

Article

Magnetic Thixotropic Fluid for Direct-Ink-Writing 3D Printing: Rheological Study and Printing Performance

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Abstract

Yield stress and thixotropy are critical rheological properties for enabling successful 3D printing of magnetic colloidal systems. However, conventional magnetic colloids, typically composed of a single dispersed phase, exhibit insufficient rheological tunability for reliable 3D printing. In this study, we developed a novel magnetic colloidal system comprising a carrier liquid, magnetic nanoparticles, and organic modified bentonite. A direct-ink-writing 3D-printing platform was specifically designed and optimized for thixotropic materials, incorporating three distinct extruder head configurations. Through an in-depth rheological investigation and printing trials, quantitative analysis revealed that the printability of magnetic colloids is significantly affected by multiple factors, including magnetic field strength, pre-shear conditions, and printing speed. Furthermore, we successfully fabricated 3D architectures through the precise coordination of deposition paths and magnetic field modulation. This work offers initial support for the material's future applications in soft robotics, in vivo therapeutic systems, and targeted drug delivery platforms.

Keywords: 3D printing; magnetic materials; magnetorheology; thixotropy



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1. Introduction

Also known as digital manufacturing or additive manufacturing [1–5], 3D-printing technology enables the fabrication of complex 3D structures using various materials, such as polymers, ceramics, metals, composites, and others. Unlike traditional manufacturing methods requiring molds or templates, this technology converts digital designs into intricate 3D products with minimal material waste [6]. Currently, 3D printing is primarily applied in the manufacturing, healthcare, construction, and aerospace fields. Three-dimensional printing techniques include stereolithography (SLA) [7], selective laser sintering (SLS) [8], fused deposition modeling (FDM) [9], direct ink writing (DIW) [10–19], and more. Notably, DIW technology facilitates 3D printing with diverse inks, such as hydrogels [20–22], ceramics [23,24], graphene [25], metals [26], and others. However, a major challenge in DIW is designing printable inks that integrate inherent material properties while meeting technical requirements for continuous and stable extrusion without nozzle clogging [27,28]. Due to the high controllability, elimination of the need for external power supply, good

biocompatibility and flexibility of magnetic materials, they are able to be applied in various types of soft robots, such as soft gripper [29], bionic soft robots, targeted drug delivery robots [30], and human stents [31,32]. When magnetic materials are used as inks in DIW 3D printing, the process becomes more complex compared to non-magnetic materials. Non-uniform dispersion of magnetic particles leads to inconsistent mechanical properties, reduced magnetic responsiveness, and nozzle clogging [33]. Additionally, external magnetic fields may interfere with ink flow, causing directional deviations or structural deformation. Moreover, magnetic inks must satisfy competing requirements: shear-thinning behavior (high viscosity at low shear rates to maintain shape, low viscosity at high shear rates for controlled extrusion) and rapid solidification under magnetic fields to support structural integrity.

Ferrofluids (FFs), magnetorheological fluids (MRFs) [34,35], and magnetic thixotropic fluids (MTFs) [36] are typical magnetic materials. FFs consist of magnetic nanoparticles (MNPs) dispersed in aqueous or organic solvents, where strong Brownian motion prevents aggregation or sedimentation. Without external magnetic fields, FFs exhibit good fluidity but insufficient viscosity to support their own weight under magnetic fields, making them unsuitable for DIW 3D printing. MRFs demonstrate Newtonian fluid behavior at zero field but experience rapid viscosity increases under magnetic fields, hindering extrusion and rendering them impractical for 3D printing. Magnetic thixotropic fluids (MTFs) are nano-self-assembled smart materials that undergo reversible solid–liquid transitions under magnetic fields. Upon field removal, gravity disrupts columnar structures, restoring initial viscosity and fluidity. The magnetic response and viscosity changes in these materials under magnetic fields are illustrated in Figure 1.

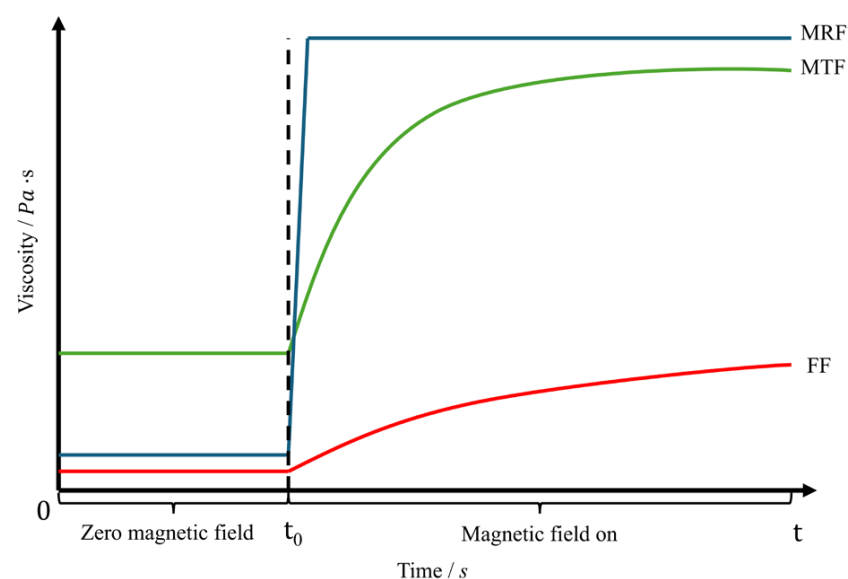


Figure 1. Viscosity variation in magnetic materials under a magnetic field.

Kim et al. [37] proposed a composite ink composed of NdFeB alloy, fumed silica nanoparticles, and silicone rubber matrix. Using DIW printing with permanent magnets or electromagnetic coils near the nozzle, NdFeB particles were magnetized and aligned along the printing direction to encode magnetic domain orientations. The printed structures exhibited rapid preset deformations under external magnetic fields, enabling crawling, folding, and grasping functions in soft robots. Kokkinis et al. [38] systematically established a theoretical framework for magnetic-field-assisted DIW and developed a multimaterial magnetically assisted 3D-printing platform (MM-3D printing). The MM-3D system integrates multimaterial dispensers and dual-component mixing units to preset magnetic

particle orientation during printing. Post-curing, structures exhibit non-uniform magnetization distributions, enabling complex deformations and motions (e.g., grasping, rolling, crawling) under external fields. However, the MM-3D system suffers from high complexity, control difficulty, and requires integrated multimaterial dispensing. Additionally, material costs are high, and magnetic particle dispersion uniformity may degrade during prolonged printing, affecting structural consistency. Inspired by cytoplasmic streaming in amoebae, Leon-Rodriguez et al. [39] proposed a magnetically controlled soft robot design based on whole-skin locomotion (WSL). The robot employs polyethylene films to construct flexible ring structures filled with ferrofluid as a magnetic-responsive material. An external electromagnetic actuation system (EMA) composed of Helmholtz and Maxwell coils generates controllable magnetic field gradients for wireless manipulation. The soft robot implies potential applications in targeted drug delivery within the digestive system and blood vessels of human beings. However, this study uses manual assembly instead of utilizing DIW 3D printing, which led to uneven magnetic material distribution and sealing variability, directly impacting magnetic response stability and repeatability.

Existing research on the printability of magnetic materials remains relatively limited, particularly regarding challenges such as ensuring particle dispersion uniformity, simplifying complex printing systems, and achieving precise structural control. To address these limitations and explore the promising application prospects, this study prepares a novel magnetic thixotropic fluid and constructs a DIW 3D-printing platform to investigate the printability of MTF. Based on the magnetorheological [40] and thixotropic [41,42] properties of MTF, the proportions of MTF and the structures of extrusion heads were designed and optimized. Rheological tests were conducted to analyze printability. Printing processes for different structures were discussed. Printing parameters (time, printing speed and magnetic field strength) were investigated for different extruders, followed by experimental analysis of printing effects.

2. Experimental Section

2.1. Preparation of Magnetic Thixotropic Fluid

MTF comprises a carrier liquid, magnetic particles, and organic modified bentonite (OMBT) [43,44]. OMBT reduces interparticle magnetic forces while imparting thixotropy. Compared to other materials, OMBT enhances thixotropy, enabling exponential viscosity reduction under external shear. Under uniform magnetic fields, MNPs and OMBT form anisotropic columnar structures, increasing interparticle cohesion, reducing fluidity, enhancing viscosity, and exhibiting good post-extrusion recovery, which meets fundamental printability requirements.

Materials used: Hydrophilic Fe_3O_4 nanoparticles (SS-F909, Jikang New Materials Co., Ltd. Hangzhou, China), organic bentonite (OMBT, BENTONE SD-2, particle size: $<1\ \mu\text{m}$, Elementis Specialties, London, UK), and L-AN32 mechanical oil (base carrier, Mojezo Petrochemical Co., Shanghai, China). MTF preparation: Quantified SD-2 bentonite was added to a container with base carrier, heated to 70°C in a water bath, and stirred at 700 rpm for 1 hour. Quantified Fe_3O_4 particles were added, followed by additional stirring for 1 hour. Through multiple experiments, the formulation of the MTF material was optimized by adjusting the ratio of Fe_3O_4 magnetic particles to OMBT particles in MTF. When the content of OMBT was fixed, we gradually increased the content of magnetic particles, obtaining formulations with 8% Fe_3O_4 -8% OMBT and 12% Fe_3O_4 -8% OMBT. However, when the content of magnetic particles was further increased, the viscosity of the material became relatively high. To reduce the viscosity, we decreased the content of OMBT, thus obtaining a formulation with 14% Fe_3O_4 , 4% OMBT. Finally, three MTF samples with different compositions were selected as the experimental materials for this

study, which are shown in Table 1: (1) 8% Fe_3O_4 , 8% OMBT; (2) 12% Fe_3O_4 , 8% OMBT; (3) 14% Fe_3O_4 , 4% OMBT.

Table 1. Three different MTF samples.

Sample Number	Fe_3O_4 (%)	OMBT (%)	L-AN32 (%)
1	8	8	84
2	12	8	80
3	14	4	82

2.2. Characterization

Figure 2a illustrates the MTF preparation process. Compared to other materials, bentonite exerts lower interparticle forces. Controlled addition imparts significant thixotropy, enabling exponential viscosity reduction under external shear. Under uniform magnetic fields, MNPs align within lamellar bentonite structures to form anisotropic columns. Upon field removal, gravitational disruption of columnar structures restores initial fluidity. The microscopic mechanism is shown in Figure 2b.

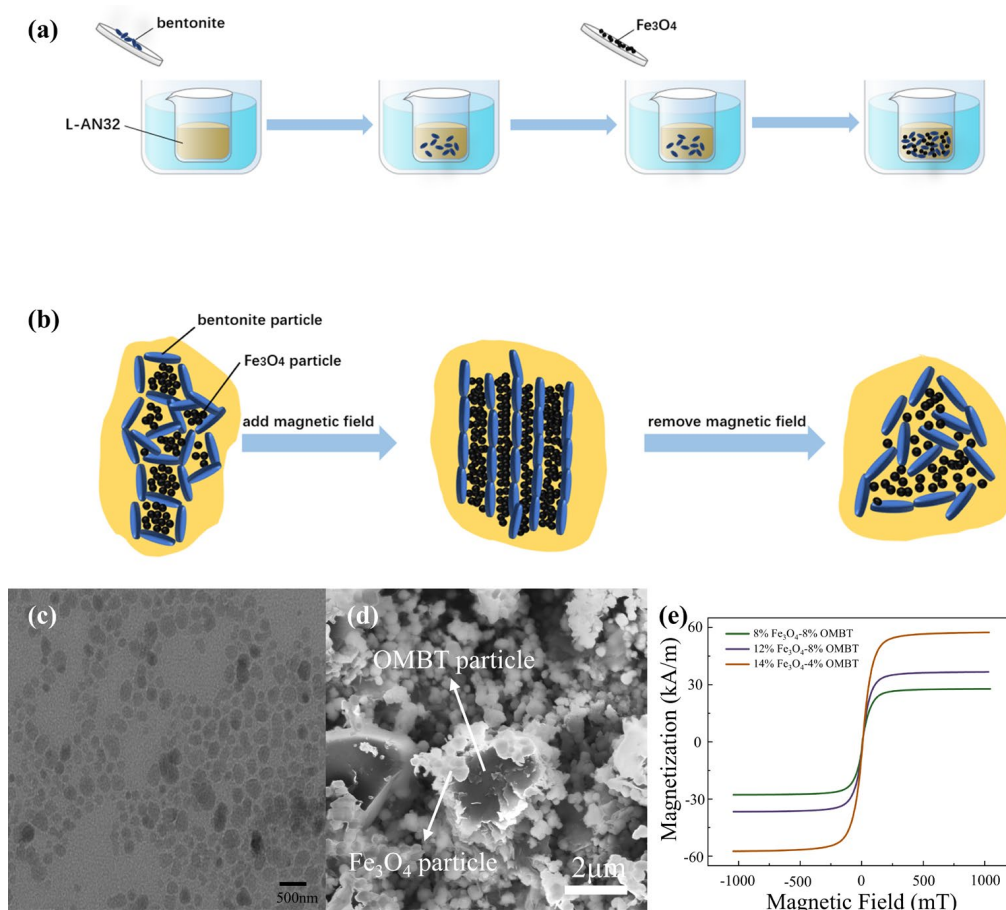


Figure 2. The preparation and characterization of MTF. (a) MTF preparation process; (b) Microstructural evolution of MTF under magnetic field application/removal; (c) TEM image of magnetic particles; (d) SEM image of MTF sample; (e) Hysteresis loops of the three MTF samples.

Fe_3O_4 particles were characterized by TEM (Figure 2c), showing uniform particle size distribution with an average diameter of 200 nm, meeting MTF requirements. After removing the oil phase, MTF samples were analyzed by SEM (Figure 2d), revealing homogeneous dispersion of magnetic particles within bentonite lamellae without surface aggregation.

Magnetic properties of the three MTF samples were characterized via hysteresis loop tests using a BKT-4500 Vibrating Sample Magnetometer (VSM), with the results shown in Figure 2e. Hysteresis loops, which basically pass through the origin, show almost overlapping magnetization and demagnetization curves. The remanence (M_r) and coercivity (H_c) of the samples are both close to zero, indicating that MTF exhibits superparamagnetic behavior. When the external magnetic field is removed, the remanence of the material is zero. The saturation magnetic field of the samples is approximately 1100 mT, exhibiting good magnetic saturation properties. The saturation magnetization of the three samples is 25.8 kA/m, 37.6 kA/m, and 55.4 kA/m, respectively, demonstrating good saturation magnetization.

Static shear stress–strain tests were performed using an Anton Paar MCR302 rheometer with an MRD170 magnetic module (20 mm cone-plate geometry, 0.084 mm gap). Shear-thinning properties were characterized at 20 °C (shear rate range: 0.001–1000 s^{−1}) under different magnetic fields. Oscillatory amplitude sweeps measured storage modulus (G') and loss modulus (G'') to analyze viscoelasticity and printability. The loss tangent ($\tan \delta$), calculated by Equation (1), indicates viscoelastic behavior:

$$\tan \delta = G'' / G' \quad (1)$$

A Cartesian 3D printer provided stable motion, high repeatability, and heavy-load capacity. Helmholtz coils generated uniform vertical magnetic fields adjustable via voltage control. Horizontal/vertical observation modules enabled real-time monitoring. Three extruders were designed based on MTF rheology: direct extrusion, stirred extrusion, and stirred-spiral extrusion. Printing trials included single-line, grid, and layer-stacking experiments to analyze parameter effects.

2.3. Direct Ink Writing 3D-Printing Experiments

A DIW 3D-printing system was developed to analyze the printability of MTF, utilizing a Cartesian 3D printer as the platform (Figure 3a). The system comprises four components: extrusion module, motion module, magnetic field generation module, and water-cooling system. This configuration ensures a stationary deposition platform with high load capacity, smooth motion, and precise positioning. Core to DIW is the extrusion system design [45], which guarantees continuous and uniform material discharge. Pneumatic extrusion [46] was adopted, consisting of a supply unit, pressure control system, and print head.

During printing, MTF exhibits significant viscosity changes under shear due to high shear-thinning, low yield stress and high flow stress. Without pre-shearing, direct pneumatic extrusion results in inhomogeneous microstructure disruption. Post-extrusion, the limited space inhibits complete structure formation under magnetic fields, causing poor uniformity, line breakage, or nozzle clogging. The schematic diagram of the direct extrusion head is shown in Figure 3b, and the printing effect is shown in Figure 3e. With pre-shearing at 100 s^{−1}, microstructures are fully disrupted, drastically reducing viscosity. During printing, material rapidly passes through a tapered nozzle where shear rates exceed 1000 s^{−1}. This makes discharge control difficult, preventing effective magnetic-field-induced solidification at normal speeds and compromising precision. The schematic diagram of the pre-stirring extrusion head is shown in Figure 3c, and the printing effect is shown in Figure 3f. Incorporating a screw section ensures material undergoes uniform shear (1 s^{−1}) after pre-shearing, slightly increasing viscosity. This optimizes homogeneity and continuity, yielding superior results. The schematic diagram of the screw extrusion head is shown in Figure 3d, and the printing effect is shown in Figure 3g.

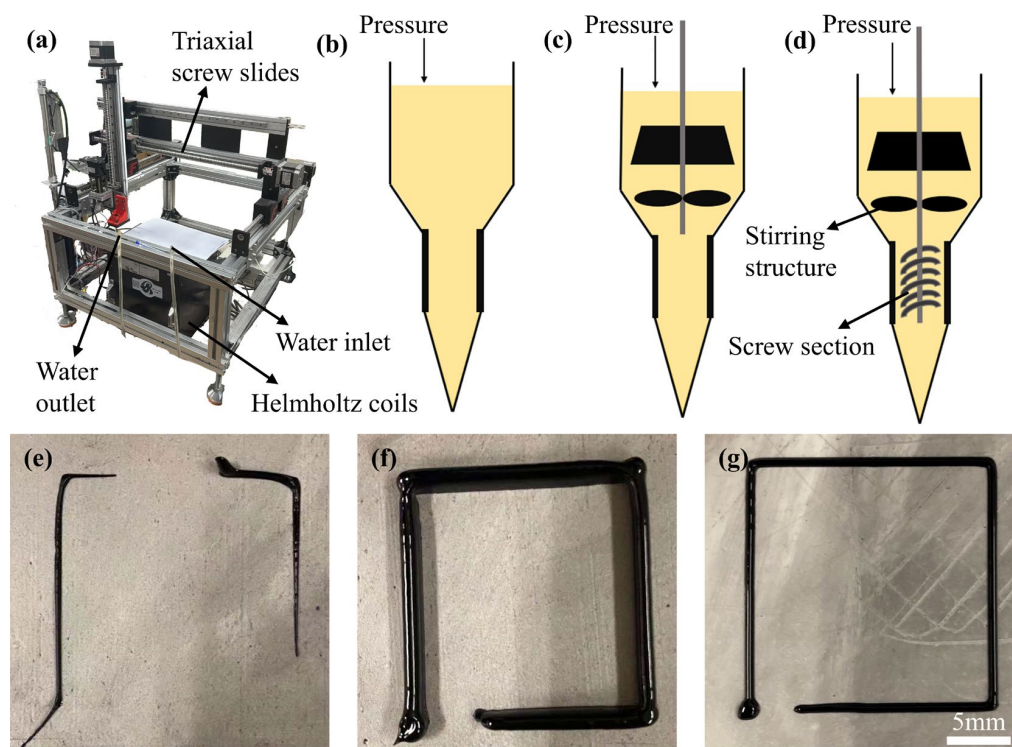


Figure 3. Comparison of the 3D-printing platform and the design and printing effects of its three types of extrusion heads. (a) The 3D-printing platform for MTF; (b) Design of the direct extrusion head; (c) Design of the pre-stirring extrusion head; (d) Design of the screw extrusion head; (e) Direct extrusion printing result; (f) Extrusion after stirring printing result; (g) Screw extrusion after stirring printing result.

3. Results

3.1. Rheological Properties of MTF

In this study, an in-depth rheological investigation of the magnetic thixotropic fluid was conducted using a rotational rheometer, which combined steady shear, large amplitude oscillatory shear tests, and thixotropic recovery experiments to analyze the printability of MTF.

Through steady shear tests, we can obtain the relationship between shear stress and shear rate for magnetic thixotropic fluids (Figure 4a) as well as the relationship between viscosity and shear rate (Figure 4b). Regarding the relationship between shear stress and shear rate, all three samples exhibit a characteristic curve where shear stress initially rises rapidly with increasing shear rate, then plateaus, and subsequently rises sharply again.

The curve is divided into three stages: low shear rate, intermediate, and high shear rate. For example, under zero magnetic field, Sample 1 (8% Fe_3O_4 + 8% OMBT) shows a gradual increase in shear stress within the shear rate range of 10^{-3} – 1 s^{-1} . At this stage, organic bentonite spontaneously forms a “house of cards” structure through hydrogen bonding, with magnetic nanoparticles uniformly dispersed within this framework. The two components form a relatively stable hybrid structure via physical interactions. The applied shear force is insufficient to disrupt the hydrogen bonds of the organic bentonite or the weak aggregates of magnetic particles, leaving the microstructure intact. As shear rate increases, the fluid begins to disrupt this structure, requiring overcoming resistance, hence the rapid rise in shear stress. In the intermediate stage, hydrodynamic forces gradually exceed the hydrogen bonding interactions of organic bentonite. The “house of cards” structure begins to disintegrate, with bentonite lamellae dispersing into smaller units. Simultaneously, aggregates of magnetic nanoparticles start to break apart. Partial disruption of the

microstructure leads to shear-thinning behavior. At high shear rates, intense shear forces completely destroy the “house of cards” structure, dispersing bentonite into individual lamellae and fully disintegrating magnetic nanoparticle aggregates into single particles. This results in enhanced fluidity and pronounced shear-thinning. Upon application of an external magnetic field, magnetic nanoparticles align along the field direction, driven by magnetic dipole forces. They interact with the isotropic structure of organic bentonite, forming a more complex hybrid microstructure. The stress corresponding to stage transitions increases significantly, indicating enhanced resistance of the internal structure to shear fields with higher magnetic field strength. The low-shear-rate stage also extends to higher magnitudes, demonstrating that compact particle alignment increases the difficulty of disrupting bentonite structures.

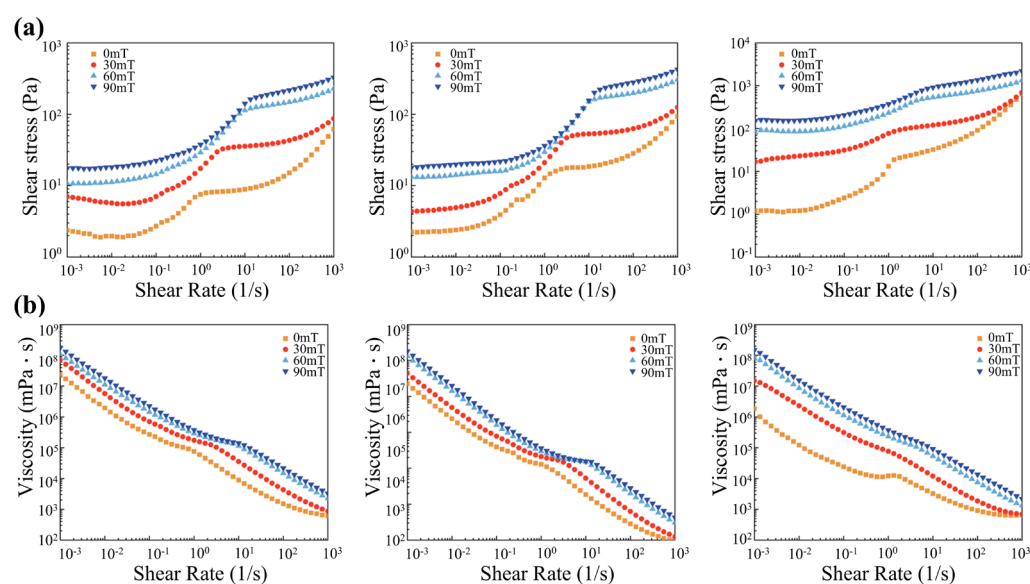


Figure 4. The steady shear rheological properties of MTF. (a) Relationship between shear stress and shear rate for the three MTF samples. From left to right: Sample 1, Sample 2, Sample 3. (b) Relationship between viscosity and shear rate for the three MTF samples. From left to right: Sample 1, Sample 2, Sample 3.

Regarding the relationship between viscosity and shear rate, all three MTF samples exhibit shear-thinning behavior under different magnetic fields. The process can be divided into two phases. For instance, at 0 mT, Sample 1 exhibits Phase I (shear rate: 0.001 – 0.4 s $^{-1}$), where viscosity gradually decreases and stabilizes, and Phase II (shear rate: 0.4 – 1000 s $^{-1}$), where progressive disruption of two distinct microstructures further reduces viscosity. Thus, pre-shearing within the print head reservoir effectively lowers the viscosity of thixotropic materials. Thixotropy is crucial for DIW 3D printing: sufficient shear enhances fluidity and extrusion efficiency while enabling shape retention post-deposition.

Beyond viscosity changes, thixotropic materials exhibit viscoelastic behavior, combining fluid-like properties with solid-like characteristics under magnetic fields. Viscoelasticity is characterized via oscillatory frequency tests. To further investigate MTF printability, dynamic oscillatory sweep tests were conducted under magnetic fields (0–90 mT) with applied sinusoidal oscillatory stress. Storage modulus (G') measures elastic responses where energy is stored and recovered upon stress removal. Loss modulus (G'') measures viscous responses where energy dissipates through flow. The loss tangent ($\tan \delta = G''/G'$) indicates whether the material behaves more like a solid ($\tan \delta < 1$) or liquid ($\tan \delta > 1$). Tests on the three samples show that increasing shear stress reduces both G' and G'' (Figure 5a,b), while $\tan \delta$ exhibits an opposite trend (Figure 5c), signifying a transition from elastic to

viscous states. In the liquid state, materials flow well in reservoirs but lack self-support for printing, necessitating magnetic field application at the deposition platform. In the solid state, materials exhibit strong self-support for printing. The timescale of structure formation in MTF is critical for successful printing of complex geometries. Thixotropic recovery tests were performed to evaluate structural stability. After applying steady shear to disrupt all microstructures, recovery of storage modulus over time was monitored under different magnetic fields (Figure 5d). MTF recovery occurs in two distinct stages. Stage I involves rapid response to magnetic fields with sharp G' increase, reducing post-printing flow and providing stable support. Stage II involves gradual structural evolution dominated by non-magnetic forces over extended periods.

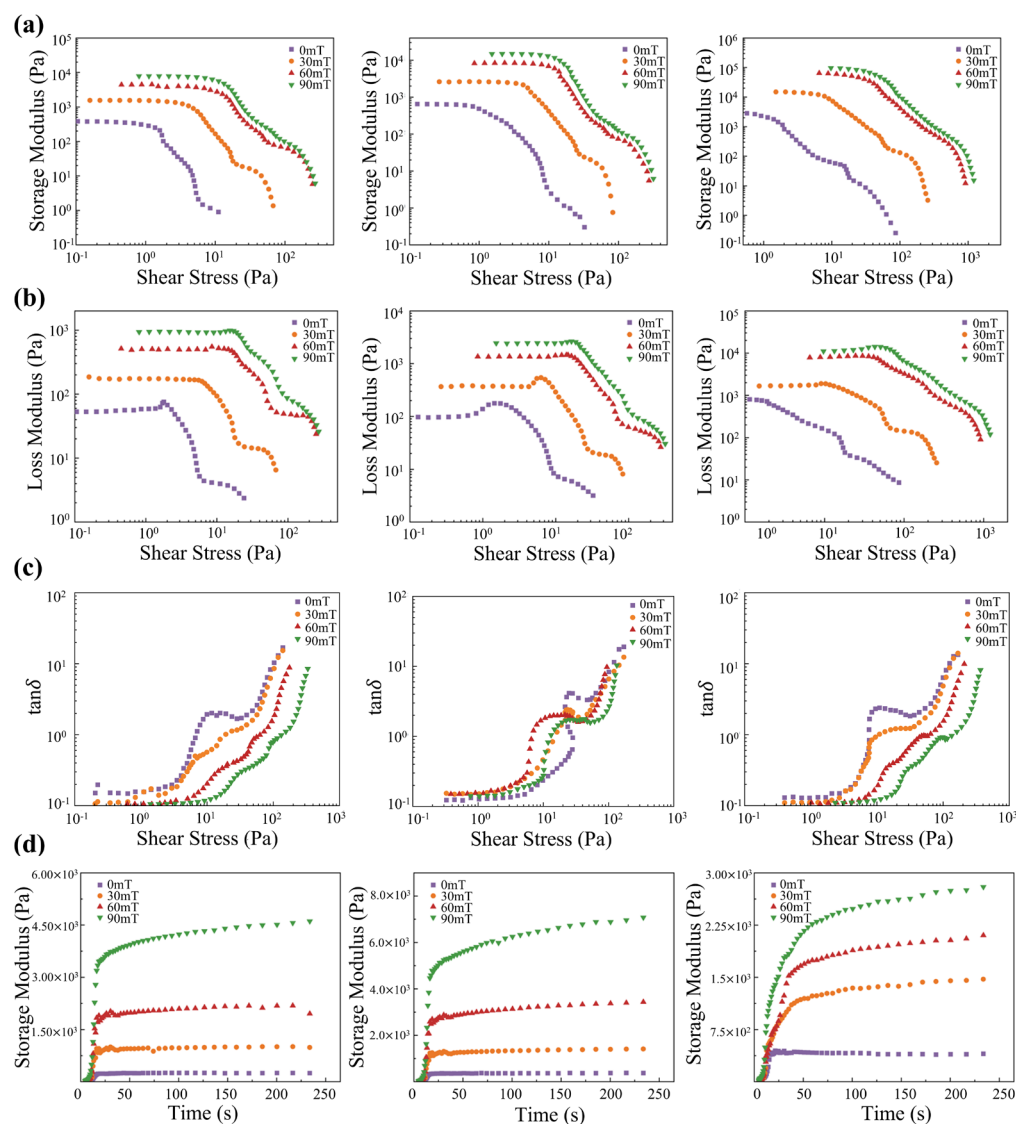


Figure 5. Large-amplitude oscillatory shear and thixotropic recovery properties of MTF. (a) Relationship between storage modulus and shear rate for the three MTF samples. From left to right: Sample 1, Sample 2, Sample 3. (b) Relationship between loss modulus and shear rate for the three MTF samples. From left to right: Sample 1, Sample 2, Sample 3. (c) Relationships between $\tan\delta$ and shear stress for MTF samples. From left to right: Sample 1, Sample 2, Sample 3. (d) Relationships between storage modulus and time under various magnetic field strengths for MTF samples. From left to right: Sample 1, Sample 2, Sample 3.

3.2. Direct Ink Writing 3D-Printing Results

Post-printing line height and width are key metrics for dimensional accuracy, interlayer bonding, and structural stability. Excessive dimensions cause over-extrusion and flattened lines; undersized dimensions cause under-extrusion and stretching; optimal dimensions slightly exceeding nozzle diameter enhance bonding and stacking. Print speed and nozzle diameter critically influence these metrics. Experiments analyzed line height/width under varied speeds (5–25 mm/s) and nozzle diameters (0.4/0.52/0.6 mm), with fixed parameters: drive pressure: 3 kg/cm², magnetic field: 30 mT, and samples: 8% OMBT-8% Fe₃O₄, 8% OMBT-12% Fe₃O₄, and 4% OMBT-14% Fe₃O₄ (Figure 6a–c). Results indicate that print speed and nozzle diameter combinations significantly impact quality. For the three MTF samples, as the printing speed, the moving speed of the printhead, increases, the line height and width with three different nozzle diameters all show a decreasing trend. Furthermore, different rheological properties dictate recovery, line height, and width. Low-viscosity materials require higher print speeds; high-viscosity materials need lower speeds to ensure continuity. The bentonite content dictates shear-thinning capability: higher bentonite ratios improve extrusion performance. At identical solid content, increased bentonite raises viscosity and yield stress, enhancing shear-thinning for more continuous extrusion.

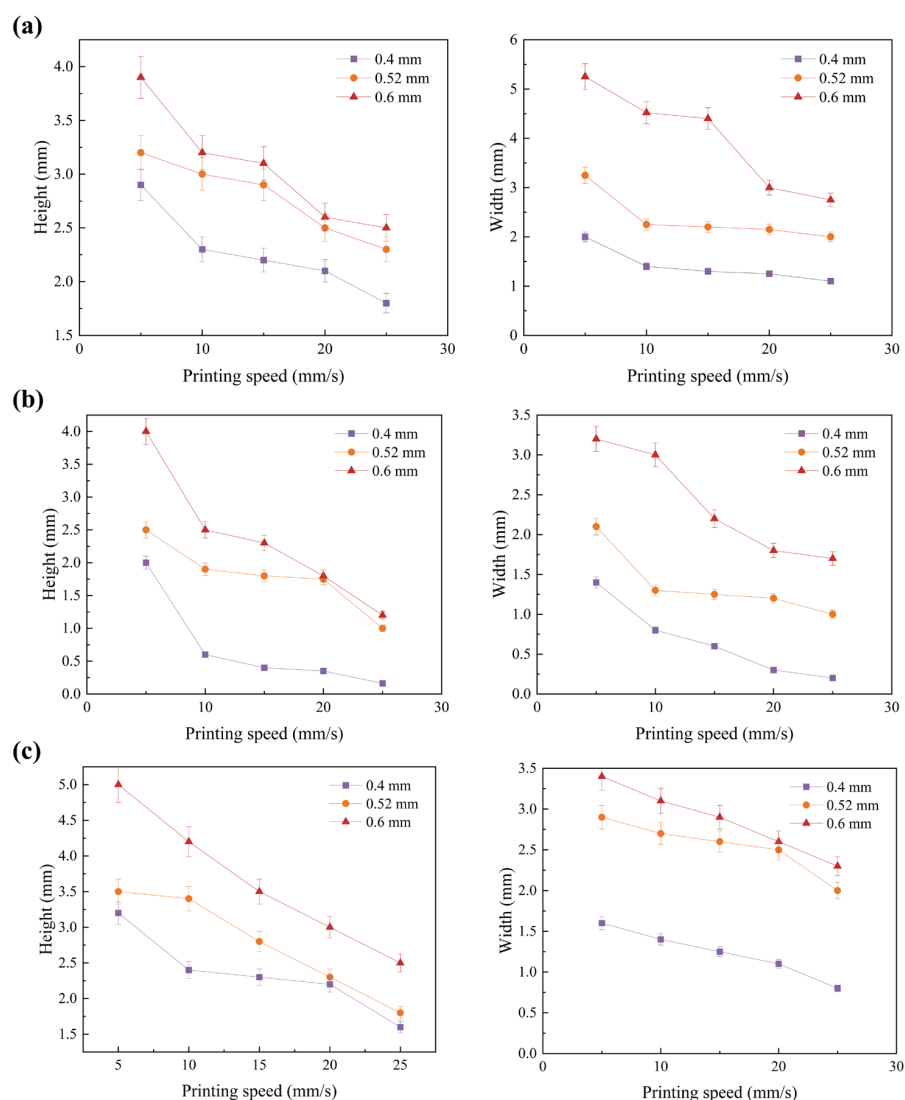


Figure 6. Relationships between line width/height and printing speed under various nozzle diameters for MTF samples. (a) Sample 1; (b) Sample 2; (c) Sample 3.

Structure formation under magnetic fields is fundamental for printing precision. Overlap tests evaluated interlayer stacking (Figure 7). When MTF is extruded after pre-shearing and the printing speed is too fast, the material's recovery is poor. The material does not fully recover under the magnetic field and does not form a sufficient anisotropic columnar structure. The intersection of lines is integrated as shown in Figure 7b, without forming overlap structures. The addition of a screw section reduces recovery time and improves printing efficiency as well as accuracy, enabling distinct overlap structures, as shown in Figure 7a.

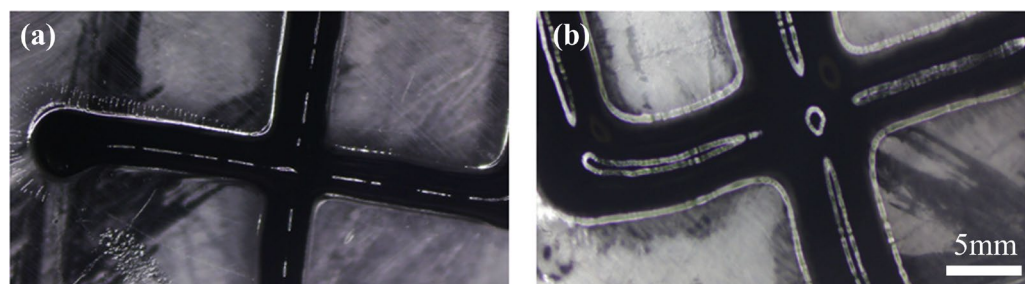


Figure 7. Results of the overlap experiments. (a) Successful overlap; (b) Failed overlap.

To further investigate the relationship between post-extrusion recovery and printing accuracy, a grid printing experiment was designed. Printing speeds of $v = 3$ mm/s, 5 mm/s, and 10 mm/s were selected while maintaining consistent extrusion volume per unit time. The grid formation status and precision were observed, with results shown in Figure 8a–c. The grid pattern consists of simple line configurations. To qualitatively evaluate the degree of solidification and printing quality, a printability parameter (Pr) was introduced, calculated as follows:

$$Pr = L^2 / 16A, \quad (2)$$

“L” is the perimeter of the internal pores in the grid structure (the total length of the edges enclosing each individual pore), and “A” is the area of the internal pores (the enclosed area bounded by the perimeter L). Essentially, Pr reflects the deviation of the pore shape in the grid structure from an “ideal square,” quantifying the filament solidification effect and interlayer support capability. Under ideal conditions, if filaments in a two-layer grid structure solidify fully without collapse or merging, pores should be perfect squares. Here, perimeter “L” and area “A” satisfy the square relationship (let the side length be “a”, then the perimeter is “4a” and the area is “a²”). Substituting into Equation (2) yields $Pr = 1$. Furthermore, the printing quality of the grid was evaluated by examining the corner angle formed at the intersections of the deposited filaments. This angle serves as a direct indicator of the material’s ability to recover its structural integrity and resist deformation under magnetic fields and different printing speeds. Based on the printed grid patterns and calculated values of Pr for MTF at different printing speeds, the results show optimal printing at 5 mm/s (Figure 8b), with Pr approximately equaling to 1 and corner angle close to the designed 90°. At a 3 mm/s printing speed, ($Pr < 1$, corner angle $> 90^\circ$), pore shapes approach circles (Figure 8a), indicating under-solidification. MTF filaments fail to fully recover structural strength within the interlayer printing interval, causing upper and lower layers to merge. This increases the pore area while decreasing the perimeter, deviating from a square shape. At a 10 mm/s printing speed, ($Pr > 1$, corner angle $\neq 90^\circ$), pore shapes exhibit irregular shapes, with possible filament breakage or local collapse (Figure 8c), indicating over-solidification. Excessive filament rigidity leads to fracture, increasing perimeter with minimal area change and deviating from a square shape. Layer-height tests examined extrusion recovery versus printing height under magnetic fields

(10/20/30 mT) for 8% Fe_3O_4 –8% OMBT (10×10 mm rectangle, 27 layers, 0.4 mm/layer; Figure 8d). The relationship between the printing height and the number of printing layers is shown in Figure 8e. According to the experiment results, as the magnetic field weakened, the extruded MTF did not form a microstructure and it fully recovered under the magnetic field. When printing the next layer, due to the weight of the material, the actual printing height of each layer was affected, and the errors accumulated, leading to structural collapse or trapezoidal deformation (“narrow top, wide base”). Full recovery of each layer ensures viscosity buildup, structural integrity, good stacking effect, and high precision of formation.

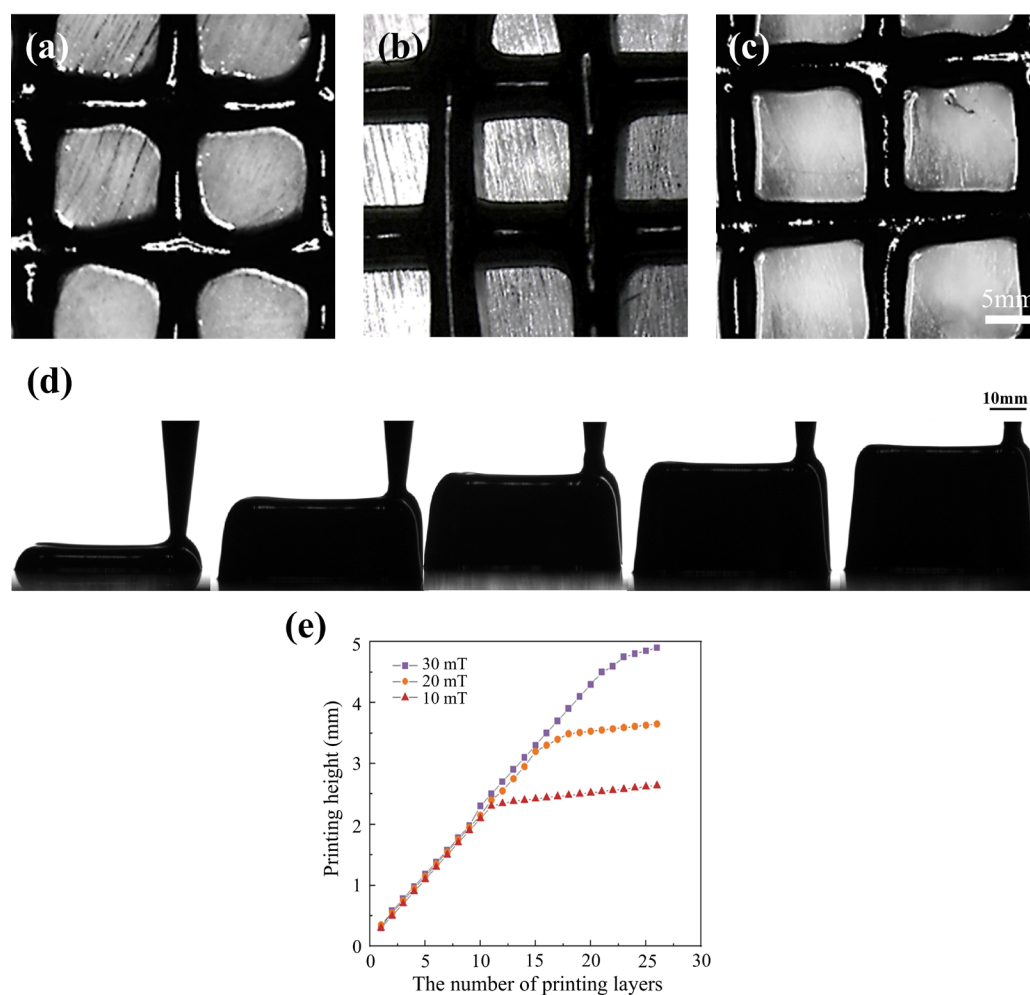


Figure 8. The post-extrusion solidification properties of MTF. (a) Grid printed at 3 mm/s; (b) Grid printed at 5 mm/s; (c) Grid printed at 10 mm/s; (d) Schematic of layer-height printing; (e) Relationship between the printing height and printing layers under various magnetic fields (10/20/30 mT) for Sample 1.

The DIW 3D-printing process for magnetic thixotropic fluids requires comprehensive consideration of both properties and rheological characteristics to establish a printability window. Through a series of experiments—including line height/width tests, overlap tests, grid pattern tests, and layer-height printing tests—the relationships among magnetic field strength (H), printing speed (v), and nozzle diameter and its influence on printing linearity and precision were investigated. The optimal printing parameters were determined as: magnetic field strength $H = 20$ mT, nozzle movement speed $v = 5$ mm/s, and nozzle diameter $d = 0.4$ mm. This combination ensures continuous and uniform material extrusion while enhancing printing quality and accuracy. Furthermore, material composition significantly impacts rheological tunability. The 4% bentonite–14% Fe_3O_4 sample

exhibited strong magnetorheological effects but poor thixotropy due to high Fe_3O_4 and low bentonite content, resulting in discontinuous extrusion and low multi-layer printing accuracy. The 8% bentonite-8% Fe_3O_4 sample, where the contents of the two components are equal, exhibited moderate thixotropy and magnetorheological effects, making it suitable for extrusion. Furthermore, this sample regained fluidity after the magnetic field was removed. For the 8% bentonite-12% Fe_3O_4 sample, although it has a relatively high Fe_3O_4 content, its overall solid content is higher than that of the 4% bentonite-14% Fe_3O_4 sample and the 8% bentonite-8% Fe_3O_4 sample. This leads to a relatively high viscosity of the material matrix and poor flowability, which hinders the magnetic field-responsive movement of Fe_3O_4 particles. Notably, when the content of Fe_3O_4 particles in MTF increases from 8% to 12%, the excess Fe_3O_4 particles exceed the accommodation limit of the “house-of-card” structures formed by OMBT. This leads to cross-linking between Fe_3O_4 particles and OMBT, preventing Fe_3O_4 particles from responding to the external magnetic field to form columnar structures along the magnetic field. Therefore, the 8% bentonite-12% Fe_3O_4 sample offers good thixotropy but weak magnetorheological response and ineffective solid–liquid transition under alternating magnetic fields.

Depending on different application scenarios, MTF material formulations with different properties can be selected. This study mainly focuses on the printability of MTF by the DIW 3D-printing system, and the selected materials should possess good thixotropy, magnetorheological properties and recovery performance. Thus, the 8% bentonite-8% Fe_3O_4 composition demonstrates preferable printability for the following DIW 3D printing. The printing of the acronym “MTF” is shown in Figure 9.



Figure 9. The printing of the acronym “MTF”. (a) Letter “M”; (b) Letter “T”; (c) Letter “F”.

4. Conclusions

This study prepared a novel MTF material and investigated its printability within a designed DIW 3D-printing system.

- Through rheological characterization, microstructural analysis, VSM magnetometry, and modulus tests, the proportions of the MTF components were designed and optimized.
- A stirring structure in the reservoir and a screw section in the extruder head were introduced, enhancing the extrusion uniformity and forming precision.
- The 8% bentonite-8% Fe_3O_4 sample was ultimately identified as having good printability ($\text{Pr} = 1$, corner angle = 90°) under the optimal printing parameters, i.e., the combination of the magnetic field strength $H = 20$ mT, the extrusion head movement speed $v = 5$ mm/s, and the extrusion head diameter $d = 0.4$ mm. The final printing quality was also validated.

Exploring the printability of magnetic thixotropic fluids provides insights into the printing of magnetic soft materials, extending to innovations in flexible wearable devices,

minimally invasive medical intervention robots, targeted drug delivery robots, and complex environment detection equipment.

Author Contributions: Conceptualization, methodology, supervision, investigation, Z.L.; methodology, investigation, and writing—original draft preparation, T.L.; investigation, formal analysis, H.C.; investigation, writing—review and editing, J.D.; resources, Z.G.; data curation, C.D.; visualization, S.Z.; project administration, Y.S.; funding acquisition, H.Z. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

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