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Polymer-Based Smart Material in 4D Printing Applications

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Abstract: The area of 4D printing is a revolutionary one that emerged from the integration of additive manufacturing and polymer science. In this area, materials can change dynamically in response to external stimuli. Complex structures with developing, shape-morphing, and adaptive behaviors can be created by integrating innovative 3D printing technology with intelligent materials, which are naturally sensitive to environmental cues. Polymer chemistry determines these smart materials and discusses the design concepts that control their responsiveness. A particular focus is on incorporating stimuli-responsive polymers, like hydrogels and shape memory polymers, into the 4D printing process. These ensuing structures suggest programmable behavior in response to light, humidity, and temperature variations in the environment. 4D printing has been designated a revolutionary technology with significant implications for sectors looking for dynamic, responsive, and personalized solutions. The study of polymer-based innovative materials in 4D printing presents novel prospects for ingenuity, presenting extraordinary chances for creating and producing materials with dynamic properties. The future of advanced manufacturing is being shaped by this research, which advances our fundamental understanding of intelligent materials and opens up novel applications in various fields.

Keywords: smart materials, 4D printing, stimuli-responsive, shape memory polymers, applications

1. Introduction

The development of polymer-based smart materials has become an exciting field of study due to their unique characteristics and usefulness in various industries. These substances can alter their physical characteristics, shape, or behavior in reversible or irreversible ways in response to external stimuli [1]. The topic of polymer-based smart materials encompasses a variety of substances with diverse uses and functions [2]. The inherent qualities and structural design of polymer-based innovative materials confer responsiveness. When exposed to specific stimuli like heat, light, moisture, pH, or electric fields, these materials may change their shape, color, transparency, conductivity, or mechanical properties [3, 4]. The response may be immediate or time-dependent, depending on the properties of the material and the type of stimulus. Polymer-based intelligent materials are highly adaptable and advantageous for a range of applications due to their capacity to dynamically adjust to environmental changes [5]. Polymer-based intelligent materials have numerous industrial uses. In the biomedical and healthcare industries, these materials are utilized in tissue engineering, drug delivery systems, biosensors, and medical devices [6, 7]. They can respond to physiological conditions, enable controlled drug release, and facilitate personalized treatment plans. Additionally, polymer-based intelligent materials find applications in robotics and actuation systems, paving the way for the creation of flexible sensors, soft robots, and artificial muscles [8, 9]. Their unique features support advancements in robotics technology and human–machine interactions. Polymer-based intelligent materials also offer benefits for the aerospace and defense sectors [10]. These components include morphing wings, adaptable frameworks, and shape-changing parts made from these materials. Engineers can enhance the aerodynamic efficiency, weight, and performance of these materials when applied in aerospace scenarios. Furthermore, polymer-based innovative materials present opportunities for adaptive architectural elements, responsive facades, and self-healing materials in design and construction. These materials can improve energy efficiency, enhance sustainability, and respond to changing environmental conditions [11, 12]. Smart materials based on polymers are evolving rapidly due to ongoing research and innovation. Researchers are exploring new materials, refining material properties, and developing production techniques to enhance these materials' capabilities. They are integrating advanced manufacturing technologies like 3D printing and nanotechnology to expand potential applications [13].

Smart materials made of polymers are closely related to 4D printing because this technology uses them to build dynamic structures that can change shape or characteristics over time. This

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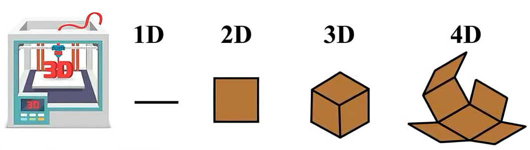
new area of study combines the 3D printing principles with the addition of time, enabling objects to change independently in response to their surroundings. Intelligent materials are essential to deliver the needed functionality [14]. The method of employing 3D printing to create items that can change or self-assemble into a specific shape in response to an external input is known as 4D printing. Heat, light, moisture, or even a magnetic field can serve as this stimulation. Innovative materials can be used in 3D printing to create objects autonomously, adjust to changing environmental circumstances, or perform specific functions [15]. The adaptability and flexibility in design that polymer-based innovative materials in 4D printing offer come from their capacity to react to various stimuli. For instance, shape memory polymers (SMPs) can be engineered to distort briefly when heated and then return to their original shape when cooled. This behavior makes the ability to fold, unfold, or change shape in a regulated way possible [16, 17]. Many industries can benefit from using intelligent materials in 4D printing. In medicine, 4D-printed implants can be designed to change, form, or release medication in response to specific biological cues, improving patient outcomes. Architectural designs that are adaptive to their surroundings can include vents that open or close in response to temperature changes. Self-assembling components can also streamline production procedures and enhance system performance in robotics and aerospace [18].

This study of polymer-based innovative materials for 4D printing is a groundbreaking fusion of technology and science. This emerging field offers materials with dynamic properties, allowing them to change and adapt over time in response to outside stimuli. The potential impact on multiple industries becomes apparent as we explore the uses of these novel materials. The versatility of 4D printing using polymer-based innovative materials promises to transform traditional production methods in various industries, including aerospace, healthcare, and architecture. The promise of improved utility, efficiency, and adaptability heralds a new age in material science and design innovation as we explore this exciting frontier. For this review, we categorize materials as smart when they can react to an external factor (such as temperature, light, humidity, pH, or magnetic fields). Throughout the manuscript, we primarily use “smart materials” to maintain consistency and clarity, along with admitting that they have similar meanings. We particularly highlight the significant contributions in 4D printing from polymer-based smart materials and new possibilities that these could create across different industries. The primary focus of this review is to appraise the variety of polymers, trigger-responsive nature, in-depth printing and programming strategies, and utility properties for solving real-world problems such as biomedical devices, soft robotics, smart textiles, etc. This article aims to compile recent developments, provide an insight into interdisciplinary connections between materials science and additive manufacturing, and explore existing challenges of the field, thus filling some gaps for other researchers. This review differs from others in that it focuses on polymers, emphasizing stimuli-responsive classifications, critical comparisons between different material systems, and tools for combining visual information. This paper concisely demonstrates the complexity of 4D printing from a broader perspective down to a detailed one by narrowing it to polymer-based smart materials.

2. 4D Printing Process

A new technology called 4D printing expands on the concepts of 3D printing by including a fourth dimension: time. It makes it possible to create objects that can alter their characteristics or shape in response to outside influences. The creation of polymer-based innovative materials now has more avenues for development thanks to this novel strategy. Compared with 3D printing, 4D printing mainly uses smart materials. After 3D printing achieves an intelligent static structure, it can convert from a static structure to a dynamic structure by giving external incentives. The main difference between 3D printing and 4D printing is shown in Figure 1. The 4D printing process consists of design, fabrication, programming, and activation, each of which is essential to achieving time-dynamic, stimulus-responsive transformations. In the design phase, computer-aided design (CAD) tools help to model complex geometries and predict deformation behaviors, frequently involving finite element analysis for material response simulations. Additive manufacturing techniques such as fused deposition modeling (FDM), stereolithography (SLA), and direct ink writing (DIW) are used in the fabrication stage to build the object layer by layer using smart polymers. During programming, the responsive behavior is encoded into the structure by manipulating the material composition, printing orientation, and/or applying pre-strain during the process. This step concludes that in response to certain stimuli (heat, light, pH, or moisture), the printed object will behave as expected. At the activation stage, when the object receives a particular external stimulus, owing to its predefined functionality, it transforms, causing it to fulfill the final functions. However, the introduction of challenges for each phase that include material restrictions, actuation time delays, stimulus selectivity, and response stability highlights the importance of integrated design-fabrication-programming workflows in further developing 4D printing technology. Incorporating SMPs and additive manufacturing processes is the core idea behind 4D printing. SMPs are a subset of intelligent materials that can “remember” their initial shape and revert to it in the presence of external stimuli. The polymer’s molecular structure undergoes a reversible phase transition to produce this feature. Researchers have expanded the possibilities of additive manufacturing to create items that can alter shape or quality over time by combining SMPs and 3D printing. Although SMPs exhibit excellent time-dependent transformations in 4D printing, their working range is often limited to a narrow temperature range and triggered by specific environmental cues. For example, body temperature-triggered SMPs are very attractive for biotech-implant uses, but their mechanical stability to cyclic loading has been a concern [19, 20]. In 4D printing, a range of polymer-based materials is employed, each with unique properties and benefits. Polylactic acid and polyurethane (PU), two thermoplastic materials with good printability and form memory, are frequently used in construction [21]. Although SMPs are less sensitive than systems based on hydrogels, as mentioned before, this class of materials cannot be used in a multi-stimuli environment. Thus, hybrid composites or multilayered constructs as an alternative to single-response (one type of SMP) restrictions are becoming a preferable combination of SMPs/hydrogels and conductive polymers. This process will require further comparative studies to optimize responsiveness while securing structural integrity. Thermoplastic SMPs can be altered by

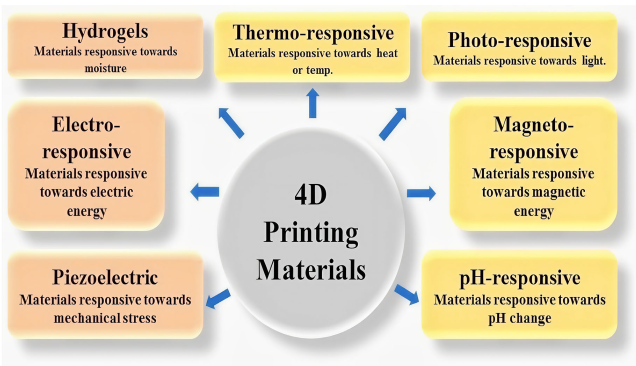
Figure 1
Progress of 4D polymer printing techniques



heating them over their glass transition temperature and then cooling them to set the modified shape. Another type of substance utilized in 4D printing is hydrogels. These water-absorbing polymers can significantly alter their volume in response to environmental temperature or pH changes. The mechanical qualities of the printed structures are also improved by using composites, which are materials made of polymers and fillers or fibers that provide reinforcement (Figure 2) [22, 23].

The steps of the 4D printing process include design, fabrication, programming, and activation. During the design phase, specific CAD software with integrated programming skills is required to specify the proper deformation sequence [24]. Designers may now construct elaborate geometries with complex structures that can change in response to certain stimuli, as demonstrated in Figure 3(a) [24]. Figure 3(b) shows additive manufacturing methods that can be used to make things. These include FDM, SLA, selective laser sintering, inkjet, and DIW. These methods allow the precise layer-by-layer deposition or curing of polymer-based materials to produce the desired item [25]. The structure needs to be programmed to start the necessary shape change after the fabrication stage. The form-memory capabilities of the polymer-based innovative materials are triggered by this programming, which entails applying stimuli or external forces. Depending on the sensitive qualities of the chosen polymer, aviation can be accomplished via various techniques, including heating, light exposure, moisture absorption, or chemical reactions [26].

Figure 2
Illustration of the various materials used in 4D printing schematically

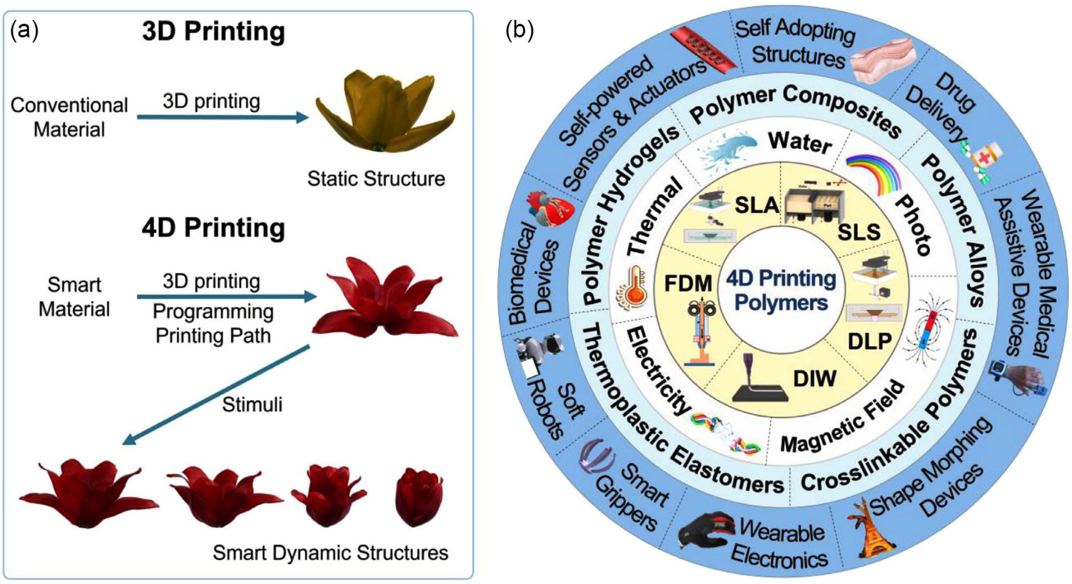


Smart materials based on polymers have various possible uses in multiple fields. By adjusting to the body's changing anatomical requirements, 4D-printed implants and prostheses can improve patient treatment. For instance, after being implanted, a 4D-printed stent may change shape and expand, offering individualized support and lowering the possibility of complications. Using 4D printing, it is also possible to create self-assembling drug delivery devices that react to particular biological cues, like pH or enzyme concentration [27]. 4D-printed buildings can have adaptable facades, roofs that can change shape, and transportable structures for disaster assistance. A potential role for 4D printing materials is the ability to expand or contract in response to temperature changes, controlling the movement of heat within a building [28, 29]. Although 4D printing with polymer-based intelligent materials holds great potential, some challenges must be addressed. Post-printing programming approaches, process optimization, and material selection require more work to increase the technology's scalability, precision, and dependability. For these materials to be widely used, it is also essential to understand their long-term stability, biocompatibility, and recycling potential. Future studies should focus on improving material characteristics, extending the range of stimuli that cause shape changes, and investigating fresh design approaches for intricate structures [30].

3. Smart Materials

Innovative materials have advanced significantly over the past two decades, revolutionizing several industries and opening up new industry prospects in electronics, aircraft, healthcare, and energy.

Figure 3
(a) A succinct contrast of 3D and 4D printing. (b) Representative printing techniques, stimuli types, printable polymeric materials, and 4D printing applications



3.1. Types of smart materials

"Smart materials" refers to a broad category of materials with distinctive features and regulated responses to external stimuli. The following are a few of the main categories of smart materials:

Shape memory alloys (SMAs) can regain their previous shape following deformation when a specific stimulus, like temperature or stress, is applied to SMAs. Alloys based on copper, iron, and nickel-titanium (Nitinol) are common SMAs. Piezoelectric materials deform when an electric field is applied, yet they create an electric charge in response to mechanical stress. Examples include quartz, polyvinylidene fluoride (PVDF), and lead zirconate titanate (PZT). Electroactive polymers (EAPs), when an electric field is applied, are polymers that can significantly deform or change shape. They are helpful for uses like artificial muscles, actuators, and sensors since they are lightweight and flexible. Dielectric elastomers, conductive polymers, and ionic polymer-metal composites are examples of common EAP types. EAPs are limited in performance concerning the actuation force and humidity stability over extended periods. Overcoming this challenge is critical for their effective use in wearable technologies and soft robotics. Magnetostrictive materials change their structure when exposed to a magnetic field. They function as sensors, actuators, and vibration reducers and display a link between magnetic and mechanical features. A typical magnetostrictive substance is terfenol-D [31].

Smart hydrogels, which are cross-linked polymer networks, exhibit a high capacity for water absorption and retention. These smart hydrogels can change their volume, release, or absorb water in response to environmental factors such as temperature, pH, or humidity. They are employed in tissue engineering, biosensors, and drug delivery systems [32]. Thermoelectric materials convert heat energy into electrical energy and vice versa. When there is a temperature difference within the material, it generates an electric current. Lead telluride (PbTe) and bismuth telluride (Bi2Te3) are two examples of such thermoelectric materials [33, 34]. Smart SMPs are a category of polymers that can alter their shape in response to specific stimuli, including changes in temperature or light. They can be temporarily deformed before returning to their original shape following stimulation. SMPs find applications in the biomedical, robotics, and aerospace fields [35, 36]. Chromogenic materials change their color or optical properties when exposed to external stimuli such as light, heat, or electric current. They are utilized in smart windows, privacy glasses, and displays. Examples include electrochromic, photochromic, and thermochromic materials [37]. Magnetorheological materials, also known as magnetorheological (MR) intelligent materials, respond to an external magnetic field by altering their viscosity or stiffness. These substances consist of magnetic particles suspended in a carrier fluid. When a magnetic field is applied, the material transitions from a liquid-like state to a solid-like state, causing the particles to align and increasing the material's apparent viscosity or stiffness. This characteristic makes MR materials beneficial in products such as dampers, shock absorbers, and haptic devices [38]. Electrochromic materials, a group of innovative materials, can change their color or opacity in response to an applied electric field. These materials undergo reversible electrochemical processes that modify their optical properties. Typical examples include tungsten oxide (WO_3), viologens, and polyaniline [37]. Conductive polymers, recognized for their electrical conductivity while retaining the malleability and processability of polymers, exhibit high electrical conductivity, adjustable conductivity, and reversible redox activity. These unique qualities enable conductive polymers to be used in various technologies, including organic electronics, sensors, energy storage, and actuators. Examples of conductive polymers include polyaniline, polypyrrole, and poly(3,4-ethylenedioxythiophene) [39]. Ferroelectric materials can reverse the spontaneous electric polarization shown by sophisticated ferroelectric materials when exposed to an external electric field. These materials can switch between polarized states due to the exceptional quality of ferroelectricity. Their reversible polarization nature makes ferroelectric materials ideally suited for a range of applications, including data storage, sensors, actuators, and transducers. Ferroelectric materials are key to numerous technical advancements and innovations in electronics, telecommunications, and medical engineering because they offer excellent reactivity, dependability, and energy efficiency [40]. Electrostrictive materials, such as PZT, are innovative electrostrictive materials commonly used in practical applications. PZT is a ceramic material with substantial electrostrictive activity, meaning that an electric field significantly alters its shape. This ability to transform electrical impulses into mechanical vibrations allows it to produce and receive ultrasound waves, making it ideal for applications like ultrasonic transducers used in medical imaging [41].

Nanomaterials (such as carbon nanotubes (CNTs) and graphene) with unique characteristics and tiny structures are referred to as nanomaterials. Examples include graphene and CNTs. Carbon atoms are arranged in a hexagonal lattice to form CNTs, which are cylindrical structures. They exhibit excellent thermal stability, strong electrical conductivity, and remarkable mechanical strength. CNTs find applications in electronics, energy storage, and composite materials. A single layer of graphite, known as graphene, is a two-dimensional substance with extraordinary qualities, such as excellent electrical and thermal conductivity [42]. Self-healing smart materials, when subjected to mechanical or environmental stress, can autonomously repair damage or restore their structural integrity. These self-healing mechanisms include crack repair, surface regeneration after damage, and the release of healing chemicals. Metal alloys like gold and gallium are employed to create hydrogels, which are water-swollen polymer networks [43]. Photocatalytic materials, when exposed to light energy, can initiate chemical reactions. This family of photocatalytic materials can degrade organic pollutants more quickly, produce self-cleaning surfaces, and generate energy through water splitting or pollutant degradation. Titanium dioxide (TiO_2) is an example of a photocatalytic innovative material, widely utilized for its photocatalytic capabilities and applications in environmental remediation, air purification, and self-cleaning coatings [44].

3.2. Smart materials properties

A class of materials known as "smart materials" has unique qualities that enable them to respond to external stimuli and alter their chemical or physical properties. Due to these materials' dynamic nature and versatility, they have numerous uses in numerous industries. Shape memory materials can deform reversibly when exposed to certain stimuli, such as temperature, light, or electrical current. Once the stimulus is gone, they may recall and return to their former shape. Applications for these features can be found in robots, aircraft components, and biomedical devices. Piezoelectricity, while subjected to mechanical stress or deformation, certain materials, such as piezoelectric ceramics or polymers, produce an electric charge. On the other hand, these materials experience mechanical deformation when exposed to an electric field. Sensors, actuators, energy harvesters, and ultrasonic devices use this property [31]. Electrochromic materials that exhibit electrochromism alter their color or optical characteristics if an electric potential is applied.

Smart windows, display technology, and privacy glass are examples of products that use this attribute, in which the transparency or opacity of the material may be adjusted [45].

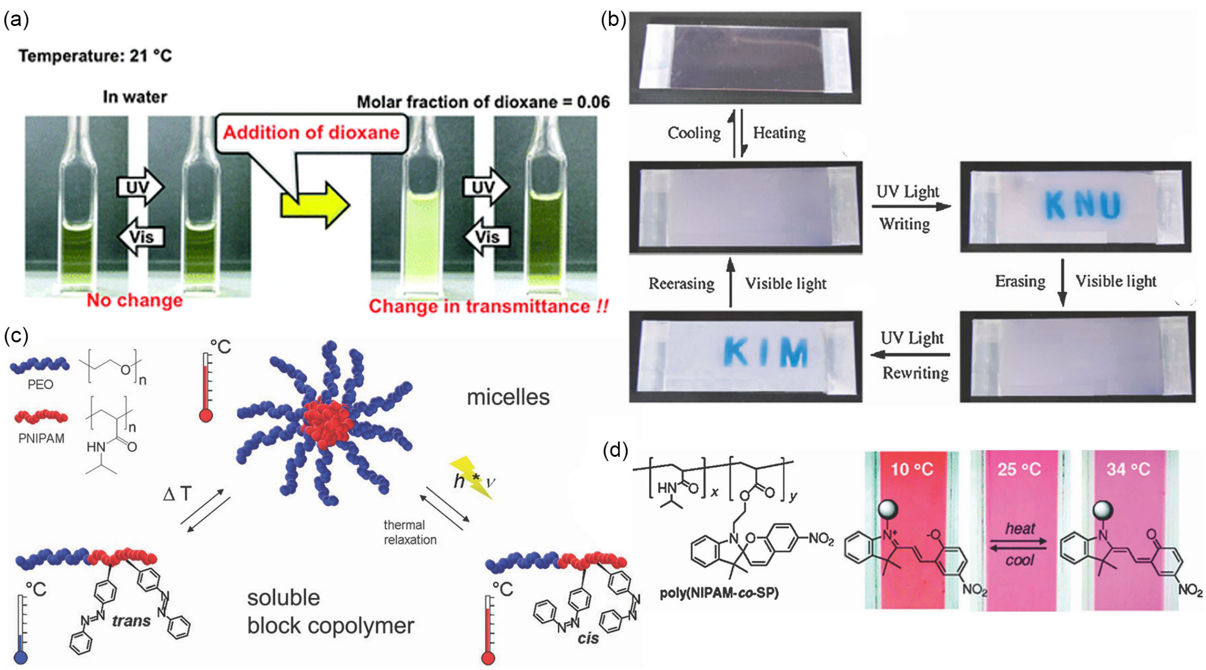
Magnetostriction: When exposed to a magnetic field, materials that exhibit this behavior alter in size or shape. This characteristic is used in sensors, actuators, and energy conversion equipment like vibration dampers and sonar systems [46].

Thermochromism: Thermochromic substances alter their color or transparency in response to changes in temperature. They are used in thermometers, smart textiles, and labels with built-in temperature sensors [47].

pH responsiveness: Some materials react by expanding or contracting when the pH level changes. Drug delivery systems, sensors, and self-healing materials use this characteristic [48]. These materials have uses in various industries, including construction, electronics, aircraft, and medicine. Their distinctive qualities improve the functionality of numerous gadgets and aid in the creation of novel technology.

Thermoelasticity: The ability of smart materials to undergo reversible changes in shape or size in response to temperature differences is known as thermoelasticity. These materials have a mechanical behavior coupled to their thermal activity, enabling them to respond to thermal stimuli with various actions. Applications for thermoelastic innovative materials include actuators, sensors, energy harvesting, and thermal management. A summary of thermoelasticity, its mechanics, and several instances of intelligent materials displaying thermoelastic behavior in this reaction [49]. The investigation of the connection between temperature and mechanical deformation in materials is known as thermoelasticity. Due to the various thermal expansion coefficients of its parts or phases, an intelligent material experiences internal stress and strain when its temperature changes. The material's dimensional changes brought on by this stress and strain can have several mechanical impacts [50]. The shape memory effect is one of the most prevalent thermoelasticity processes. SMAs are a class of intelligent materials that have unusual behavior. After being deformed by a thermal or mechanical stimulus, they may "remember" their previous shape and return to it. SMAs have a two-way shape memory effect, which means that they may be trained to have a particular shape at a high temperature (austenitic phase) and then, upon cooling, transition to a lower temperature phase (martensitic phase) with a different shape. When heated again, the SMA returns to its original shape. The reversible phase transition between the austenitic and martensitic phases causes the shape memory phenomenon in SMAs. The material's modulus, strength, and thermal expansion coefficient all undergo a considerable shift along with this phase transformation. The shape memory effect applications in SMAs include robotics, aircraft parts, automotive systems, medical devices (stents, orthodontic wires), and robotics [51, 52]. Thermally sensitive polymers are another type of thermoelastic innovative material. These polymers can significantly alter their physical characteristics due to temperature changes, such as shape, volume, or modulus. Thermally responsive polymers' glass transition temperature (Tg) or lower critical solution temperature is frequently used to predict how specific polymers behave. The polymer can experience significant variations in its mechanical properties above or below these critical temperatures, as shown in Figure 4 [53, 54].

Figure 4
(a) UV-irradiation on PNIPAM polymers with azobenzene end-groups in water/1,4-dioxane (6 mole percent dioxane) at room temperature reversibly changes a turbid suspension into a clear solution. (b) PNIPAM hydrogels incorporated with spironaphthoxazine are applicable in optical data recording. With heating and cooling, the hydrogel placed between two glass plates could be transitioned from sol, (c) the creation and disintegration of micelles that stem from PEO-b-PNIPAM block copolymer with azobenzene groups in the thermo-responsive segment were investigated under the dual control of temperature and light, and (d) copolymer, poly(NIPAM-co-SP), of N-isopropylacrylamide and spiropyran units can serve as a colorimetric thermometer with a UV-induced temperature



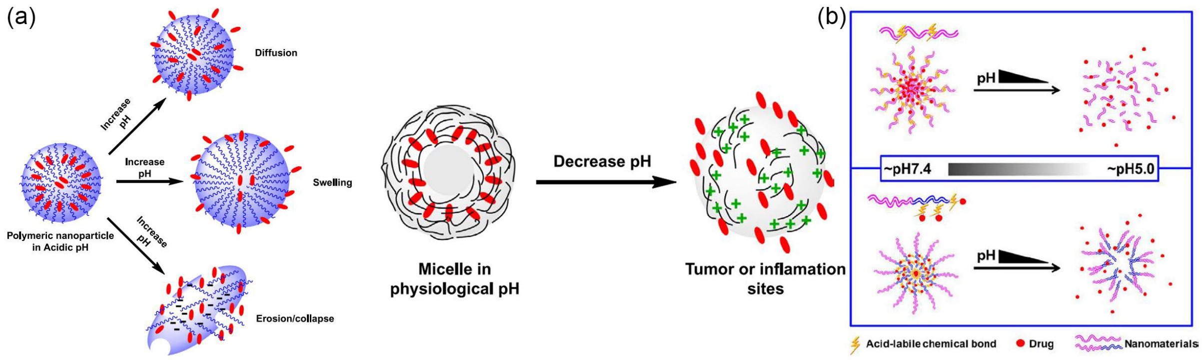
Thermally sensitive polymers have been utilized in applications such as medication delivery systems, wherein a medicine is released based on changes in body temperature through a volume change. Additionally, they are used in soft robotics, which utilizes shape changes for actuation and movement. Other intelligent materials, such as piezoelectric ceramics, electrostrictive polymers, and MR fluids, display thermoelastic behavior in addition to SMAs and thermally sensitive polymers. These materials have been used in actuators, energy-harvesting devices, and adaptive dampers because they can alter their mechanical properties, such as strain, stiffness, or damping, in response to temperature changes [55]. A thorough comprehension of the underlying principles and exact control over material composition, microstructure, and processing methods are necessary to design and develop thermoelastic intelligent materials. The thermoelastic behavior of these materials can also be predicted and optimized thanks to computational modeling and simulation approaches [56].

Pseudoelasticity, a class of advanced materials known as "smart materials," has unique qualities and abilities that enable it to react to outside stimuli in a regulated and adaptive way. One of the notable characteristics displayed by certain innovative materials is pseudoelasticity, which allows them to experience significant deformations and recover to their former shape when the imposed force has been removed. This article discusses the fundamental processes of pseudoelasticity in intelligent materials, highlights some of its essential applications, and offers an overview of the phenomenon. For additional investigation, references to pertinent research studies and academic journals are included [57]. The capacity of a material to experience significant deformations while retaining its original shape upon unloading is known as pseudoelasticity, also known as superelasticity or reversible phase change. SMAs and some polymers are typical examples of materials where it is often seen that a reversible phase transformation occurs [58]. SMAs are a class of metallic alloys that behave in a pseudoelastic manner due to their distinct thermal and crystallographic characteristics. Nickel-titanium alloy (Nitinol) is one of the SMAs that has been the subject of the most research. Nitinol can be found at low temperatures in a martensitic phase with a less regular crystal structure. The martensitic phase permits substantial deformation when a load is applied. The material undergoes a reversible phase shift back to the austenitic phase upon unloading or heating, regaining its original shape, as seen in Figure 5 [59]. The thermoelastic structural phase transition between the austenitic high-temperature phase and two low-temperature phases, martensitic and stress-induced martensitic, is the cause of pseudo elasticity in smart materials, particularly SMAs. This transition causes reversible deformations in SMAs. The substance changes into the martensitic phase, characterized by a less organized crystal structure, when cooled below the martensite start temperature (M_s). Significant distortion is possible during this stage without suffering long-term harm. The material returns to the austenitic phase and regains its former shape upon unloading or heating over the austenite finish temperature (A_f). SMAs are the best choice for applications that call for shape memory effects and significant deformations since the reversible nature of this phase transformation allows for pseudoelastic behavior. Developing the thermoelastic structural phase transition is crucial for utilizing the unique properties of smart materials in various industries, including robotics, aerospace, and biomedical engineering [60].

Some polymers, including hydrogels and SMPs, also display pseudoelastic behavior. Due to their distinctive cross-linked architecture, SMPs can experience significant deformations. These materials can be programmed to take on a transient shape and then change to their original shape in response to an external stimulus (such as heat, light, or moisture). Numerous industries, including aeronautical engineering and biomedical technologies, find uses for this feature [61]. Pseudoelastic materials have unique qualities and characteristics that make them useful in various applications. Pseudoelastic materials are capable of large deformations, frequently going beyond the capabilities of regular materials. Because of this property, they are suitable for applications that call for flexible or shape-changing components [62]. Unlike conventional materials that display plastic deformation, pseudoelastic materials can regain their previous shape after loading. For applications where recurrent or cyclic deformations are anticipated, this reversibility is essential. Intelligent materials, like SMAs, can store and release large amounts of energy during phase shift. They can function effectively as actuators or dampers in a variety of engineering systems thanks to this feature [63]. Smart materials made of pH-sensitive polymers modify their characteristics or behavior in response to changes in the environment's pH (acidity or alkalinity). These materials are made of polymers with specific pH-responsive capabilities, allowing them to react in a planned and regulated manner. Numerous industries use biomedicine, medication delivery systems, sensors, and environmental monitoring [64]. pH-responsive functional groups or moieties are

Figure 5

(a) Schematic illustrations of potential drug release pathways from pH-responsive DDSs. Drug release from a micelle when it destabilizes in acidic microenvironments, and (b) drug release from a polymeric nanocarrier as the pH is elevated, for example, while traveling from the stomach fluid to the intestinal fluid



incorporated into the polymer structure to create pH-sensitive polymer-based intelligent products. Typical examples of pH-responsive groups include phenols, amines, carboxylic acids, and imidazoles. In reaction to pH variations, these groups can undergo ionization or protonation/deprotonation processes, changing the material's characteristics [59]. Alterations in solubility, swelling behavior, mechanical characteristics, charge, and conformational alterations are only a few of the pH-dependent aspects of these materials. The polymer can expand or contract at particular pH ranges, changing its size, porosity, or permeability. The charge and electrostatic interactions within the polymer matrix can also change due to the ionization of functional groups [65]. Several mechanisms control the pH response in polymer-based intelligent materials, including ionization/dissociation, complexation, hydrophobic/hydrophilic transitions, and electrostatic interactions. The responses of the substance to pH variations, such as structural modifications, drug release, or modifications in optical or mechanical properties, are determined by these mechanisms [66]. pH-responsive polymers have shown promise, especially in targeted therapy for malignancies, as shown in Figure 5. As a result of these polymers' pH-dependent characteristics, including diffusion, swelling, and erosion, regulated medication release is made possible in response to the tumors' acidic milieu [67]. Polymers that respond to pH can control medication release by diffusion. The polymer matrix experiences swelling or alterations to its porous structure in an acidic environment, such as the tumor microenvironment. This makes it easier for drug molecules to diffuse out of the polymer, which enhances medication release at the tumor location. pH-responsive polymers may swell or vary in volume in response to pH changes. The polymer chains may protonate at an acidic pH, which causes electrostatic repulsion and enhanced hydration. The polymer matrix is disturbed by this swelling impact, facilitating medication release. In contrast, the polymer maintains its compact state at neutral or alkaline pH levels, reducing drug release [68].

In response to pH changes, some pH-responsive polymers erode. Drugs that have been encapsulated can be released when polymer chains degrade or dissolve under acidic circumstances. This medication release method, based on erosion, enables controlled and ongoing distribution. Cancer-targeting solid tumors have an acidic tumor microenvironment as a distinguishing feature. This property is exploited by pH-responsive polymers, which selectively release medications in response to the lower pH of tumor tissues. This targeted drug administration increases treatment efficacy by improving medication accumulation at the tumor site while minimizing systemic side effects [67]. PH-responsive polymers offer a versatile platform for precise drug administration in tumor therapy by utilizing diffusion, swelling, erosion, and tumor targeting. These polymers can release drugs locally and continuously, improving therapeutic results and reducing side effects.

A group of materials known as light-sensitive smart materials, often referred to as photoresponsive materials, possesses unique characteristics and responds differently to light stimuli. When exposed to light, these materials can undergo reversible changes in their physical or chemical properties. This explanation will examine the workings, characteristics, and prospective uses of light-sensitive innovative materials. Depending on the specific material, different mechanisms underlie light-sensitive intelligent materials. However, photoexcitation and photo-response are the two universal phases present in these materials. Electrons within the molecular structure of a light-sensitive innovative material are excited by photon absorption, which occurs when light interacts with the material. Various mechanisms, such as electron transfer, energy transfer, or changes in molecular configuration, might lead to this excitation. After being photoexcited, a material experiences a photo-response, which is a change in its chemical or physical properties. This reaction may manifest in various forms, such as changes in color, shape, transparency, conductivity, or the release of stored energy. The composition and design of the material determine the specific response [69, 70].

Smart materials responsive to light have several distinctive qualities that make them useful in various applications. Reversibility: When the light source is turned off, the modifications that the light has caused in these substances frequently return to how they were. This reversibility enables many applications by permitting repeated activation and deactivation cycles [71]. Innovative materials are highly sensitive to light stimuli, responding quickly and effectively to changes in light. Light-sensitive response innovative materials react quickly and effectively to changes in illumination due to their great sensitivity to light stimuli. They are helpful for applications demanding immediate and accurate control because of this characteristic. Selectivity differentiates materials that respond selectively to various light wavelengths or colors due to their different absorption spectra. This selectivity enables customized applications and the capacity to elicit particular reactions [72]. Tunability can be achieved by modifying the composition, molecular structure, or exposure circumstances of light-sensitive innovative materials, and desired reactions can be created. This adaptability allows for modification for specific applications and needs [73]. Light-sensitive smart materials have many uses in a variety of industries. Examples that stand out include materials that change color when exposed to light, known as photochromic materials. As an illustration, consider *Spirogyra*, which turns colorless to color when exposed to light. Photochromic lenses employ photochromic components, which darken in response to ultraviolet light, shielding the eye from harmful rays [74, 75]. Thermochromic substances react to temperature changes by changing their hue. Surfaces can be painted with light-sensitive thermochromic pigments to show temperature changes. Thermal indicators, for instance, use liquid crystal thermochromic materials to depict temperature changes graphically [76]. Polymers that change upon exposure to light in terms of their physical characteristics, such as form or elasticity, are called photoresponsive polymers. These materials have uses in soft robotics, where the movement and shape of robotic parts can be controlled by light. Materials used in photovoltaic cells, such as silicon or perovskite-based materials, are light-sensitive and can convert visible light into electrical energy. These materials make it possible to produce electricity from sunlight, which helps develop renewable energy sources [77].

The piezoelectric effect is a peculiar characteristic of the intriguing class of piezoelectric materials. The name "piezo" is derived from the Greek word for pressure and describes these materials' capacity to produce an electric charge in reaction to pressure or mechanical stress. On the other hand, they can also change shape or deform in response to an applied electric field. Because of their dual feature, piezoelectric materials are highly adaptable and valuable in various applications, such as sensors, actuators, energy-harvesting devices, and acoustic transducers [78]. The material's crystal structure serves as the foundation for the piezoelectric effect. Natural crystals like quartz, tourmaline, and Rochelle salt are piezoelectric materials, as are synthetic ceramics and polymers. These materials have an asymmetrical crystal structure and an asymmetrical atom arrangement. When the material is mechanically deformed, its non-centrosymmetry causes the separation of positive and negative charges within the material [79]. When mechanical pressure or force is applied to a piezoelectric material, the crystal structure changes, displacing charged particles and producing electric dipoles. This displacement creates a voltage and an electric field across the material. Piezoelectric materials can act as sensors for measuring force, pressure, acceleration, and other physical parameters since the size of the electric charge generated is precisely proportional to the applied mechanical stress [80].

On the other hand, a piezoelectric material deforms or changes shape when an electric field is applied to it. This property enables piezoelectric materials to precisely control and manipulate mechanical motion, using actuators as one example. Precision positioning systems, micro-robotics, and adaptive optics can all use piezoelectric actuators to produce exact displacements using shifting electric fields [81]. Piezoelectric materials are used in energy harvesting as well. When subjected to vibrations or mechanical stress, they can transform mechanical energy into electrical energy. This electrical energy can then be captured and powered by small electronic devices or recharged batteries. This potential has sparked the creation of wireless sensor networks, wearable technology, and self-powered sensors that can function without external power sources [82]. Additionally, the discipline of acoustics makes substantial use of piezoelectric materials. They are used in various transducers, including speakers, microphones, and ultrasound equipment. Electrical signals are converted from mechanical vibrations by sound waves in microphones, whereas mechanical vibrations are brought on by electrical signals in speakers to produce sound. To produce and detect high-frequency sound waves for use in medical imaging, nondestructive testing, and distance measuring, ultrasound devices utilize the piezoelectric effect [83]. New piezoelectric materials with higher performance properties have recently been created due to materials science and engineering developments. These include several polymer-based piezoelectric materials and PZT, one of the most popular piezoelectric ceramics. Additionally, scientists are looking at the possibilities of cutting-edge substances like nanowires, thin films, and composites to improve piezoelectric capabilities and open up new applications [84, 85].

4. Application of Smart Materials

4D printing is a cutting-edge rapid prototyping technology with enormous potential for use in a variety of technical areas, including biomedicine, electronics, robotics, food, automotive, construction, and aerospace. However, 4D printing of polymer composites produces a variety of materials for unique and exciting applications that were previously impossible to achieve using traditional manufacturing procedures. For example, targeted electrical stimulation of piezoelectric active implants promotes bone formation while reducing bone resorption. Piezoelectric materials can significantly increase the integration of bone marrow [86–88].

4.1. Soft robotics

In today's world, soft robots and actuators have become important focal areas for 4DP applications. Programming strategies in soft robotics often revolve around shaping the way SMPs or hydrogels are placed and oriented within the printed structure. Actuation sequences can be encoded in the material by defining the path directions of printing and layer composition carefully (e.g., bending or crawling within an actuating with a decentralized slight delay). However, temperature-responsive hydrogels can be designed to swell asymmetrically, which in turn can give rise to motion in soft actuators. The challenge here is the logistics of horrific deformation mechanics in the face of real-world loads and cyclic products [89]. The advent of (SMPC-based) shape memory polymer composites smart materials has also aided in achieving substantial structural deformation compared to robots built using standard methods [90]. These 4D-printed robots help to reduce size while simultaneously increasing functionality. Additionally, SMPC-based soft robots can be used in underwater robotic applications [91]. Similarly, many researchers created biomimetic actuators using SMP- and PNIPAM-based smart hydrogels and hydrogel-based smart materials [92]. Micro-robots in the human stomach model were effectively completed by completing the active movement of freight in the form of pharmaceuticals, despite several physical difficulties, such as the wrinkled surface of the human stomach model, as shown in Figure 6 [93]. Thus, printed soft millirobots have enormous potential in medical treatment, drug administration, and bioengineering.

4.2. Biomedical devices

SMP, a smart material, has a wide range of applications in the healthcare sector, including manufacturing dynamic and smart biomedical devices and artificial skins. Developing a polycaprolactone (PCL)-based customizable medical device to treat tracheobronchomalacia that could change shape under tissue growth and resorption settings [94, 95]. 4D printing technology enables the creation of customized items such as stents. The specific chemical details of the scaffold could be programmed into hydrogels or other materials, and material properties (e.g., transition temperature for SMPs) can be tailored to induce shape changes in physiological conditions (like in situ). Programming has to make sure that these devices can fold or unfold based on body temperature or pH without any harm. In robotics, programming is different; it needs to be biocompatible, slow-acting, and noninvasive when deployed. SMP-based medical devices may be restricted by their slow degradation and low recovery stress, which might not be suitable for all load-bearing applications. So, future work should compare biodegradable SMPs critically with non-degradable alternatives to find the best choice for each clinical situation. SMP-based printed stents also reduce the surgical incision's diameter during implantation by momentarily programming it. The body temperature helps the printed stent to re-establish its original diameter upon insertion [96, 97]. 4D printing technology also manufactures protective equipment during pandemics and rare situations such as coronavirus disease 2019 [98]. Designed a device for selective drug release in the intestinal tract. In another study, Zu et al. [99] used an extrusion approach to create a capsule shell from a plant stomata-inspired, UV-cross-linked PNIPAM-based hydrogel. Because of the reduced critical solution temperature-induced swelling/shrinking properties, the produced PNIPAM polymer capsules exhibited microstructure alterations and temperature-responsive drug release, as illustrated in Figure 7 [100, 101]. Using in vitro drug release tests, the PNIPAM-based hydrogel capsules controlled drug release characteristics based on ambient temperature differences.

4.3. Drug delivery system

Drug delivery is the creation of innovative materials or carrier systems for the efficient therapeutic delivery of medications. Hydrogels are appealing prospects for drug delivery applications because they enable geographic and temporal control over the release of various therapeutic agents, such as chemical medicines, tiny biomolecules, and cells. Hydrogels swell quickly in aqueous settings such as bodily fluids. This may result in the burst (short-term) release of medicines, particularly for tiny molecules smaller than the hydrogel mesh size. Thus, drug–polymer interactions are critical for regulating medicines' release from hydrogels [102].

Figure 6

A metamaterial approach to soft robotics. Robot responses can be programmed into their squishy bodies by harnessing flexible metamaterials based on beams, origami, and kirigami and reinforced architectures: (i) inchworm locomotion, (ii) buckling-induced auxetic actuators, (iii) untethered propulsion, (iv) bistable origami wing, (v) an origami-inspired foldable robotic hand, (vi) rectilinear locomotion enhanced with kirigami skin, (vii) knitted and woven artificial muscles, (viii) a morphable knitted blooming flower, and (ix) chiral composite actuators

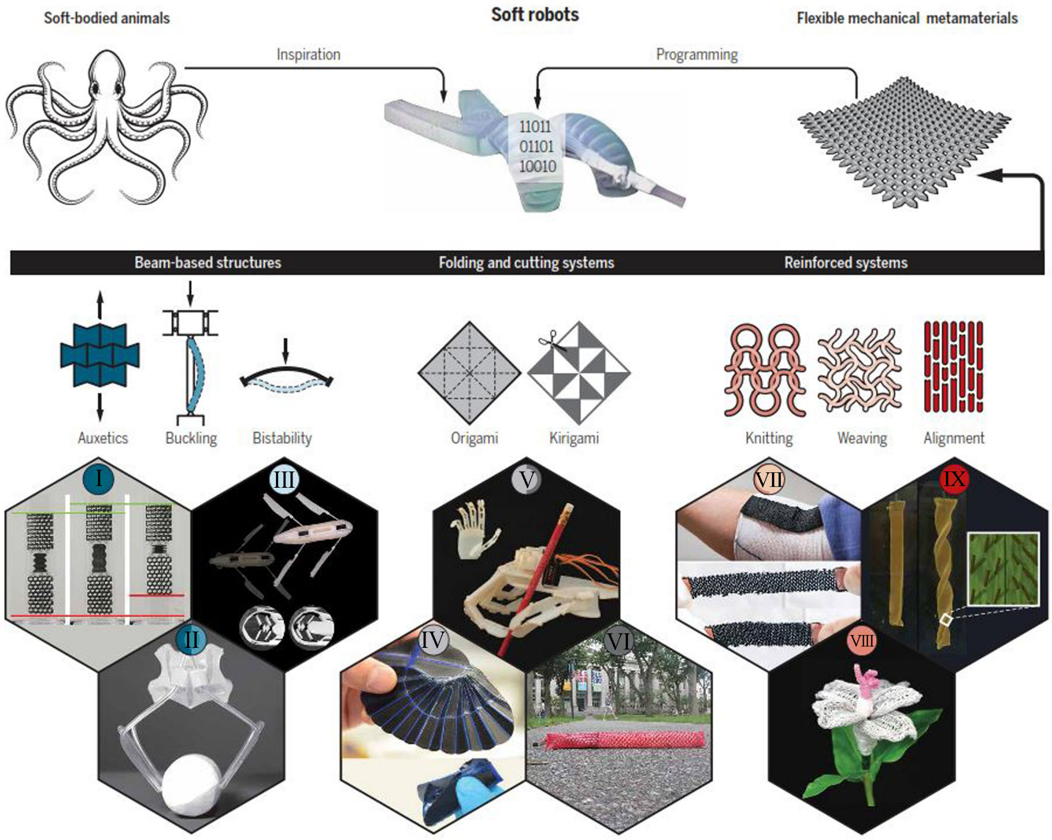


Figure 7

(a) PCL-based 4D-printed electrical device, (b) Electrical devices based on form memory are fabricated. The temperature sensor was fabricated in both its on and off states (top and bottom). (c) Stereolithography (STL) illustration. All patients' tracheobronchial splint fits are virtually evaluated using a segmented primary airway model. The last 3D-printed PCL tracheobronchial splint for the patient and the development of the right bronchus, the splint included a 90° spiral to the open angle of the apparatus

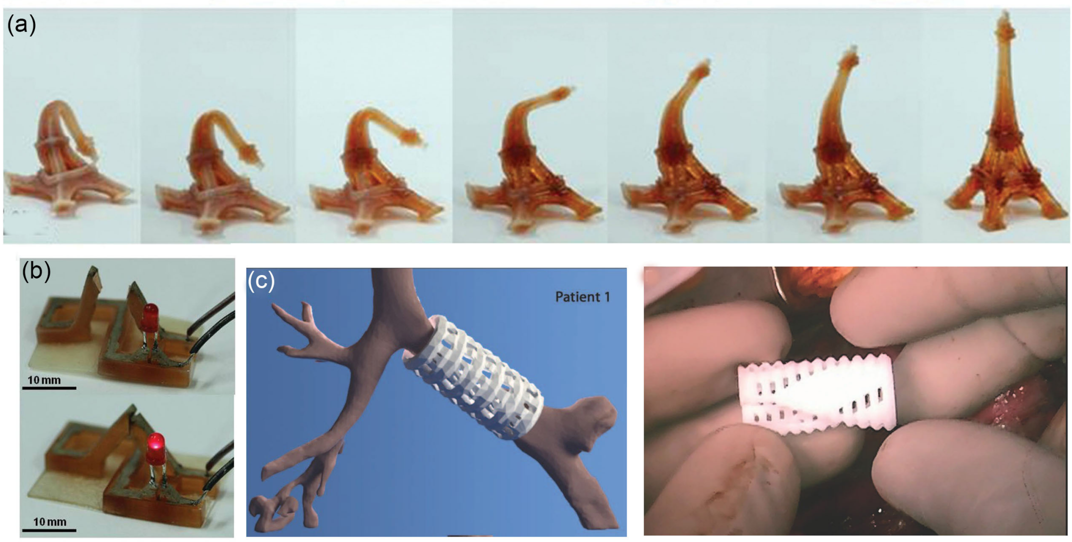


Table 1 illustrates the use of 4D printing in medicine delivery systems. Medication routes must be designed to achieve optimal medication release function. The advancement of progressive manufacturing techniques, such as 3D printing, has enabled the creation of complicated medication delivery systems that would not be possible using traditional methods. 4D printing takes this a step further, allowing for the creation of more advanced medication methods of administration [103]. The four-dimensional technique is also used to increase the tissue retentiveness of systems that deliver medications. For instance, Melocchi et al. [104] investigated the feasibility of 4D printing a retentive device for intravascular medication delivery in Figure 8 [105]. The device is designed to release medications into the bladder over time and is based on a water-induced shape memory reaction of polyvinyl alcohol (PVA). The tool was built using an FDM-based printer, and its shape memory characteristics were studied.

Table 1
Summary of emerging 4D printed hydrogels for drug delivery applications

Printing techniques	Hydrogels	Drug and loading method	External stimulus	Drug release profile	Ref.
Direct Ink Writing (DIW)	Pluronic diacrylate macromer and alginate	Methotrexate co-mixing	Ion (calcium chloride)	Rapid release for up to 6 hours, followed by sustained release for up to 12 hours.	[106]
Direct Ink Writing. (DIW)	Poly(N-isopropyl acrylamide)	Brilliant blue and lemon yellow Injection	Temperature (22 °C)	Quickly release for up to 15 hours, with medium release for up to 48 hours.	[107]
Direct Ink Writing (DIW)	Gelatin methacryloyl	Heparin–co-mixing	Solvent (water)	Fast release up to 8 hours, followed by continuous release for up to 28 hours.	[108]
Digital Light Processing (DLP)	4-hydroxybutyl acrylate. Urethane-polyethylene glycol-polypropylene glycol (PU-EO-PO)	Doxorubicin and ovalbumin—Immersion	Magnetic field (1 MHz)	High release in 4 hours (doxorubicin) or 30 minutes (ovalbumin), followed by moderate release for 50 hours and steady release for 75 hours.	[109]
μSLA	Poly(ethylene glycol) diacrylate	Rhodamine B immersion	Ion (phosphate-buffered saline)	Fast release in 1 min, followed by medium release up to 2.5 h, and slow release up to 3 h	[110]
FDM	Poly(vinyl alcohol)	Caffeine co-mixing	Solvent (water)	Fast release up to 2 h, followed by steady release up to 6 h	[111]

4.4. Soft biosensors

The biosensors can be extremely useful in tissue engineering applications, particularly in the maintenance of 3D (three-dimensional) cell cultures [112] and the development of "organs-on-chips" models, in which biomolecule concentrations such as glucose, adenosine, and hydrogen peroxide levels play important roles in determining the fate of cells and tissues. Living cells are well known for transmitting a variety of physical and chemical signals, including changes in oxygen consumption, pH, membrane potentials, ion concentrations, and the release of metabolic chemicals and molecules [113]. Monitoring these analysts can provide real-time information on cellular activity. In clinical applications, biosensor-based blood glucose concentration monitoring has emerged as a key diagnostic approach for precisely tracing diabetes with high levels of glycated hemoglobin (HbA1c) in Figure 9 [114]. In tissue engineering applications, however, continuous glucose monitoring in culture media is used as an indicator of cell metabolic activity [115].

4.5. Surgical tools

Additive manufacturing is utilized to make various orthopedic tools, dental surgical tools, and aids (implant supporting bars and abutments). Using this technology, clinicians may construct guides that accurately follow a patient's unique anatomy and find surgery tools with high accuracy. These tools can operate in intricate and tiny areas while ensuring patient safety in Figure 10 [116, 117]. Artificial medical devices' resident life in the human body can be increased by making the coated material more resistant to the tribological and corrosive difficulties they face in a physiologically relevant environment [118].

4.6. Intelligent textile

Intelligent fabrics have entered a new phase of innovation thanks to the incorporation of smart materials, especially polymers and those created by 4D printing. Due to their ability to perform tasks beyond those of traditional fabrics and their wide range of potential uses, these materials have completely changed the textile industry [89]. Because they combine flexibility, reactivity, and adaptability, polymer-based smart materials are widely used in intelligent textiles. Textiles that may react dynamically to external stimuli are made

Figure 8
(a) depicts an overview of the evolution of drug delivery systems (DDS), and (b) a diagrammatic depiction of active and passive targeting. Passive targeting relies on the carrier's physicochemical features, such as size, charge, and shape. Furthermore, surface modification with poly (ethylene glycol) enhances targeting and circulation time. Active targeting displays a large number of ligands and their matching size range

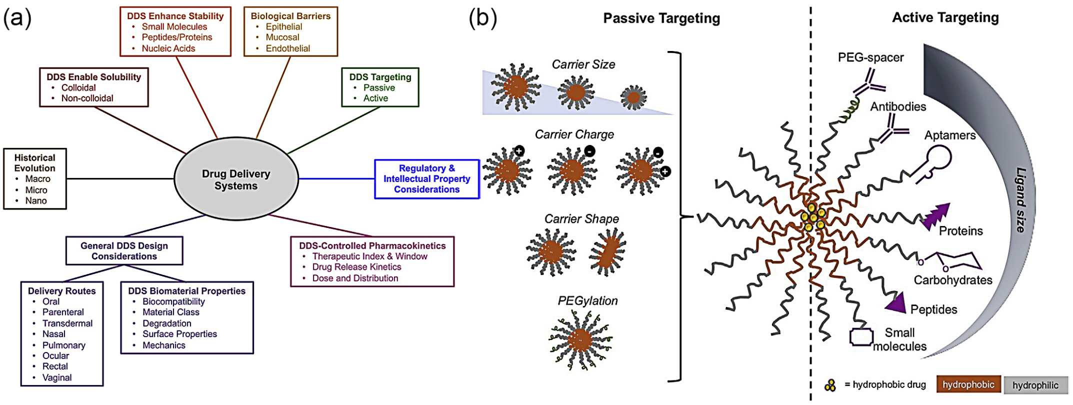


Figure 9
(a) Fused filament fabrication (FFF) dynamic sensor design in a single process with specified dimensions; (b) for an FFF piezoelectric PVDF film, coordinate the system and mode response directions

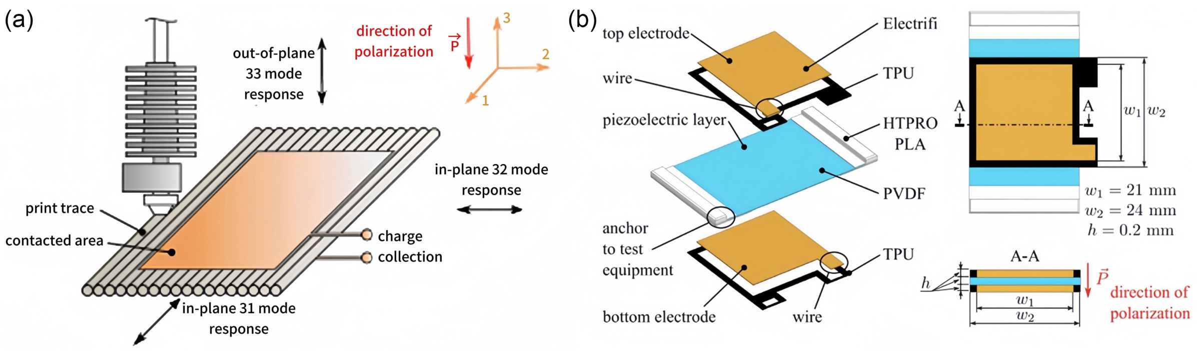
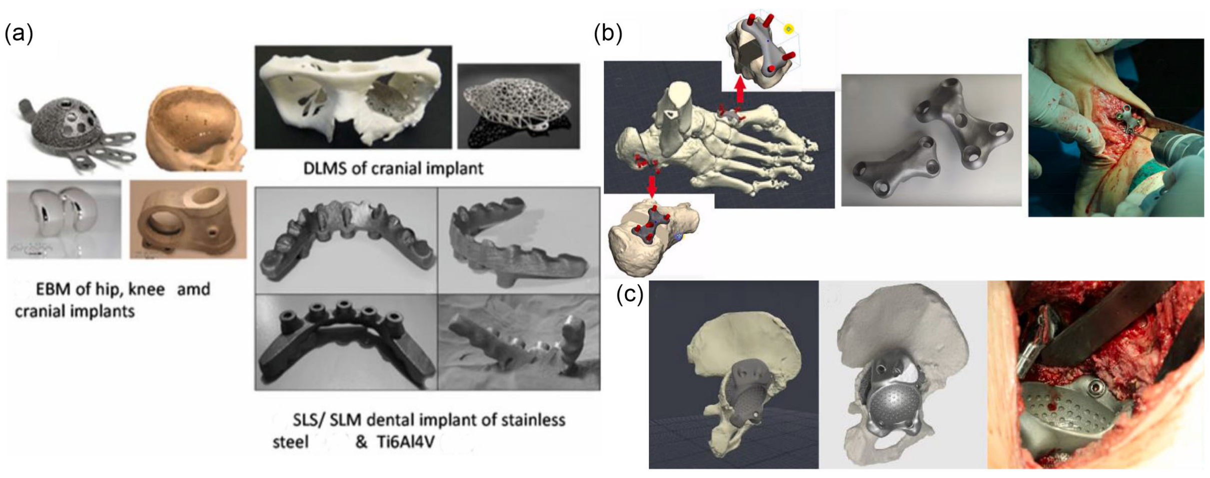


Figure 10
(a) Depicts the three-dimensional planning process for the future implant's contour, connecting locations with the bone and screw holes. The final titanium implant (b) was polished and sterilized before the operation. Surgical/implant replacement (c), followed by hip replacement



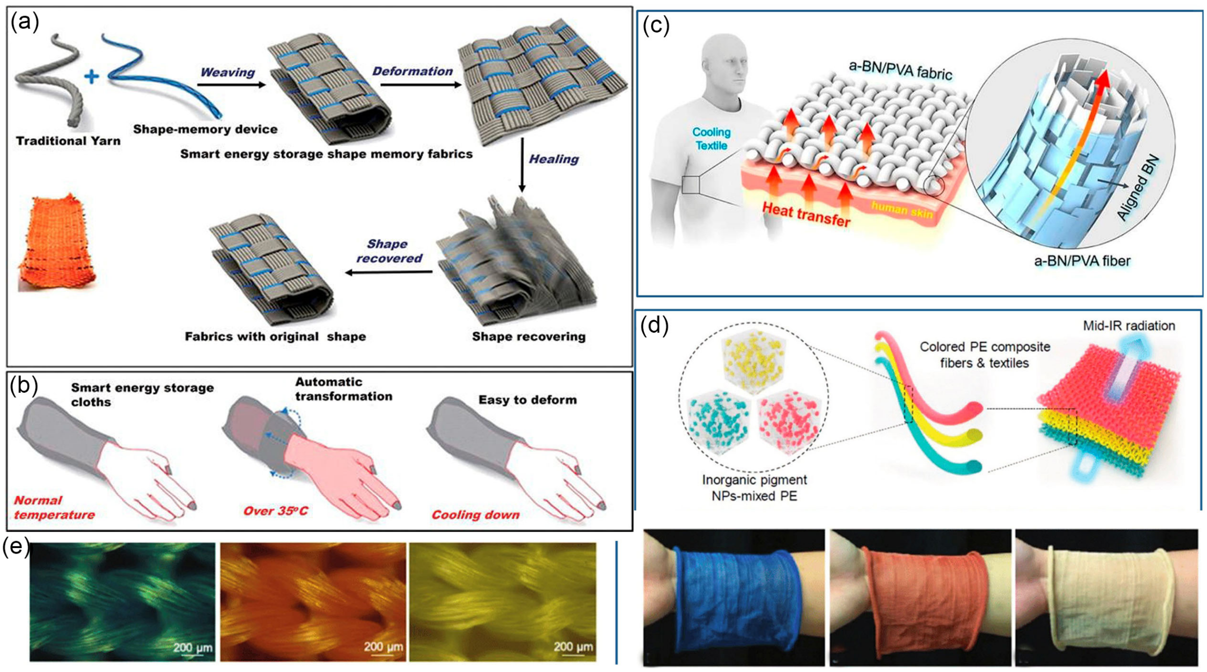
possible by smart polymers, including conductive and shape memory polymers. These materials have been used to make clothing that may change shape or other characteristics in response to temperature changes, giving wearers more comfort and utility. SMPs are essential to the field of intelligent textiles because they can reversibly change their shape in response to external stimuli, like heat. This property allows fabric designers to create customized and adaptive fits by altering their structure or conforming to the wearer's body shape. Sportswear that adjusts to optimize aerodynamics and medical textiles that mold to the wearer's body for improved therapeutic effects are just two examples of the applications for SMPs. Another type of smart material is conductive polymers, which are a subset of smart materials that aid in the development of textiles with electronic features. By conducting electricity, these polymers open the door for the direct integration of sensors, actuators, and other electronic components into textiles. It is possible to create intelligent textiles with conductive polymers that can track physiological factors like body temperature and heart rate, giving important information for fitness and health applications [119]. The potential of intelligent textiles gains a temporal dimension with the introduction of 4D printing, an extension of 3D printing. With this method, fabrics can be made to change in a regulated way over time in reaction to certain stimuli. Concerning textiles, 4D printing makes it possible to create clothing that may alter in texture, color, or shape in response to the user's preferences or the surroundings. Utilizing materials that can react to outside stimuli, such as heat or moisture, to cause preprogrammed structural alterations in the fabric is the integration of 4D printing in intelligent textiles. In reaction to increasing body temperature, a textile printed using 4D technology has the potential to modify its porosity, hence improving its breathability. Textiles become more functional as a result of this dynamic responsiveness, which transforms them from passive coverings into active elements that might improve user experience, as shown in Figure 11 [120]. Furthermore, the use of 4D printing and smart polymers in intelligent fabrics goes beyond comfort and style. These materials allow textiles to be made with mechanical intelligence integrated into them. It is possible to create clothes that offer extra support or protection when needed by using fabrics that are engineered to react to particular mechanical stresses. Because fabrics in sportswear may dynamically respond to the intensity of physical activity, this use is very relevant [120].

4.7. Piezo actuator

The incorporation of polymer-based smart materials with 4D printing technology is bringing in a new era of accuracy, responsiveness, and versatility in the field of piezo actuator applications. Polymers, adaptable materials that provide the basis for creating sophisticated components, are at the center of this innovation. Particularly, since they can offer the controlled degradation and biocompatibility needed for piezo actuator applications, biocompatible polymers like PCL and poly(lactic-co-glycolic acid) are becoming more and more popular. The transition from 3D to 4D printing signifies a significant advancement in manufacturing capacity [121, 122]. The temporal dimension is introduced by 4D printing, enabling printed structures to change over time in reaction to outside stimuli dynamically. This refers to the development of components that may experience regulated movements or change shape in the context of piezo actuators, providing previously unheard-of levels

Figure 11

Healthcare uses smart materials and intelligent fabrics. (a) Diagram of a hybridized shape memory supercapacitor made of conventional fabric; (b) illustration of the smart shape memory textile used in an intelligent garment; (c) a schematic illustration of how thermal conductive fabric, also known as highly aligned boron nitride (BN)/poly (vinyl alcohol) (PVA) fabric (referred to by the authors as a-BN/PVA fabric), can enhance the thermal transport characteristics of textiles for personal cooling; (d) a colored textile used for personal cooling where the cooling temperature determines the color; (e) optical micrographs and photographs of the knitted colored textile with good wearability for blue PB-PE, red Fe_2O_3-PE, and yellow Si-PE



of precision and adaptability. For applications where complex, sensitive, and programmable movements are crucial, this technology holds great promise. A wide range of industries use polymer-based smart materials in 4D printing for piezo actuators. These actuators can be used in robotics to build flexible, soft robotic systems that can imitate the movements of living things. These actuators' versatility is especially useful in the medical field, where they can be incorporated into assistive equipment for those with mobility issues or surgical instruments for minimally invasive treatments [123].

Piezo actuators made of 4D-printed smart materials are used in the field of micro- and nano-electromechanical systems to position and manipulate minuscule objects precisely. This has ramifications for the development of optics, electronics, and medical diagnostics, fields where exact control over minute components is critical. Furthermore, the incorporation of piezo actuators into wearable technologies presents the possibility of customized and adaptable gadgets. Intelligent textiles and textile products with 4D-printed piezo actuators can offer dynamic, personalized support by adjusting to the wearer's movements or reacting to particular environmental factors [124].

4.8. Nuclear industries

The application of innovative materials in nuclear engineering is still very conceptual, but it remains an up-and-coming field. SMPs and conductive polymers, with their unique responsiveness to stresses and potential functionality as monitoring equipment, maintenance, and safety features, represent two of the most common classes of materials for these applications. The pseudoelastic recoverable deformation of SMPs in combination with actual shape recovery can be implemented as a dynamic seal in heat exchangers in reactors that can accommodate the changing shape due to changes in temperature or mechanical load. However, none of these concepts was applied on a large scale within reactors. Two recent studies imply that such recoverable materials can be used to reverse the deformation induced by an earthquake or a thermal load, which increases the resilience of the construction. Smart materials are revolutionizing the nuclear industry by transforming how we approach various aspects of nuclear applications. The pseudo elasticity of SMPs makes sealing effective even under changing circumstances, thereby enhancing safety in nuclear plants [125]. Conductive polymers and their nanocomposites with radiation resilience are considered a promising material for widespread temperature and pressure sensing equipment to use in reactor systems. The use of conductive polymers, which may act as sensors to keep an eye on a variety of parameters, is advantageous for the nuclear industry as well. The nuclear business has new prospects thanks to the temporal dimension of 4D printing. Manufacturing and maintenance processes can be affected by the capacity to design components that can alter over time in terms of shape or characteristics [126]. The idea of sub-Kelvin radiation exposure and its subsequent action can be used to craft 4D-printed SMPs that will repair themselves within tens of seconds. While some conductive polymers were able to heal themselves in some controlled tests, they still lack scalability and are prone to external stress. This skill makes developing components for nuclear reactors with optimal mechanical and thermal qualities possible. In terms of upkeep, 4D printing opens up possibilities for structures that can mend themselves. With the use of 4D printing, intelligent materials can be designed to initiate repair mechanisms in response to particular stimuli, such as heat or radiation exposure. This characteristic may increase the longevity of crucial nuclear reactor components, lowering maintenance expenses and downtime. Reactor components can deliberately incorporate these materials to lessen the effects of outside forces and vibrations. This contributes to the overall system's safety and lifespan, in addition to guaranteeing the reactor's structural integrity. The creation of sophisticated nuclear fuel assemblies is another area in which 4D printing and smart polymers are applied. Through the utilization of polymer flexibility and 4D printing accuracy, engineers can create fuel assemblies that exhibit improved structural integrity and thermal conductivity. This invention maximizes heat transport and eliminates possible weak points, which raises the overall safety and efficiency of nuclear reactors. Additionally, radiation shielding is included in the nuclear industry's integration of smart materials. Workers' protective gear in nuclear facilities can be made of polymers that can absorb radiation. This application lowers radiation exposure and offers a lightweight substitute for bulky, conventional shielding materials, both of which improve worker safety. The auspicious nature of the 4D-printed polymer-based innovative material application in nuclear reactors is still conceptual and under-evaluated. Therefore, further research should be aimed at their space radiation testing, mechanical performance under radiation, and possible integration with actual reactor systems to develop applicable and validated tools [127].

4.9. Nano-systems

A revolutionary era of precise engineering, responsiveness, and flexibility at the nanoscale is being ushered in by the combination of 4D printing technology and smart materials based on polymers. A key element of this paradigm is smart materials, which improve the performance of nano-systems. A crucial function is played by SMPs, which can hold onto a certain shape and return to it in response to external stimuli like temperature [128]. This property is utilized to create nano-actuators that can be programmed to change shape and then revert to their original form. It is a crucial component of precise control in nano-robotics and other nanotechnology applications. A level of complexity is added to nano-systems through the use of stimuli-responsive polymers. Nanoscale responsiveness and fine-grained control are made possible by these polymers' ability to respond to outside stimuli like electrical signals. This feature has potential for use in nanosurgical devices and medication administration systems, for example, where accurate and quick movements are necessary. Advancements in environmental monitoring, medical diagnostics, and other nanoscale sensing applications are made possible by these nano-sensors' ability to react to changes in their surroundings and provide important information. Moreover, the creation of nano-actuators with hitherto unheard-of powers is made possible by the incorporation of polymer-based smart materials into 4D printing technology. These actuators can be used to precisely manipulate nano-objects, which will enable breakthroughs in the building of nanodevices with complex architectures and the assembly of nanostructures [129]. The combination of 4D printing with polymer-based smart materials in the field of nano-systems represents a major advancement in nanoscale precision engineering and adaptability. The possibilities are vast, ranging from nano-robotics and medicine delivery to nano-sensors and actuators. This convergence of technology not only opens up new avenues for groundbreaking discoveries with broad applications across a variety of industries but also pushes the envelope in terms of control and responsiveness [130].

5. Conclusion and Outlook

The studies of polymer-based novel materials and their incorporation into 4D printing technologies represent an innovative intersection of science and technology. Due to these materials' unique qualities, which enable them to respond dynamically to external stimuli, a wide range of applications across several industries has become conceivable. The ability of polymer-based intelligent materials to modify either irreversibly or reversibly in response to various stimuli, including heat, light, moisture, pH, and electric fields, contributes to their versatility. This versatility has created the potential for revolutionary applications in biomedical engineering, aircraft, robotics, and architecture. These materials are applicable in tissue engineering, drug delivery, biosensors, and medical devices within the biomedical field. They offer customized treatment regimens and regulated reactions to biological processes. Innovative materials based on polymers now have greater possibilities due to the advent of 4D printing, which introduces time as a fourth dimension. 4D printing enables the creation of dynamic structures that can change shape or properties over time by combining SMPs with advanced additive manufacturing processes. This development has significant implications for various industries, such as architecture and medicine, where 4D-printed implants can adapt to changing conditions by responding to biological stimuli. Although the capabilities of 4D printed smart polymers have been increasing, there are a few key hurdles to overcome for full acceptance. Difficulty in scaling up is still one of the main drawbacks, with many 4D-printed structures confined to lab-scale prototypes. Future work should address the development of a high-conversion mass production process by combining scaling up with accuracy and responsivity. For biomedical applications, biocompatibility is a significant issue as well. Despite the early promise of some innovative materials on their in vitro performance, a more rigorous evaluation is necessary to understand their long-term effects in vivo and their degradation behavior. Finally, cost-effectiveness is a further limitation of the technology, as many high-performance stimuli-responsive materials, along with an advanced 4D printing system, carry a heavy economic burden. One direction is to develop low-cost alternatives such that the functionality of the system is not compromised. In the future, 4D printing paradigms are envisioned to be reengineered by emerging technologies, including artificial intelligence (AI) and machine learning. AI can enable predictive behavior modeling of materials, optimize print paths, and power automatic programming of multi-stage actuating with complex structures. Integration with digital twins, real-time sensing, and intelligent feedback systems could also realize an adaptive 4D system and a self-monitoring, corrective sub-system implemented. As a result, this will not only improve performance but also speed up the creation of new 4D-printed products with applications across landscape healthcare and aerospace.

In conclusion, studying novel materials based on polymers for 4D printing represents a significant advancement in material science and design innovation. The potential to transform conventional production techniques in several industries and usher in a new era of utility, efficiency, and flexibility lies in these materials' dynamic characteristics and versatility. The automation of programming the materials and structures in advance so that they will be able to respond to external stresses is a core technical enabler of 4D printing. Unlike traditional 3D printing, programming dictates the way shape transformations unfold over time. Thus, strategies differ according to the application; biological systems may use temperature or enzyme activation, whilst soft robotics can exploit mechanical gradients and light-induced swelling. Existing routes have made significant progress yet have not solved challenges, such as high precision control of multi-state actuations, robust reversibility over repeated cycles, and compatibility with diverse triggers in complex environments. This is the area where things are still lacking and universal but adaptable programming protocols for 4D printing continue to be a significant research frontier. The technology field is about to transform due to the impact this research has on other industries, including aircraft, healthcare, and architecture.

Ethical Statement

This study does not contain any studies with human or animal subjects performed by any of the authors.

Conflicts of Interest

The authors declare that they have no conflicts of interest in this work.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Author Contribution Statement

Md. Abu Shyeed: Conceptualization, Resources, Writing – original draft. **Jannatul Ferdaus:** Resources, Writing – original draft, Writing – review & editing. **Md Faruk Hossain:** Resources, Writing – original draft. **Md Alal Hossain:** Writing – review & editing. **Khan Rajib Hossain:** Conceptualization, Software, Writing – review & editing, Supervision.

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