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3D Printing for Explosive and Propellant Applications

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ABSTRACT

3D printing technology is considered the perfect modern manufacturing technology for military/industrial enterprises worldwide. Applying 3D printing in explosive and propellant fabrication enables precise performance control and accurate structure formation, revolutionizing traditional manufacturing concepts and improving continuous, automated, integrated, and flexible explosive and propellant manufacturing. As key components in the 3D printing of explosives and propellants, adhesives/binders play a crucial role in determining the formation rate, stability, and structural integrity of explosive formulations. This paper provides an overview of the four major 3D printing technologies suitable for explosive and propellant manufacturing: vat photopolymerization, binder jetting, fused deposition modeling, and direct ink writing, with their typical production processes, technical characteristics, principles, and limitations discussed. Specific solutions to the limitations of vat photopolymerization (printing speed), binder jetting (low accuracy and limited applicable materials), fused deposition modeling (poor mechanical properties and dimensional stability), and direct ink writing (product performance defects) are presented. Additionally, future development directions and prospects for the 3D printing of explosives and propellants are discussed, thus providing valuable insights into the application of 3D printing technology in the fields of explosives and propellants.

Keywords: 3D printing; Manufacturing technologies; Explosives and propellants; Outlook and prediction

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1. Introduction

Explosives and propellants play crucial roles in enhancing the power, firepower, and effectiveness of weapons [1]. The performance of explosives is determined by their components, structure, and processing methods, with the forming method being a key factor that limits their safe processing and large-scale manufacturing. Traditional manufacturing processes, such as casting, granulation, melt casting, and compression, face challenges in achieving high solid contents and complex cross-sectional shapes for explosive and propellant charges, considerably hindering the development of high-performance and controllable energy output explosion loading technologies [2, 3]. With its digital manufacturing approach, 3D printing technology offers precise, rapid, controllable, and safe

processing, thus overcoming the constraints of traditional manufacturing methods and facilitating the precise formation of complex structural components; consequently, this technology has been widely adopted in various fields [4–10]. Therefore, integrating 3D printing technology with explosive and propellant manufacturing technology can help overcome the limitations of traditional methods, achieve processes previously impossible or difficult, and produce disruptive effects. This integration has significant research implications and promising applications [11–14]. In 3D printing systems for explosives and propellants, adhesives are critical components that fulfill the basic curing function and possess fast shaping and strong bonding capabilities. Adhesives are essential for 3D printing explosives and propellants and should exhibit extensive suitability for most 3D printing processes [15–18]. Thus, the design and precise control of the adhesive/binder structure plays a crucial role in the curing rate, stability, and structural integrity of the explosive and propellant formulations. With the increasing solid loading in explosive and propellant formulations, commercially available adhesives and binders with single-curing functionalities, such as photocuring or thermocuring, are no longer sufficient to meet the 3D printing requirements of current explosive and propellant formulations, thus highlighting an urgent need to develop new adhesive/binder materials for 3D printing of explosive and propellant formulations.

Hence, we reviewed the research progress in 3D printing technology for explosives and propellants, focusing on the unique characteristics and application directions of 3D printing technology for solid propellants, gun propellants, explosives, and initiating explosive devices. The forming principles and process characteristics of vat photopolymerization, binder jetting, fused deposition modeling, and direct ink writing are summarized. In addition, existing problems in the corresponding studies were analyzed, the importance of 3D printing technology for explosive and propellant manufacturing processes was evaluated, and development direction and trends in 3D printing were predicted. Considering 3D printing technology of explosives and propellants should be systematically studied according to the application background, the design and preparation of energetic adhesives for the 3D printing of explosives and propellants, the process adaptability of adhesive materials, the creation of integrated multifunctional structures to overcome size limitations, adaptation to the extreme environment of the battlefield, and the sustainability of 3D printable adhesives were systematically studied to provide a reference for the application of 3D printing technology in explosives and propellants.

2. Historical Development of 3D Printing Technology for Explosives and Propellants

The development of 3D printing technology for explosives and propellants has a domestic and international history. Advanced countries and regions, such as the United States (U.S.), Europe, and Japan, were among the early pioneers in

researching rapid prototyping technologies. In the late 1970s, Lu et al. [19] from the United States proposed the concept of rapid prototyping. Charles W. Hull, also from the United States, first proposed the concept of laser irradiation to solidify liquid photosensitive resins and layer-by-layer curing for three-dimensional object formation in his doctoral thesis [19]. In 1984, Hull built a stereolithography apparatus (SLA) and obtained a patent for this technology (US4575330A) in the same year [20]. In 1988, 3D Systems developed the SLA-250, the first commercially available 3D printer that accounted for approximately 50% of the international market. With continuous research and innovation in photopolymer-based rapid prototyping technology, 3D systems have subsequently manufactured models, such as SLA 190, 250, 400, and 500 [21]. Other foreign companies such as EOS, Teijin Seiki, Mitsui Zosen, and CMET have also entered the field of 3D printing and rapid prototyping technology and have gained considerable market share, driving the rapid development of the entire 3D printing industry [22]. In 1992, EOS introduced the first commercial model, the FDM-1650; in 1997, they successfully launched the FDM-Quantum—the first fused deposition modeling (FDM) equipment to adopt the extrusion head magnetic levitation positioning system. This machine achieved dual-head printing technology for the first time and increased the printing speed five-fold.

Owing to military secrecy and competition in the field of explosives and propellants, publicly available information on the application of 3D printing technology in these areas remains limited [23]. As early as 1999, the Defense Advanced Research Projects Agency (DARPA) in the United States introduced 3D printing technology to the field of energetic materials. Significant achievements have been made in the research on material performance and printing processes. According to reports, the U.S. Department of Defense has used 3D printing technology to fabricate various miniature initiating explosive components, complex-shaped gun propellants, solid propellants, and multi-point initiation explosive columns to verify the manufacturing processes of critical initiating explosive components and precision microscale initiating explosives for guided weapons, thus addressing the issues of unintentional detonation caused by long production processes, unreliable contact between charges, and inconsistent loading densities. The U.S. military is also conducting systematic research on the application of 3D printing in the fields of double-base solid propellants and gun propellants. The U.S. Defense Threat Reduction Agency has proposed the development and validation of the capability to rapidly manufacture energetic material payloads and ammunition using additive manufacturing technology. The U.S. Marine Corps' Next Generation Logistics Office tested 3D-printed ammunition at the Naval Surface Warfare Center in Indian Head, Maryland, which demonstrated improved lethality compared with traditionally manufactured ammunition while offering enhanced safety and precision. Rocket Crafters Inc. (RCI) in the United States announced that its 3D printing technology for hybrid rocket engine grains has been granted a patent. This technology enables the design and production of flawless high-performance fuel grains for hybrid rocket engines, significantly improving the combustion rate during rocket engine operation. RCI plans to apply this technology to orbital launches, with countries and regions such as Australia, the European Union, China, and India actively involved in this research. Australia has initiated a joint R&D program on 3D printing technology for energetic materials, while the European Defense Agency launched a four-year joint research program on 3D printing technology for energetic materials involving 15 energetic materials

manufacturing companies from seven countries: Germany, France, Finland, the Netherlands, Poland, Sweden, and Norway. China has proposed applications of additive manufacturing technology in solid propellant manufacturing and has conducted related experiments at multiple research institutions. The Indian Scientific Research Institute has established an energetic materials additive manufacturing research laboratory and initiated a research and development project on energetic material additive manufacturing technology.

Explosives and propellants are combustible materials that contain energetic groups or oxidizers, have high energy densities, and are inherently unstable. They can undergo independent oxidation/reduction reactions and release energy upon stimulation by external energy sources. However, during the manufacturing and shaping processes of energetic materials, they are highly susceptible to accidents caused by environmental factors such as temperature or load. Owing to the unique characteristics of the explosive industry, conventional manufacturing techniques, such as casting, pressing, and pouring, are predominantly used for explosive loading. However, these methods present several issues, including high risk for operators during loading, low production efficiency, significant environmental pollution, and the inability to meet the production requirements of complex or heterogeneous charges. Therefore, the current limitations of ammunition manufacturing technology are attributed to traditional design concepts and manufacturing processes, which make it difficult to drive the development and progress of the next generation of high-quality weapons and equipment, thus highlighting a need for in-depth research in the areas of explosive selection for additive manufacturing, rapid prototyping of explosives, and integration of explosive and propellant manufacturing systems. Building on materials and technology, developing a 3D printing device platform that meets the requirements of safe and efficient manufacturing of explosives and propellants is fundamental for promoting the deep integration of explosives, propellants, and 3D printing technology. The material systems, structural characteristics, and functionality of explosives, particularly their operational safety, impose a series of requirements on the device platform, including safety, functionality, automation, and digitization.

Table 1. Timeline of key milestones in the development of additive manufacturing technology.

Year	Key milestones
1986	American scholar Charles W. Hull invented stereolithography (SLA), a technique for creating three-dimensional objects by curing photopolymer with light.
1986	3D systems, the world's first additive manufacturing equipment manufacturing company, was founded.
1988	3D systems developed the SLA-250, the first publicly available 3D printer that used selective photopolymerization to solidify liquid resin.
1988	Dr. Scott Crump invented fused deposition modeling (FDM) and established Stratasys, a company specializing in this technology.
1989	Scholar C.R. Dechard invented selective laser sintering (SLS) technology.
1992	Helisys developed the laminated object manufacturing (LOM) technique and introduced the first commercial prototyping system.
1993	Massachusetts Institute of Technology (MIT) obtained a patent for 3D printing technology.
1995	Z-Corporation acquired the exclusive license from MIT and began developing 3D printers.

- 1999 The Defense Advanced Research Projects Agency (DARPA) started researching additive manufacturing with energetic materials.
- 2005 Z-Corporation developed the Spectrum Z510, the world's first high-precision color 3D printer.
- 2005 The U.S. Naval Surface Warfare Center is also conducting research on pyrotechnic systems and miniaturized explosive sequences for use in rapid prototyping of fuzes/safing and arming devices. The rapid prototyping pyrotechnic system has undergone deep-sea launch tests for a 6.25-inch high-speed anti-torpedo.
- 2008 The U.S. Defense Laboratory has successfully incorporated energetic materials or pseudo high-energy explosives into inkjet printing technology, enabling the inkjet printing of polymer entity.
- 2010 Researchers, including Ihnen, experimented with direct writing of explosive initiators using inkjet-printed materials containing hexogeen (RDX).
- 2011 Los Alamos National Laboratory chemist Alex Muller has proposed a design concept for an arrayed porous charge structure based on photopolymerization additive manufacturing technology, enabling unprecedented control over the behavior of explosives by manipulating their microstructure.
- 2013 The Netherlands Organization for Applied Scientific Research (TNO) conducted experiments with additive manufacturing of energetic materials using *p*-trinitrotoluene (TNT).
- 2015 The National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland, USA, has proposed a method for manufacturing monodisperse particulate explosives using voltage-based inkjet printing technology.
- 2015 The National Institute of Standards and Technology (NIST) used on-demand piezo inkjet printing to produce micrometer-sized explosive particles.
- 2015 The European Union launched the "Support Action for Standardization in 3D Printing" project.
- 2016 The U.S. Marine Corps' Logistics Innovation Office printed and tested 3D-printed ammunition at the Indian Head Naval Surface Warfare Center.
- 2017 TNO successfully printed porous propellant (energetic material with a solid loading of 75%) using SLA.
- 2017 Lawrence Livermore National Laboratory in the United States has proposed a method based on DIW (Direct Ink Writing) technology to control the shock wave characteristics of energetic materials. They have achieved control over the output shock wave of the front end of the energetic materials.
- 2017 Purdue University has designed a dual-nozzle inkjet control device that utilizes platform movement and alternating nozzle inkjet to achieve nanoscale aluminum-based energetic ink formulations.
- 2018 Companies like ATK in the United States have conducted static explosion tests on 3D-printed hypersonic warheads.
- 2018 Gaston et al., from the U.S., proposed a design scheme for circumferential MEFY (Multi-Effect Fragmentation Yield) warheads using 3D printing. In comparison to traditional ammunition manufacturing processes, 3D printing not only enhances production and assembly efficiency while reducing research and development cycles but also lowers the waste rate in MEFP warhead production, presenting considerable application prospects.
- 2018 The Defense Science and Technology (DST) Group of the Australian Department of Defense Industry collaborates with industry and academia to leverage additive manufacturing technology for the production of explosives, propellants, and pyrotechnics, aiming to improve the safety of industrial explosives and stimulate the development of advanced weapon systems.
- 2018 The Indian Institute of Science successfully produced composite solid propellants with different internal bore shapes using additive manufacturing.
- 2019 The Defence Science and Technology Laboratory (DSTL) in the UK researched 3D printing of energetic materials using a LabRAM resonant acoustic mixer.
- 2020 TNO completed ignition tests for a 30 mm caliber projectile loaded with 3D-printed propellant.
- 2020 The Logistics Office of the U.S. Marine Corps quietly printed and detonated an indirect fire munition at the Naval Surface Warfare Center in Maryland.
- 2020 The UK Ministry of Defence (MOD)-funded Defence Science and Technology Laboratory (DSTL) proposed design schemes for additive manufacturing of energetic materials.
- 2022 The UK Ministry of Defence 3D printed multidimensional "shaped" explosives.
- 2023 Researchers from the University of Iowa and Iowa State University in the United States collaborated to utilize pressure-assisted binder jetting 3D printing technology for the fabrication of solid propellants. They also analyzed the influence of printing parameters on the composition and performance of the solid propellant.

Table 2. Types and properties of 3D printing technology.

Process	Representative materials	Polymers material	Performance requirements
Vat photopolymerization	Photopolymer resins	Polyurethane acrylate, epoxy acrylate, epoxy compounds, vinyl ethers, etc	Ability to undergo polymerization reaction upon exposure to a specific wavelength of ultraviolet (UV) light (25–420 nm) for photopolymerization.
Binder jetting	Photopolymer resins/thermoplastic polymers	Polylactic acid, silicone rubber, hydrogels	Gelation, appropriate viscosity, shear thinning index of 1.5–4, good stability.
Fused deposition modeling	Polymer filaments	ABS, polylactic acid, polycarbonate, polysulfone, polyether ether ketone	High mechanical strength, low shrinkage rate, suitable melting temperature.
Direct ink writing	Polymers	Thermoplastic resins: polystyrene, polyamide, polypropylene. Thermosetting resins: epoxy resin, unsaturated polyester, phenolic resin, amino resin, polyurethane, hydrogels, etc.	Suitable solidification, viscosity, excellent flowability, minimal shrinkage, low internal stress, high strength and resistance to aging.

3. Types of 3D Printing Technologies Suitable for Printing Explosive and Propellant Materials

According to the additive manufacturing standards published by ASTM-F42 (Committee on Additive Manufacturing Technologies), 3D printing is classified into seven types [24]. Four of these types—vat photopolymerization, material jetting, fused deposition modeling, and selective laser sintering—can be used for 3D printing and shaping explosive materials, as outlined in Table 2. Among the four technologies suitable for 3D printing and shaping explosive materials, the rapidly formable adhesive system is the most critical component.

3.1. Vat photopolymerization

The vat photopolymerization 3D printing technology includes stereolithography (SLA) [25], digital light processing (DLP) [26], continuous liquid interface production (CLIP) [27], and calculated axial lithography (CAL) [28]. The formation principles of these technologies are based on the photopolymerization of liquid photosensitive resins, in which the photosensitive substances in the resin system undergo photochemical reactions triggered by UV light, generating reactive fragments that initiate the polymerization and crosslinking of monomers and prepolymers, eventually resulting in the rapid formation of solid products. Photosensitive resins generally consist of prepolymers, reactive diluents, photoinitiators, and additives (such as organic solvents and surfactants). The composition of the photopolymerization adhesive system for 3D printing—mainly comprising photoinitiators, binders, plasticizers, and auxiliary additives—is shown in Fig. 1.



Fig. 1. Components of photocurable binder matrix.

SLA is the earliest and most widely applied photopolymerization 3D printing technology with the most mature applications. Fig. 2 illustrates the forming principle of an SLA printer. A UV laser with a specific wavelength is used to irradiate the surface of the photosensitive resin, solidifying it from points to lines and then to layers. After each layer is solidified, a leveling process is performed to reduce the warping and deformation of the printed object. The main function of the scraper during printer operation is to evenly spread the liquid material onto the printing bed, ensuring high printing accuracy and a smooth surface finish. This technology has played a significant role in traditional mold manufacturing and rapid casting. However, owing to the slightly larger laser spot size, this technology is not suitable for ultra-high-precision printing; moreover, the printing speed is relatively slow.

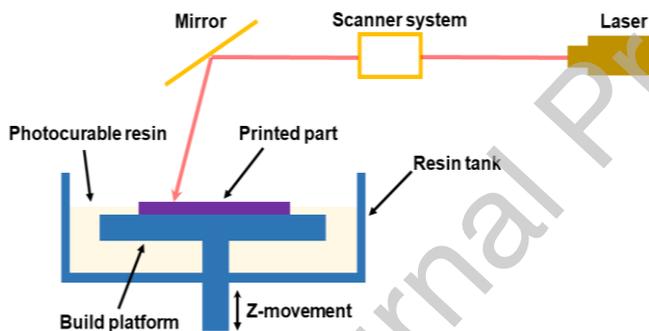


Fig. 2. Forming principle of an SLA printer [25].

DLP technology uses a specific wavelength of UV light to project a cross-sectional image of the model onto the surface of a photosensitive resin, solidifying it in a layered manner. This approach improves the low printing speed and lengthy printing process associated with conventional photopolymerization. The DLP principle is illustrated in Fig. 3.

CLIP technology, proposed by Carbon 3D and researchers from the University of North Carolina, utilizes an oxygen-permeable, UV-permeable membrane and oxygen to create a liquid-dead zone, enabling high-speed continuous liquid interface printing. The maximum printing speed can reach 500 mm/h, 100 times faster than that in traditional SLA processes [29]. The CLIP principle is illustrated in Fig. 4.

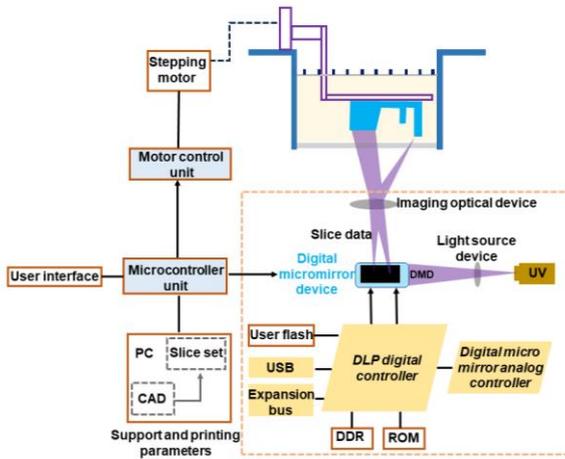


Fig. 3. Forming principle of a DLP printer [26].

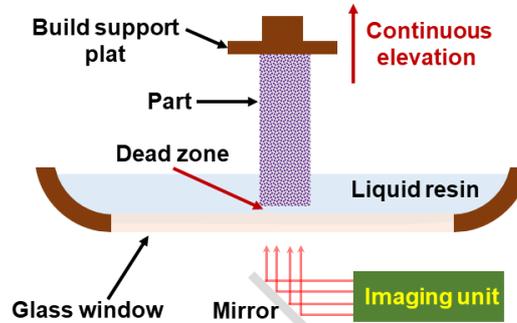


Fig. 4. Forming principle of a CLIP printer [27].

In 2019, Kelly et al. from the University of California, Berkeley introduced a CAL 3D printing technology based on reverse CT scanning [28]. This technology involves calculating a series of reverse computed tomography (CT) images of a 3D model from multiple angles and projecting them onto a rotating container containing acrylic resin. The rotation angle of the container changes with the projected reverse CT image angle. When the absorbed energy reaches the threshold, the acrylic resin undergoes a polymerization reaction and becomes a solid polyacrylic resin, as shown in Fig. 5.

CAL technology does not require fluidity of the medium during the printing process, does not need support structures, can print discontinuous structures, and can generate new structures outside existing objects, thus making it suitable for mass production of printed part sizes reaching 0.5 mm with discernible feature lengths in the sub-millimeter range. CAL can also process weakly absorbing photosensitive resins, thus offering potential for applications in optical part manufacturing.

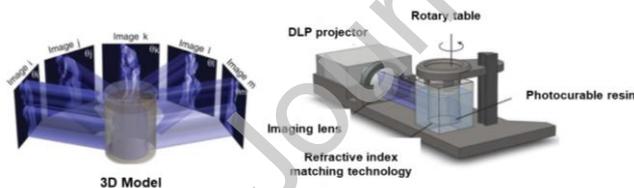


Fig. 5. CAL 3D printing principles [28].

Comparison of SLA, DLP, CLIP, and CAL technologies (Table 3):

Photopolymerization Method: SLA, DLP, CLIP, and CAL undergo photopolymerization. SLA uses a laser focused on a liquid photopolymer, typically forming points to lines and then to layers. DLP projects a cured photopolymer using a digital light processor in a layered manner. CLIP is a surface-forming process that employs image projection through a semi-transparent membrane using high-transparency UV light and oxygen to create a liquid dead zone, thus facilitating continuous solidification without requiring layer separation and repositioning, resulting in the fastest printing speed. CAL is an upgraded version of the DLP technology that is formed in a layered manner.

Printing Speed: SLA is formed from points to lines and lines to layers, resulting in the lowest printing speed. DLP and

CAL enable solidification in a layered manner, resulting in faster printing speeds than that of SLA. SLA and DLP are layer-by-layer printing processes that are not continuous, making it difficult to achieve high printing speed and excellent printing accuracy simultaneously. CLIP significantly differs from SLA/DLP in that it involves using high-transparency UV light and oxygen to create a liquid dead zone, facilitating continuous solidification and achieving printing speeds significantly faster than those of SLA and DLP.

Printing Accuracy: While SLA, DLP, and CAL technologies can achieve high printing accuracies, CAL offers the potential for higher accuracy owing to its reverse CT scanning-based approach. CLIP technology also offers high printing accuracy but may have limitations in achieving the same level of accuracy as SLA and DLP in some cases, owing to the continuous printing process.

Surface Finish: SLA, DLP, CLIP, and CAL technologies can achieve smooth surface finishes on printed objects. However, SLA and DLP may require additional post-processing steps, such as rinsing and curing, to remove excess uncured resin and improve surface quality.

SLA, DLP, CLIP, and CAL technologies have a wide range of applications. SLA is widely used in various industries, such as prototyping, jewelry, and dentistry, while DLP technology is commonly used in industries such as jewelry, dentistry, and consumer products. The CLIP technology has found applications in the automotive, aerospace, and medical industries, where high-speed production is required, while the CAL technology offers the potential for mass production and optical part manufacturing.

In summary, vat photopolymerization 3D printing technologies, such as SLA, DLP, CLIP, and CAL, utilize the photopolymerization of liquid photosensitive resins to create solid objects. Each technology has advantages and applications, with differences in printing speed, accuracy, surface finish, and suitability for specific industries.

Table 3. Comparison of vat photopolymerization 3D printing technologies.

Technology	Photopolymerization method	Print speed	Main advantages	Main disadvantages
SLA	Scanning	Slow	High cost-effectiveness	Slow printing speed
DLP	Surface projection	Relatively fast	Higher resolution compared to SLA	Quality limited by pixel size
CLIP	Mask projection	Fastest	Fastest printing speed	High cost; requires highly specialized photopolymer resins
CAL	Surface projection	Relatively fast	Higher resolution compared to DLP	Not suitable for printing non-transparent materials

3.2. Binder Jetting

Binder jetting utilizes a printing head similar to that of an inkjet printer to spray precise layers of photosensitive polymer resin, usually partially surrounded by a support material, which is instantly cured using UV light. To maintain a precise layer thickness and compensate for minor variations in droplet size, current devices employ a mechanical leveling mechanism that removes excess material after each deposition using a print head [30,31] (see Fig. 6).

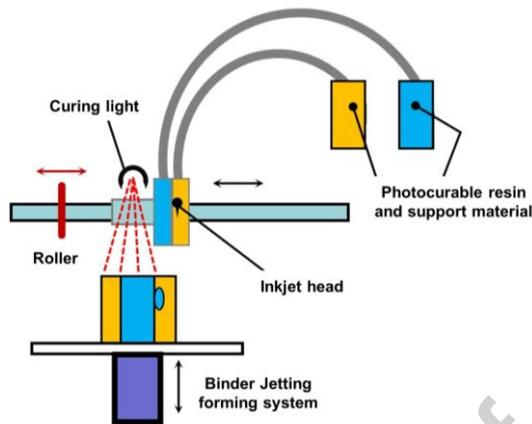


Fig. 6. Simplified binder jetting molding 3D the main components of the printer; each layer printed is planed and cured immediately after UV exposure [30].

On-demand droplet-based microjet freeform fabrication is based on microdroplet jetting and fluid dropletization principles. The shaping process involves periodically ejecting a continuous fluid (ink) as discrete droplets from the nozzle tip via controlled external driving forces (such as pneumatic or piezoelectric actuation). These droplets were stacked layer-by-layer on a substrate to form a three-dimensional solid.

Limitations: Ink viscosity considerably impacts the effectiveness of material jetting. The micro-jet heads available on the market can only spray low-viscosity "inks" (such as acrylic resin), which offer high accuracy and resolution without requiring complex laser or electron beam scanning. However, in the 3D printing industry, the current microjet resolution does not satisfy high-quality printing requirements.

Therefore, the main areas of technological innovation in material jetting focus on the nozzle and innovative "ink" design.

3.3. Fused Deposition Modeling

Fused deposition modeling (FDM)—the most widely used 3D printing process in the field of energetic materials and belonging to the field of material extrusion—involves extruding molten thermoplastic polymer material through a heated nozzle, which is then deposited and solidified at specific positions to form the desired shape [32,33] (see Fig. 7).

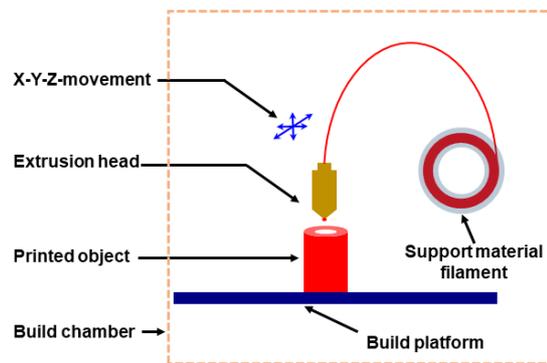


Fig. 7. Principles of popular FDM processes: melting and extruding plastic fiber materials using X - Y - Z shaft hot melt nozzle [32].

The processing temperature must be compatible with the melting point of the material used and controlled accordingly, such as by heating the build platform or even the entire build chamber, to reduce post-deposition thermal shrinkage. The most used polymers in this process are acrylonitrile butadiene styrene (ABS) and polypropylene; however, advanced printers can also process engineering materials such as polyamide, polycarbonate, and even polysulfone. Considering the raw material used in this method is a thermoplastic polymer, the mechanical properties of the final parts are similar to those of traditionally molded or machined products.

This process resembles squeezing toothpaste and is a relatively simple procedure that does not require complex equipment. Moreover, this technology is mature and the products have good dimensional accuracy and storage performance, making them widely used in low-end 3D printing devices. However, FDM parts exhibit noticeable surface textures, low strength between layers, and long printing times.

Limitations: Owing to the working principle of layer-by-layer extrusion and deposition in a molten state, FDM is only suitable for producing small-to-medium-sized models. The surfaces of the formed parts exhibited visible ridges, with the dimensional accuracy of the final product affected by thermal and molecular orientation shrinkage of the thermoplastic material during the melting, extrusion, and cooling processes. The generated internal stresses also result in inferior mechanical properties of the finished product. Additionally, the bonding strength between adjacent cross-sectional layers is limited, resulting in a weaker structural strength in the thickness direction of the printed parts, slow printing speed, and low efficiency.

Therefore, the main focus of innovation lies in achieving precise and orderly deposition of the molten material, rational and scientific structural design, and optimization of the process parameters. To address the issue of dimensional shrinkage, size compensation can be introduced during the CAD modeling process, and well-designed structures can be employed.

3.4. Direct Ink Writing

DIW technology is a 3D printing technique that involves the continuous extrusion of ink-based suspensions through a printing nozzle, followed by specific post-processing steps—such as solvent evaporation or light curing, depending on the material properties—to obtain 3D fabricated samples (see Fig. 8). DIW offers unparalleled advantages at the micro/nanoscale compared to traditional manufacturing methods and has wide applications in various fields, including semiconductor materials,

electronic devices, optical instruments, tissue engineering scaffolds, colloidal materials, photonic crystals, and microelectromechanical system (MEMS) sequential explosive charges.

DIW exhibits several notable advantages, such as simple processing, low equipment requirements, low manufacturing costs, a wide range of applicable raw materials, high precision in shaping, manufacturing flexibility, and high densification of the formed body after sintering. Moreover, DIW meets the demands of customized structures and designs [34,35].

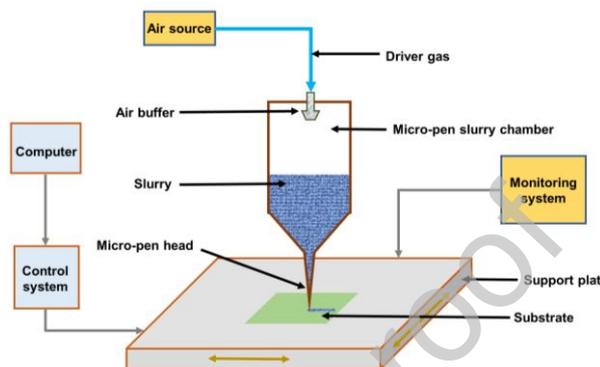


Fig. 8. Direct ink writing (DIW) process diagram. The powder diffuses from the supply tank to the construction tank in the form of a thin layer, which is fused to the component with a powerful infrared laser [34].

Limitations: The dimensional accuracy of printed products relies heavily on the properties of the printing ink, making it challenging to improve the printing formulation further. Post-printing processes such as drying and debinding are required, adding complexity to the overall processing and resulting in lower dimensional accuracy of the fabricated products. The final accuracy of the produced components depends on the formulation of the ink material, physicochemical properties, viscosity, and rheological performance, and on the parameters of direct writing, including nozzle diameter, needle size, pressure, speed, and other variables. In recent years, researchers have explored the use of external factors such as light, heat, rotation, and vibration to assist the DIW 3D printing process [36]. This approach has expanded the range of DIW material manufacturing and enhanced its applicability and functionality.

4. Research Progress of 3D Printing Technology in the Fields of Explosives and Propellants

3D printing technology has attracted significant attention in the field of energetic materials, both domestically and internationally, owing to its ability to achieve precise control and accurate formation of specialized and functional explosive structures [37]. However, owing to military secrecy requirements and the unique nature of the explosives industry, information regarding the application of 3D printing technology in the defense industry, especially in advanced weapons and equipment manufacturing, remains lacking. Nevertheless, comprehensive research has indicated that the US military has been systematically studying the application of 3D printing in the fields of explosives and propellants in recent years [38, 39], while other countries, including the United Kingdom, Australia, and India, have actively pursued research in this area. These

countries have already mastered the preparation of miniature pyrotechnic components, complex-shaped propellants, and multipoint initiation explosive columns using 3D printing technology to address specific challenges in practical applications and promote the development of 3D printing for energetic materials [40–42]. The Indian Institute of Science identified additive manufacturing technology for explosives as a key area for development and initiated a research and development project on the additive manufacturing of composite solid propellants [43]. This study successfully produced solid propellants with complex grain configurations and controllable burn rates. Currently, the research directions in China and abroad are generally consistent. However, compared to other countries, the 3D printing of explosives and propellants in China is still in the research stage. Representative universities and institutions, such as Nanjing University of Science and Technology, Beijing Institute of Technology, North Industries Group, and Xi'an Modern Chemistry Research Institute, have actively conducted exploratory research on 3D printing technology in the field of explosives, achieving progress in equipment, processes, materials, and other aspects. Their research focused on two major challenges that must be overcome in 3D printing technology for explosives: creating a suitable molding process and selecting appropriate 3D printing formulations for explosives. According to the literature, research on 3D printing technology in the field of explosives and propellants has mainly focused on solid propellants, gun propellants, explosives, and initiating explosive devices [44].

4.1. Applications of 3D printing in solid propellants

In 2005, the Xi'an Modern Chemistry Research Institute conducted preliminary work, including the use of SLA technology to shape a mixture of photopolymer and aluminum (Al) powder, utilization of surrogate systems to simulate hydroxyl-terminated polybutadiene (HTPB) propellant formulations, and the application of piston extrusion additive manufacturing technology in forming experiments. These studies demonstrated the feasibility of additive manufacturing technology in the field of propellant grain formation [45].

In 2017, Nanjing University of Science and Technology developed a light-curing 3D printing technology for propellant molding [46] and applied it for patent protection. This technology enables the formation of propellants at lower temperatures and pressures, thereby enhancing the safety of 3D printing of solid propellants. However, light-curing printing has the drawback of internal photopolymerization, which makes it difficult to achieve complete curing within a short period.

In the same year, Groven and Mezger investigated the fabrication of printed solid propellant models [47]. They used a valve system with spiral components to extrude a printing material consisting of HTPB and ammonium perchlorate (AP) as an inactive binder with a solid content of 85 wt%. However, the printed structures exhibited inadequate dimensional tolerance precision, and the shape of the printed propellant columns was not ideal.

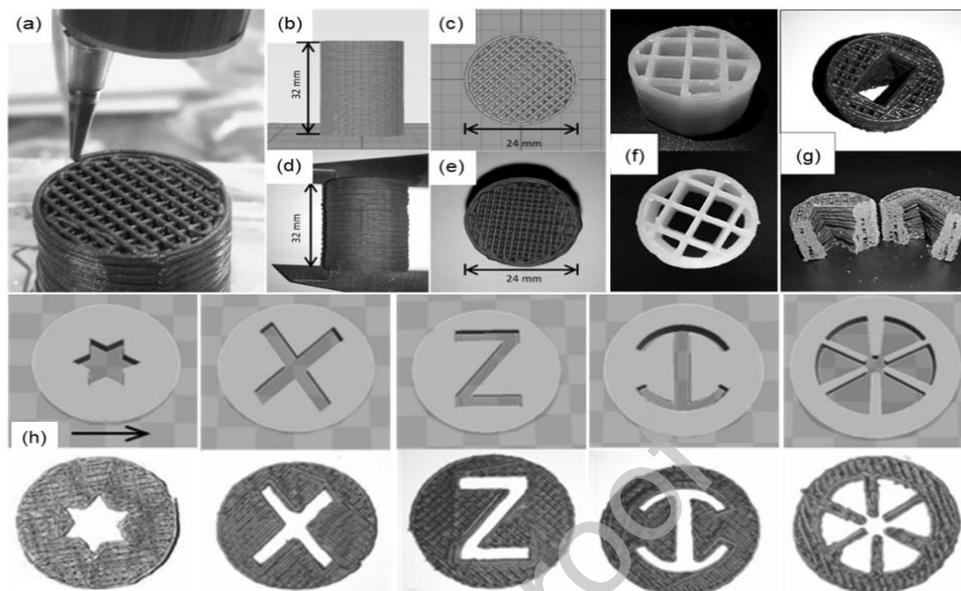


Fig. 9. (a) 3D printing process; (b, c) CAD models; (d–g) 3D-printed composite propellant grains; (h) CAD cross-sections of port geometries and corresponding 3D-printed propellant grains [48,49].

In 2017, Chandru et al. from the Indian Institute of Science [48,49] utilized a single-nozzle inkjet printing technology to produce solid propellant grains with multi-dimensional porous networks comprising 78 wt% AP and 22 wt% HTPB binders, plasticizers, and curing agents, as shown in Fig. 9. By varying the internal pore shapes and the type and density of the fillers within the pores, propellant grains with varying energy densities were obtained using this approach. In addition, the printed propellant grains were characterized and tested, with the experimental results showing that the performance of the printed propellant grains was similar to that produced by conventional vacuum casting. However, this process also had certain limitations: without external support structures, the propellant grain samples collapsed and sagged as the height increased during the printing process, affecting the precision of grain formation and significantly extending the curing time for each propellant grain sample.

In 2018, Gunduz et al. [50] successfully printed structures using various energetic materials, such as Al-based polymers, with the assistance of high-amplitude ultrasonic vibration (HAUV) and utilized this technique to 3D print HTPB-based propellants with an AP content as high as 85 wt.%. In the same year, Sandia National Laboratories [51] proposed another direct-write fabrication method called automated ink-injection molding. In this printing process, the extruded liquid ink immediately maintained its shape after deposition owing to its shear-thinning characteristics. Using this strategy, Durban et al. [52] and Doorenbos et al. [53] performed automated ink injection molding using water-based inks based on Al or copper oxide (CuO) and aluminum–thermite mixtures, respectively. The test results showed continuous combustion of the printed aluminum-thermite ribbon at a rate of 12 cm/s. Moreover, the deposition of nano-aluminum-thermite ink on the propellant using the automated ink injection molding method showed no cracking. Nafday et al. [54] used a commercial silicon nitride pen to pattern PETN and HMX in acetonitrile.

In 2019, McClain et al. [55] utilized a novel conical nozzle with an added ultrasonic vibration device at the extrusion end

to print high-viscosity HTPB propellant samples and prevent material clogging and found that the rheological properties of the high-viscosity slurry inside the channel significantly improved under ultrasonic vibration. However, the nozzle had to move at a shorter and faster speed to avoid a decrease in printing accuracy owing to machine recoil and vibration. The existing manufacturing techniques for composite solid propellant grains involve using hazardous chemicals and specialized molds for casting and curing processes. This process involves the polymerization of oligomers and functionalization of isocyanates. Moreover, the mold structure constrained the geometric structure of the propellant, limiting the pressure vs. time curve of the rocket engine to certain predefined configurations. However, the storage time of the components in composite solid propellant grains falls far short of military warfare requirements. To address these challenges, in 2021, researchers from the Polytechnic University of Turin, Italy [56] proposed and filed a patent for an additive manufacturing process for propellant grain production based on UV curing. The mechanical and physical characteristics of the different formulations were tested using dynamic mechanical thermal analysis, thermogravimetric analysis, and stress-strain tests. This curing method, which involves printing and solidification, facilitates using specific pressure vs. time curves or local component adjustments and innovatively utilizes UV-sensitive prepolymer components instead of isocyanate binders, significantly reducing chemical hazards to operators. This technology enables the production of more complex propellant grain geometries, thus providing the foundation for applying UV-cured propellants in complex propulsion tasks. In addition, in terms of propellant formulations, ammonium sulfate was used instead of ammonium perchlorate, with HTPB and polybutadiene diacrylate (PBDDA) considered as binders to prepare samples with and without aluminum to evaluate the effects of opaque materials produced during the UV curing process. The results showed similar experimental outcomes for the two novel UV-cured materials, confirming the feasibility of propellant production using a non-isocyanate process.

In our literature survey, we found it challenging to obtain research results on the combustion characteristics of propellant formulations at the fine scale (millimeter level). In 2021, researchers from Purdue University in the U.S. [57] used 3D printing technology to obtain propellant grains on a fine scale, successfully producing propellant grains with a faster-burning inner layer containing 1 % iron oxide or 5 % nano-aluminum as well as a two-layer grain with a slower-burning outer layer consisting of 85% AP and HTPB. The combustion characteristics of the inner-layer propellant were tested, with the results indicating an increase in the burning surface area in the pressure range of 3.45–10.34 MPa. The absence of interlayer delamination suggests that the driving force behind the increased burning rate was the difference in the interlayer burning rates. Furthermore, compared with traditionally cast nano-aluminum propellants, 3D-printed nano-aluminum propellant layers exhibit a more stable burn rate exponent. Adding a small amount of the burn-rate catalyst was sufficient to enhance the burn rate of the matrix fuel. This research provided the foundation for on-demand 3D printing of designed solid propellant grains with tailored thrust curves.

Embedding fully consumed reaction lines in propellants can effectively increase the surface area involved in combustion to enhance the burning rate [58]. However, this phenomenon can only be observed through the invasive windows near the embedded reaction lines. To address this issue, in 2021, researchers from Purdue University in the U.S. [58] developed an approach to customize the internal burning curves of propellants with embedded printable reaction lines and developed a dynamic X-ray imaging technique to qualitatively and quantitatively characterize the complex internal burning surface development. The method involved embedding printable reaction lines of aluminum/polyvinylidene fluoride into various

shapes, such as single lines, multiple forks, U-shapes, and V-shapes. A nano-aluminum-based formulation generated a conical burning surface at 1 atm, with dynamic X-ray imaging used to analyze the evolution of the internal burning curves of propellants with embedded additive manufacturing reaction components. This strategy avoids heat loss at the windows and prevents the ejection of unburned propellants, even in the vicinity of multiple embedded wires.

In 2021, researchers from the Utah State University Propulsion Research Laboratory [59] utilized 3D printing technology to develop a high-performance "green" solid-liquid hybrid fuel column using ABS. An efficient heat-transfer mechanism was achieved by increasing the mass concentration of copper in the fuel column to 6 % and uniformly mixing it with the ABS fuel. This mechanism enabled deep radiative heat transfer between the flame region and solid fuel, significantly improving the pyrolysis efficiency and regression rate of the fuel. The researchers systematically described the production and manufacturing methods of this solid propellant and presented the results of hot-fire tests. The results showed that the injection of copper significantly increased the regression rate of the 3D-printed fuel, providing higher thrust while maintaining the fuel volume without affecting the characteristic velocity of the propellant or the overall specific impulse of the system. Additionally, the copper injection resulted in an increased burning rate and solid fuel density, thus improving the specific impulse density of the propellant. Researchers have also proposed a method for injecting materials with lower molecular weights and higher thermal conductivities, such as graphene and carbon nanotubes. This study offers significant potential for applications in small spacecrafts, where available spaces are at a premium.

Applying 3D printing technology facilitates ABS fabrication into almost any desired structural model. In 2021, researchers from the Florida Institute of Technology in the U.S. [60] used the FDM method to 3D print ABS solid-liquid hybrid fuel columns with spiral ports. The test results of the fuel columns demonstrated that the spiral ports significantly enhanced heat transfer, thereby improving the burning rate of the fuel column. Using a skeletal structure also notably influenced the combustion performance of the solid propellant, whereas the combination of multiple ports increased the diversity of the propellant structure. Furthermore, the vortex effect has been proven to increase the regression rate, serving as an important direction for exploring the configuration of fuel columns with multiple spiral ports. The FDM method opens new avenues for optimizing the performance of solid-liquid hybrid rocket engines. In 2023, Tan and Liu [11,14] designed and synthesized two novel photothermal dual-curing adhesives—acrylate-type hydroxyl-terminated polybutadiene and acrylate-type hydroxyl-terminated polyethers—utilizing cationic ring-opening polymerization and an active monomer mechanism for the photothermal dual-curing reaction. The prepared adhesives have lower viscosity and excellent mechanical properties at low temperatures. The mechanical properties, thermal stability, and shrinkage properties of the photothermal dual-curing elastomers were systematically investigated. In addition, the best curing parameters for the photothermal dual-curing system and the optimum material ratio were determined. The experimental results indicate that the adhesive exhibits excellent thermomechanical properties. Therefore, the target adhesive satisfied the requirements of the printing process in terms of both thermodynamic properties and viscosity. Finally, the photothermal dual-curing adhesive formula was verified through a 3D printing experiment, with a satisfactory printing effect obtained. In summary, this study solved the problems of slow curing speed and incomplete curing in a short period of time for traditional photocured 3D printing, thus providing a solid foundation for overcoming the difficulties of accurate rapid prototyping and precise performance control in 3D printing with conventional propellants and explosive column handling.

In 2023, researchers from the University of Iowa collaborated to use pressure-assisted binder jet 3D printing technology to fabricate solid propellants [61]. They also analyzed the influence of the printing parameters on the composition and performance of solid propellants. Although 3D printing technology enables precise control over the thrust of a propellant by adjusting its macroscopic and microscopic structures, this approach often sacrifices the solids content, density, mechanical properties, and combustion performance of the propellant. To address these challenges, ammonium perchlorate with high density and strong thermal stability was selected as the oxidizer, with hydroxyl-terminated polybutadiene (HTPB) with low-temperature curability selected as the fuel binder, respectively. The researchers employed a pressure-assisted binder-jetting technique to print novel solid propellants. The study revealed that by varying the applied pressure, layer thickness, and binder content of each layer, the solid content and density of the propellant could be adjusted, thereby controlling its combustion behavior. The experimental results demonstrated that the printed solid propellants achieved a maximum density of 85.5 % and a maximum solid content of 96.1 %, surpassing existing reports on 3D-printed solid propellants. Furthermore, the solid propellants exhibited a tensile strength of 0.88 MPa, an elastic modulus of 20.7 MPa, and an elongation of 9.1 % at break. Additionally, researchers have successfully printed solid propellant samples with complex shapes, such as spirals, hollow cylinders, and double-helix cores using this technique. Hence, these studies provide a feasible pathway for manufacturing geometrically complex and adjustable-thrust solid propellants to satisfy specific application requirements, including high burning rates.

3D printing of solid propellants is currently undergoing rapid development as it offers unparalleled advantages over traditional processes in terms of freedom in solid propellant design, compactness of shaped charges, and product consistency, with safety and process adaptability issues preliminarily addressed through further research. Ensuring combustion performance, providing improved processing performance and higher adaptability in solid propellant formulations, and developing and improving scalable 3D printing technologies suitable for solid propellant preparation are expected to solve the key issues of high hazard and low efficiency in solid propellant manufacturing.

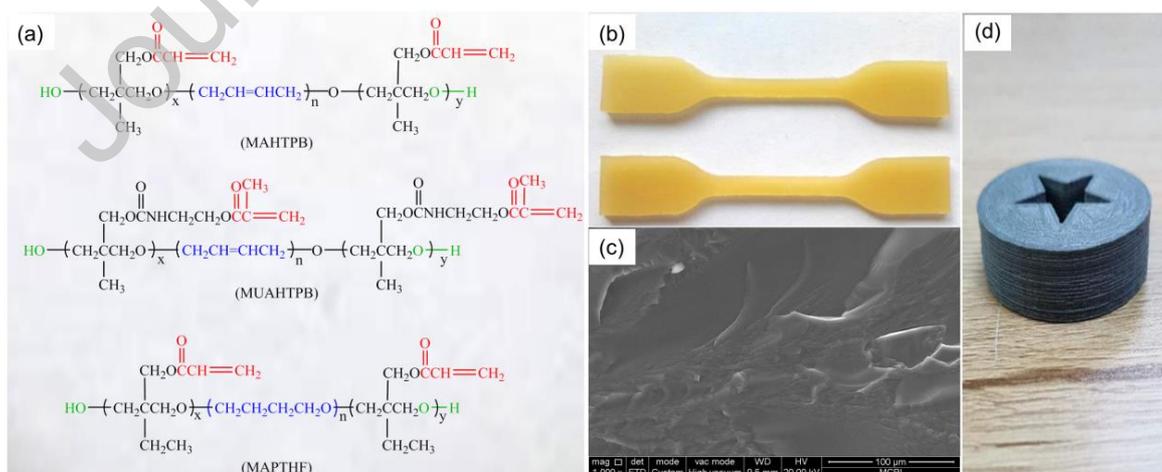


Fig. 10. (a) Structures of three photo-thermal dual-curable binders; (b, c) Photos and cross-section SEM image of elastomers formed from MAHTPB after curing; (d) Photos of 3D printed propellant grain formed from MAHTPB/RDX/AP/Al

formulation after curing [11,14].

4.2. Applications of 3D printing in gun propellants

Currently, propellants are manufactured using traditional solvent methods and molded through extrusion techniques, resulting in relatively simple structures such as granules, flakes, tubes, seven-hole columns, and nineteen-hole columns. However, with the development of weapons and increasing demand for long-range and high-power capabilities, higher requirements for the combustion performance of propellants have emerged. Using complex structures with high progressive burn rates has become one of the main approaches for improving the muzzle pressure efficiency of artillery systems.

To address these challenges, in 2013, the National Academy of Applied Science in the US achieved the 3D printing of *p*-trinitrotoluene (TNT) using the fused deposition modeling method and introduced TNT/RDX explosive formulations. In 2015, they completed 3D printing of a propellant consisting of 50 % RDX and 50 % inert binder using photopolymerization methods [62]. In 2017, the Netherlands Organization for Applied Scientific Research [63] used UV photopolymerization 3D printing technology to produce high-density propellant grains and propellant charge disks with perforated low-vulnerability ammunition (LOVA), as shown in Fig. 11. The performances of these propellants have been extensively studied and characterized. Their 3D printing approach utilized a basic propellant formulation comprising 50 % HMX and 50 % inert binders.

In 2018, the Swedish company TNO [64] successfully printed a propulsion formulation system composed of a UV-curable adhesive and energetic solid components using an injection-based extrusion nozzle. They also incorporated a UV light source at the nozzle to enable rapid curing of the extruded material, thereby avoiding material flow during extrusion. In the same year, the U.S. Department of Defense initiated four research and development projects on the additive manufacturing of energetic materials, with one involved in functionalizing nitrocellulose with acrylates and methacrylates and using UV photopolymerization technology to fabricate propellants [65].

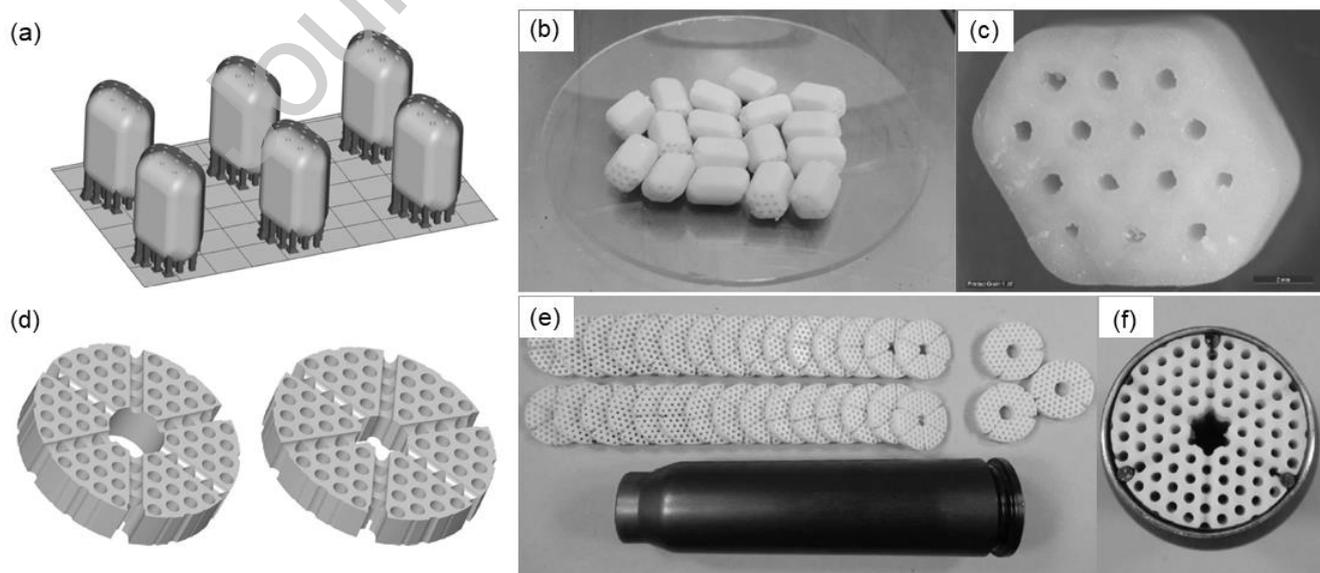


Fig. 11. (a) Build configuration with support and (b, c) photos of high packing density propellant grains and corresponding cross-section; (d) Model diagrams and (e, f) photos of propellant charge disks before and after loading [62,63].

In 2020, Yang et al. [66] obtained porous gun propellants using photopolymerization-based 3D printing technology. The formulation consisted of 25% UV-curable epoxy acrylate resin, 50 % RDX, 12.5 % energetic plasticizer Bu-NENA, 12.5 % reactive diluent, and other additives. The authors comprehensively studied the safety, mechanical strength, combustion performance, and other characteristics of 3D-printed propellants. They evaluated the performance of the printed propellant using a 30 mm test gun for porous disc propellants (MPD), achieving the expected results in terms of mechanical strength and combustion performance. In 2020, Hu et al. [67] used RDX and an energetic photosensitive resin to develop a novel propellant via 3D photopolymerization printing technology. The feasibility of the principle was demonstrated, with relevant performance studies conducted, resulting in a complex-structured propellant with a mechanical strength comparable to that of conventional propellants. The energetic photopolymerization adhesive exhibited excellent compatibility with conventional energetic solids such as RDX and CL-20. Compared to inert photopolymerization adhesive formulations, the energy of the 3D-printed propellants increased by more than 200 J/g. Hence, this study is of great significance for improving the energy performance of 3D-printed explosives and making 3D-printed propellants practically feasible.

To address the issue of relatively low energy levels in propellant formulations formed using photopolymerization curing technology with a solid content below 60 %, Yang et al. [68] used extrusion-based 3D printing technology in 2022. They formulated a photopolymerization-based 3D-printed propellant using epoxy acrylate resin (EA) as the binder, 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (TPO) as the photoinitiator, and 70 % mass fraction of CL-20 as the energetic solid additive. The experimental results showed that the printed samples had fewer defects than conventional nitrocellulose-based propellants. The 3D-printed photopolymerization propellant exhibited higher tensile and compressive strengths but reduced toughness compared to conventional propellants. In addition, this propellant demonstrated a high burning rate but a low burning rate coefficient and high-pressure exponent characteristics. This study provides support for exploring the compatibility between extrusion-based printing technology and photopolymerization propellants.

To address the issues of high viscosity and flammability of propellants, which hinder high-temperature heating, Zhou et al. [69] from Nanjing University of Science and Technology designed an extrusion system and built a flexible heating system for propellant-extrusion-based 3D printing in 2021. They used a propellant formulation predominantly composed of nitrocellulose (NC) and prepared material formulations with different concentrations: 27.3 %, 33.3 %, 38.5 %, 42.9 %, 46.7 %, and 50 %. The researchers obtained the corresponding printed samples and found a polynomial function relationship between the inner diameter of the nozzle and the material concentration. They determined the optimal printing process parameters: filling velocity range of 2–4 mm/s, filling ratio range of 70 %–90 %, and bed temperature range of 25–45 °C. Using a self-built propellant 3D printer, they printed the target propellant and conducted compression tests on the printed samples to achieve a maximum compressive strength of 230 MPa.

To address the challenge of relatively simple structures of propellant samples obtained using existing propellant manufacturing processes, which cannot meet the increasing demand for complex structures, Zhou et al. [70] conducted a study in 2022 to establish an extrusion-based 3D printing deposition model and determined the important process parameters for

extrusion-based 3D printing. Researchers have systematically investigated the influence of process parameters, such as the inner diameter of the nozzle, printing speed, and bed temperature, on the dimensional accuracy and tensile strength of printed propellant samples. Experimental results showed that the optimal propellant sample dimensions were achieved with a nozzle inner diameter of 0.7 mm, printing speed of 3 mm/s, and bed temperature of 35 °C. The highest tensile strength of the propellant samples was obtained with a nozzle inner diameter of 0.7 mm, printing speed of 4 mm/s, and bed temperature of 35 °C.

Overall, research on the 3D printing of launch-gun propellants is still in its early stages. Although safety and process adaptability issues have been preliminarily addressed through further research, several unresolved problems remain. Therefore, improving intelligence reduces human involvement, increases the safety of the printing process, and produces mobile 3D printers that can adapt to different environments. In conclusion, introducing 3D printing technology into the field of gun propellants is a revolutionary change that can overcome the limitations of traditional structural design and fully utilize the changes in the burning rate and burning surface during the combustion process, thus advancing the production of gun propellants into a new stage. 3D printing technology can significantly reduce the time and cost associated with transportation, prototyping, and equipment application while minimizing the environmental impact of the production process. Additionally, 3D printing technology makes it possible to facilitate the preparation of gun propellant-loading structures with unique performance and promote the development of new types of warhead ammunition.

4.3. Applications of 3D printing in explosives

The application of 3D printing in the field of explosives has been reported by the US National Laboratory of Chemical Science and Technology [71]. They developed an ink made of RDX and nano-aluminum that can be used for inkjet printing. The ink was printed on a mixed cellulose ester membrane filter and quantitatively on ashless filter paper using inkjet technology. Gas chromatography–mass spectrometry and UV–Visible spectroscopy were used to analyze the concentrations of the ink materials and explosives, with the results confirming the repeatability of ink-printing quality.

Madeline et al. [72] used thermal inkjet printing and coating deposition to print suspensions of TNT, RDX, and ammonium nitrate onto gold-plated silicon substrates. The results demonstrate that inkjet printing has high deposition accuracy and repeatability.

Brain et al. [73] developed a series of ink formulations for a CL-20-based explosive ink. They used a two-component binder system composed of water-soluble organic solvent systems of ethyl cellulose and polyvinyl alcohol. One of the formulations, named EDF-11, met all the requirements: viscosity ranging from 31000–35000 mPa/s, with 95 % of the total solid content constituted by energetic solids. EDF-11 was successfully graphically printed on the MEMS scale components. Detonation experiments revealed that the explosion could continue through right-angle initiation or even larger angles, with the EDF-11 formulation achieving stable detonation at a thickness of 0.50 mm with a critical dimension of 86 μm . High-speed photography measured the detonation velocity to be 7150 m/s. The MEMS initiator loaded with EDF-11 received full qualification certification from the US military. Although direct visual evidence of the application of this technology in the manufacture of explosive charges is not available because of confidentiality, the successful preparation of related samples indirectly confirms the applicability of 3D printing technology in the field of explosives and its practical use in multi-

dimensional explosive charge structures.

In China, initial developments have been made in the use of 3D printing technology to fabricate complex-shaped structures of composite explosives. Wang et al. [74] from Southwest University of Science and Technology used GAP as a binder and incorporated N-100 for curing to prepare a submicron CL-20 composite printing formulation. They employed 3D printing technology to achieve three-dimensional periodic structures (Fig. 12(a)), with the results confirming that the explosive ink could reliably transmit detonations on microdevices with a minimum size of 0.4×0.4 mm.

Xiao et al. [75], from the Nanjing University of Science and Technology, independently developed a 3D printing prototype for casting explosives. By adjusting the formulation and process parameters of the casting explosive, they successfully printed columns of nanometer-sized octogens (HMX) and TNT composite explosives. The extrusion speed was 40–60 mm/s, the layer thickness was 0.25–0.3 mm, and the printing nozzle temperature was 105–115 °C. The density of the printed column reached 1.653 g/cm³, exhibiting high stability and good formability. This technology enabled the preparation of HMX and TNT composite explosive columns with various structures.

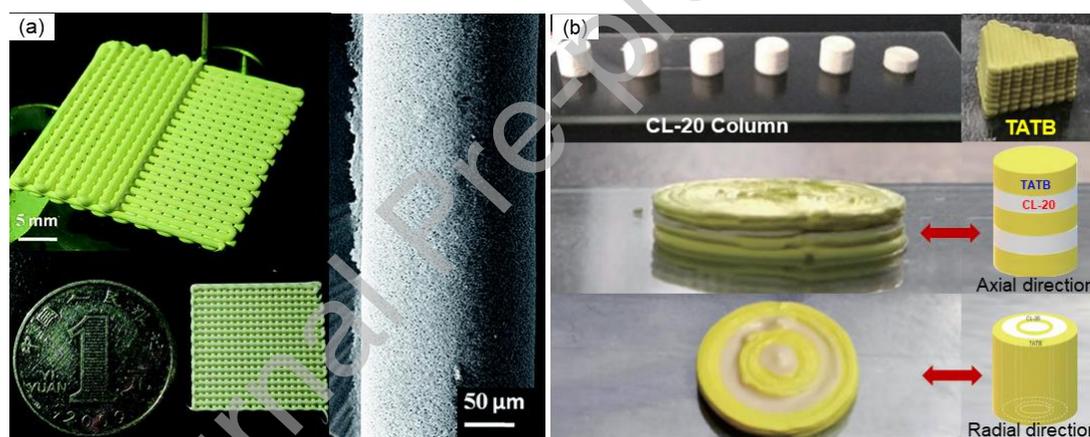


Fig. 12. (a) Optical image for the direct ink writing (DIW) of CL-20/GAP ink for 3D structure and SEM image of deposition filament after curing; (b) Photos of CL-20, TATB, and composite charge structures for TATB/CL-20 [74,76].

Wang et al. [76] from the Institute of Chemical Materials, China Academy of Engineering Physics proposed the use of 3D printing technology to fabricate novel composite charge structures with axial multilayers, radial multilayers, and axial/radial composite structures. They established printing systems for CL-20/GAP/N100 and TATB/GAP/N100 explosive formulations, used 3D printing technology to construct three novel composite charge structures of TATB and CL-20, as shown in Fig. 12(b), and studied the influence of the binder content and 3D printing process parameters on the stability of the charged microstructures. The impact sensitivity evaluation results showed that the characteristics of the axial/radial composite multi-dimensional charge structure (with a CL-20 mass fraction of 90 %) reached 72.00 cm, 3.14 times higher than the homogeneous CL-20 charge with the same mass, indicating significantly improved safety performance. However, this process presents several challenges. Controlling the viscosity of the propellant slurry during printing is difficult. When the viscosity of the slurry is too low, the propellant grains collapse, making it challenging to achieve a proper formation. However, excessively

high slurry viscosity can cause nozzle clogging. In addition, a certain level of deviation is inevitable in terms of the accuracy and dimensional tolerance of the printed propellant grains compared with the designed model. Furthermore, surface smoothness and uniformity of the formed propellant grains were not precisely achieved.

Rhoads et al. [77] conducted a study on the 3D printing of aluminum/polyvinylidene fluoride (PVDF) energetic materials using FDM technology. They compared the performance of energetic samples with that of standard 3D printing materials. The experimental results demonstrated that the print quality of high-energy filaments was comparable to that of standard materials such as ABS. Differential scanning calorimetry and thermogravimetric analysis were employed to investigate the energy and thermal responses of the printed and nonprinted materials. The results indicate that the printing process did not compromise the energy performance of the materials. In 2018, Fang et al. [78] proposed a new 3D printing jetting method to address the issues of long traditional forming times, complex processes, multiple control factors, and difficulties in forming irregular PBX explosive products. Based on the theory of 3D printing jetting, this method utilizes high-precision jetting nozzles to spray the material onto the substrate point-by-point to achieve a three-dimensional formation. The authors conducted theoretical modeling of the contact between single droplets and the substrate, as well as droplet stacking, and defined the factors influencing the surface roughness of the explosive formation. They used Fluent software to simulate and analyze the jetting process and identified the main factors, such as the nozzle diameter, needle stroke, and driving pressure. Finally, orthogonal experiments were designed to determine the relationship between the influencing factors, confirming the consistency between the simulation results and theoretical analysis. These results provide theoretical and methodological support for the integrated processing and formation of PBX explosives.

To address the issues of poor adaptability, low safety, complex processes, and high costs of forming irregular energetic columns, Chen et al. [79] applied photopolymerization 3D printing technology to the field of energetic column formation, aiming to provide a theoretical and technical foundation for the 3D printing of irregular energetic columns. First, a single-factor optimization method and an orthogonal experimental design were used to determine the composition of the photopolymerizable resin. They improved the dispersion of Al in the photopolymerizable resin by modifying it through organic monomer copolymerization and enhanced the suspension of AP in the resin by refining it through recrystallization, which ensured that both Al and AP met the requirements of solid fillers for 3D printing pastes. Subsequently, an energetic paste for 3D printing was prepared, with an X8.9 photopolymerization 3D printer used to print irregular energetic columns. The printed columns exhibited high precision and good overall performance. The performance of the columns was tested, with the experimental results showing that the surfaces of the photopolymerization 3D printed columns were smooth and the internal structure was dense, with no defects such as bubbles or cracks. The density of the columns was 1.606 g/cm^3 , 3.7% higher than that of columns formed by mold casting. The density exhibited good uniformity and stability. They conducted combustion tests on the columns, and the results showed that the columns burned vigorously, exhibiting a "plateau effect" during combustion, indicating uniform burning. The average burning rates of the columns are 7.11 mm/s. Differential scanning calorimetry revealed that the columns underwent three stages during the heating process: heat absorption, heat release, and secondary heat release, with a heat release enthalpy of 758.10 J/g. In addition, quasi-static mechanical property tests were conducted, with the average compressive strength of the columns determined to be 9.83 MPa, 315 % higher than that of the columns formed by mold curing. The compression rate was 2.1 %, 90.9 % higher than that of the mold-cured columns. The printed test specimens

exhibited a tensile strength of 9.8171 MPa, 11.76 % higher than that of the mold-cured specimens, and a tensile fracture stress of 9.08 MPa, 39.96% higher compared to the mold-cured specimens.

Stec et al. [80] deposited a slurry of CL-20-based mixed explosives using direct writing technology. The dried thin layers achieved a theoretical maximum density (TMD) of 90 % and exhibited an appropriate mechanical strength without cracks or voids. However, owing to the complexity of the properties, such as the hazardous nature and viscosity of energetic components, controlling the process conditions is challenging. Chirolì et al. [81] attempted a similar composition with a slurry comprising 60 wt% nitrocellulose (NC), 40 wt% acetone, and additives. Stec III et al. [82] further developed a process using the Micro-PenTM system to print specific patterns based on a CL-20 slurry. The results showed the successful explosion of the prepared samples under both constrained and unconstrained conditions. An explosive ink based on CL-20, called EDF-11, has obtained certification from the US Army. Groven [83] applied direct writing technology to produce three-dimensional lattice structures of aluminum and fluoropolymer, with a thickness of 400 μm and dimensions of 3 mm \times 5 mm. Combustion tests revealed that the burning rate approached 30 m/ms for single and multi-layer materials with micro/nano-sized aluminum.

In 2017, Bukovsky et al. [84] used binder jetting technology with an ExOne@M-Lab printer to deposit aluminum particles with a diameter of 15 μm and a binder, followed by casting with TNT melt to obtain the explosive columns. Wang et al. [85] prepared a CL-20/GAP-based composite explosive ink with CL-20 as the main charge, GAP as a binder, and N100 as a curing agent. The ink was then printed and solidified using DIW, resulting in well-formed explosives without cracks or voids. Wei et al. [86] designed and prepared a GAP/CL-20-based composite explosive using GAP as the binder and CL-20 as the solid filler. They utilized microinjection loading technology to print the composite into a small-scale detonation network and tested and analyzed the performance of the formed explosives.

In 2017, Wang et al. [87] dissolved a CL-20 explosive and an NC binder in an ethyl acetate solution to obtain an explosive ink. They used inkjet-printing technology to deposit and shape the ink, achieving a single-layer thickness of 2.4 μm . Lu et al. [88] investigated the melt-deposition modeling of energetic materials and successfully 3D-printed cylindrical energetic charges with bar, single-hole, and star-hole geometries using a self-built experimental system. Ding et al. [89] developed a 3D printer for energetic materials based on a fused deposition modeling machine and successfully printed energetic material samples, albeit limited to two-dimensional structures. Han et al. [90] built a 3D printing system capable of printing liquid energetic materials and successfully printed samples resembling emulsion explosives; however, no specific studies on printing energetic materials have been conducted.

The US Naval Surface Warfare Center [91] employed single-nozzle extrusion printing technology to print multiple explosive formulations sequentially, resulting in the production of PBX explosives with energy-density gradients. This technique has been utilized in the mass production of multiple rocket launchers. Song et al. [92] employed a combination of simulation and experimental methods to study the direct writing technology of CL-20-based explosive ink. They prepared explosive inks consisting of submicron-scale CL-20 as the main explosive component along with WPU and EC as binders and tested the performance of the deposited explosive ink. Xu et al. [93] used a micro-controlled direct-writing process to fabricate a self-made soluble CL-20-based explosive ink and characterized the properties of the resulting composites. Ye et al. [94] formulated a CL-20/GAP/EC/RGO composite energetic ink suitable for direct micropen writing. Inkjet printing of all-liquid inks based on PETN, CL-20, and 3,4-dinitrofurazan-furoxan with theoretical maximum densities (TMD) of up to 93% have

been reported [95–98]. The explosive inks were solutions of the two explosives (BNFF, DNTF, and RDX) and two binders (GAP and ethyl cellulose).

In 2020, the Ministry of Defence (MOD) of the United Kingdom sponsored the Defense Science and Technology Laboratory (DSTL) to initiate the development of 3D-printed energetic materials for explosives [99]. This project employs intricate 3D printing designs to establish new avenues for various explosive effects while reducing transportation and storage costs. The production of novel energetic formulations through additive manufacturing is part of the MOD's "Future Energetics Program," aimed at training experts and developing new technologies. The project focuses on material extrusion and printer capabilities, aiming to develop various shapes of materials for operational tasks in the theater of war. 3D printing enables customization of the required charges while reducing transportation and material costs. This capability ensures rigorous testing and evaluation of vehicles and systems against current and future threats, thereby guaranteeing the necessary protection for military forces.

Van Driel et al. [100] used FDM technology to deposit TNT from a TNO melt; however, the results showed that the deposition structure of 300 layers of TNT was irregular and not ideal. In 2021, Cong et al. [101] employed 3D printing melt deposition technology to address the shortcomings of the casting processes for cast explosives. They selected HMX and RDX, which exhibit good detonation performances, as solid energetic components and prepared HMX/RDX-TNT-based cast explosives of different compositions. They conducted printing and molding tests by varying six main process parameters—nozzle diameter, extrusion speed, layer thickness, printing speed, packing density, and bed temperature—and obtained optimal process parameters for the accurate fabrication of HMX/RDX-TNT-based cast explosives.

Nanjing University of Science and Technology [102] developed a prototype printer for thermoplastic energetic materials, achieving initial success in 3D-printed composite structure cast explosives. This equipment has made significant technological breakthroughs in key components such as material homogenization, stable delivery, continuous and uniform extrusion, and rapid solidification systems. Applying FDM technology to prepare HMX/RDX-TNT-based cast explosives makes it possible to obtain cylindrical charges with uniform density and continuous internal structure, which exhibit significantly improved mechanical stress resistance compared to traditional casting methods [103–105]. The propellant charges fabricated through the FDM process exhibited more complete combustion, significantly enhancing uniformity and continuity and improving the energy release efficiency and reaction rates. The layer-by-layer solidification process effectively avoids the shrinkage caused by cooling. The pressure applied to the molten slurry during the extrusion process effectively suppressed the formation of internal voids, ensuring the reliable initiation and propagation of the explosion. This innovative FDM process, characterized by mold-free automated manufacturing, high precision, low cost, safety, and efficiency, provides a reliable technological approach for the innovation and development of propellant manufacturing processes in China and offers a technical solution to improve casting efficiency and address the issues of unstable product quality, low production efficiency, and low material utilization.

3D printing technology can also break through existing design and development modes in the field of explosives. Research on printable explosive systems is being conducted to satisfy existing requirements of energy, safety, and mechanics. Specific research areas involve key characteristics such as the rheology, formability, and stability of energetic systems for 3D printing, which includes studying the influence of adhesive/binder molecule construction on the rheology and formability of composite explosive formulations, the impact of explosives and high-energy metal particle size on the rheology and

formability of the formulation system, the interface behavior and mechanisms of solid particle/polymer in energetic systems, the rheological characteristics and variations of explosive systems under shear, and formulation design criteria for composite explosive systems to develop formulations that allow for stable and rapid shaping. Techniques such as layered radial loading, density, or composition gradient loading make it possible to distribute different types of explosives and explosive densities in a specific spatial area, thereby enabling the design and manufacture of warheads with multiple damage modes. This new structural development and application requires extensive design proposals, experimental exploration, and process validation. Developing integrated continuous manufacturing technologies for multi-material structures based on 3D printing technology and integrating them with digitization and intelligence can rapidly produce target energetic materials, achieve customized structures and functions, and promote the development of forward design modes that meet the technological requirements of process adaptability, safety, and quality stability for dimensional charges. In addition, in recent years, the process advantages of fine control over the microstructure of explosive formulations using 3D printing technology have become a research hotspot for improving comprehensive performance by controlling microstructural improvements.

4.4. Applications of 3D printing in initiating explosive devices

As early as 1999, the Defense Advanced Research Projects Agency (DARPA) [106] in the US began researching the application of 3D printing technology to energetic materials. This process involves combining inkjet printing technology with traditional pyrotechnic techniques to primarily liquefy different energetic materials, such as initiators and high explosives, along with binders and organic solvents, and load them into the different print heads of a 3D printer. Following the principles of 3D printing, various energetic materials are printed as inks onto the desired positions on a substrate. Subsequently, through drying or UV light curing, the required ignition or explosion sequences for the pyrotechnic device are accomplished, directly fabricating most or all of the pyrotechnic chips, eventually resulting in the formation of MEMS micropropulsion chips. From the late 20th century to the early 21st century, DARPA [107] conducted research on 3D printing rapid prototyping technologies, with 7 out of 79 military-related projects involving the manufacturing of pyrotechnic systems. Rapid prototyping of pyrotechnic systems successfully conducted a deep-sea launch test on a 6.25-in high-speed anti-torpedo. In 2010, Ihnen et al. [108–110] experimented with the direct writing of initiators using RDX as the energetic material and a mixture of ethyl acetate, cellulose, and polyethylene acetate as the binder. The obtained RDX energetic ink is suitable for inkjet printing systems, producing energetic material ink patterns that meet the requirements for high resolution. In the same year, Fuchs et al. [111] developed an energetic ink-writing system capable of printing complex explosive propagation and initiation networks using EDF-11 as the energetic ink material. In 2017, Rocket Crafters Inc (RCI) [112] announced the acquisition of a US patent for 3D printing technology for hybrid rocket engine grains. This technology enables the design and manufacturing of flawless, high-performance, and operationally safe fuel grains for rocket engines, significantly improving the combustion rate during the rocket engine operation; as such, the company is preparing to apply this technology to future orbital launches.

In 2003, Xu [113] researched the application of 3D printing technology to chemical chips. Initially, they designed and assembled a hardware platform based on the principles of the SLA. In 2005, Zhu et al. [114] used 3D printing photopolymerization SLA technology to manufacture energetic chips, selecting polyacrylate, epoxy acrylate, EO-TMPAT, TPGDA, and the photoinitiator D-1173 as the main chip materials. By analyzing the adhesion of the materials, they achieved a

resin formulation by combining the materials in appropriate proportions. They selectively scanned a liquid photosensitive resin using a UV laser and achieved layer-by-layer curing and formation. The process mainly involves model design, slicing, data processing (including contour recognition, spot compensation, and scan-path generation), molding, and post-curing. In 2006, Wang et al. [115] combined photopolymerization molding with inkjet 3D printing technology to manufacture chemical chips for the rapid and safe loading of microsized charges. They formulated energetic materials as UV-curable inks to improve their safety and homogeneity. Based on the layer data of the prototype, they achieved a rapid and safe formation through inkjet deposition and UV irradiation. This research demonstrated the advantages of inkjet rapid prototyping technology in the rapid, safe, precise, and highly automated loading of micro-sized charges with no wastage of agents. In 2011, Zongren Xing et al. [116] researched a 3D printing manufacturing technology based on lead thiocyanate (LTNR) and identified a suitable energetic ink system and a compatible needle size.

In 2012, Zhang et al. [117] applied the advanced manufacturing concept of 3D printing to pyrotechnic technology and researched printing processes suitable for printing energetic materials. Experimental studies have promoted the development of miniaturized and automated pyrotechnic devices aligned with the direction of pyrotechnic development. Leveraging the precision and high automation advantages of rapid prototyping technology facilitates the direct writing of initiators, MEMS micropropulsion chips, and other high-complexity, high-precision, and overload-resistant pyrotechnic devices or precise charges.

In 2010, Andrew et al. [118] designed an energetic ink using nano-RDX as the main explosive mixed with organic solvents. The ink was applied using a direct writing technique to study the fuses, as shown in Fig. 13. The results revealed that this ink can be used in inkjet printing systems to produce high-resolution graphics. However, owing to the slow movement speed of the printhead, they could not create properly sized molded samples suitable for performance testing. Additionally, when the formed samples had a thickness of 500 μm , they could only ignite but not achieve full detonation.

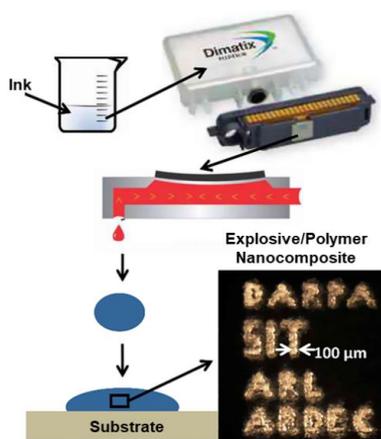


Fig. 13. Illustration for Nano RDX inkjet printing [118].

In 2013, Zhu et al. [119] used refined CL-20 as an energetic ink material and selected PVA and EC as binders, with water and IPA used as solvents to prepare the writable explosive ink composite, CL-20/PVA/H₂O/EC/IPA. The influence of different

binders, solvents, and their composition ratios on the performance of the energetic inks was studied. In 2015, Wang et al. [120] demonstrated that a resin/RDX formulation cured by light had better charge-loading effects than an NC/RDX formulation, further validating the feasibility of 3D printing light-curing rapid prototyping for energetic material charges.

In 2016, Hu et al. [121], based on the characteristics of partial energetic materials with an ignition point higher than their melting point by more than 15 °C, melted powdered energetic materials and controlled a 3D motion control platform to print them on a substrate. This approach offers the advantages of low cost, simplicity, and reduced production time. In the same year, Yao et al. [122] discovered that nanoscale CL-20 explosive ink using direct writing technology could meet the requirements for the microscale loading of MEMS initiators. However, research on ink formulations suitable for MEMS initiator loading remains limited. To address this issue, we used nanoscale CL-20 as the energetic component and composed a binder system using nitrocellulose, a UV curing agent, EA, and TMPTA to obtain an energetic ink formulation. Three different ink formulations were obtained by adjusting the composition ratios. The influence of factors such as needle diameter, writing pressure, writing height, and viscosity on the linewidth of direct writing were studied. For example, when the needle diameter increased from 0.15 mm to 0.33 mm, the line width significantly increased and the magnitude of the widening of the line width also increased. However, excessively large diameters lead to an uneven linewidth distribution. Direct writing technology is conducted in air; thus, if the amount of energetic ink is too large, air can be trapped in the ink, affecting the printing results. In addition, the influence of the solid filler particles of nanoscale CL-20 explosives on the UV curing reaction in a mixed system remains unclear and requires further experimental exploration.

In 2019, Guo et al. [123] continued research on energetic ink formulations suitable for the microscale loading of MEMS initiators. They used TPO as a photoinitiator, PUA as a UV-curable adhesive, and CL-20 as the explosive component to prepare UV-curable energetic ink, studied the micro-sized loading of CL-20-based UV-curable explosive ink using direct writing technology, and evaluated the curing rate, morphology, crystal type, impact sensitivity, and detonation performance of the samples. The experimental results showed that the CL-20-based UV-curable ink achieved complete curing within 7 min after 3 min of UV exposure, demonstrating rapid curing performance. The critical detonation size was 0.078 mm, and the detonation velocity was 7357 m/s, indicating low internal defects and low impact sensitivity. This study further expanded the types of energetic ink formulations suitable for the microscale loading of MEMS initiators. The excellent performance of this UV-curable explosive ink indicates its potential application in microblasting systems.

In 2020, He et al. [124] prepared a GAP/NC/DNTF microscale energetic composite using inkjet printing and polymer crosslinking technologies, as shown in Fig. 14. Under the condition of a 1 mm charge width, the critical detonation thickness of the DNTF-based inkjet printing sample is 0.015 mm, with a detonation velocity reaching 8686 m/s. This process demonstrates excellent energy performance and remarkable microsized detonation capability, thus providing technical support for preparing energetic material loading and energetic devices in micro-nano structures.

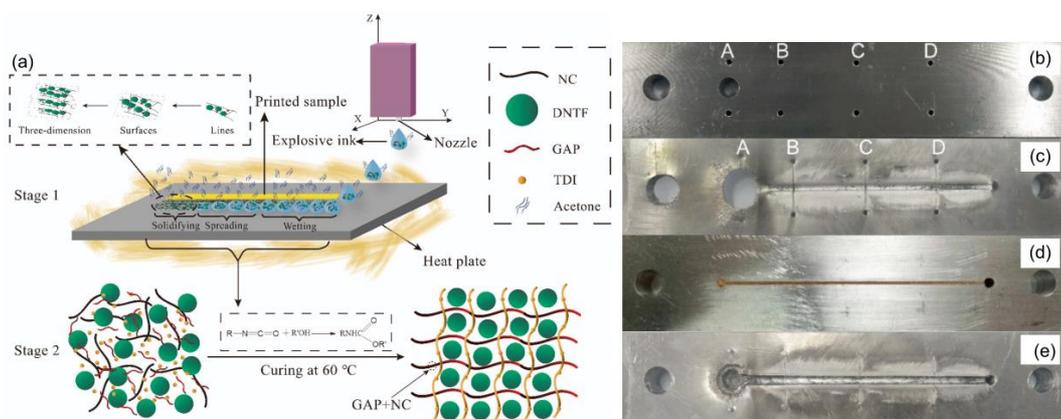


Fig. 14. (a) Diagrammatic sketch of (Stage 1) inkjet printing and (Stage 2) curing reaction of DNTF-based explosive ink; Detonation velocity test specimen images of GNT printed samples: optical images of (b, c) cover plate and (d, e) GNT explosive-deposited plate before and after detonation [124].

Regarding the issues of surface passivation of nano-aluminum powder with inert aluminum oxide shells and nanoparticle agglomeration during production, storage, and use, which limit the reactivity and safety of nano-aluminum powder, Zheng et al. [125] effectively reduced the agglomeration phenomenon of nano-aluminum powder and improved its safety using 3D printing technology to prepare fluorinated aluminum thermite ink. The unique molecular properties of fluoropolymers enhance the mechanical performance of aluminum thermite inks. Additionally, fluoropolymers react with the surface aluminum oxide and facilitate the reaction between aluminum and fluoropolymers. The authors prepared a polytetrafluoroethylene (PTFE)-based aluminum thermite ink adapted to the rheological characteristics of 3D printing and studied the influence of the thermal decomposition performance, combustion performance, and composition ratio of the Al/PTFE/F2311 ink formulation. They also printed various composite structures and found that the different structures exhibited unique combustion characteristics. However, 3D printing control and material delivery systems need to be improved to achieve higher printing accuracy. Furthermore, to achieve the large-scale production and wholesale application of high-energy inks, various complex nozzles must be designed to coordinate the use of multiple formulations, thereby enabling customized high-precision and large-scale applications of energy and structure.

To investigate the influence of the structural parameters of the extrusion system nozzle channel (cone angle, outlet diameter, and forming section length) on fluid flow in the extrusion process of energetic materials using DIW technology, Yang et al. [126] established a high-viscosity energetic material extrusion model based on a Polyflow Extrusion module. In 2023, extrusion experiments will be conducted under DIW 3D printing conditions to validate the model. The research results showed that the simulated trends were consistent with the actual experiments, providing reliable predictions of the flow field changes under different conditions. In addition, a cone angle of 100° and a nozzle outlet diameter of 1.5–1.75 mm resulted in a relatively stable extrusion process with minimal expansion, and the growth of the forming section reduced the expansion effect at the outlet while increasing the required inlet pressure.

3D printing technology can drive innovation in the initiation of explosive device manufacturing. Manufacturing technologies and processes in the industry are predominantly intermittent, with multiple steps, complex procedures, and a

high reliance on manual labor. Some process technologies are outdated, leading to low levels of automation and manufacturing efficiency, thus hindering the development of explosive devices. Therefore, leveraging 3D printing technology in combination with advanced mixing preparation techniques, such as resonant and ultrasonic mixing, can potentially establish a new technological process chain for initiating explosive device manufacturing and transform existing multi-step intermittent processes into continuous, single-step processes, thus simplifying the manufacturing process and improving automation levels and manufacturing efficiency while eliminating the manufacturing challenges posed by intermittent processes. In particular, in the field of loading miniature energetic components, 3D printing technology possesses unique process advantages such as network loading and MEMS energy devices. Developing the 3D printing technology can advance loading techniques for initiating explosive devices at the microscale, perfectly addressing challenges such as high manual labor, low reliability, high safety risks, and low manufacturing efficiency, thereby comprehensively enhancing the technological level. Additionally, developing low-viscosity ink formulations suitable for low-temperature printing processes is one of the main research directions for the 3D printing of explosive devices in the future.

In summary, 3D printing technology has become a modern process in defense and military industries worldwide, providing an efficient tool for repeated design and rapid prototyping and features such as design flexibility, on-demand printing, low cost, safety, and short development cycles. As a significant branch of 3D printing technology, the 3D printing of explosives is a highly efficient tool for repeated design and rapid prototyping, transforming the manufacturing process in the fields of explosives and ammunition, thus providing unprecedented flexibility. Recently, active research has been conducted in the field of 3D printing technology for energetic materials, focusing mainly on solid propellants, gun propellants, explosives, and initiating explosive devices. The printed products obtained were applied to the new LOVA launch charges. 3D printing technology for energetic materials can innovate ammunition loading and shaping processes, ensuring reliable high-efficiency destruction of new strategic weapons and advanced conventional warheads. This technology provides new methods for researching high-efficiency destruction technologies for advanced weapons and ammunition, offers new processes and equipment for the development and production of future weapons and equipment, and facilitates high-density consistency, absence of internal defects, and low void fraction loading of small- and complex-shaped warheads.

5. Conclusion and Outlook

The feasibility and unique advantages of 3D printing technology for energetic materials were verified, disrupting the traditional development model of explosive and propellant manufacturing industries. Achieving the precise, efficient, and safe preparation of energetic materials and enhancing the rapid response capability of high-tech weapon ammunition production can substitute traditional personnel and weapon reserves with advanced process equipment, ensuring mobilization capability during wartime and support for the development and batch production of high-tech equipment.

The feasibility and unique advantages of the 3D printing technology for energetic materials were validated. However, compared with other fields, 3D printing technology for energetic materials is still in the research stage and can

thus only print energetic products with low solid content. Traditional printing materials have difficulty meeting the requirements of high solid content, high viscosity, and rapid prototyping of energetic material formulations. Moreover, while small-scale preparation of energetic material samples has been achieved, large-scale production of various energetic materials such as explosives, propellants, and solid rocket fuels has not been realized. Moreover, research and development of high-performance adhesives/binders is crucial for advancing explosive and propellant technologies. To further develop the 3D printing technology for explosives, developing new adhesive/binder materials that can rapidly and completely cure within a short period, specifically tailored for 3D printing in explosive and propellant formulations, is essential. In the future, the key focus of research and development in various countries will be the design and preparation of energetic binders suitable for 3D printing technology, process adaptability of binders, overcoming size limitations by creating integrated multifunctional structures, achieving precise and efficient 3D printing in extreme battlefield environments, and the sustainable preparation of binders.

5.1. Design and fabrication of energetic binders for 3D-printed explosives and propellants

Currently, binders used in 3D-printed explosives and propellants are derived from traditional 3D-printing binder materials. However, existing binder materials must be modified to achieve multi-dimensional and functionally diverse formulation printing of explosives and propellants. Fully leveraging the structural characteristics and performance relationships of the reported binders for explosives and propellants could help in enhancing or improving the properties of existing binders. Based on the structural and performance characteristics of multifunctional binders for 3D-printed explosives and propellants, energetic units can be incorporated into polymerizable monomers to form energetic monomers and polymers, thus providing a simplified and highly safe process for the simultaneous polymerization and solidification of energetic binders. Additionally, there is an urgent need to develop new varieties of energetic binders to meet the requirements of special application environments such as high/ultralow temperatures and high humidity for specialty propellants and gun propellants.

5.2. Process compatibility of 3D-printed energetic binders

Process compatibility is the foundation for the practical application of binder systems in 3D-printed explosives and propellants. High-performance energetic binders must exhibit low sensitivity, good compatibility, excellent chemical stability, good storage performance, and low toxicity. However, developing printing equipment that can handle various formulations and binder material structural properties to create high-precision micro- and macro-scale three-dimensional dynamic models for matching binders is crucial. These models can be converted into printing programs to facilitate the creation of functionally graded energetic materials, intelligent energetic materials, and disruptive energetic material architectures. Furthermore, the printing process selected for binder fabrication should demonstrate good compatibility with the simultaneous printing of different types of explosive formulations, synchronous reinforcement of printing paths and structural types, and synchronous modification through physical and chemical treatments of the printed structures.

5.3. Integration of multifunctional structures to overcome size limitations

Currently, most 3D-printed explosives and propellants at small and conventional scales are limited to printing with a

single material and utilizing a single process, making it challenging to manufacture explosives and propellants with multi-scale and multi-dimensional structures. Ideally, 3D printing of explosives and propellants should encompass multiple scales (including macro-, meso-, and microscales), multiple materials (integrating rigid and flexible materials), and multiple processes (switching between traditional 3D printing and subtractive manufacturing for complete integration and autonomous fabrication). Meso-, micro-, and nanoscale explosives and propellant products can be printed directly using 3D printers, while large-scale explosive and propellant structures can be fabricated through a "bottom-up" 3D printing and a whole-structure 3D printing strategy. The "bottom-up" 3D printing strategy involves segmenting the large-scale explosive-related structures into appropriately sized components, printing these different components, and then assembling them using connectors. Whole-structure 3D printing involves dividing a large-scale explosive structure into layers of suitable thickness and then printing the large structure layer by layer.

5.4. Precise and efficient 3D printing adapted to extreme battlefield environments

The 3D printing of explosives and propellants must meet the printing requirements in extreme battlefield environments, which pose high risks to operators. Therefore, using remotely controlled and automated 3D printing robots is crucial in these environments. In addition, to achieve efficient and precise control of 3D printing of explosives and propellants in extreme battlefield conditions, ensuring the safety of the printing process and the intended goals and functionalities of the final printed structure, developing quantitative relationships in printing control equations that match the desired goals with the printing process, materials, and printer is necessary. In this process, printing control must be guided by a database of material adaptability for printing to facilitate precise and efficient 3D printing of explosive structures adapted to extreme battlefield conditions.

5.5. Sustainability of adhesives for 3D-printed explosives and propellants

Adhesive materials for 3D-printed explosives and propellants are typically disposable throughout their life cycle, and costs can sometimes exceed affordability in wartime economies, thus highlighting a need for further optimization of the design of adhesive materials for 3D-printed explosives and propellants, as well as in the production and extraction of adhesive raw materials; preparation, transportation, and delivery of printable materials; and the recycling and reuse of these materials. In addition to developing novel adhesive materials specifically for 3D-printed explosives and propellants, transforming a significant amount of waste generated from daily life and production into printable adhesives can be a sustainable approach to maximize resource utilization and reduce adhesive production costs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Bojun Tan: Writing – original draft, Conceptualization, Resources, Writing – review & editing, Funding

acquisition; **Jinkang Dou**: Conceptualization, Writing – review & editing; **Yujia Wen**: Writing – review & editing; **Binghui Duan**: Writing – review & editing; **Hongchang Mo**: Writing – review & editing; **Zongliang Wei**: Writing – review & editing; **Jing Zhang**: Writing – review & editing; **Yongfei Pan**: Writing – review & editing; **Xiaoyong Ding**: Writing – review & editing; **Ning Liu**: Writing– review & editing, Funding acquisition.

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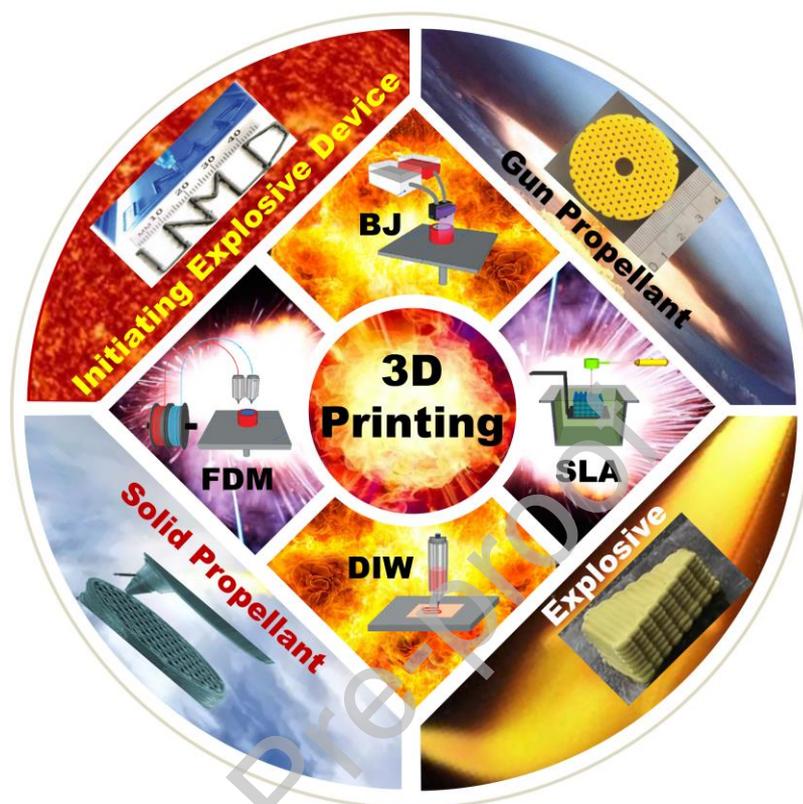
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Graphical Abstract



This paper provided an overview of four major 3D printing technologies suitable for explosives and propellants manufacturing, which were vat photopolymerization, binder jetting, fused deposition modeling and direct ink writing. Additionally, future development directions and prospects for 3D printing of explosives and propellants were discussed, providing valuable insights for the application of 3D printing technology in the fields of explosives and propellants.

Conflict of Interest

The authors declare no conflict of interest.