



4D printing of self-healing and shape-memory hydrogels sensitive to body temperature

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ABSTRACT

The development of thermoresponsive shape-memory hydrogels (SMHs) that combine robust mechanical properties, self-healing capabilities, and 4D printing potential holds great promise for advanced biomedical and smart material applications. Such hydrogels with trigger temperatures close to but below 37 °C are ideal for biomedical use. Despite their potential, developing SMHs that meet the right trigger temperature along with sufficient mechanical strength remains a significant challenge. We present here a simple strategy to create 4D-printed mechanically robust, self-healing and shape-memory supramolecular hydrogels with a Young's modulus and tensile strength of 51 ± 1 MPa, and 6.0 ± 0.3 MPa, respectively. They exhibit a trigger temperature between 32 °C and 40 °C that can be adjusted by the composition of the hydrogel network. The hydrogels are prepared by terpolymerizing hydrophobic, crystallizable hexadecyl acrylate (C16A), hydrophilic N,N-dimethyl acrylamide (DMAA), and methacrylic acid (MAAc) monomers in the presence of TPO photoinitiator using a commercial stereolithography (SLA) device without any solvent, or cross-linker. Strong hydrogen bonding interactions between DMAA and MAAc units contribute to the mechanical properties of the hydrogels by creating reversible cross-links while the hexadecyl side chains of C16A units further increase the mechanical strength by forming crystalline domains in the hydrogels with a melting temperature between 32 and 40 °C. All the hydrogels exhibit complete heat-induced self-healing and shape-memory functions due to their entropic elasticity. The successful 4D printing of shapes like a flower and a paper clip showcases the adaptability of these hydrogels for functional devices such as smart packaging and drug delivery systems.

1. Introduction

Four-dimensional printing (4D printing) represents a revolutionary advance in additive manufacturing technology, whereby smart polymeric materials are used to create three-dimensional objects in a layered fashion, enabling them to alter their shape or intrinsic properties in response to external stimuli over time [1,2]. This innovative approach combines the precision of additive manufacturing with the dynamic capabilities of responsive materials, thereby creating new opportunities for exploitation across a range of industrial sectors [3,4]. The smart materials utilized in 4D printing are capable of responding to a variety of stimuli, including temperature, pH, light, and electrical fields [2,5]. This enables the fabrication of adaptive and self-transforming structures. The

potential applications of 4D printing are numerous and diverse, spanning various sectors including healthcare, manufacturing, consumer goods, and construction [6–10].

Among the 4D printable polymeric materials, shape memory hydrogels (SMHs) are a fascinating category of smart materials that can be temporarily fixed in one or more programmed shapes and recover their permanent shape when exposed to suitable stimuli [11,12]. Over the past decade, SMHs have garnered significant research attention due to their potential applications in drug delivery matrices, tissue engineering scaffolds, soft actuators, and biomedical materials [13–16]. Unlike traditional shape-memory polymers, SMHs are water-rich, giving them soft and wet characteristics [17]. This makes them particularly suitable for biomedical applications, where they can be used as

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implantable materials.

Thermoresponsive SMHs have been extensively studied due to their rapid response rate, high shape fixity, and shape recovery ratios [18–20]. These properties are highly desirable for various applications, particularly in the biomedical field, where the materials must function effectively within the human body [21,22]. For biomedical use, thermoresponsive SMHs must meet two essential criteria, namely an appropriate temperature to trigger the shape-memory effect, and good mechanical properties [23,24]. The trigger temperature is crucial, as excessively high temperatures can cause tissue damage. In contrast, temperatures above 37 °C require an external heat source, complicating the application process and increasing the risk of overheating. Therefore, thermoresponsive SMHs with trigger temperatures close to but below 37 °C are ideal for biomedical applications. Despite their potential, developing SMHs that meet the right trigger temperature along with sufficient mechanical strength remains a significant challenge.

A considerable effort has been devoted in the past decade for the development of mechanically strong hydrogels capable of exhibiting thermoresponsive shape-memory effect at body temperature [25–28]. For instance, the inclusion of physical interactions such as crystalline domains or hydrophobic interactions in hydrogels creates thermoresponsive SMHs with significant mechanical strength [25,28]. However, achieving the shape-memory effect in such hydrogels at body temperature requires precise tuning of the composition and structure of the hydrogel network [18,25,28–30]. The hydrogel needs to be strong enough to maintain its shape under physiological conditions but also sensitive enough to respond slight temperature variations typical of body temperature. For instance, a temperature-responsive SMH prepared by introducing fluorocarbon hydrophobes into a hydrophilic network exhibits hydrophobic associations acting as reversible cross-links that endow the hydrogel with good mechanical properties and shape-memory effect [28]. However, the trigger temperature of this hydrogel was higher than the body temperature, around 45 °C. Hydrogels containing *n*-alkyl (meth)acrylate units with 18 carbon atoms on their side chains together with hydrophilic monomer units have been prepared by free-radical polymerization via bulk or micellar polymerization [18,31–33]. Although the hydrogels exhibited good mechanical properties, their trigger temperature was between 38 °C and 56 °C hindering their biomedical applications. It was shown that the trigger temperature of the hydrogels could be lowered by reducing the size of alkyl side chains of acrylates [6,34]. For instance, the copolymerization of acrylic acid and hexadecyl acrylate (C16A) produce hydrogels with a trigger temperature between 38 and 40 °C which is, however, still higher than the body temperature [6]. In this context, a strategy relying on hydrophobic and hydrogen-bonding interactions was also developed for preparing SMHs with body temperature responsivity and good mechanical performances [35]. The hydrogels prepared by copolymerization of acrylamide and 2-phenoxyethyl acrylate acting as hydrophilic, hydrogen bonding monomer, and hydrophobic comonomer, respectively, exhibit a maximum tensile strength of 5.1 ± 0.16 MPa and a good shape-recovery ratio at 37 °C [35].

We present here a simple strategy to create 4D-printed mechanically robust, self-healing and shape-memory supramolecular hydrogels with a Young's modulus and tensile strength of 51 ± 1 MPa, and 6.0 ± 0.3 MPa, respectively, exhibiting a trigger temperature between 32 °C and 40 °C that can be adjusted by the composition of the hydrogel network. 4D printed hydrogels were synthesized by terpolymerizing hydrophobic, crystallizable hexadecyl acrylate (C16A), hydrophilic *N,N*-dimethyl acrylamide (DMAA), and methacrylic acid (MAAc) monomers in the presence of diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO) photoinitiator using a commercial stereolithography (SLA) device without any solvent, or cross-linker. This approach avoids the potential toxic side effects of solvents and chemical cross-linkers, which are critical concerns for potential medical applications. Strong hydrogen bonding interactions between DMAA and MAAc units contribute to the mechanical properties of the hydrogels by creating reversible cross-links

while the hexadecyl side chains of C16A units further increase the mechanical strength by forming crystalline domains in the hydrogels with a melting temperature between 32 and 40 °C that could be adjusted by the amount of C16A in the reaction system.

2. Results and discussion

The terpolymerization of C16A, DMAA, and MAAc monomers in the presence of TPO as a photoinitiator was carried out by vat-photopolymerization based on stereolithography (SLA) resin printer. The reactions were carried out without any solvent, or chemical cross-linker to eliminate their potential toxic side effects. Two sets of gelation experiments were conducted. In the first set, the amount of C16A in the monomer mixture was fixed at 40 mol % while the composition of DMAA/MAAc mixture represented by the mole fraction of DMAA (x_{DMAA}) was varied. In the second set, the amount of C16A was varied at a fixed x_{DMAA} of 0.50. Hereafter, molar concentrations of C16A are abbreviated as %.

Prior to initiating a non-commercial resin printing process with a commercial printer, it is essential to optimize the printing parameters, including bottom exposure time, normal exposure time, motor speed, and light-off delay. The term “bottom exposure time” denotes the curing duration of the initial layers printed directly onto the steel platform. It differs from the normal exposure time due to the distinctive interaction between the resin and the platform. A prolonged bottom exposure time results in a more robust foundation for subsequent layers. The normal exposure time represents a crucial parameter in the curing process for layers beyond the initial base, as precise adjustments are essential to guarantee uniform curing across all layers. Furthermore, the speed of the motor must be carefully calibrated. High speeds can potentially result in breakages, whereas low speeds may impair effective detachment of the print from the resin vat. Additionally, the light-off delay allows the resin to settle before UV curing, enhancing the precision of the print.

In order to achieve the most optimal printing results for hydrogel monomers, a systematic adjustment of the key parameters was conducted using a dummy model, thereby ensuring the proper curing of the printed hydrogel structures. The results demonstrated that the normal exposure time was the most critical factor affecting printability. Fig. S1 illustrating the impact of varying exposure times on printed models demonstrates a discernible enhancement in print quality, particularly in the central regions, as exposure time increases. A comparison of the test prints allowed us to determine the optimal settings, which were found to be a bottom exposure time of 70 s, an exposure time of 10 s, a motor speed of $3 \text{ mm} \cdot \text{s}^{-1}$, and a light-off delay of 8 s. These settings provided the best balance of print quality and structural integrity for our hydrogel formulation, enabling the printing of various intricate structures, including a flower and a paper clip (Fig. S2).

The microstructure of 4D-printed hydrogels was investigated by recording FTIR spectra of dried hydrogel specimens. Fig. 1a, b shows the spectra of DMAA/MAAc copolymer, and C16A/DMAA/MAAc terpolymer, respectively, together with the spectra of the homopolymers. C=O stretching vibrations of MAAc units appear at 1703 and 1691 cm^{-1} while the absorption peaks for the DMAA units appear at 1600 and 1607 cm^{-1} for the copolymer and homopolymer, respectively (Fig. 1a). The characteristic peaks of C16A units in the terpolymer appear at 2850–2918 cm^{-1} due to stretching vibrations of the alkyl groups, and at 1727 cm^{-1} due to the C=O stretching vibrations of esters. All the characteristic peaks of the monomer units can be detected in the terpolymer hydrogels. Indeed, the gel fraction W_g was found to be unity in both sets of experiments revealing that all the monomers in the reaction system are incorporated into the network structure. Fig. 1c presents the equilibrium water content EWC of the hydrogels for the 1st set (x_{DMAA} varied) and 2nd set of experiments (mol % C16A varied). Increasing x_{DMAA} at a fixed C16A content slightly increases the EWC of the hydrogels which is attributed to the higher hydrophilicity of DMAA as compared to MAAc. Indeed, the hydrophobicity of DMAA and MAAc

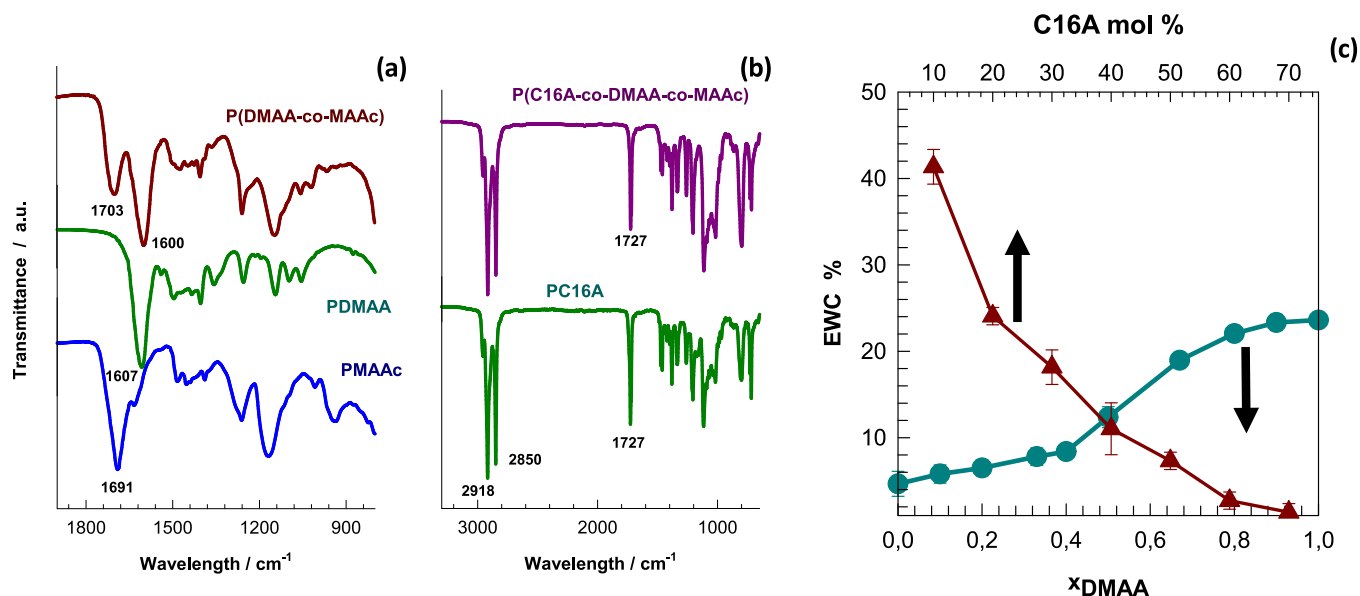


Fig. 1. (a, b): FTIR spectra of DMAA/MAAc (1:1 by mole) copolymer, and C16A/DMAA/MAAc (2:1:1 by mole) terpolymer hydrogels, respectively, after their drying, together with the spectra of the homopolymers. (c): The swelling degree of the hydrogels for the 1st set (x_{DMAA} varied) and 2nd set of experiments (% C16A varied) in terms of the equilibrium water content EWC.

in terms of normalized log P values are -0.29 and 4.82 , respectively [36], indicating more hydrophobic character of the latter monomer. Moreover, increasing C16A content significantly decreases the equilibrium water content due to increasing hydrophobicity of the network chains.

Fig. 2a–c shows stress–strain curves (a), and mechanical parameters (b, c) of the printed and equilibrium swollen hydrogels in water prepared at 40 % C16A but at various x_{DMAA} . In the absence of DMAA ($x_{\text{DMAA}} = 0$), i.e., C16A/MAAc copolymer hydrogel exhibits brittle behavior with a very low toughness W ($0.06 \text{ MJ}\cdot\text{m}^{-3}$), and fracture strain ϵ_f (2 %) while incorporation of DMAA units into the hydrogel network at a level of $x_{\text{DMAA}} = 0.5$ creates a brittle-to-ductile transition

accompanied with a significant increase in the fracture strain and toughness, 90 % and $2.2 \pm 0.2 \text{ MJ}\cdot\text{m}^{-3}$, respectively. Simultaneously, Young's modulus E of the hydrogels rapidly decreases as DMAA content is increased from 30 to 50 %. The significant effect of DMAA/MAAc composition on the mechanical performance of terpolymer hydrogels is attributed to the carboxyl group of MAAc and carbonyl group of DMAA acting as the H-bond donor and acceptor, respectively (Fig. 2d) [37]. This leads to the formation of 1:1 hydrogen-bonded complex between MAAc and DMAA units of the hydrogels [37]. Previous works show formation of hydrogen-bonded clusters of copolymers in MAAc/DMAA hydrogels which are strengthened by the hydrophobic α -methyl groups of MAAc units [36,38]. The polymer-rich clusters within the hydrogel

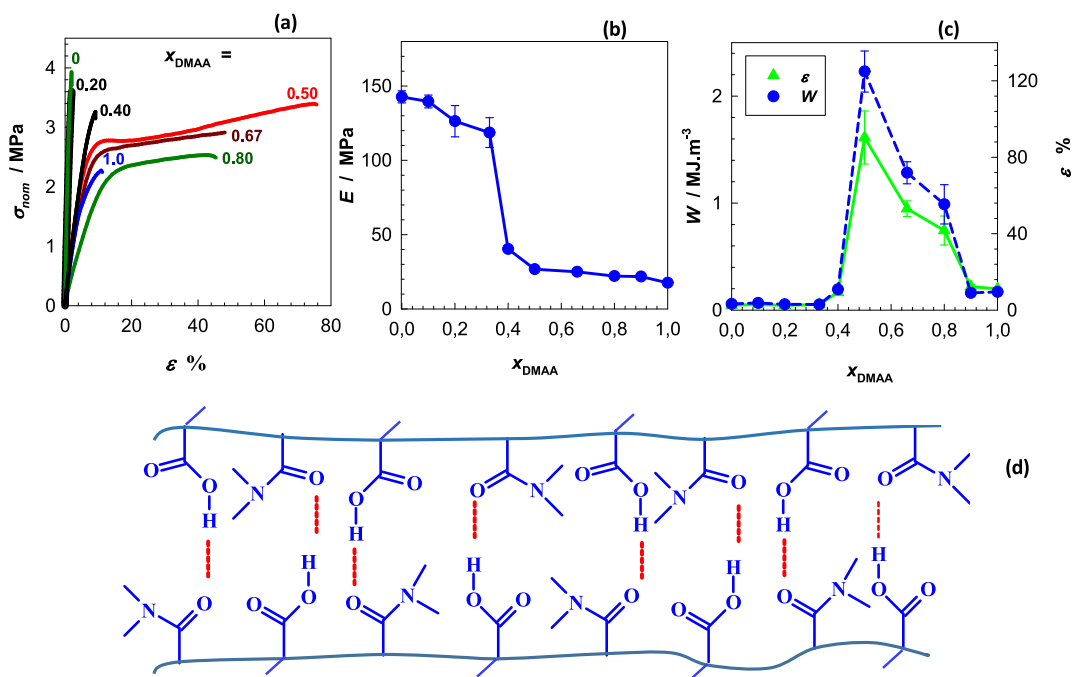


Fig. 2. (a–c) Stress–strain curves (a), and mechanical parameters (b, c) of the hydrogels prepared at various x_{DMAA} as indicated. C16A = 40 %. (d) Scheme presenting H-bonding interactions between MAAc and DMAA segments in the hydrogels.

undergo a sacrificial rupture when subjected to stress which helps to dissipate energy, preventing the hydrogel from breaking down completely. Thus, multiple hydrogen-bonds between MAAc and DMAA units create tough hydrogels, and the toughness reaches a maximum value at equimolar ratio of MAAc - DMAA units.

The presence of H-bonding interactions between MAAc and DMAA segments in the hydrogels was also reflected by their solubility in aqueous solutions of urea which is a hydrogen bonds breaking agent. For instance, MAAc/DMAA (1:1) copolymer hydrogels prepared in the absence of C16A were insoluble in distilled water for at least two weeks while they could easily be dissolved in 7 M aqueous urea solution. This indicates existence of strong H-bonding interactions between DMAA and MAAc units withstanding dissolution in water. Moreover, terpolymer hydrogels containing 10 % C16A units disintegrated within a few days while standing in 7 M urea solution, whereas those containing larger amounts of C16A exhibited a higher degree of swelling in the same solution as compared to water (Fig. S3). For instance, EWC of the hydrogel containing 20 % C16A was 24 ± 1 and 72 ± 1 % in water and 7 M urea solution, respectively, at 25 °C after two weeks, indicating partial dissolution of the network chains in urea solution. All these findings reveal presence of H-bonding interactions contributing to the cross-link density of the hydrogels.

Because the hydrogels prepared in the 1st set of experiments contain a fixed amount of C16A, their melting T_m and crystallization temperatures T_{cry} as well as the degree of crystallinity f_{cry} remained unchanged at 35.7 ± 0.5 °C, 25 ± 1 °C, and 15 ± 6 %, respectively, independent on DMAA/MAAc composition. In contrast, increasing C16A content in the 2nd set of experiments significantly increased the transition temperatures and the crystallinity of the hydrogels. Fig. 3a, b presents heating and cooling DSC scans of the hydrogels prepared at $x_{DMAA} = 0.50$ and at various C16A contents. The intensity of the melting peak increases and

the peak temperature shifts to a higher temperature as the C16A amount is increased indicating increasing stability of the crystalline domains. T_m and T_{cry} increase from 31.8 ± 0.5 to 40 ± 1 °C, and from 21 ± 1 to 25 ± 1 °C, respectively, with increasing C16A content from 10 to 70 % (Fig. 3c). The T_m 's recorded as 35.4 ± 0.8 °C, 36.6 ± 0.2 °C, and 37.9 ± 0.3 °C for the hydrogels containing 30, 40, and 50 % C16A, respectively, are ideal trigger temperatures for biomedical applications. Simultaneously, the degree of crystallinity f_{cry} increases from 0.8 ± 0.2 to 40 ± 3 % revealing increasing number of C16A units forming crystalline domains (Fig. 3d). Fig. 3e presents XRD scans of the hydrogels at various C16A contents. The broad peak at around $2\theta = 16^\circ$ is characteristic for amorphous polymers such as DMAA/MAAc (1:1) copolymer, as indicated by "0" in the figure. This peak gradually disappears with the incorporation of C16A units, and a sharp peak at 21.3° appears (0.42 nm d-spacing), which is a characteristic feature of the crystalline structure found in side-by-side packed paraffin-like alkyl chains such as hexadecyl side-chains of terpolymer network [33,39–41].

The presence of crystalline domains in hydrogels introduces a mechanism for switchable viscoelasticity, which can be controlled by temperature changes, particularly around the melting temperature of the crystalline domains. Fig. 4 presents the storage modulus G' and loss factor $\tan \delta$ of the hydrogels with various C16A contents subjected to a thermal cycle between 25 and 65 °C at a constant rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ plotted against time and temperature. The thermal cycle consists of five steps as indicated in the figure, namely,

- (i) isothermal at 65 °C,
- (ii) cooling from 65 to 25 °C,
- (iii) isothermal at 25 °C,
- (iv) heating from 25 to 65 °C, and
- (v) isothermal at 65 °C.

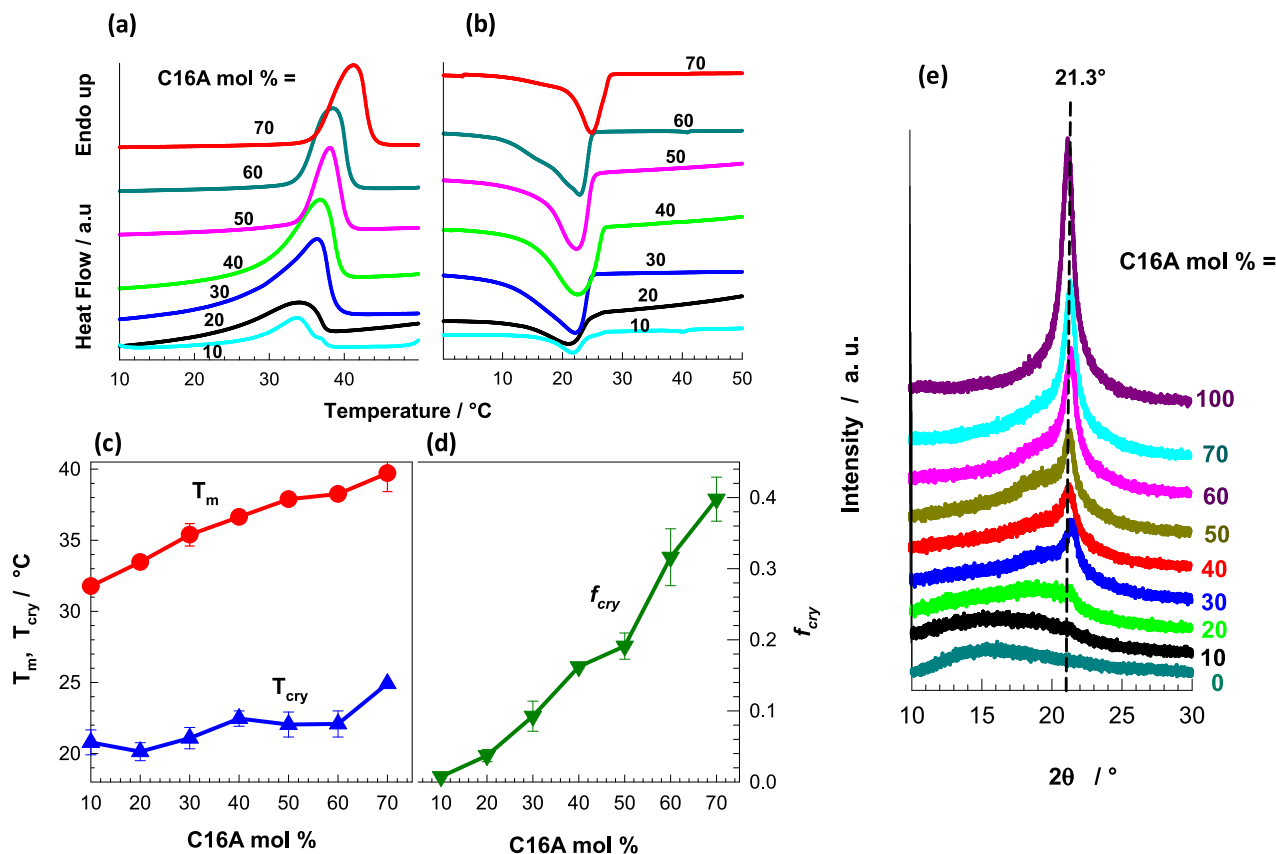


Fig. 3. (a, b) Heating (a) and cooling DSC scans (b) of the hydrogels prepared at various C16A contents. $x_{DMAA} = 0.50$. (c, d) T_m and T_{cry} temperatures (c), and crystallinity degree f_{cry} (d) of the hydrogels shown as a function of C16A %. $x_{DMAA} = 0.50$. (e) XRD scans of the hydrogels at $x_{DMAA} = 0.50$ and at various C16A %.

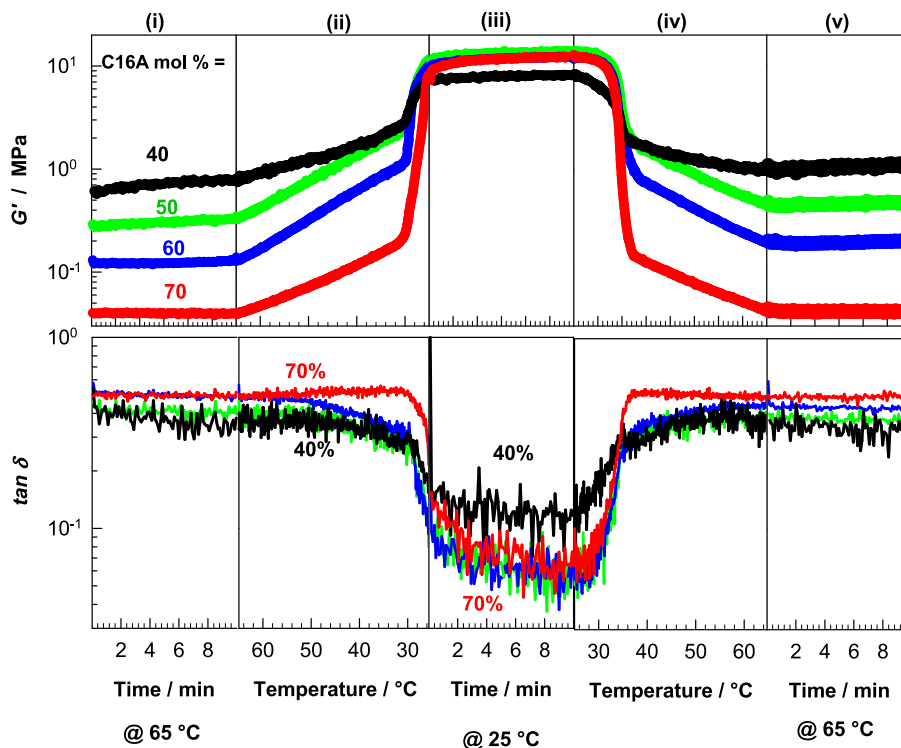


Fig. 4. The variations of G' and $\tan \delta$ of the hydrogels with various C16A % during a thermal cycle between 65 and 25 °C plotted against time and temperature. Heating and cooling rates = 5 °C·min⁻¹.

The hydrogels exhibit reversible changes in their viscoelastic properties, e.g., the storage modulus G' of the hydrogel with 70 % C16A 300-fold reversible changes between 40 kPa and 12 MPa when the temperature is varied between 65 and 25 °C. The magnitude of the modulus change increases with increasing C16A % which is attributed to the simultaneous increase in the crystallinity. Moreover, in the molten state, the hydrogel with a low amount of C16A, i.e., at a high DMAA/MAAc content exhibits higher modulus due to the strong H-bonding interactions (Fig. 2b) while an opposite behavior appears below T_m due to increasing crystallinity.

Fig. 5a,b presents stress-strain curves of the hydrogels with various C16A % at a constant strain rate ($\dot{\epsilon}$) of $1.9 \times 10^{-2} \text{ s}^{-1}$ together with their mechanical parameters, namely Young's modulus E , toughness W , fracture stress f_σ , and fracture strain f_ϵ . The hydrogels with > 30 % C16A exhibit distinct yielding behavior represented by a loss of tensile stress at a low strain due to the rapid crack growth immediately after crack initiation. The yielding behavior of the hydrogels gradually disappears above 50 % C16A which is accompanied with reduced mechanical properties. Moreover, the mechanical parameters of the hydrogels show a bell-shaped curve when plotted against C16A content with a peak at 50 % C16A. For instance, the toughness of the hydrogels 8.2-fold increases with increasing amount of C16A from 30 to 50 % while further increase in C16A content to 70 % reduces the toughness to its initial value. The maximum modulus, toughness and fracture stress achieved at 50 % C16A are $51 \pm 1 \text{ MPa}$, $8 \pm 1 \text{ MJ}\cdot\text{m}^{-3}$, and $6.0 \pm 0.3 \text{ MPa}$, respectively, at which the hydrogel sustains $166 \pm 12 \%$ stretches. We may attribute the bell-shaped behavior to the competition of factors that affect the cross-link density of the hydrogels which is determined by H-bonding interactions and crystalline domains. As seen in Fig. 2b, c, the mechanical parameters of the hydrogels depend on the composition of MAAc/DMAA mixture. Increasing x_{DMAA} above 40 % significantly reduces the modulus of the hydrogels at a fixed C16A content of 40 % revealing formation of weaker H-bonding interactions. In contrast, increasing C16A content leads to an increase in the degree of crystallinity and hence in the modulus of the hydrogels. The competition of

these two opposite effects on the modulus results in the appearance of a maximum at 50 % C16A content.

The stress-strain curves of the hydrogels exhibited strain rate dependence, as seen in Fig. 5c for the hydrogel with 50 % C16A. The yield stress σ_y increases while the fracture strain ϵ_f decreases with increasing strain rate $\dot{\epsilon}$ from 0.95×10^{-2} to $4.54 \times 10^{-2} \text{ s}^{-1}$. This behavior, which is typical for tough physically cross-linked hydrogels [42], is due to the decreasing relaxation time of the network chains as $\dot{\epsilon}$ increases. Thus, the network chains are more elongated at a given strain as $\dot{\epsilon}$ is increased, leading to higher yield stresses σ_y , and facilitating breaking of the H-bonds at lower strains, and hence decreasing elongation at break [31,42]. Assuming that the polymer segments exceed the energy barrier at the yield point, Eyring theory gives a linear relationship between the yield stress σ_y and the logarithm of the strain rate $\dot{\epsilon}$ by [43–45],

$$\sigma_y = \frac{2kT}{V_a} \ln\left(\frac{\dot{\epsilon}}{\dot{\epsilon}_0}\right) + \frac{2E_a}{V_a} \quad (1)$$

where V_a is the activation volume representing the volume of the polymer segments that move together as a unit during the yielding process. ϵ_0 is a constant pre-exponential factor, E_a is the activation energy, and kT is the thermal energy. According to Eq. (1), σ_y linearly increases with $\ln(\dot{\epsilon})$ with a slope yielding the activation volume V_a . The filled symbols in Fig. 5d represent σ_y vs. $\dot{\epsilon}$ data in a semilogarithmic plot of two independent measurements conducted on different specimens with 50 % C16A while the solid lines are the best fitting to Eq. (1) leading to an activation volume (V_a) of $2.1 \pm 0.1 \text{ nm}^3$. For comparison, the experimental data reported in the literature for semicrystalline copolymer hydrogels based on DMAA/C18A and AAc/C16A units are also shown in Fig. 5d by the open symbols [6,31,32]. From the slopes, the average activation volume V_a for the copolymer hydrogels was found to be $12 \pm 1 \text{ nm}^3$ which is about 6-fold larger than the terpolymer hydrogels. This suggests activation of smaller species in terpolymer hydrogels, like polymer-rich aggregates rupturing under stress by

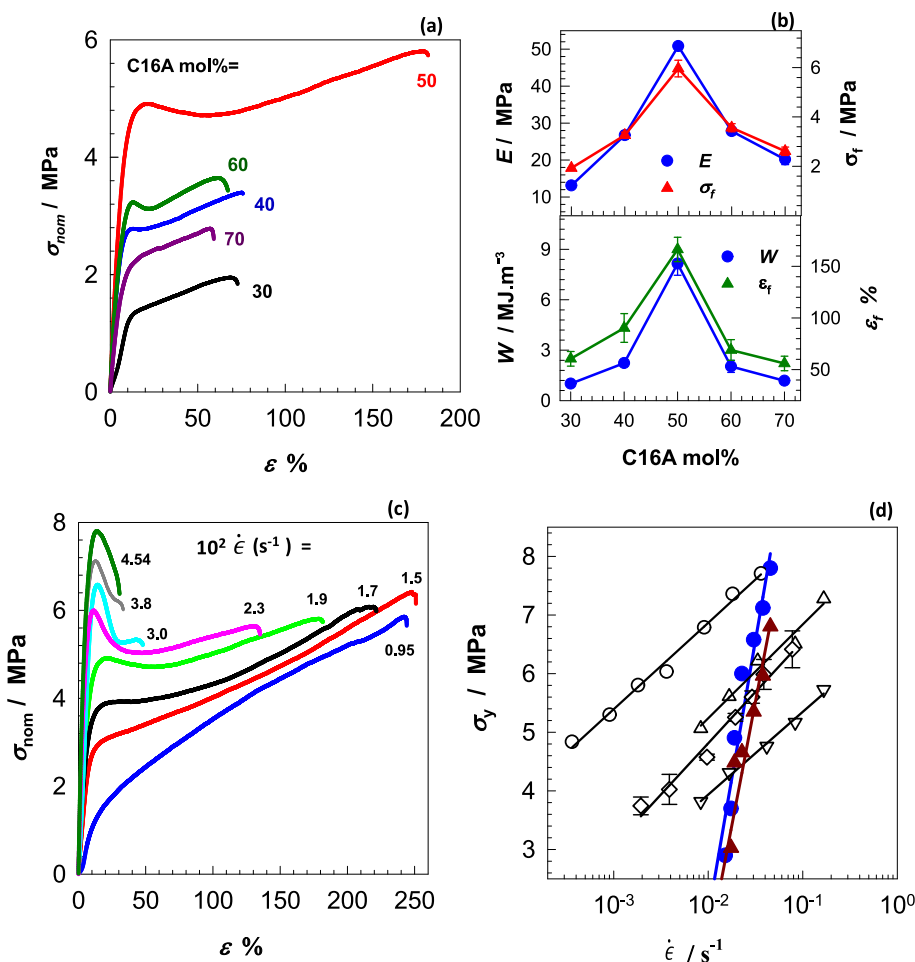


Fig. 5. (a, b) Stress-strain curves (a) and the mechanical parameters (b) of the hydrogels containing various amounts of C16A. $\dot{\epsilon} = 1.9 \times 10^{-2}$ s⁻¹. (c) Strain-rate dependence of the stress-strain curves of the hydrogels. C16A = 50 %. (d) σ_y vs. $\dot{\epsilon}$ data of the hydrogels in a semilogarithmic plot. The filled symbols are data of the present work while the open symbols were taken from ref. [6] (circles), ref. [32] (triangles up), ref. [32] (triangles down), and ref. [31] (diamond). The solid lines are the best fitting to Eq. (1).

dissipating energy. This also suggests existence of stronger H-bonds in terpolymer hydrogels as compared to copolymer ones decreasing the size of activation volume.

All the hydrogels exhibited complete heat-induced self-healing and shape-memory functions due to their entropic elasticity. Fig. 6A presents a hydrogel specimen (60 × 10 × 2 mm) after cutting into two parts, and coloring one of the parts (a), after bringing the cut surfaces together followed by immersing in water at 60 °C for 10 min (b), and after cooling to 25 °C to complete healing (c). The healed specimen can be stretched, bended or twisted without a failure (d–g). Additionally, complete healing was also observed at 60 °C even after three cuts were made in the hydrogel specimens. Moreover, the healing temperature was crucial for recovering the original properties of the hydrogel. Below the melting temperature T_m of the crystalline domains, the cut ends of the specimens did not adhere to one another, resulting in no healing. In contrast, at temperatures above T_m , such as 60 °C, complete healing was observed. To quantify the healing efficiency, the hydrogel specimens mentioned above were subjected to the tensile tests under identical conditions. The solid and dashed curves in Fig. 7a show stress-strain curves of virgin and healed hydrogels, respectively, with 50 to 70 % C16A while the inset present the healing efficiencies with respect to the modulus f_E , fracture stress f_σ and strain f_ϵ . A healing efficiency of 100 % with respect to the modulus is observed indicating a complete recovery of the virgin microstructure. The healing efficiency with respect to the fracture stress is around 80 % while the efficiency further decreases when fracture strain is considered. This could be related to the difficulty in coinciding

the cut ends of the hydrogel specimens. The healing mechanism of the hydrogels is based on the reversible transition between semicrystalline and flexible states of the network chains depending on the temperature. In addition, the dissociation and reformation of intermolecular hydrogen bonds may also contribute to the self-healing efficiency of the hydrogels. For example, heating a damaged region of the hydrogel above T_m of its crystalline cross-links significantly reduces its stiffness so that the hydrogel becomes much softer and more flexible in the damaged region. This reduction in stiffness occurs because heating above T_m causes the crystalline cross-links to melt, and intermolecular hydrogen bonds to dissociate, disrupting the structured network that provides rigidity and strength, thereby dramatically altering the mechanical properties of the hydrogel in the heated region due to the entropically most favorable coiled conformation of the amorphous chains. When the hydrogel is cooled below T_m , the crystallizable groups that were released during heating reassemble or recrystallize in the affected area. This reformation of crystalline cross-links allows the hydrogel to regain its original mechanical properties, including stiffness and strength, effectively restoring the hydrogel's integrity and functionality.

The images in Fig. 6B illustrate shape-memory behavior of a hydrogel specimen with 50 % C16A. Heating the specimen to 65 °C provides melting of its crystalline domains so that it can easily be bended to create a bended-shape. Cooling the specimen to 25 °C followed by removing the force fixes the temporary shape due to the locking of the bended chain conformation. The original (permanent) shape of the specimen can be recovered by re-heating it to 65 °C providing breaking

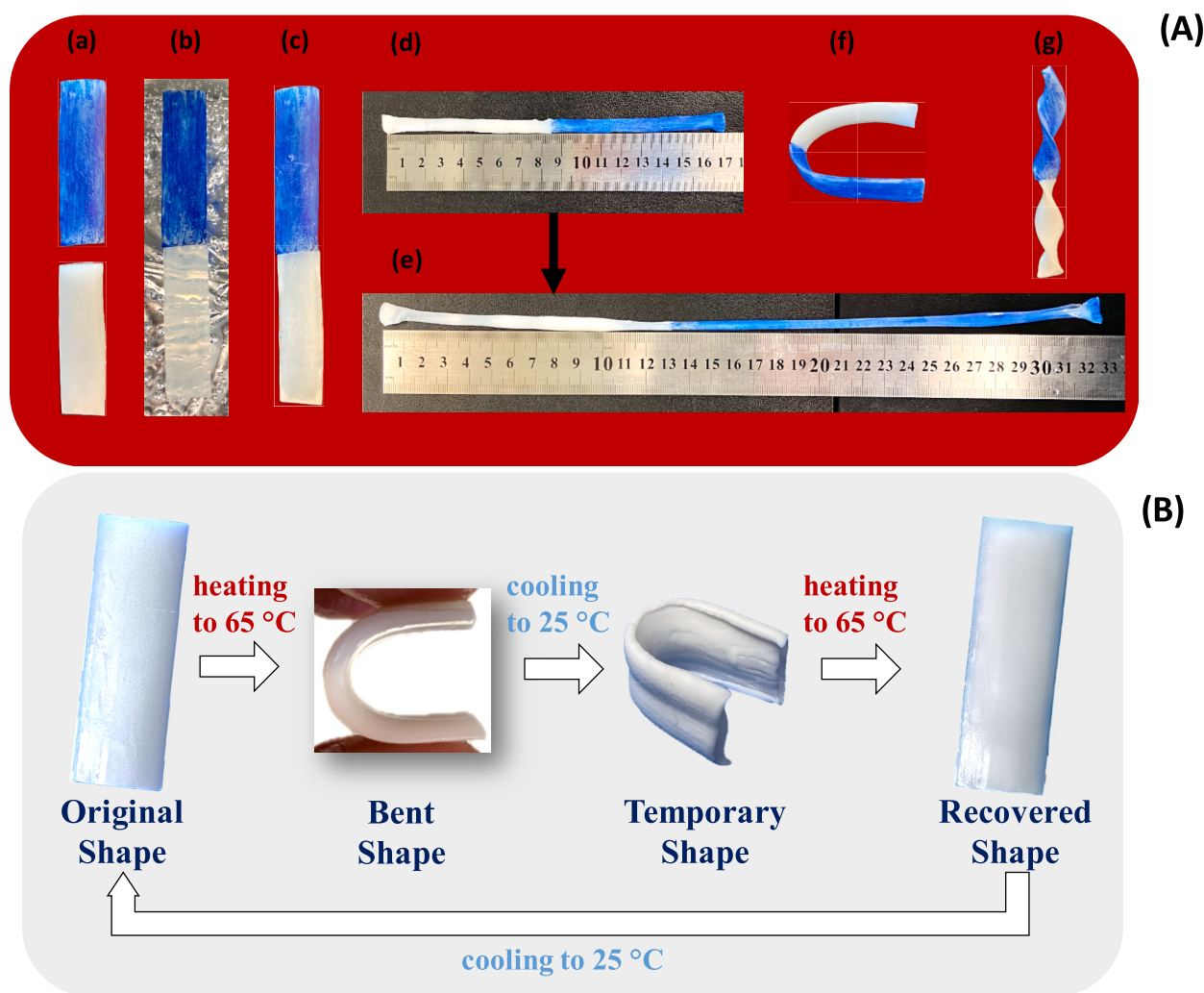


Fig. 6. (A) Images of a hydrogel specimen with 70 % C16A demonstrating its self-healing function. The images show the specimen after cutting into two parts (a), after bringing the cut surfaces together followed by immersing in water at 60 °C for 10 min (b), and after cooling to 25 °C for complete healing (c). The healed specimen can be stretched, bended or twisted without a failure (d–g). (B) The images of a hydrogel specimen with 50 % C16A illustrating its shape-memory behavior.

of the locks, followed by cooling to room temperature. The shape-memory behavior of the hydrogels with 40 to 70 % C16A was estimated quantitatively by a simple bending recovery test. The shape-fixity ratio $R_f(\theta)$ was found to be complete for all hydrogels studied. Fig. 7b shows the temperature dependence of the shape-recovery ratio $R_r(\theta)$ of the hydrogels. Except the hydrogel with the lowest C16A content of 40 %, they all exhibit a complete shape-recovery between 35–38 °C which increased with increasing C16A content due to simultaneous increase in T_m . The shape-memory effect in hydrogels can be explained by the presence of reversible physical cross-links such as H-bonds, hydrophobic associations, and crystalline domains. At 25 °C, the physical cross-links limit the mobility of the network chains so that the programmed temporary shapes are fixed, whereas when heated to 35–38 °C, the polymer chains regain their mobility due to the dissociations of the physical cross-links leading to the shape-recovery. Thus, the physical cross-links in the hydrogels function as molecular switches that can either fix or release programmed temporary shapes in response to temperature changes. This is a key feature of the shape-memory effect observed in such hydrogels.

Finally, the 4D printing capabilities of hydrogels were successfully demonstrated through printing of a flower and a paper clip prior to the creation of a temporary program (Fig. 8). The flower shape was conceptualized with the objective of developing a controllable drug delivery system with potential medical applications. This design

exemplifies the capacity of the hydrogel to undergo a predefined transformation, which could be initiated by alterations in temperature. This property is particularly advantageous in medical scenarios where precise control over drug release is crucial, as it allows for the precise regulation of the rate and extent of drug release. On the other hand, the design of the paper clip was inspired by the field of smart packaging and/or smart tool applications. This design illustrates the potential of the hydrogel to be utilized in everyday objects that require adaptability and responsiveness to environmental conditions. In both instances, the hydrogels demonstrated an exceptional capacity to revert to their original configurations when subjected to typical body temperature, thereby exhibiting shape-memory characteristics (Video S1 and S2). This rapid response to temperature changes highlights the practical utility of these materials in real-world applications. These findings not only underscore the versatility and functionality of 4D-printed hydrogels but also open up new avenues for their application in fields ranging from medicine to smart packaging. The ability to design and fabricate objects that can change shape in response to environmental stimuli represents a significant advancement in material science and engineering. Future research could explore further customization of these hydrogels to enhance their responsiveness and expand their range of applications, potentially leading to innovative solutions in various industries.

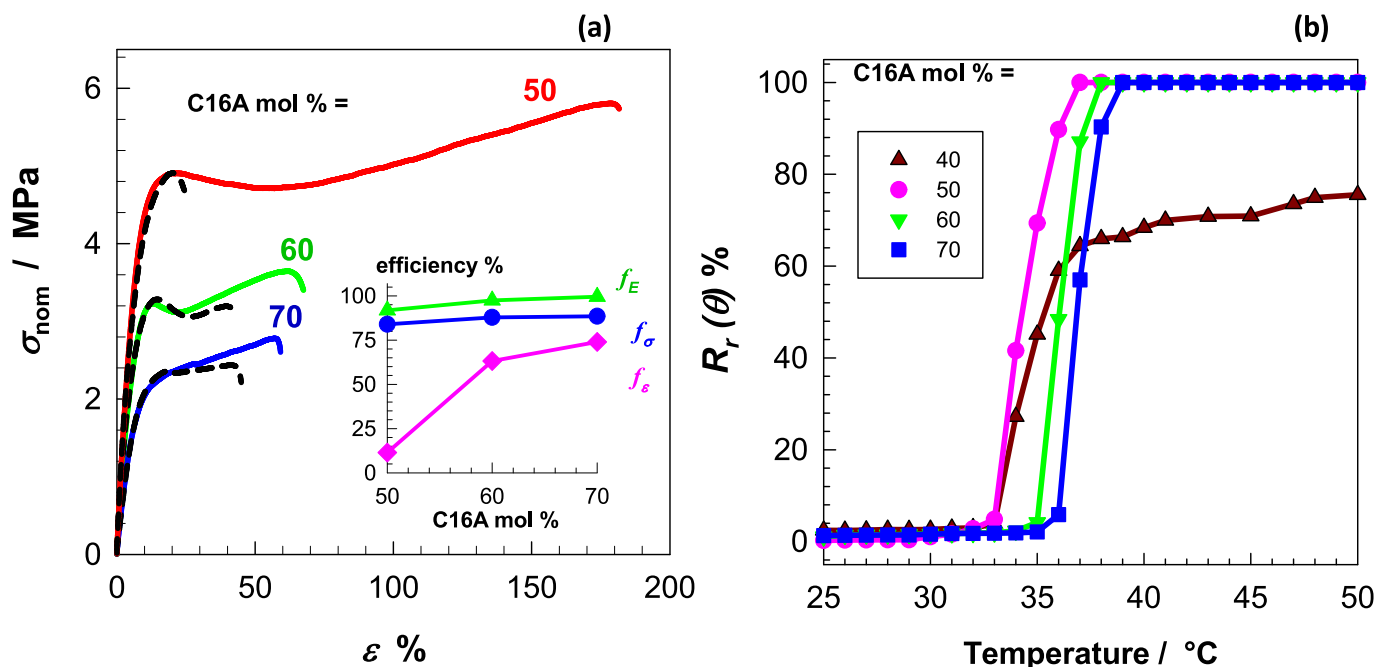


Fig. 7. (a). Stress–strain curves of virgin (solid curves) and healed hydrogels (dashed curves) with 50 to 70% C16A, as indicated. The inset presents the healing efficiencies with respect to the modulus f_E , fracture stress f_σ and strain f_ϵ plotted against C16A %. (b) The temperature dependence of the shape-recovery ratio $R_r(\theta)$ of the hydrogels.

3. Conclusions

Thermoresponsive SMHs with trigger temperatures close to but below 37 °C are ideal for biomedical applications. Despite their potential for various applications in biomedical field, developing SMHs that meet the right trigger temperature along with sufficient mechanical strength remains a significant challenge. We presented here a simple strategy to create mechanically robust, self-healing and shape-memory supramolecular hydrogels exhibiting a trigger temperature between 32 °C and 40 °C that can be adjusted by the composition of the hydrogel network. The hydrogels are prepared by terpolymerizing hydrophobic, crystallizable C16A, hydrophilic DMAA, and MAAC monomers in the presence of TPO photoinitiator using a commercial stereolithography device without any solvent, or cross-linker. This approach avoids the potential toxic side effects of solvents and chemical cross-linkers, which are critical concerns for potential medical applications. Strong hydrogen bonding interactions between DMAA and MAAC units contributed significantly to the mechanical properties of the hydrogels. For instance, in the absence of DMAA, i.e., C16A/MAAC copolymer hydrogel containing 40 % C16A exhibited brittle behavior with a very low toughness ($0.06 \text{ MJ}\cdot\text{m}^{-3}$), and fracture strain (2 %) while incorporation of DMAA units into the hydrogel network at equimolar amounts of MAAC created a brittle-to-ductile transition accompanied with a significant increase in the fracture strain and toughness, 90 % and $2.2 \pm 0.2 \text{ MJ}\cdot\text{m}^{-3}$, respectively. The significant effect of DMAA/MAAC composition on the mechanical performance of terpolymer hydrogels is attributed to the carboxyl group of MAAC and carbonyl group of DMAA acting as the H-bond donor and acceptor, respectively. Increasing amount of C16A units in the hydrogels further increased the mechanical properties of the hydrogels. The maximum modulus, toughness and fracture stress achieved at 50 % C16A are $51 \pm 1 \text{ MPa}$, $8 \pm 1 \text{ MJ}\cdot\text{m}^{-3}$, and $6.0 \pm 0.3 \text{ MPa}$, respectively, at which the hydrogel sustains $166 \pm 12 \%$ stretches. The melting temperatures T_m of the crystalline domains of hydrogels containing 30, 40, and 50 % C16A are 35.4 ± 0.8 °C, 36.6 ± 0.2 °C, and 37.9 ± 0.3 °C, respectively, which are ideal trigger temperatures for biomedical applications. Simultaneously, the degree of crystallinity f_{cr} increases from 0.8 ± 0.2 to $40 \pm 3 \%$ revealing increasing number of

C16A units forming crystalline domains. All the hydrogels exhibit complete heat-induced self-healing and shape-memory functions due to their entropic elasticity. 4D printing capabilities of the hydrogels are successfully demonstrated through printing of a flower and paper clip shapes which are conceptualized as drug delivery devices and smart packaging applications, respectively.

It is important to note that, aside from our recent study indicating that AAC/C16A hydrogels exhibit a trigger temperature between 38 and 40 °C, higher than body temperature [6], there are no prior studies in the literature specifically addressing C16A-containing self-healing or shape-memory hydrogels. Additionally, compared to AAC/C16A hydrogels, the terpolymer hydrogels we investigated offer a broader range of mechanical and thermal properties by varying the parameters of x_{DMAA} and C16A percentage.

4. Experimental section

4.1. Materials

Hexadecyl acrylate (C16A, TCI), *N,N*-dimethylacrylamide (DMAA, Sigma-Aldrich), and methacrylic acid (MAAC, Merck) monomers and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, Sigma-Aldrich) photoinitiator were used as received.

4.2. Preparation of hydrogels

The UV polymerization of the monomers in the presence of TPO photoinitiator was conducted at 23 ± 2 °C in the absence of a solvent and a chemical crosslinker. Since the hydrogels were comprised of both hydrophilic (DMAA, MAAC) and hydrophobic constituents (C16A), the effect of each group of monomers on hydrogel properties was evaluated by designing two sets of gelation experiments. Thus, there are primarily two experimental parameters, namely the mole fraction of DMAA in the DMAA/MAAC mixture (x_{DMAA}), and the mole percentage of C16A in the overall precursor mixture (C16A %) which are calculated by,

$$x_{DMAA} = \frac{n_{DMAA}}{n_{DMAA} + n_{MAAC}} \quad (2a)$$

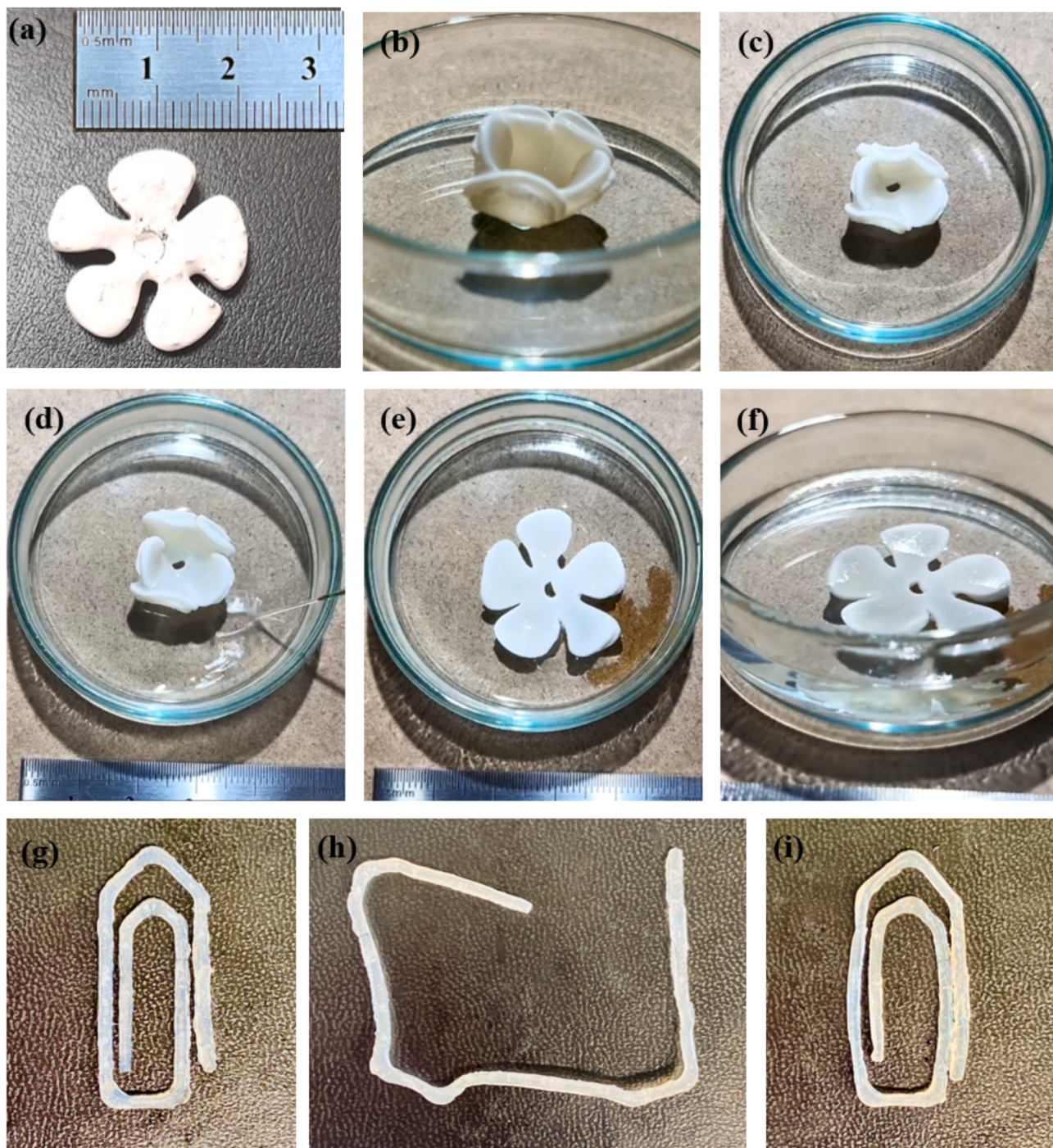


Fig. 8. (a–f). Real-time shape recovery images of a flower-shaped hydrogel with 50 % C16A. $x_{DMAA} = 0.5$. (a) 3D-printed flower in permanent shape, (b, c) programmed temporary shape view from the side (b) and up (c). (d) transition to permanent shape as dispensing hot water from a syringe, (e, f) recovered permanent shape view from up (e) and side (f). (g–i). 4D-printed paper clip-shaped hydrogel with 50 mol% C16A. $x_{DMAA} = 0.5$. (g) the printed shape, (h) programmed temporary shape, and (i) recovered permanent shape. We should note that it was difficult to achieve higher resolution print using our hydrogels.

$$C16A \% = \frac{n_{C16A}}{n_{C16A} + n_{DMAA} + n_{MAAc}} \times 10^2 \quad (2b)$$

where n_i is the mole of the monomer i . In order to determine the optimal hydrogel properties, the first set of gelation experiments was designed using various x_{DMAA} but at a fixed C16A content of 40 % as indicated in Table 1. In the second set of experiments, the amount of C16A was varied from 10 to 70 % at a fixed x_{DMAA} of 0.50 (Table 2). The polymerization of the monomers was carried out by vat-photopolymerization based on stereolithography (SLA) resin printer,

Creality Halot-One (405 nm wavelength). The liquid monomer mixtures composed of C16A, DMAA, and MAAc, together with TPO initiator were poured into vat section, followed by bulk polymerization under 405 nm laser beam on the printer's platform. Then, the cured hydrogel samples were delicately scraped from the platform with a steel spatula. A typical procedure to prepare hydrogels at $x_{DMAA} = 0.50$ and C16A = 50 % was as follows: The monomer mixture was prepared by first melting C16A (13.6 g) at 35 °C on a magnetic stirrer and then, it was mixed with the liquid DMAA (2.28 g) and MAAc (1.98 g) monomers. After adding TPO (358 mg, 2 wt% relative to total monomers) and cooling to 23 ± 2 °C,

Table 1

Preparation conditions of hydrogels at various mole ratios of DMAA to MAAC + DMAA (x_{DMAA}). C16A = 40 %.

x_{DMAA}	DMAA (g)	MAAC (g)	TPO (mg)
0.00	0	5.52	364
0.10	0.63	4.94	363
0.20	1.26	4.36	363
0.33	2.08	3.61	362
0.40	2.48	3.24	362
0.50	3.09	2.68	361
0.67	4.08	1.77	361
0.80	4.86	1.06	360
0.90	5.44	0.53	360
1.00	6	0	360

Table 2

Preparation conditions of hydrogels at various C16A contents. $x_{DMAA} = 0.5$.

C16A (%)	C16A (g)	DMAA (g)	MAAC (g)	TPO (mg)
10	5	7.52	6.53	381
20	8.28	5.53	4.81	372
30	10.6	4.13	3.59	366
40	12.3	3.09	2.68	361
50	13.6	2.28	1.98	358
60	14.7	1.64	1.42	355
70	15.6	1.11	0.97	352

printing was accomplished on a SLA printer at a layer thickness of 50 μm . The bottom exposure time and overall exposure time were set at 70 s and 10 s, respectively. After printing each layer, the printing program allowed the printed part to cool down for 5 s before printing the following layer. The printed specimens were then cured under 405 nm laser light for 10 min and then immersed in a large volume of water for two days to facilitate physical cross-linking. Besides printing, syringes were also used as templates to enable rapid and same-sized hydrogel preparation. After preparing the precursor, syringes were simply loaded with the liquid and placed into the printer's vat to be cured for 5 min using the printer's "Clean" function. The Clean function is commonly used to cure any residual resin within the vat, yet in our study, it also served as a UV-lamb to cure samples in syringes. Four repetitions of the Clean function were performed on the syringes, with alternating rotations to ensure full polymerization. Subsequent to the curing process, the syringes containing hydrogel samples were stored in a refrigerated environment at 2 °C overnight to remove the samples easily from syringes. The assessment of swelling and rheological properties was conducted on samples acquired from 1 mL and 20 mL syringes, respectively.

4.3. Characterization

The synthesized hydrogel samples were immersed in an excess amount of distilled water for 2 days to promote physical cross-linking via hydrogen bonds, prior to any characterization process. Swelling measurements were conducted using a minimum of three samples, and the standard deviation was calculated accordingly. The as-prepared mass of the samples was recorded as m_0 and measured using an analytical balance before immersing in water. After immersing samples in excess water, the masses of the specimens were collected daily until they reached equilibrium, which took 2 days. After reaching equilibrium, mass of the swollen samples was recorded as m_{sw} . Afterwards samples were dried in an oven at 30 °C along 2 weeks under vacuum. Lastly, mass of the dried samples was recorded as m_{dry} . The equilibrium water content EWC of the hydrogels, and the gel fraction (W_g) which is the mass fraction of the incorporated monomers into the 3D network of the hydrogels were calculated as.

$$EWC = 1 - \frac{m_{dry}}{m_{sw}} \quad (3)$$

$$W_g = \frac{m_{dry}}{m_0 C_0} \quad (4)$$

where C_0 is the total concentration of the monomers in the polymerization mixture. The structure analysis of hydrogels was accomplished with Agilent Technologies Cary 630 Fourier-transform infrared spectroscopy (FTIR) spectrometer equipped with attenuated total reflection (ATR) accessory. The spectra were recorded in the wavenumber range of 4000–400 cm^{-1} . The measurements were conducted on five solid polymer specimens obtained after drying of the hydrogels, namely poly (C16A-co-DMAA-co-MAAC) terpolymer, poly(DMAA-co-MAAC) copolymer, poly(C16A), poly(DMAA), and poly(MAAC) homopolymers.

The thermal characteristics of hydrogels were evaluated using Perkin-Elmer Diamond DSC 4000 differential scanning calorimetry (DSC). During testing, nitrogen gas at a flow rate of 19.8 $\text{mL} \cdot \text{min}^{-1}$ was circulated through the cell to prevent sample interaction with the environment.

DSC analyses were carried out on hydrogels at their equilibrium swollen states in distilled water. The hydrogel specimens that were cut into pieces of around 10 mg were placed in an aluminum crucible and scanned at a rate of 5 °C $\cdot \text{min}^{-1}$ between heating-cooling cycles ranging from −20 °C to 80 °C. T_m and T_{cry} temperatures were determined from endothermic and exothermic peaks in the DSC curves, respectively. Melting enthalpies of C16A (ΔH_m) were calculated from the area under the melting peak while the fraction of crystalline domains (f_{cry}) caused by C16A was calculated using the equation,

$$f_{cry} = \frac{q_w w_{C16A} \Delta H_m}{\Delta H^0} \quad (5)$$

where w_{C16A} is the weight fraction of C16A, ΔH_m and ΔH^0 are the melting enthalpies of the specimen (in $\text{J} \cdot \text{g}^{-1}$) and 100 % crystalline C16A (149 $\text{J} \cdot \text{g}^{-1}$) [46], respectively, and q_w is the equilibrium weight swelling ratio with respect to dry state, i.e., $q_w = (1 - EWC)^{-1}$. The crystallinity of hydrogels was characterized by Bruker D8 Advance X-ray powder diffraction (XRD) instrument. For this purpose, swollen hydrogel samples were first dried at 30 °C for 2 weeks. They were then ground into powder form using a mortar and pestle. Eventually, powdered samples were put into XRD examination. Scanning of the samples was carried out between $2\theta = 0$ and 45°. XRD analysis was carried out on eight specimens, namely terpolymers with various C16A content between 10 to 70 wt%, and additionally poly(DMAA-co-MAAC) copolymer as a control group.

Rheological tests were conducted using Bohlin Gemini 150 rheometer (Bohlin Instruments, UK) equipped with a Peltier temperature control unit. A parallel plate 20 mm in diameter was employed during the tests. Water trap was also used to prevent solvent vaporization at elevated temperatures. Temperature-sweep oscillation tests were carried out to determine temperature sensitivity of the hydrogels during a thermal cycle. Disc-shaped specimens of 20 mm diameter and 1 mm thickness were placed between the rheometer's parallel plates. Rheometer was then programmed to conduct a cooling-heating cycle between 65–25 °C at a fixed angular frequency (ω) of 6.3 rad/s and strain amplitude (γ_0) of 0.1 %. The thermal cycles were conducted at a constant heating-cooling rate of 5 °C $\cdot \text{min}^{-1}$.

The mechanical properties of printed hydrogels equilibrium swollen in water were examined using uniaxial tensile testing on a Zwick Roell Z0.5 TH universal testing equipment with a 500 N load cell. The tests were performed on dog-bone-shaped specimens printed in accordance with the International Organization for Standardization (ISO 527) standard. Each test was carried out at 23 ± 2 °C, and all specimens were water-swollen hydrogels. The nominal stress (σ_{nom}) and strain (ϵ) of the printed hydrogels were recorded with Zwick/Roell equipment's

testXpert III Testing Software. The tests were repeated for at least three times for each sample and standard deviations were calculated accordingly. Collected data were then plotted into σ_{nom} - ϵ graphs and used to establish the mechanical properties such as Young's modulus (E), fracture stress (σ_f), fracture strain (ϵ_f), toughness (W). The slope of the initial linear region of stress-strain curves between 2 and 6 % strain was chosen to determine E while σ_f and ϵ_f were calculated as the stress and strain values at the point of rupture, respectively. W was computed as the area under the stress-strain curves until the point of failure. During uniaxial tensile tests, the sample length was set as 23 mm and strain rate was fixed at $1.9 \times 10^{-2} \text{ s}^{-1}$. Tensile tests were also carried out at different strain rates to calculate the activation volume.

The healing efficiency of the hydrogels was determined using cut-and-heal tests conducted on rectangular-shaped hydrogel specimens ($60 \times 10 \times 2 \text{ mm}$). Each specimen was first cut in half and, after bringing the cut surfaces together, it was immersed in water at 60°C for 10 min to induce healing. The healing efficiencies with respect to the modulus f_E , fracture stress f_σ and strain f_ϵ were calculated from the stress-strain curves of virgin and healed hydrogels equilibrium swollen in water.

Shape memory property of hydrogels was evaluated using a bending test. The tests were conducted using rectangular-shaped ($40 \times 12 \times 1 \text{ mm}$) hydrogel specimens with 40, 50, 60, and 70 % C16A and $x_{DMAA} = 0.5$ under the same conditions. The specimens were first heated to 65°C in water. The rectangular shape of the specimen was bent at 65°C to an angle $\theta_0 = 180^\circ$, and then cooled to 25°C for a minute to maintain a temporary form. Bent rectangular samples were then gradually heated from 25 to 65°C , increasing one degree at a time. Meanwhile, after waiting five minutes at each temperature, the angle between the two edges was recorded as the recovery angle θ_r . Angular shape-recovery efficiency $R_r(\theta)$ and angular shape-fixity ratio $R_f(\theta)$ were calculated accordingly. $R_r(\theta)$ is defined as ability of the material to return back to its original shape while $R_f(\theta)$ is the indicator of the fixing ability of the switching domains of material. $R_r(\theta)$ and $R_f(\theta)$ were calculated as,

$$R_r(\theta) = \frac{\theta_d - \theta_r}{\theta_d - 180^\circ} \quad (6a)$$

$$R_f(\theta) = \frac{\theta_f - 180^\circ}{\theta_d - 180^\circ} \quad (6b)$$

where θ_d , θ_r and θ_f are deformed angle under load, recovery angle and fixed angle after un-loading, respectively.

CRediT authorship contribution statement

Gamze Aydin: Writing – original draft, Methodology, Investigation, Data curation. **Turdimuhammad Abdullah:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition, Conceptualization. **Oguz Okay:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

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

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Appendix A. Supplementary material

The following files are available free of charge: Fig. S1 (Printed dummy models with normal exposure times of 5, 6, 7, 8, 9, and 10 s.); Fig. S2 (CAD models and real image of the printed flower and paper clip using the hydrogel resin); Fig. S3 (Hydrogel specimens immersed in water and aqueous 7 M urea solution after one day). Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eupolymj.2024.113651>.

Data availability

Data will be made available on request.

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