulsion systems shows that hydrocolloid effects are strongly formulation-specific.

The most transferable design principle is consequently a molecular-to-process framework in which hydrocolloid type, concentration, charge density, molecular weight, branching, and gelation trigger are selected against the intended deposition conditions rather than optimized in isolation. The review concludes with a practical formulation map, evidence-based design rules, and research priorities for scalable, multi-material, and stimuli-responsive food printing.

KEYWORDS: 3D food printing; Molecular structure; Rheology; Personalized nutrition; Hydrocolloids

1. INTRODUCTION

Three-dimensional food printing (3DFP) is an additive-manufacturing route in which a digitally defined geometry is converted into a physical food structure through sequential deposition. Extrusion-based systems are particularly attractive because they can handle pastes, gels, protein-rich dispersions, and other semi-solid formulations without requiring a fully rigid powder feedstock. Early reviews emphasized customization of shape, texture, colour, flavour, and nutrition as the major opportunity of 3DFP (Godoi et al., 2016; Sun et al., 2015).

The formulation challenge can be expressed as a printability envelope. A printable ink must be sufficiently mobile under the stresses generated in the nozzle, sufficiently cohesive to produce a continuous filament, sufficiently resistant to gravity-driven deformation after deposition, and sufficiently compatible with successive layers to avoid delamination or distortion. Kim et al. (2019) demonstrated the usefulness of standardized hydrocolloid reference materials for classifying deformation behaviour and dimensional stability across foods, while Guo et al. (2019) showed that model-building and slicing decisions can themselves affect printing quality. (Liu, Zhang, Bhandari, et al., 2018) linked the rheological behaviour of mashed potatoes to actual printing performance and showed a clear optimum rather than a monotonic relationship between formulation solids and printability. Their observation is consistent with the wider review of Pérez et al. (2019), which concluded that yield stress, consistency, and viscoelastic parameters can predict printability only when interpreted together with printer variables. Vancauwenberghe et al. (2018) further demonstrated that pectin-based inks could be used to manufacture food honeycombs with controlled porosity and that the fidelity of the actual printed geometry influences how well model-based texture predictions match the final structure.

In food formulations, hydrocolloids can contribute viscosity at low concentration, alter water mobility, stabilize dispersed particles or droplets, generate physically associated networks, or provide specific gelation triggers. Saha and Bhattacharya (2010) emphasized the distinction between thickening and gelling functions; the difference is highly relevant to 3DFP because a thickener can improve low-shear stability without necessarily generating a fast post-deposition solidification mechanism.

Rinaudo (2008) similarly showed that polysaccharide behaviour depends on chemical structure and ionic environment rather than simply polymer concentration.

2. Classification and Molecular Structure of Functional Food Hydrocolloids

In 3DFP, hydrocolloids play a key role as thickening and gelling agents for smooth extrusion. Commonly used hydrocolloids in 3DFP are xanthan gum (Demircan et al., 2023; Sahu et al., 2026), gellan gum (Vijayan et al., 2025), guar gum (He et al., 2023), k-carrageenan (Pant et al., 2021), agar (Jeon et al., 2024), konjac gum, pectin, gelatin, flaxseed gum, carboxymethylcellulose, etc.

Hydrocolloids encompass a broad family of hydrophilic polymers, including polysaccharides and proteins, that form viscous dispersions or gels in aqueous media. Their behaviour in food inks is governed by backbone chemistry, molecular weight, branching, charge density, degree of substitution, flexibility, and interactions with water, salts, proteins, starch, and other hydrocolloids (Rinaudo, 2008; Saha & Bhattacharya, 2010). A useful classification for 3DFP is: neutral polysaccharides, anionic hydrocolloids, cationic hydrocolloids, and protein-polysaccharide composite systems.

Neutral polysaccharides include starch-derived structures, guar gum, locust bean gum, and curdlan. Starch is unusual because it is both a polymer and a particulate semi-crystalline material before gelatinization; its amylose and amylopectin fractions determine swelling, paste development, gelation, and retrogradation. Guar and locust bean gum are galactomannans whose relatively flexible, highly hydrated chains can produce large increases in low-shear viscosity. Curdlan is a linear β-(1→3)-glucan with a distinctive thermally induced gelation behaviour. McIntosh et al. (2005) showed that curdlan's rheological and thermal properties arise from its chain architecture and association into ordered structures, making it fundamentally different from a simple soluble thickener. In food printing, this distinction matters because curdlan can create a persistent network after a thermal trigger, whereas a neutral thickener may mainly increase resistance to flow.

Anionic hydrocolloids include xanthan, alginate, pectin, gellan, and carrageenan. Their negative charge strongly influences chain conformation and their response to cations. Fialho et al. (2008) described gellan as an anionic polysaccharide whose acylation state changes the balance between elastic, soft gels and firmer, more brittle structures. Geonzon et al. (2020) and Hilliou (2021) similarly showed that carrageenan gelation is a multi-scale process involving helix formation, association, and network organization rather than a single molecular event. Alginate has a different advantage: calcium ions can generate physical junctions between guluronate-rich regions, so gel formation can be spatially and temporally controlled. Divalent-cation-induced alginate gels and emphasized that ionic environment is an integral part of the material design (Rinaudo, 2008).

Cationic hydrocolloids are represented most prominently by chitosan. Protonation of the polymer's amino groups in acidic conditions changes its solubility and electrostatic interactions, allowing it to interact with anionic polysaccharides and other negatively charged food components. Direct 3DFP literature on chitosan is smaller than the literature on xanthan, alginate, pectin, and carrageenan; therefore, the role of chitosan should not be generalized from biomedical hydrogel behaviour alone. Nevertheless, Feng et al. (2022) provide direct food-printing evidence that chitosan can alter water distribution, rheology, and printing stability in a starch-based hydrogel, demonstrating that its cationic character can have a practical food-ink consequence (Feng et al., 2022).

Protein hydrocolloids and protein-polysaccharide complexes represent a second design dimension. Gelatin, whey proteins, soy proteins, milk proteins, and plant proteins can interact with polysaccharides through electrostatic attraction, hydrogen bonding, hydrophobic association, depletion, steric effects, and, under suitable conditions, complex coacervation. Milk-protein concentrate inks with different hydrocolloids generated different complex networks and markedly different zero-shear viscosity, thixotropy, and structural retention (Liu et al., 2022). Similarly, gelatin and sodium alginate could modify the rheology and textural properties of soy-protein-based inks without requiring covalent cross-linking during the printing conditions (Chen et al., 2019). These findings demonstrate that hydrocolloids should be treated as a family of structure-building molecules rather than a single functional ingredient.

The comparison across these classes produces an important formulation principle. Neutral polymers mainly alter hydration, chain overlap, and physical entanglement; anionic polymers add electrostatic and ion-mediated control; cationic polymers introduce pH-responsive association; and protein-polysaccharide mixtures create composite networks in which the structural state of one biopolymer can constrain the other. The most effective food ink is often a deliberately combined network rather than a single hydrocolloid.

Table 1. Molecular structure and function for hydrocolloids relevant to 3DFP

Class	Examples	Molecular feature	Mechanism	Rheological consequence	3DFP relevance	References
Neutral polysaccharide	Starch	Amylose/amylopectin; semi-crystalline granules before gelatinization	Gelatinization, hydrogen bonding, retrogradation	Changes paste viscosity, yield stress and recovery; solids can improve buildability but impair extrusion at excess levels	Starch-based pastes and doughs	(Liu, Zhang, Bhandari, et al., 2018)

Neutral polysaccharide	Guar gum	Highly hydrated branched galactomannan	Hydration and chain entanglement	Strong low-shear thickening; can reduce syneresis but may raise extrusion resistance	Starch and vegetable inks	(Liu, Zhang, & Bhandari, 2018)
Anionic polysaccharide	Xanthan gum	High-MW heteropolysaccharide with charged side chains	Hydration, rigid-chain association and entanglement	Strong shear-thinning and low-shear structure; high elasticity may contribute to die-swell	Mashed potato, vegetable and composite inks	(Liu, Zhang, & Bhandari, 2018; Sahu et al., 2026)
Anionic polysaccharide	Alginate	M/G sequence-dependent uronic-acid copolymer	Ca^{2+}-mediated ionic cross-linking	Rapid post-extrusion or in-line gelation; useful for shell/core architectures	Produce, gels, multi-material printing	(Vancauwenberghe et al., 2018)
Anionic polysaccharide	Pectin	Galacturonan-rich plant polysaccharide; degree of methylation controls behaviour	Ca^{2+} cross-linking for low-methoxyl pectin; acid/sugar gelation for high-methoxyl pectin	Water binding and network formation; suitable for defined texture and cellular structures	Fruit-based and pectin food simulants	(Vancauwenberghe et al., 2018)
Anionic polysaccharide	Carrageenan	Sulfated galactan; κ/ι/λ forms differ in substitution	Coil-to-helix transition and ionic-assisted association	Thermo-responsive viscoelasticity; strong influence on G′ and gel temperature	Protein and starch composite inks	(Liu et al., 2019)
Protein hydrocolloid	Gelatin	Partially hydrolyzed collagen; amphoteric protein	Thermoreversible helix-associated junctions	Temperature-sensitive viscosity and recovery; supports layer setting on cooling	SPI and protein-rich inks	(Chen et al., 2019)
Neutral bacterial polysaccharide	Curdlan	Linear β-(1→3)-glucan	Thermal self-association and ordered gel formation	Persistent thermal gel network; potential for structural locking	Meat analogues and thermal post-processing	(McIntosh et al., 2005)
Cationic polysaccharide	Chitosan	Deacetylated chitin with protonatable amino groups	Electrostatic association and hydrogen bonding	pH-sensitive hydration and network interactions; can alter water mobility	Starch/functional inks	(Feng et al., 2022)
Protein-polysaccharide composite	SPI/MPC + hydrocolloid	Heterogeneous protein-particle/polymer network	Electrostatic, hydrogen-bond, steric and associative interactions	Composite rheology can be tuned for shear-thinning, elasticity and recovery	Protein-rich, emulsion and meat-analogue inks	(Chen et al., 2019)

3. Hydrocolloid-Water and Hydrocolloid-Biopolymer Interactions at the Molecular Scale

Hydration is the first event. A hydrocolloid that disperses efficiently in water increases the effective hydrodynamic size of its chains and changes the fraction of free, weakly bound, and strongly associated water. The result is not merely an increase in viscosity; water becomes part of the structure of the ink. Liu, Zhang and Bhandari (2018) used nuclear magnetic resonance and infrared approaches to show that different gums altered water mobility and molecular interactions in mashed potato systems. Feng et al. (2022) extended this concept to a β-carotene-loaded yam starch hydrogel, finding that hydrocolloid type influenced water migration, rheology, texture, microstructure, and print stability. Notably, chitosan promoted migration from weakly bound toward more tightly associated water, illustrating that the same nominal concentration of different hydrocolloids can generate different molecular states.

Hydrogen bonding provides another route to network formation. In starch-rich systems, water competes with polymer-polymer interactions, while heating, cooling, and concentration determine when chains become sufficiently associated to create a mechanically coherent network. Liu, Zhang and Bhandari (2018) showed that gum addition changed FT-IR and NMR signatures in mashed potato formulations alongside changes in viscosity, modulus, and printing performance. Chen et al. (2019) provided an important counter-example to the assumption that every formulation improvement requires chemical cross-linking: their soy-protein/gelatin/alginate formulations improved printability and texture even though no chemical linkage between SPI

and gelatin was detected under the tested mixing and printing conditions. The practical implication is that reversible physical association can be sufficient when its kinetics match the extrusion process (Chen et al., 2019).

Carrageenan illustrates the importance of hierarchical assembly. κ-, ι-, and λ-carrageenan differ in their ability to form networks because of sulfate substitution and helix-forming behaviour (Geonzon et al., 2020). Hilliou (2021) emphasized the relationship between carrageenan structure and elastic properties and noted that a consensual description involves a coil-to-helix transition followed by helix aggregation. In a 3DFP context, this means that the apparent storage modulus measured at a fixed temperature reflects not only polymer concentration but also whether chains have already entered an ordered state. Thermo-responsive printing therefore requires control of temperature history as much as polymer chemistry (Hilliou, 2021).

Ionic cross-linking adds spatial control to molecular association. Alginate-calcium systems are the canonical example: divalent calcium coordinates with carboxylate-rich alginate regions to create junctions. Although, food hydrocolloids emphasize that ion availability and polysaccharide sequence distribution determine the resulting gel structure (Saha & Bhattacharya, 2010). In printing, this can be advantageous because the formulation can be extruded in a relatively mobile state and subsequently set by exposure to calcium, reducing the need to force the full strength of the final gel through the nozzle.

Protein-polysaccharide complexation adds another layer because the network can become spatially heterogeneous. Through microscopy and rheology, that κ-carrageenan, pectin, guar gum, and sodium alginate formed different associations with milk-protein concentrate, whereas xanthan behaved differently and did not always maximize structure retention (Liu et al., 2022). Ji et al. (2022) provided a complementary starch-protein example in which casein altered starch molecular dimensions and the multi-scale gel structure, improving printing precision even though structural recovery decreased. These studies caution against equating stronger rheology with better printing: a molecular change that increases elasticity or modulus can improve dimensional stability while simultaneously reducing recovery kinetics or extrudability (Ji et al., 2022).

4. Molecular Conformation to Non-Newtonian Extrusion Rheology

Extrusion-based 3DFP is a transient non-Newtonian process. The material experiences a low-stress storage state, a high-shear transport state, and a post-deposition recovery state. No single steady-shear measurement captures all three.

For yield-stress fluids, the Herschel-Bulkley relation is a practical representation: $\tau = \tau_0 + K\dot{\gamma}^n$, where τ is shear stress, τ_0 is the fitted yield-stress parameter, K is the consistency index, $\dot{\gamma}$ is shear rate, and n is the flow-behaviour index. When $n < 1$, the fluid is shear-thinning. Barnes (1999) noted that yield stress is a complex material concept rather than a universal thermodynamic constant; this distinction is important in food printing because different experimental protocols can produce different apparent yield-stress values. In the printing context, the parameter is best treated as a comparative descriptor of the stress required to initiate substantial flow under a defined test method.

The strongest direct evidence comes from mashed-potato studies. Liu, Zhang, Bhandari, et al. (2018) reported that unmodified mashed potato with 0% added potato starch had a yield stress of approximately 195.90 Pa and developed sagging after printing. At 2% added potato starch, yield stress increased to about 312.16 Pa and the formulation showed improved printability; at 4%, structural retention remained high but extrudability worsened because viscosity and consistency increased excessively. This non-monotonic response is a central lesson for hydrocolloid engineering: the target is an intermediate rheological window rather than the highest possible modulus or viscosity.

Liu, Zhang and Bhandari (2018) also evaluated xanthan, guar, κ-carrageenan, and κ-carrageenan/xanthan combinations in mashed potatoes. Gum addition generally increased viscosity and the dynamic moduli, but the magnitude and direction of change depended on the individual gum. Their NMR and FT-IR observations linked these macroscopic changes to altered water mobility and molecular interactions. The multicomponent study of Liu et al. (2019) strengthened this conclusion by showing that carrageenan-xanthan-starch formulations could be tuned to generate greater viscosity, yield stress, storage modulus, shear-thinning, and thixotropic recovery, while the optimum printability was still determined by the combined response rather than by any single parameter.

Beyond steady shear by applying three-interval thixotropy testing to starch-based inks containing xanthan, methylcellulose, hydroxypropyl methylcellulose, alginate, and starch. They showed that deformation and structural recovery influenced object stability and that the time interval between deposited layers could affect printing accuracy. This finding directly connects material relaxation time with process planning: even a formulation with acceptable single-filament properties can lose fidelity when the layer cycle is too rapid for the network to recover before being loaded by subsequent layers (Heckl et al., 2023).

Pérez et al. (2019) reviewed the wider literature and concluded that storage modulus, yield stress, consistency index, and flow behaviour index all contribute to printability, while nozzle speed and layer height also influence final geometry. Kim et al. (2018) reached a similar systems-level conclusion through a hydrocolloid reference framework: dimensional stability and handling must be evaluated together. These findings argue against universal numerical thresholds for τ_0 or n. An apparently ideal rheogram can still produce a poor print when particle size, nozzle diameter, thermal history, or layer timing is inappropriate.

Three-interval thixotropy tests are particularly valuable because they reproduce the sequence of resting, high-shear destruction, and recovery (Vijayan et al., 2025). The relevant metric is not simply the magnitude of recovery but the kinetics and reproducibility of recovery. A formulation that recovers only after several minutes may be unsuitable for continuous layer deposition even when its final plateau modulus is high. In contrast, a moderately stiff network with fast recovery can maintain fidelity more effectively.

Thus, rheology should be treated as a time-dependent process rather than a single material fingerprint. Steady shear describes nozzle transport; yield stress and low-shear rheology describe the propensity for post-deposition flow. Figure 1 shows the graphical analysis of apparent viscosity with shear rate and storage modulus with time.

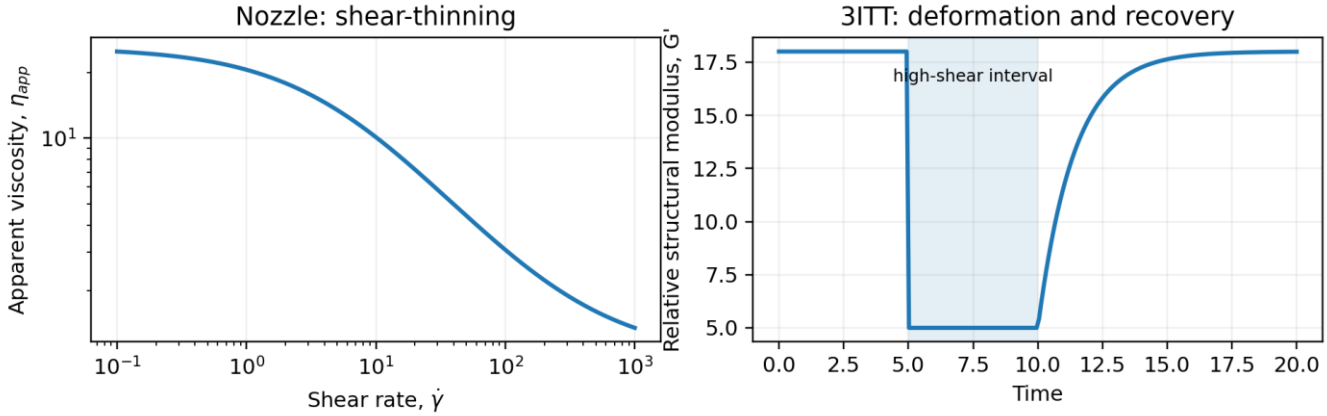

Figure 1. Apparent viscosity decreases under nozzle shear, while the structural modulus is disrupted during high shear and then rebuilds after deposition. The curves are illustrative and not tied to a specific food formulation.

5. Effect of Hydrocolloids Across Specific Food Ink Matrices

The effect of hydrocolloids is strongly matrix-specific because the food matrix determines what the hydrocolloid can interact with.

Starch systems are particularly sensitive to hydrocolloid addition because gelatinization, amylose leaching, amylopectin swelling, and retrogradation change both the particulate and molecular structure of the ink. Altering potato starch content in mashed potatoes changed yield stress, viscosity, modulus, and shape retention (Liu, Zhang, Bhandari, et al., 2018). Furthermore, xanthan, guar, and carrageenan could further modify mashed-potato rheology, water mobility, microstructure, and extrusion printing. The interpretation is mechanistic: gum addition modifies the continuous phase around starch particles and changes how water is distributed during deformation (Liu, Zhang, & Bhandari, 2018).

The multicomponent carrageenan-xanthan-starch study of Liu et al. (2019) provides a useful contrast because it deliberately combines several hydrocolloid functions. Carrageenan contributes thermo-responsive gelation, xanthan contributes high low-shear viscosity and shear-thinning, while starch modifies the particulate and gel structure. The authors connected these rheological transitions to printability and showed that multicomponent design can produce a broader processing window than a single polymer (Liu et al., 2019). Feng et al. (2022) reached a related conclusion in β-carotene-loaded yam starch hydrogels, where guar gum, carrageenan, xanthan-guar blends, chitosan, and gum arabic altered apparent viscosity, G′, G″, water migration, crystallinity, and print stability in different ways.

Heckl et al. (2023) add an important process-level dimension. Their comparison of five hydrocolloid systems demonstrated that network deformation and recovery, not just initial viscosity, affect printing accuracy. They found xanthan and pre-gelatinized starch particularly effective at stabilizing the cereal-based materials studied and showed that the interval between deposited layers could change structural accuracy. Ji et al. (2022) further demonstrated that protein addition can change the multi-scale starch structure and improve printed line definition, even when structural recovery of the gel is reduced. Together, these studies indicate that starch printing performance is a balance among particle packing, polymeric continuous-phase viscosity, elastic recovery, and moisture distribution.

The purple-sweet-potato study of Hu et al. (2023) broadens the evidence base beyond potato starch and shows that hydroxypropyl methylcellulose, xanthan gum, guar gum, and flaxseed gum generally improved 3D printing performance, whereas κ-carrageenan did not provide the same benefit under their tested conditions. Importantly, tanδ was strongly related to printability, and hydrocolloid addition changed water mobility and hydrogen-bond signatures. This is a valuable contrast to the carrageenan-positive results in the multicomponent starch study: hydrocolloid performance cannot be transferred across matrices without accounting for polymer-protein-starch interactions and the specific thermal state of the formulation (Hu et al., 2023).

Fresh produce has a different challenge: high water content and a comparatively weak internal network make the material prone to slump after deposition. Pant et al. (2021) systematically tested xanthan, κ-carrageenan, and locust bean gum in fresh and frozen vegetable formulations designed for dysphagic foods. Their work combined rheological, textural, microstructural, and syneresis measurements and demonstrated that printable formulations could be obtained at relatively low hydrocolloid levels while limiting water seepage. The study is important because it connects printability to sensory and swallowing functionality rather than considering geometry alone.

Pectin-based printing provides another mechanism. Vancauwenberghe et al. (2018) used pectin food inks to manufacture honeycomb structures and then compared predicted and actual texture. The study did not treat the pectin simply as a thickener; it demonstrated that controlled material formulation can be used to translate geometric porosity into controlled mechanical

texture. The implication for fruit purées is that a hydrocolloid network can be used to engineer structure while preserving a high-water food matrix, provided the network is strong enough to withstand deposition and subsequent loading.

The evidence across starch and produce systems converges on four design requirements: adequate low-shear stability, strong but not excessive yield stress, rapid recovery after nozzle shear, and control of water mobility. The most reliable hydrocolloid is therefore the one that solves the dominant matrix failure mode without shifting the ink into an over-structured state (Table 2).

Table 2. Evidence-based matrix comparison from direct 3DFP studies

Matrix	Hydrocolloid	Main observation	Mechanistic interpretation	References
Mashed potato	Potato starch	0% starch: $\tau_0 \approx 195.90$ Pa with sagging; 2% improved yield stress and printability; 4% retained shape but increased resistance to extrusion.	Optimum rather than monotonic response; viscosity and yield stress must be balanced.	(Liu, Zhang, Bhandari, et al., 2018)
Mashed potato	Xanthan/guar/κ-carrageenan	Gums changed viscosity, G′, G″, water mobility and FT-IR/NMR signatures; blend effects differed by gum.	Hydrocolloid chemistry changes the continuous phase and water distribution.	(Liu, Zhang, & Bhandari, 2018)
Starch/carrageenan composite	Carrageenan + xanthan + starch	Multicomponent formulation increased viscosity, yield stress, G*, shear-thinning and thixotropic response in a controlled manner.	Complementary hydrocolloid functions can widen the processing window.	(Liu et al., 2019)
Yam starch + β-carotene	GG/XG/CG/XG-GG/chitosan/GA	Several hydrocolloids increased viscosity and moduli; chitosan and guar improved resolution/formability under the tested conditions.	Water migration, crystallinity and rheology jointly affect print stability.	(Feng et al., 2022)
Cereal-based ink	Xanthan/MC/HPMC/alginate/starch	3ITT revealed that deformation and recovery affected accuracy; layer interval influenced the final structure.	Transient recovery must be matched to layer cycle time.	(Heckl et al., 2023)
Purple sweet potato	HPMC/XG/GG/flaxseed gum/KC	Most tested hydrocolloids improved printing performance; tanδ correlated with printability.	The same hydrocolloid may behave differently across starch-rich matrices.	(Hu et al., 2023)
Fresh/frozen vegetables	XG/KC/LBG	Low-level hydrocolloid formulations improved rheology, structure and syneresis control for dysphagia foods.	Hydrocolloid dosage must preserve water-rich sensory functionality.	(Pant et al., 2021)
Pectin food simulant	Pectin	Pectin inks enabled honeycomb printing and model-based texture control.	Material fidelity is necessary for digital-to-texture translation.	(Vancauwenbergh e et al., 2018)

6. Protein-Based Meat Analogues and Emulsion-Gel Systems

Protein-rich foods and emulsion gels present a more complex molecular problem because the printing network must often provide both structural strength and a desirable bite, juiciness, lubrication, or release behaviour. Proteins can aggregate, unfold, adsorb to interfaces, and interact electrostatically with hydrocolloids; lipids can separate or destabilize under shear; and thermal processing can cause additional network rearrangement.

Chen et al. (2019) provide one of the clearest direct demonstrations. Soy protein isolate mixed with sodium alginate and gelatin showed shear-thinning behaviour and could be printed into stable geometries. Gelatin reduced viscosity and elastic modulus at 35 °C relative to the protein-only formulation, while cooling increased the rheological index and supported deposited layers. Importantly, no chemical cross-linking between SPI and gelatin was detected during the tested printing conditions. This result challenges a common assumption that stronger printing always requires irreversible cross-linking; reversible protein-polysaccharide association and temperature-dependent gelatin structure were sufficient to generate printability.

Liu et al. (2022) examined milk-protein concentrate with multiple hydrocolloids using microscopy, steady shear, SAOS, thixotropy, creep recovery, and structural characterization. κ-Carrageenan, pectin, guar gum, and sodium alginate significantly

increased zero-shear viscosity, thixotropy, and solid-like behaviour, whereas xanthan did not produce the same direction of response. The work is mechanistically important because the hydrocolloids did not merely dilute or thicken a homogeneous protein solution; they formed mixed networks around protein particles. The different outcomes among hydrocolloids illustrate how charge, chain conformation, and association kinetics govern the resulting composite structure.

Soluble protein-polysaccharide blends to soy-protein-based emulsion gels for reduced-fat meat analogues. Their work showed that biosurfactants with higher effective volume and molecular weight produced stable emulsion-gel networks, increased elastic properties, and improved creep-recovery behaviour. The formulation consequence is important for 3DFP: a hydrocolloid-rich or biopolymer-rich continuous phase can immobilize droplets and provide the recoverable structure needed for extrusion, reducing the tendency for the oil phase to coalesce or migrate (Shahbazi et al., 2021).

Ji et al. (2022) provide a complementary protein-starch system. Adding casein to cassava starch gel increased the average molecular dimensions of starch after thermal processing, reduced printed line width, and increased the centre height of printed structures. At the same time, structural recovery decreased. This apparent contradiction is scientifically useful: improved printing precision does not necessarily mean the fastest recovery response. A stiffer or more compact network may maintain geometry under load while recovering more slowly.

The broader meat-printing literature also shows why formulation and architecture must be considered together. Constraints of meat printing, emphasizing the importance of extrusion characteristics, texture, and structure. More recent experimental work reinforces the move toward multifunctional plant-protein inks (Bhandari et al., 2019). Studies reported that partial oil substitution using aloe gel and flaxseed mucilage could help balance lubrication and structural integrity in 3D-printed plant-based meat analogues, directly linking hydrocolloid-rich biopolymers to the competing requirements of flow and mouthfeel (Fan et al., 2026). Although, soy-protein-stabilized high-internal-phase emulsions containing Arabic gum, xanthan gum, or iota-carrageenan could exhibit shear-thinning, viscoelasticity, and post-shear recovery suitable for 4D food printing; xanthan at the tested high level produced particularly stable, fine droplets and strong recovery (Kim et al., 2025).

These studies collectively show that hydrocolloids in protein and emulsion systems serve at least three functions: they reinforce the continuous phase, control interfacial or particle interactions, and create time-dependent recovery after shear. However, excessive strengthening can impair extrusion, reduce lubrication, or generate an overly elastic response.

7. Structural Fidelity, Layer Stacking Capacity, Die-Swell, and Post-Processing Stability

Structural fidelity is the final expression of all preceding molecular and rheological processes. After the material leaves the nozzle, the printed filament must preserve its intended width, height, curvature, and layer-to-layer contact while resisting gravity, subsequent loading, and post-processing. Two phenomena are particularly important: elastic die-swell immediately after extrusion and progressive lateral slump during layer stacking.

Die-swell, or the Barus effect, results from elastic stresses stored during flow through a narrow die. Highly entangled and/or strongly elastic polymer networks develop normal-stress differences as chains orient and stretch. On leaving the nozzle, part of that stored deformation is recovered, causing the filament to expand. The mechanism is well established in polymer rheology (Barnes, 1999) and is relevant to food hydrocolloids because xanthan, gellan, and other high-molecular-weight polymers can have substantial elastic contributions. In practical 3DFP, die-swell should not be eliminated by indiscriminately reducing polymer concentration; rather, nozzle geometry, extrusion rate, temperature, and the formulation's elasticity must be balanced. Liu, Zhang, Bhandari, et al. (2018) and Heckl et al. (2023) demonstrate that dimensional fidelity depends on the combined evolution of flow and recovery.

Vancauwenberghe et al. (2018) demonstrated the practical consequence using pectin-based honeycomb structures. The designed porosity and the actual printed geometry were not identical, yet the predicted and measured texture values followed the same trend. This indicates that model-based design is only as accurate as the physical fidelity of the print. Hydrocolloid formulation therefore becomes part of digital food design because it determines whether the path generated by the slicer is reproduced as the actual material structure.

Post-processing introduces another structural challenge. He et al. (2020) showed that changing potato-flake content and pH altered rheology, modulus, moisture state, and shape fidelity, and that dual extrusion could be used to create a multi-material, colour-changing food. Kim et al. (2019) demonstrated a complementary route in cookie dough: 0.5 g/100 g xanthan gum enabled smooth printing and improved retention during thermal post-processing, while excessive xanthan could raise extrusion hardness and reduce printability. The comparison is instructive because it shows that a formulation can be structurally stable after printing but still fail during the extrusion stage.

Thermal hysteresis and gelation temperature are equally important. Gelatin and some carrageenan systems can be designed to melt or flow at one temperature and re-form a gel at another. Curdlan and ionically cross-linked alginate, in contrast, can provide more persistent networks once their triggers have been applied. The optimal mechanism depends on whether the printed object is intended to be eaten cold, heated, cooked, or cured after deposition. The post-processing review by He et al. (2020) emphasizes that pretreatment and post-treatment should be regarded as an integrated part of food-material design rather than an afterthought.

Layer stacking can be understood through a simple stress balance (Figure 2). The growing structure imposes a downward load on the lower layers. If the local stress exceeds the compressive or shear resistance of the hydrocolloid-reinforced network, filaments deform laterally. Increasing hydrocolloid concentration can raise this resistance, but it also changes the nozzle-flow

requirements. The formulation must therefore satisfy a ratio of load-bearing capacity to extrusion resistance rather than a single absolute property.

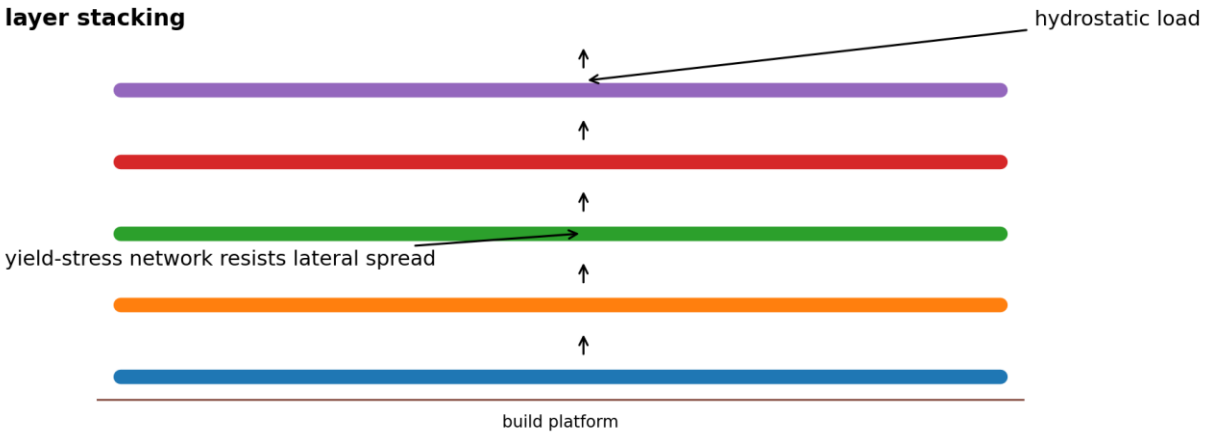

Figure 2. Layer-stacking stress balance. The load imposed by upper layers must remain below the deformation resistance of the hydrocolloid-reinforced network to prevent lateral slump.

8. Future Prospects, Industrial Scalability, and 4D Food Printing

The future of hydrocolloid-enabled 3DFP lies in moving from empirical formulation to predictive material-process co-design. Multi-material and coaxial strategies are attractive because they decouple flow from final gelation. An alginate-containing phase can be extruded while a calcium-containing phase provides local cross-linking, allowing the material to remain comparatively mobile during transport and become structurally stronger immediately after or during deposition. More broadly, dual extrusion has been demonstrated in food systems for colour and composition control (He et al., 2020). The engineering challenge is controlling diffusion, interfacial bonding, and viscosity matching between streams so that the core-shell or multi-material interface remains stable.

4D food printing extends this concept by deliberately programming a time-dependent response. He et al. (2020) demonstrated spontaneous colour change in a dual-extrusion potato/purple-sweet-potato system, showing that pH-responsive anthocyanins can transform an initially static printed structure. Pulatsu et al. (2022) showed how ethyl cellulose could participate in an osmotically driven, anisotropically actuated edible composite, pointing to a broader strategy in which swelling and contraction are spatially encoded into the printed material. The molecular prerequisite for such systems is anisotropic or differential response: hydrocolloids and starches with different swelling or gelation behaviours can create programmed strain gradients.

Recent protein-hydrocolloid work suggests an additional pathway toward responsive foods. Kim et al. (2025) developed soy-protein/hydrocolloid-stabilized high-internal-phase emulsions for 4D printing and linked hydrocolloid addition to hydrogen bonding, droplet size, post-shear recovery, and printing precision. The significance is not simply that the system responds to pH; it demonstrates that a functional hydrocolloid can simultaneously control interfacial structure, rheology, and stimulus responsiveness.

Industrial scaling remains the largest translation barrier. A formulation that behaves predictably in a 10-20 mL syringe may behave differently in a larger reservoir because mixing, thermal gradients, residence-time distributions, air entrainment, and pump-induced shear become more important. The industrial-perspective analysis of Jayaprakash et al. (2020) identified economic, technological, and consumer constraints that remain relevant to commercial food printing. From the materials perspective, the same scale-up problem means that hydrocolloid hydration and network development must be reproducible over the entire process train, not just at the printer nozzle.

Recent work also points toward circular and data-driven manufacturing. Agricultural side-streams can supply fermentable substrates or fibre-rich components, while machine learning can potentially connect ingredient composition to rheological and printing outcomes. However, prediction should be constrained by mechanistic understanding. A model trained only on bulk viscosity may fail when the governing variable is recovery time, interfacial gelation, thermal transition, or phase separation.

Regulatory considerations must be incorporated into the design stage. Established food hydrocolloids have long histories of food use, but genetically modified production hosts, novel microbial polymers, chemically modified derivatives, or new use levels require jurisdiction-specific safety assessment. The scientific priority is therefore to achieve the necessary printability using food-relevant materials and processes wherever possible, and to document molecular identity, purity, residual processing aids, allergen implications, and intended exposure for any novel ingredient.

9. CONCLUSION

Hydrocolloids are central to extrusion-based 3D food printing because they operate at the interface between molecular structure and process mechanics. Their charge, molecular weight, branching, substitution pattern, thermal response, hydration behaviour, and ability to associate with proteins or starch determine the network that a printer actually sees. That network governs viscosity

under shear, apparent yield stress, elastic and viscous moduli, recovery after deformation, and ultimately the fidelity of the deposited food structure.

The literature reviewed here shows that the strongest evidence is not for a universal best hydrocolloid, but for matrix-specific combinations. In starch systems, xanthan, guar, carrageenan, and other gums can improve rheology and shape retention when used within an optimum range. In protein systems, gelatin, alginate, carrageenan, pectin, and related polymers can build composite networks whose performance depends on protein state and temperature. In produce systems, hydrocolloids reduce the instability associated with high water content. In emulsion gels, they can stabilize the continuous phase and provide recoverable structure after shear. Across all cases, improvements in one rheological property can be offset by losses in extrudability or recovery, making multi-parameter characterization essential.

The most generalizable design rule is therefore molecular-process matching. A hydrocolloid should be selected according to the desired sequence of events: hydrate and disperse without phase separation; shear-thin sufficiently inside the nozzle; resist excessive elastic recoil; rebuild rapidly after deposition; carry the hydrostatic load of subsequent layers; and remain stable through intended thermal or chemical post-processing. When these requirements are considered together, hydrocolloids become more than additives: they become programmable structural elements of the food ink. Future progress will depend on integrating molecular characterization, transient rheology, digital process control, and food-quality outcomes. Such integration is necessary to move 3DFP from successful laboratory demonstrations toward reproducible, scalable, nutritionally customized, and structurally complex food manufacturing.

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