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The use of moisture-responsive materials in 4D printing

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ABSTRACT

Purpose: The objective of this research paper is to compile a list of key moisture-sensitive smart materials used in 4D printing. These materials have applications in various fields, including industrial and medical, and the list can be used as a reference for creating 4D-printed sensors and actuators.

Design/methodology/approach: The smart materials used in 4D printing are discussed, and a description of each material is given, including its principle, applications and areas of use.

Findings: We have discovered a large number of different materials that are sensitive to moisture and have identified those that are most essential for use in 4D printing.

Research limitations/implications: According to the results of this research, the moisture-sensitive materials used in 4D printing have very limited use and application, and the majority of these materials are still in the research and development stage.

Originality/value: This review article provides researchers interested in using smart materials to exploit 4D printing in the industrial and medical fields, as well as in many other disciplines, with a means to identify the most widely used and prevalent moisture-sensitive materials.

Keywords: Additive manufacturing, 4D printing, Shape-memory materials, Smart materials, Moisture-responsive

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MATERIALS

1. Introduction

In traditional manufacturing, several procedures are required to turn raw materials into finished items, including planning and executing many manufacturing processes. This process takes a long time, is labour-intensive, and drives up production costs. Additive manufacturing allows us to rapidly-produce a broad range of objects, even those with complex designs. These technological advancements have been classified into the following seven groups: Selective Laser Sintering (SLS), Fused Deposition Modelling (FDM), Direct Metal Laser Sintering (DLMS), Directed Energy Deposition (DED), material jetting, sheet lamination and binder jetting. Time, money, and manufacturing steps may

all be saved by streamlining this process. Three-dimensional printing has recently gained attention for its usage in producing functional components for a wide range of products.

Bone, organs, and body parts are just some of the plastic objects that have shown promising results when constructed using 3D printing technology. Through computer-aided design and pre-operative simulation, we have come to the point where we can 3D-print plastic bones in precise dimensions for individual patients. The medical field, the food business, electrical components, aerospace, and soft robotics are just a few of the places where these technologies have found a use. Professor Skylar Tibbits is credited with first using the word "4D printing" when speaking at the MIT Conference. He explained what he meant by "4D printing": "Using the 3-D printer in the creation of objects that could transform their form whilst they are eliminated from the 3-D printer". The phrase "4D printing" describes a revolutionary approach that incorporates phase change materials (PCMs) with traditional 3D printing processes.

Due to their interactions with their surroundings, the shape of these PCMs may change over time. This causes shifts in the characteristics of its constituents, spawning the existence of a 4th dimension, the time. The three most prominent types of phase change materials are known as "shape memory materials" (SMMs), "self-healing materials," and "metamaterials". The phrase "shape memory materials" (SMMs) are those that can "self-organize" or "self-assemble" in response to an external stimulus. Self-healing materials, as their name implies, have the potential to mend themselves anytime damage or defect presents itself by replacing the damaged or defective area with a whole new one. The term "metamaterials" refers to man-made substances that possess characteristics that cannot be found in naturally occurring substances.

The investigation of "smart materials" that make use of polyvinyl chloride (PVC) is one of the most recent developments in this area of research. The researchers made a 3D-printed PVC with shape-memory effects investigated the material's structural characteristics. The findings point to the possibility of useful shape-memory effects for PVC in 4D printing applications.

In addition, the researchers have discovered a method for 4D printing that makes use of shape-memory polymers (SMPs) with continuous carbon fibre reinforcement. Because of its high strength-to-weight ratio and shape memory qualities, the newly developed material may be used in various fields, including the aerospace, automotive, and biomedical sectors. As one of the most promising functional materials, SMPs have been shown to have the potential to incorporate the fourth dimension.

SMPs may be made to adapt their form or characteristics in response to variations in humidity. This is helpful in places like greenhouses and grain silos where humidity levels must be precisely managed for plant growth and food safety. SMPs, for instance, may be used to make humidity-sensitive sealing for silos, ensuring that no moisture will get in and ruin the grains. Adjustable plant supports that react to variations in humidity using SMPs are a great way to ensure that greenhouse plants get the care they need. Improved agricultural practices and greater food security may be achieved by using SMPs' humidity-response impact. Humidity-sensitive materials might benefit from this technique, but it is not yet commercially viable due to its high price and the inability to scale it up [1-7]. In this article, we well discover that the most frequent 4D printing smart materials are moisture-sensitive.

2. Cellulose

Cellulose is a sustainable material that has recently drawn the interest of scientists due to the possibility that it might be used in producing films that are sensitive to moisture. As a result of the water vapour absorbing and releasing processes that take place on the surface of these films, they can fold and unfold reversibly. Zhang et al. have created a moisture-responsive film that can stand independently out of sustainable cellulose. Initially, the cellulose was altered by stearoyl moieties, which resulted in the production of cellulose stearoyl esters (CSEs) with different degrees of substitution (DSs). CSE films with a DS of 0.3 were sensitive to the presence of moisture, in contrast to CSE films with DSs of 1.3 or 3. Because of the water vapour absorbing and releasing processes that take place at the film's surface, the films having a CSE of 0.3 can fold and unfurl reversibly within a local moisture gradient. Films that react to moisture while having a nonwetting exterior that may undergo continual morphing and shape-shifting on the water with fast bending and unbending were produced by spray-coating CSE3 nanoparticles (NPs) over CSE 0.3 films. These films were developed by spray-coating CSE3 nanoparticles (NPs) over CSE 0.3 films. Combination moisture and temperature responsiveness was seen in dual-layer films that had one layer of CSE0.3 and one layer of CSE3. Because different mechanical resistances are encountered at different thicknesses of CSE 0.3 film, the minimum degree of bend that may be achieved can be adjusted accordingly. This makes the degree of bend possible to start on the thinner side (Fig. 1) [8].

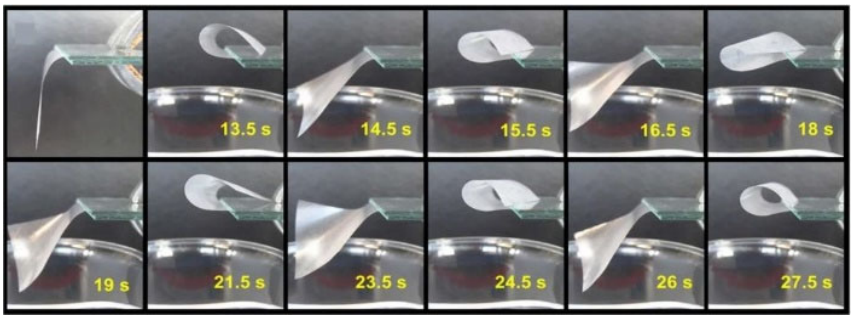

Fig. 1. Characteristics of CSE films

Table 1.
Measurement of the degree of polymerisation and the synthesis and characterisation of CSEs [8]

No	samples	status	Stearoyl chloride	DS[a]	DP_W[b]	DP_n[b]	DP_W[b]/ DP_n[b]	yield
1.	$CSE_{0.3}$	homogeneous	1 mol/mol AGU	0.3	862	185	4.65	99.3%
2.	$CSE_{1.3}$	homogeneous	2mol/mol AGU	1.3	213	65	3.25	98%
3.	CSE_3	heterogeneous	6 mol/mol AGU	3	430	210	2.04	98%

Figure 1 is a comparison of the properties of CSE 0.3, CSE 1.3 and CSE 3 films using a width of 21.2 ± 1.6, 20.6 ± 1.6 and 20.3 ± 2.2 µm, each in order. One side of the film is mounted on glass plates; when 37 degrees Celsius of warm water was placed beneath the film, the moisture-responsive motions occurred instantly. The relevant Table 1 contains data on the synthesised CSEs described in this investigation [8].

The DS for each CSE may be calculated according to the elemental analysis. Number-averaged degrees of polymerisation (DPW and DPn) for the CSEs are also included in the table. It is important to note that a refractive index (RI) detector was used to precisely measure the DP of CSE 0.3 because of its solubility in DMF/LiCl solution. This table most likely contains extensive data on the characteristics of the CSEs synthesised and described in this analysis [8].

Cui et al. developed artificial muscles in a hydrogel with a tendril-like structure by integrating tunicate cellulose nanocrystals (TCNCs) into polymeric networks through host-guest interaction. This allowed for the creation of artificial tendons. The hydrogel muscles increased their actuation rate in response to the stimuli while simultaneously displaying actuation strain and maintaining their shape. The trigger qualities of hydrogel muscles vary depending on their chirality, tension, twisting rate, and transient shape, as shown in Figure 2. The biomedical sector has many opportunities thanks to hydrogels because of their high water content and the fact that they can flex like genuine muscles [9].

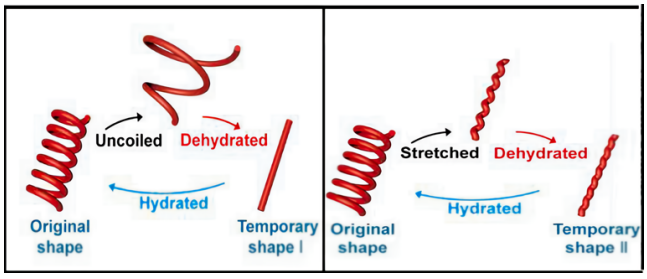

Fig. 2. Hemochloric hydrogel behaviour

Regarding printing responsive structures using 4D technology, Mulakkal et al. described the development and physical characterisation (stability, swelling potential, and rheology) of the cellulose-hydrogel composite to demonstrate its applicability. The carboxymethyl cellulose (CMC) hydrocolloid with integrated cellulose pulp fibres was used to make an ink that has a high total cellulose content and an efficient dispersion of fibres inside of the hydrogel matrix, as shown in Figure 3. A resistive humidity sensor with excellent sensitivity and linearity was developed by covering the cellulosic paper with carboxylic acid functionalised carbon nanotubes (CNTs). This is the most useful use of cellulose [10,11].

Figure 3 present a stimuli responsive cellulosic pulphydrogel composite ink was developed and the petal architecture fabricated using this ink could deploy to flat configuration upon hydration and recover from drying [10].

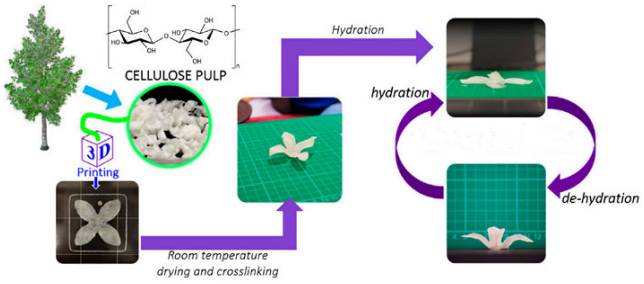

Fig. 3. A stimuli responsive cellulosic pulphydrogel composite ink

3. Silk fibroin films

Silk fibroin films have distinctive actuation properties, which may be modified by adjusting the ratio of water to ethanol in the vapor generator. These properties can be used to create a variety of effects. Ganesan et al. demonstrated that the multivapor responsive actuation is entirely reversible and bidirectional by making use of regenerated silk fibroin sheets in their experiment. In a film consisting of a single layer of silk fibroin, it is possible to achieve a multi-vapor response. The silk fibroin films buckle upward in reaction to the presence of water and ethanol vapor, but they maintain their pliability when they are exposed to air. Confirmation that the film shrunk because of vapor pressure may be obtained by straightforward testing using silica gels that had varied degrees of hydration. They are focusing on how the quantity of water that is present in the regenerated silk fibroin films impacts the overall efficiency with which they may be utilized to conduct actuation. This is because the amount of water that is present may have a significant impact. Notably, in conditions of higher humidity, the actuation efficiency of ethanol vapor improves compared to that of water vapor, and vice versa. The researchers proved that they were able to control the amplitude, direction, and velocity of the actuation by altering the percentage of water to ethanol in the vapour generator. In addition to this, the actuation capacity of the film may be fully muted by choosing the correct water-to-ethanol ratio in a binary combination. This comes as a good extra benefit. The vapour pressure of water significantly impacts the amplitude of the actuation, in contrast to the impact that the vapour pressure of ethanol has, which is to reduce the amplitude. A continuous undulating wavy motion is shown using the one-of-a-kind actuation features of multivendor-responsive homogenous single-layer silk fibroin films. Within the field of biomedicine, silk fibroin may be used in several different ways to accomplish various goals. This technology can be utilizedutilised in various fields, including bone tissue engineering, eye regeneration, nerve regeneration, skin tissue engineering, cartilage regeneration, vascular tissue engineering, spinal cord tissue engineering, gene therapy, and biological drug delivery [12,13].

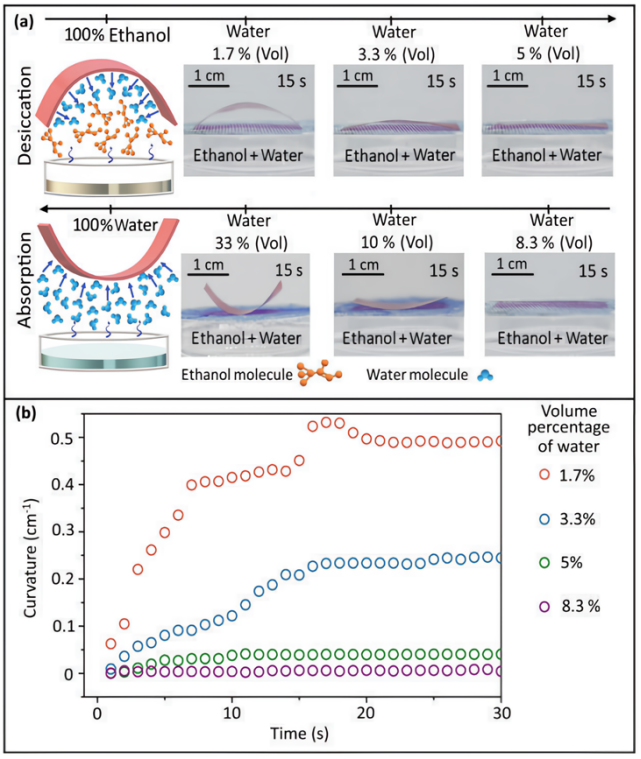

Fig. 4. Silk fibroin film actuation in response to binary water and ethanol vapour mixtures

The response of a silk fibroin film to binary mixes of ethanol and water is shown in Figure 4a, where the film's actuation behaviour is shown to vary with the mixture's ethanol concentration. Film bowing upwards when exposed to ethanol indicates a considerable increase in water content. Figure 4b shows the silk fibroin films were exposed to vapours from a binary combination of water and ethanol at concentrations of 1.7, 3.3, 5, and 8.3%, and their curving changed with time [12].

4. Smart polyurethane (PU)

Because it can be produced from materials other than petroleum, polyurethane (PU) is considered to have a lower impact on the environment. The formation of PU results from the combination of isocyanate functional groups and

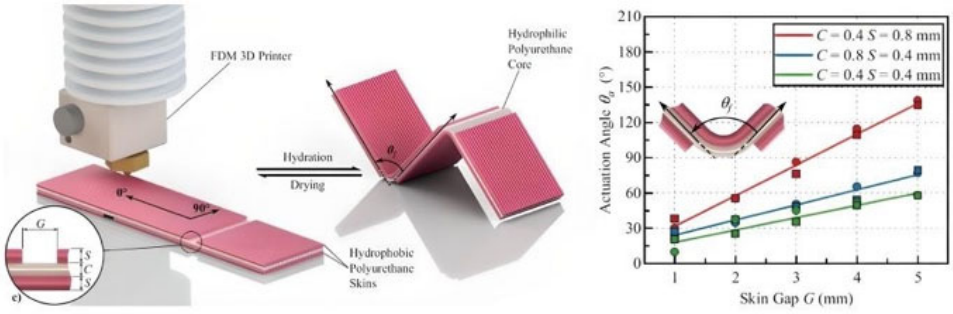

Fig. 5. 3D printed moisture-responsive polyurethane elastomer

polyol groups. The diisocyanate and the chain extender are the two components responsible for forming the hard segments. Polyol, on the other hand, is responsible for creating flexible segments that enhance the PU and elasticity. Shape memory PU (SMPU) Polyols may be produced from either fossil fuels or renewable resources, and considerable advancements have been achieved in 3D and 4D printing using smart PU composites. Polyols can be created from both petroleum and natural resources. Even if the majority of printed PU or SMPU composites are still in prototype form, there is reason to believe that they will play an important role in producing functioning things in the future, notably in electronics and biomedical engineering. On the other hand, PUs get their actuation reaction force from the desorption or sorption of moisture [14,15].

Origami structures consisting of three layers, each having a polyurethane elastomer skin and a polyurethane hydrogel core, were created by Baker et al. using 3D printing. It was necessary to fabricate discrete localized holes in the elastomeric skin to construct active hinges. The result of the hydration-induced shape shifts was the formation of a variety of intricate origami fold patterns. As shown in Figure 5, the geographical distribution of hinges was the primary factor in determining these patterns [16].

Figure 5 shows an origami-inspired trilayer structure folding upon hydration (core from polyurethane hydrogel and skins from polyurethane elastomer) [17].

5. Polyethylene glycol diacrylate (PEGDA)

Polyethylene glycol diacrylate, often known as PEGDA, is a substance that reacts to the presence of moisture and has been put to use in various applications, one of which is the creation of hydrophilic membranes. Chan et al. effectively grafted PEGDA onto a microporous polypropylene membrane by using UV light and benzophenone as a photoinitiator. This process took place in the presence of UV light. According to the contact angle measurements, the surface modification turned what was formerly a hydrophobic polypropylene membrane into a more hydrophilic one. In response to an increase in humidity, the PEGDA membrane grafts expanded to a greater extent (Fig. 6). Because of this membrane's sensitivity to moisture, it may be more effective in preventing diseases liquids would carry it than otherwise. In response to increased relative humidity, grafted PEGDA membranes showed signs of expansion. However, the membrane's receptivity to water may boost its effectiveness in warding off pathogens carried in liquid form [18].

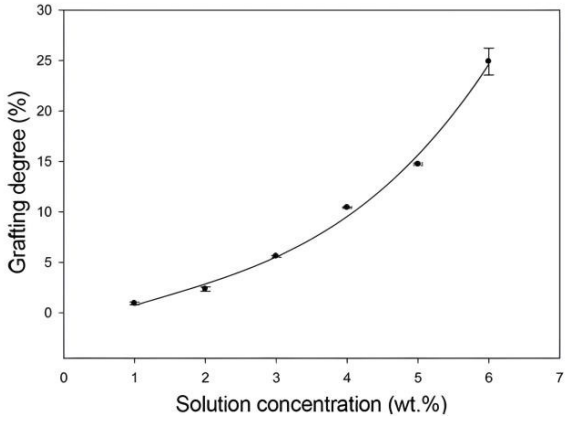

Fig. 6. Effect of solution concentration on the grafting degree of PEGDA

6. Poly (N-isopropylacrylamide-co-acrylic acid) (pNIPAM-AAc)

Poly(N-isopropylacrylamide-co-acrylic acid), often referred to as pNIPAM-AAc, is a well-known smart material that finds use in various applications, including microgripper joints. This material is famous for its reversible actuation,

Table 2.
pNIPAM-AAc soft-hydrogel parameters before and after enzymatic crosslinking and with atypical hinge designs

No	Specification	pNIPAM-AAc soft-hydrogel	Enzymatically Crosslinked pNIPAM-AAc soft-hydrogel	pNIPAM-AAc soft-hydrogel with Unconventional Hinge Designs
1.	Mechanical Stability	Moderate to Low	High	High
2.	Strength	Moderate to Low	High	High
3.	Overswelling Prevention	Limited	Effective	Effective

which can be performed by changing the saturation point via temperature changes. Breger et al. used gradient crosslinked pNIPAM-AAc soft-hydrogels throughout the manufacturing process of their microgripper joints. The saturation point may be altered, which permits reversible actuation, by either heating or cooling the water in which the gripper is submerged. This is done so that the gripper can be used in either direction. Altering the temperature of the water will result in the opposite of the desired effect.

The mechanical stability and strength of pNIPAM-AAc soft-hydrogels are found to be significantly increased after enzymatic crosslinking, which is another method for preventing overswelling. In addition, using hinges with unconventional designs is yet another method for preventing overswelling [19,20].

There is a clear improvement in the mechanical properties of pNIPAM-AAc hydrogels after enzymatic crosslinking, as shown in Table 2, which compares the properties of the hydrogels before and after crosslinking and also shows the effect of crosslinking on swelling and mechanical properties.

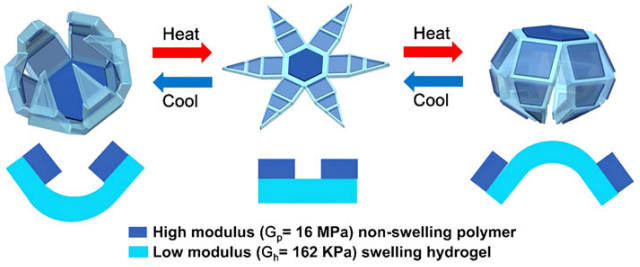

Fig. 7. The reversible self-folding of pNIPAM-AAc soft microgrippers

Figure 7 is a simplified illustration of the temperature-induced self-folding of pNIPAM-AAc soft microgrippers. When the temperature drops below 36 degrees Celsius, water is absorbed by the pNIPAM-AAc, causing it to expand and push the microgripper open before closing oppositely, exposing its pNIPAM-AAc layer to the environment [21].

7. Double cross-linked polymer

A new kind of polymeric network that can sense and react to humidity has been created by Jiang et al.. Acid ether hydrogen bonds can undergo fast deformation in response to changes in humidity because of the extraordinary sensitivity with which they can detect even minute fluctuations in the relative humidity of their environment. Because of the stretch deformity made possible by the strong cross-linking of coordination compounds, reversible actuation may be made simpler and more easily achieved in response to variations in humidity. The structural integrity of the double-crosslinked polymer can be maintained despite the material's ability to be repeatedly bent and straightened out. In addition, if you wanted to fine-tune the trigger attitude produced by humidity, you would have to adjust the layer width. Applications in artificial muscles, soft robotics, and humidity-sensitive polymeric actuators may all benefit from this double-crosslinked polymer [22].

Figure 8a shows double cross-linked polymer bending quickly (thickness = 50 μm). If one put the film in a humid environment (relative humidity between 22 and 95 per cent), the polymer will curve away from the moisture. The Figure 8b is a schematic depicting the humidity-induced development of the double-crosslinked hydrogel displaying a swelling-ratio-gradient, plus solid ion liaison and stability Cross-linkers have a potential to improve the film's elasticity and stiffness, allowing it to straighten out after being bent as it dries [22].

8. Discussion

In recent years, moisture-responsive materials have attracted much interest due to the many potential uses they offer in various sectors, including biomedicine, soft robotics, and environmental monitoring, amongst others. Table 3 offers a comprehensive review and comparison of the moisture-sensitive materials that are most often utilised.

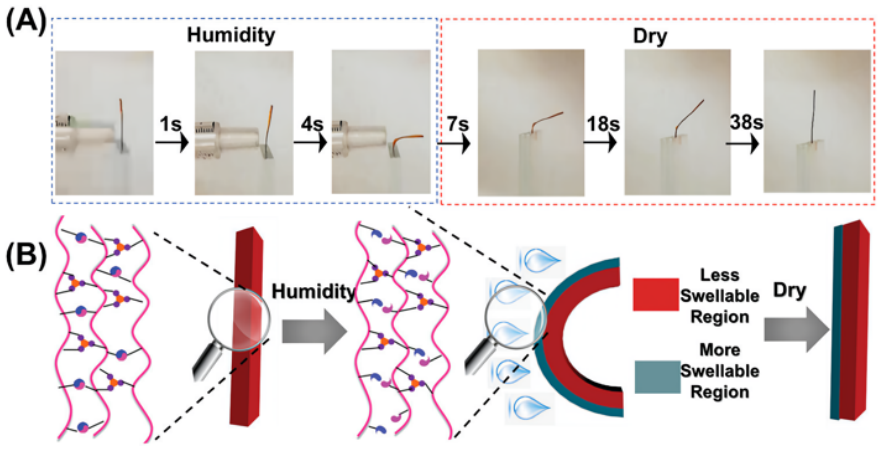

Fig. 8. Present The double cross-linked polymer reacts to changes in humidity

Table 3.
A survey of the most popular moisture-responsive materials and their uses in a variety of applications

No	Material	Advantages	Disadvantages	Applications
1.	Cellulose	Renewable, biodegradable, low cost	High degree of crystallinity, limited water responsiveness	Packaging, textiles, sensors
2.	Silk fibroin films	Biocompatible, biodegradable, high tensile strength	Limited water responsiveness, expensive	Biomedical applications, sensors
3.	Smart polyurethane (PU)	Excellent mechanical properties, high water responsiveness	Non-renewable, potential toxicity concerns	Actuators, drug delivery systems
4.	Polyethylene glycol diacrylate (PEGDA)	Highly tunable water responsiveness, simple modification process	Limited mechanical strength, potential toxicity concerns	Sensors, drug delivery systems
5.	Poly (N-isopropylacrylamide-co-acrylic acid) (pNIPAM-AAc)	Excellent water responsiveness, reversible actuation	Limited mechanical strength, potential toxicity concerns	Microgrippers, actuators
6.	Double cross-linked polymer	High water responsiveness, excellent mechanical stability	More complex synthesis process	Artificial muscles, soft robotics

Table 3 shows how cellulose, silk fibroin films, smart polyurethane, polyethylene glycol diacrylate, poly(N-isopropylacrylamide-co-acrylic acid), and double cross-linked polymer all fare when exposed to water. Response time, actuation strength, mechanical qualities, and prospective applications are only a few metrics used to evaluate and contrast the materials.

It is clear from Table 3 that different materials have different properties that make them more or less suited to certain uses. Silk fibroin films, for instance, are well-suited for usage in both sensors and actuators because of their short reaction time and high actuation strength. Cellulose, on the other hand, is well suited for biomaterials and textiles despite its delayed reaction time due to its superior mechanical characteristics.

The fact that the reaction time and actuation strength of different materials tend to be inversely related is also intriguing. When compared to PEGDA, whose response time is slower but whose actuation strength is higher, smart PU's are a good example. This trade-off emphasises the need to choose a material meticulously according to the needs of a certain application and the desired level of performance.

It is essential to keep in mind that the mechanical characteristics of the materials have the potential to significantly influence the applications to which they may be

put. For instance, since it has high levels of both elasticity and stiffness, a double cross-linked polymer is an excellent candidate for use in artificial muscles and soft robotics.

9. Conclusions

This article compiled a list of the most prevalent kinds of moisture-sensitive materials used in 4D printing today. Based on our results, it is clear that the lack of suitable materials is limiting advancement in this area. Engineering and research professionals attempting to create devices using moisture-sensitive materials may find this study an invaluable resource and reference.

We compared the moisture-sensitive materials that we found in our research and discussed each one separately to find the characteristics that set them different from the other types of materials. This study is a great resource for researchers/scientists and engineers working on developing moisture-responsive materials. Researchers may create more reliable and effective moisture-responsive devices by carefully evaluating the qualities of the materials and selecting the most suitable material for their particular purpose, which. That will assist in developing sensors, actuators, and soft robotics in the context of further technological research.

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