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(54) Title: HEXADECYL ACRYLATE-BASED PHOTO-CURABLE RESINS FOR 4D PRINTING OF BODY TEMPERATURE RESPONSIVE HYDROGELS WITH SHAPE MEMORY AND SELF-HEALING PROPERTIES

(57) **Abstract:** The present invention relates to a photo-curable resin and its use in the additive manufacturing (three-dimensional printing) of hydrogels with shape memory and self-healing. The resin according to the invention comprises hexadecyl acrylate, one or more hydrophilic monomers and one or more photoinitiators. The resin cured by copolymerising the hydrophobic hexadecyl acrylate and the hydrophilic monomer under ultraviolet light forms a shape memory hydrogel. The resin is suitable for hydrogel production by vat photopolymerisation techniques at room temperature. The hydrogel according to the invention has the ability to return to a programmed shape and heal itself at temperatures close to human body temperature.

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HEXADECYL ACRYLATE-BASED PHOTO-CURABLE RESINS FOR 4D PRINTING OF BODY TEMPERATURE RESPONSIVE HYDROGELS WITH SHAPE MEMORY AND SELF-HEALING PROPERTIES

Technical Field

The present invention relates to a photo-curable resin and its use in the additive manufacturing (three-dimensional printing) of hydrogels with shape memory and self-healing.

Prior Art

The use of alkyl acrylate monomers forming long chains for the production of shape memory polymers is known in the art. However, the reaction of these monomers at high temperatures limits their use and requires specialised production equipment due to their high melting points.

Shape memory polymers can return to their initial shape by applying controlled conditions such as temperature after plastic deformation. Self-healing materials, on the other hand, can repair the damaged area and integrity damage such as tears by forming new bonds between the relevant surfaces.

Additive manufacturing methods can be used to create structures consisting of polymer-based materials with shape memory and self-healing. The production of shape memory or programmable materials by additive manufacturing methods is called four-dimensional (4D) printing. For the production of such materials, especially vat photopolymerisation techniques can be used, in which layers are formed by applying a deposition pattern created by a visible or near-visible wavelength light source to polymer precursors in liquid form in a pool. Examples of pool photopolymerisation techniques include stereolithography, microelectromechanically controlled projection systems such as DLP (digital light processing), continuous liquid interface production (CLIP), liquid crystal display controlled systems.

The document numbered CN107075015A discloses a branched polymer for use as a thickener in a surfactant system. The polymer may comprise a hydrophilic component selected from acrylic acids or acrylamides together with various alkyl acrylates including hexadecyl acrylate. The possible use of this molecule as a three dimensional printing material is also mentioned.

The document numbered JPH07292040A discloses a temperature-sensitive shape memory hydrogel. Exemplary embodiments disclose the use of stearyl acrylate and hexadecyl acrylate as the hydrophobic component and acrylic acid as the hydrophilic component. It is shown that low transition temperatures as low as 38 °C can be obtained in samples containing hexadecyl acrylate, and the variation of the transition temperature depending on the alkyl group chain length is mentioned. A particular composition containing 8 parts acrylic acid and 2 parts stearyl acrylate is also described. Since N,N'-methylenebisacrylamide was used as a crosslinker, the hydrogel obtained does not exhibit self-healing properties.

In the document titled "3D printing of shape memory hydrogels with tunable mechanical properties" (Shiblee, M. N. I., Ahmed, K., Khosla, A., Kawakami, M., & Furukawa, H. (2018). *Soft matter*, *14*(38), 7809-7817.), shape memory hydrogels and their three-dimensional printing by stereolithography are described. These hydrogels contain stearyl acrylate and lauryl acrylate as the hydrophobic components and dimethyl acrylamide as the hydrophilic component. Since N,N'-methylenebisacrylamide was used as a crosslinker, the hydrogel obtained does not exhibit self-healing properties.

In the document titled "Semicrystalline physical hydrogels with shape-memory and self-healing properties" (Okay, O. (2019). *Journal of Materials Chemistry B*, *7*(10), 1581-1596.), the use of n-alkyl acrylates, in particular n-octadecyl acrylates, for three-dimensional printing of shape-memory and self-healing hydrogels is described. The production of gels using octadecyl acrylate as hydrophobic monomer with acrylic acid, acrylamide, N-isopropylacrylamide and N-t-butylacrylamide in a molar ratio of 65 to 35 is described. It is stated that if octadecyl acrylate is replaced with dodecyl methacrylate at a molar ratio of 0.2%, the brittleness of the obtained hydrogel can be eliminated and the hydrogel exhibits necking behaviour.

Objects of the Invention

The object of the present invention is the development of a resin for use in the additive manufacturing of hydrogels with shape memory and self-healing.

Another object of the present invention is the development of a photo-curable resin suitable for the additive manufacturing of hydrogels by additive manufacturing methods, in particular by stereolithography. It is also intended that the resin should have a transition temperature close to room temperature so that no further heating is required during additive manufacturing.

A further object of the present invention is the development of a resin for use in the additive manufacturing of a hydrogel whose transition temperature between weak and strong gel forms is close to body temperature, and which is therefore capable of self-healing and assuming a programmed shape at these temperatures.

The invention also aims to develop an additive manufacturing method based on the use of said resin and a hydrogel thus obtained.

Brief Description of the Invention

The resin according to the invention comprises hexadecyl acrylate, one or more hydrophilic monomers and one or more photoinitiators. The resin preferably comprises acrylic acid as the hydrophilic monomer. The resin cured by copolymerising the hydrophobic hexadecyl acrylate and the hydrophilic monomer under ultraviolet light forms a shape memory hydrogel. The resin is suitable for hydrogel production by vat photopolymerisation techniques at room temperature.

The hydrogel according to the invention has the ability to return to a programmed shape and heal itself at temperatures close to human body temperature. The hydrogel obtained with the resin having a composition suitable for the preferred embodiments of the invention also exhibits necking behaviour.

Detailed Description of the Invention

The resin realised to achieve the objects of the present invention is described with reference to the attached figures.

Figure 1 shows the differential scanning calorimetry (DSC) graphs of some resins according to the invention, depicting the data obtained during heating (**a**) and cooling (**b**).

Figure 2 shows the FTIR graphs of some hydrogels according to the invention.

Figure 3 shows the differential scanning calorimetry (DSC) graphs of some hydrogels according to the invention depicting the data obtained during heating (**a**) and cooling (**b**).

Figure 4 shows the storage modulus (**a**) and loss factor (**b**) graphs of some hydrogels according to the invention.

Figure 5 shows the stress-strain curves of some hydrogels according to the invention.

Figure 6 shows the Young's modulus, breaking stress, strength graphs obtained according to the curves in Figure 5.

Figure 7 shows the stress-strain curves of some hydrogels according to the invention.

Figure 8 shows the yield strain graph obtained according to the curves in Figure 7.

Figure 9 shows the bending (**a**) and elongation (**b**) rate of return curves of some hydrogels according to the invention.

Figure 10 shows photographs of a hydrogel according to the invention in the state of plastic deformation and during restoration due to shape memory.

Figure 11 shows the stress-strain curves of some hydrogels according to the invention before cutting and after restoration (**a**) and the restoration efficiencies of the breaking stresses, elongations at break and Young's moduli obtained according to these curves (**b**).

Figure 12 shows the scanning electron microscopy (SEM) images of a hydrogel according to the invention before incision (**a1**), after incision (**a2**) and after healing (**a3**) and energy dispersive X-ray spectroscopy (EDX) maps before incision (**b1**), after incision (**b2**) and after healing (**b3**).

Figure 13 shows the differential scanning calorimetry curves of some hydrogels according to the invention.

Figure 14 shows the melting and crystallisation temperature graphs obtained according to the curves in Figure 13.

Figure 15 shows the stress-strain curves of some hydrogels according to the invention.

Figure 16 shows the Young's modulus, breaking stress and strength graphs obtained according to the curves with DMAA molar ratio of 0.5, 0.66 and 0.8 in Figure 15.

Figure 17 shows a schematic view of a resin according to the invention (**a**), a polymeric gel obtained with this resin (**b**) and a hydrogel according to the invention obtained by soaking the polymeric gel with water (**c**). The side chains formed in the hexadecyl acrylate units and the physical cross-links formed by them in water are shown by solid lines and the region where hydrophobic interactions take place is shown by dashed lines. Triangles indicate the photoinitiators.

The resin according to the invention essentially comprises hexadecyl acrylate (C16A), one or more hydrophilic monomers and one or more photoinitiators. The hydrophilic monomers and photoinitiators are selected from those miscible with hexadecyl acrylate.

Hydrophilic monomers can be selected from compounds such as acrylic acid (AAc), methacrylic acid (MAAc), N-N-dimethylacrylamide (DMAAm), 3-trimethylammonium propyl (meth)acrylamide, N-(3-(dimethylamino)propyl)acrylamide, n-propylacrylamide, n-tert-butylacrylamide and their mixtures.

In a preferred embodiment of the invention, acrylic acid is used as the hydrophilic monomer. Hexadecyl acrylate is mixed with acrylic acid in a ratio of 10 to 75% by mole, in particular in a ratio of 40:60.

The photoinitiators can be selected from among compounds such as 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TPO), 2,4,6-trimethylbenzoylpenylethoxyphosphine oxide, 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959), bis(2,4,6-trimethylbenzoyl)-phenylphosphinoxide (Irgacure 819), 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (Irgacure 907), 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (Irgacure 369), 2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one (Irgacure 379), 4-benzoyl-4'-methyl diphenyl sulphide (Chivacure BMS), 4,4'-bis(diethylamino)benzophenone (Chivacure EMK), 4,4'-bis(N,N'-dimethylamino)benzophenone and mixtures thereof.

The photoinitiators are mixed in the mixture of hexadecyl acrylate and hydrophilic monomer at 1.5 to 3.5 %, in particular at 2 to 3%, by weight of the monomer mixture.

Due to the use of hexadecyl acrylate, the resin according to the invention is in a molten state at temperatures close to room temperature. Thus, the resin can be used with common commercial additive manufacturing equipment without the need for further heating and temperature maintenance.

For the additive manufacturing of a hydrogel according to the invention, essentially, the process steps

- mixing of hexadecyl acrylate, one or more hydrophilic monomers miscible with hexadecyl acrylate and one or more photoinitiators miscible with hexadecyl acrylate,
- deposition of the mixture by a vat photopolymerisation technique,
- impregnating the deposited structure, i.e. the polymeric gel, with water

are performed. By impregnating the polymeric gel with water, a shape memory and self-repairing hydrogel is produced. For photo curing of the mixture, the light wavelength can be determined depending on the choice of photoinitiator and ultraviolet wavelengths are commonly used. Hydrogel production is preferably carried out using a mixture at 23±2 °C and vat photopolymerisation for printing. Photopolymerisation is carried out with irradiation in the wavelength range 360-480 nm.

The invention provides a hydrogel consisting of copolymers of hexadecyl acrylate and one or more hydrophilic monomers. The resulting hydrogel contains hydrophilic units together with hydrophobic units with a predominance of crystallised hexadecyl acrylate. Physical cross-links are established within the hydrogel. During the printing of polyacrylic acid-based self-healing and shape memory physical hydrogels, hydrophilic and hydrophobic monomers are copolymerised without a solvent in the presence of a photoinitiator. Subsequently, during swelling in water, i.e. water impregnation, the hexadecyl side chains in the hexadecyl acrylate units act as physical cross-linkers and strong hydrophobic interactions take place between the hexadecyl acrylate units, leading to the formation of a supramolecular hydrogel.

Exemplary embodiments of the invention using acrylic acid as a hydrophilic monomer and the experiments carried out in order to demonstrate the effectiveness of the resin according to these exemplary embodiments and the hydrogels obtained using this resin are described below.

Acrylic acid as hydrophilic monomer and diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (TPO) as photoinitiator were used together with n-hexadecyl acrylate. Samples 1-4 containing 20%, 30%, 40% and 50% hexadecyl acrylate by mole in the monomer mixture, respectively, and sample 5 containing 100% hexadecyl acrylate as a control were prepared. Firstly, hexadecyl acrylate was melted at 35 °C and then the determined amount of acrylic acid was mixed with the help of a magnetic stirrer. Then, TPO was added to the monomer mixtures at the rate of 2% by weight of the monomer mixture and the mixtures were cooled to 23±2 °C. These mixtures were deposited with stereolithography equipment to form 50 μm thick layers. The deposited material was cured with a 405 nm laser. During printing, the base layer was exposed to the laser for 70 s, the other layers for 10 s, and each layer was allowed to stand for 5 s before printing the subsequent layer. The printed samples were exposed to laser treatment for 10 min. The cured samples were immersed in plenty of water for 2 days to form physical cross-links. Each sample was immersed in approximately 150 mL of distilled water to absorb as much water as possible.

Measurements were carried out on liquid resin samples and printed hydrogel samples by diamond differential scanning calorimetry. For this purpose, the liquid resin samples were heated from 20 °C to 40 °C at a rate of 5 °C/min and cooled to 20 °C at the same rate. The printed hydrogel samples were heated from 0 °C to 80 °C at 5 °C/min and cooled to 0 °C at the same rate. The measurements were carried out in a nitrogenous environment to prevent the samples from reacting with the environment.

The melting and crystallisation temperatures of the resin obtained with hexadecyl acrylate and acrylic acid, whose melting temperatures are 17 °C and 14 °C, respectively, are below room temperature as shown in Figure 1. This allows additive manufacturing with the resin of the invention to be carried out without the need for specialised equipment having functions such as heating and thermal insulation.

Fourier transform infrared spectroscopy (FTIR) was used for characterisation of the printed hydrogels. FTIR plots of the poly(acrylic acid-co-hexadecyl acrylate) containing hydrogel obtained with various ratios of hexadecyl acrylate are shown in Figure 2. Here, the band corresponding to the stretching of carbonyl groups is around 1730 cm^{-1}, and the peaks corresponding to the carbon hydrogen bond stretching in alkyl groups are seen at 2854 and 2920 cm^{-1} values. The intensity increases with increasing hexadecyl acrylate ratio. No significant deviation is observed in the adsorption bands. This indicates that the interactions between acrylic acid and hexadecyl acrylate units of the copolymer are predominantly physical rather than chemical.

Using the enthalpy data obtained, the degree of crystallisation of the hydrogel samples was calculated by $f_{cry} = w_{C16A} \cdot \frac{m_s}{m_d} \cdot \frac{\Delta H}{\Delta H^o}$. In this formula, w_{C16A} his the weight fraction of hexadecyl acrylate, m_s is the weight of the water-impregnated sample, m_d is the weight of the dry sample, ΔH is the melting enthalpy of the sample, ΔH^o is the melting enthalpy of crystallised hexadecyl acrylate.

The equilibrium water content (*EWC*) of the samples is calculated as $EWC = \frac{m_s}{m_d} - 1$.

The temperature dependent phase change observed due to the crystallised hexadecyl acrylate units in the water soaked hydrogels was also demonstrated by differential scanning calorimetry. As seen in Figure 3 and Table 1, the melting temperature (T_m) increases from 38 °C to 40 °C and the crystallisation temperature (T_{cry}) decreases from 29 °C to 25 °C as the hexadecyl acrylate content increases. The interval between melting and crystallisation temperatures calculated as $\Delta T = T_m - T_{cry}$ is also shown in the table. By increasing the hexadecyl acrylate molar ratio from 20% to 50%, the degree of crystallisation, i.e. the proportion of hexadecyl acrylate fragments forming alkyl crystals, increases from 7.5% to 15%. However, the water content in the equilibrium decreases from 51% to 7%.

Table 1 – Melting and crystallisation temperatures, degree of crystallisation and equilibrium water content for various hexadecyl acrylate ratios

C16A (%mol)	T_m (°C)	T_{cry} (°C)	ΔT (°C)	f_{cry} (%)	EWC (%)
20	38.0±0.2	28.6±0.4	9.4	7.5±0.1	51±5
30	38.0±0.1	27±1	11	12±1	24±3
40	39.9±0.3	27±1	13	15±1	16±1
50	40.4±0.6	25±1	15	15±1	7±2

The rheological behaviour of the printed hydrogels was also evaluated by temperature-sweep oscillation tests. For this purpose, a disc-shaped sample with a diameter of 20 mm and a thickness of 1 mm was positioned between parallel plates and a cooling and heating cycle was applied in the range of 25-65 °C under an angular frequency (ω) of 6.28 rad/s and a strain amplitude of 0.1%.

The effect of temperature on the storage modulus (G') and loss factor ($tan\delta$) of the hydrogel is also shown in Figure 4. The hydrogel melting and crystallisation temperature ranges are also marked with dashed lines. The storage modulus increases with increasing hexadecyl acrylate content at temperatures lower than the melting temperature and decreases with increasing hexadecyl acrylate content at temperatures higher than the melting temperature. The most pronounced changes of the storage modulus were observed for samples containing 50% hexadecyl acrylate, where the storage modulus varied between 14 MPa and 8 kPa during the temperature change between 25 and 65 °C. Meanwhile, the loss factor varies between 0.04±0.01 and 0.5, consistent with the reversible transformation between hydrogels with strong and weak viscoelastic behaviour. The temperature dependent transition between strong and weak hydrogels with such a reversible storage modulus change indicates that the hydrogel according to the invention is suitable for soft robotics and 4D printing applications.

Stress-strain data were collected with dog bone shaped specimens in accordance with the ISO 527 standard and Young's modulus was also calculated using the stress-strain curves corresponding to 0.5-1% strain. According to these curves, the yield stress and strength of the sample were calculated. A constant strain rate ($\dot{\varepsilon}$) of $1.8\times10\text{-}2\ s^{-1}$ was applied to the samples. Figure 5 shows the stress-strain curves for samples with different hexadecyl acrylate ratios. Figure 6 shows the corresponding Young's modulus (E), breaking stress (σ_f) and strength (energy required for breaking) (W). The modulus of elasticity increases significantly with increasing hexadecyl acrylate content, reaching 216±8 MPa at 50 mol%. This increase indicates an increase in the number of crystallised units forming physical cross-links. Furthermore, a transition from brittle to ductile behaviour is observed in the printed hydrogels with decreasing hexadecyl acrylate content below 50 mol%. At 40 mol% and below, necking behaviour is also observed with high yield stress, which provides high durability. At this ratio, the brittle crystalline units break at the microscopic scale and dissipate energy, while the weak cross-links between the hydrophobic units maintain the integrity of the hydrogel.

The dependence of the physical cross-links in the hydrogel structure on the time scale of the mechanical tests is also seen in light of the stress-strain curves presented in Figure 7 for hydrogels containing 40 mol% hexadecyl acrylate at different strain rates. With increasing strain rate, Young's modulus, yield stress (σ_y) and stress at break increase, while the elongation at break decreases. This behaviour coincides with the physical hydrogel behaviour with high mechanical strength due to the formation and dissolution of cross-links. Figure 8 shows the yield strain as a function of strain rate. The yield strain can be modelled as $\sigma_y = \frac{2\,kT}{V_a} ln(\dot{\varepsilon}/\varepsilon_o) + \frac{2E_a}{V_a}$. Here, V_a is the activation volume, ε_o is the preexponential factor, E_a is the activation energy and kT is the thermal energy. Accordingly, the activation volume is found to be 12.6±0.3 nm^3 using the correct fit to the data presented in Figure 8. This indicates that side alkyl chain crystals are also activated during elongation.

In order to evaluate the hydrogels according to the invention in terms of their shape memory after elongation and bending, the samples in accordance with ISO 527 standard were extended to twice their initial length at 42 °C and the samples with dimensions of 30×20×1 mm were folded at 42 °C. After that, these samples were immersed in water at 25 °C under force to preserve these shapes. The samples were then heated to 50 °C at a rate of 1-2 °C per minute while the length (λ_d) and bending angle (θ_d) were monitored. The rate of return for elongation was calculated as $R_\lambda = \frac{2\lambda_o - \lambda_d}{\lambda_o}$ and for bending as $R_\theta = \frac{\theta_d}{180}$. The rates of return for elongation and bending are shown in Figure 9a and Figure 9b. It is seen that the ability to maintain the transient shape below the melting temperature also increases with increasing hexadecyl acrylate ratio. Except for the samples containing 20% hexadecyl acrylate by mole, all of the samples can return to their permanent shape in a narrow temperature range of 37-42 °C, close to human body temperature.

In order to demonstrate the effectiveness of hydrogels according to the invention in 4D printing applications, a robotic hand measuring 48×38×5 mm was also printed. A temporary shape was formed on the robotic hand by extending one finger and bending another finger at 45 °C and the robotic hand was cooled to 20 °C to maintain this shape. Then, the robotic hand was immersed in water at 43 °C to restore the initial shape. As shown in Figure 10, both the extended and bent finger returned to the initial shape in a short time.

In order to evaluate the self-healing ability of the hydrogels according to the invention, the samples were divided into two parts by cutting. Then the samples were kept at 65 °C for one day with the cut surfaces touching each other. After the samples reached room temperature, uniaxial tensile tests were performed.

In Figure 11a, the initial (pre-cutting) stress-strain curves for different hexadecyl acrylate molar ratios are presented with solid lines and the post-healing stress-strain curves are presented with dashed lines. The healing efficiencies of the respective breaking stresses, elongations at break and Young's moduli are also shown in Figure 11b. As can be seen, the healing efficiencies of stress at break and Young's modulus are above 90% for all hexadecyl acrylate ratios. The healing efficiency of elongation at break increases with increasing hexadecyl ratio.

The healing process was also observed by scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDX). For this purpose, an incision was made on a hydrogel sample containing by moles 40% hexadecyl acrylate and the healing of the incision site was monitored at 43 °C for 2 minutes. SEM images of the incision site before incision, after incision and after healing are shown in Figures 12a1, 12a2 and 12a3, respectively. EDX maps of the incision site before incision, after incision and after healing are shown in Figures 12b1, 12b2 and 12b3, respectively. In these maps, carbon atoms are marked with a dark colour and oxygen atoms with a light colour. As seen in Figures 12a3 and 12b3, even after a short period of time such as 2 minutes, a decrease in the thickness of the incision zone and the formation of a bridge in the region marked with an arrow are observed. In light of the EDX images, it appears that the homogeneous distribution of acrylic acid and hexadecyl acrylate units is also maintained during incision formation and healing.

Other exemplary embodiments of the invention using methacrylic acid and dimethylacrylamide as hydrophilic monomers are described below.

To obtain the resin, mixtures of 40% by mole of hexadecyl acrylate and 60% by mole of methacrylic acid and dimethylacrylamide were prepared, followed by the addition of 2.5% by weight of TPO to the monomer mixture. Mixtures of methacrylic acid and dimethylacrylamide were prepared in molar ratios of 0:1, 1:9, 1:4, 1:2, 1:1, 2:1, 4:1, 9:1, 1:0 (X_{DMAAm} = 1; 0.9; 0.8; 0.67; 0.5; 0.33; 0.2; 0.1; 0, respectively). In addition, resins containing hexadecyl acrylate from 10 to 75% (30, 40 and 50%) by mole (molar ratio of methacrylic acid and dimethylacrylamide 4:1) were also produced. The molar ratios of the monomers used in the resin are shown in Table 2.

Table 2 – Molar composition of the resin containing hexadecyl acrylate, methacrylic acid, dimethylacrylamide (TPO ratio is indicated by total monomer weight.)

C16A	MAAc	DMAAm	TPO
40	0	60	2.5
40	6	54	2.5
40	12	48	2.5
40	20	40	2.5
40	30	30	2.5
40	40	20	2.5
40	48	12	2.5
40	54	6	2.5
40	60	0	2.5
50	40	10	2.5
30	56	14	2.5

The differential scanning calorimetry curves of the hydrogels obtained by using resins with different methacrylic acid, dimethylacrylamide ratios and resins with different hexadecyl acrylate ratios with methacrylic acid, dimethylacrylamide molar ratio of 4:1 are shown in Figures 13a and 13b, respectively. The corresponding melting and crystallisation temperatures are also shown in Figures 14a and 14b. It is seen that the dimethylacrylamide doping has no effect on the thermal properties of the printed copolymer network. The melting and crystallisation temperatures do not change significantly with the composition ratio of hydrophilic monomers. The mean value of the melting temperature is 35.7±0.5 °C with a standard deviation of 1.4%.

The melting temperature of the sample with a ratio of methacrylic acid to dimethylacrylamide of 4:1 at around 35 °C is also close to human body temperature.

Stress-strain curves for hydrogels obtained using resins with different methacrylic acid, dimethylacrylamide ratios are also presented in Figure 15. There is a difference in the mechanical characteristics of the hydrogel with the change in the mole ratio of dimethylacrylamide:methacrylic acid. In samples with mole ratios of 0; 0.1; 0.2; and 0.33 dimethylacrylamide, the hydrogel exhibits predominantly brittle behaviour, i.e. low elongation rate. At mole ratios of 0.5 and above, it exhibits ductile behaviour, i.e. high strain rate. The most superior mechanical parameters can be obtained with an equimolar ratio of monomers in which the number of hydroxyl groups of methacrylic acid units and the number of carbonyl groups of dimethylacrylamide are equal, i.e. 0.5 mol each. At mole ratios of 0.66 and 0.8 dimethylacrylamide, the ductile material behaviour continues. At molar ratios of 0.9 and 1 dimethylacrylamide, the contribution of hydrogen bonding to the mechanical properties of the material is minimised. Thus, the brittle-ductile behaviour of the hydrogel can be controlled by means of the ratios of dimethylacrylamide and methacrylic acid, which are hydrophilic monomers.

CLAIMS

1. A resin suitable for the additive manufacturing of hydrogels with shape memory and self-healing, comprising a hydrophobic monomer, one or more hydrophilic monomers miscible with the hydrophobic monomer and one or more photoinitiators, characterised in that the hydrophobic monomer is hexadecyl acrylate.

2. A resin according to claim 1, characterised in that the hydrophilic monomer is acrylic acid, methacrylic acid, N-N-di methylacrylamide, 3-trimethylammonium propyl (meth)acrylamide, N-(3-(dimethylamino)propyl)acrylamide, n-propylacrylamide, n-tert-butylacrylamide or a mixture thereof.

3. A resin according to claim 2, characterised in that the hydrophilic monomer is acrylic acid and the mixture of acrylic acid and hexadecyl acrylate comprises 10 to 75% by mole of hexadecyl acrylate.

4. A resin according to claim 2, characterised in that the hydrophilic monomer is a mixture of methacrylic acid and dimethylacrylamide, and the mixture of the hydrophilic monomer and hexadecyl acrylate comprises 10 to 75% by mole of hexadecyl acrylate.

5. A resin according to claim 1, characterised in that the photoinitiator is 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 2,4,6-trimethylbenzoylpenylethoxyphosphine oxide, 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone, bis(2,4,6-trimethylbenzoyl)-phenylphosphinoxide, 2-methyl-4'-(methylthio)-2-morpholinopropiophenone, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, A resin as in claim 1, characterised in that it is 2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one, 4-benzoyl-4'-methyl diphenyl sulphide, 4,4'-bis(diethylamino)benzophenone, 4,4'-bis(N,N'-dimethylamino)benzophenone or a mixture thereof.

6. A resin according to claim 5, characterised in that it comprises between 1,5 and 3,5 % by weight of photoinitiator.

7. A hydrogel production method by additive manufacturing with shape memory and self-healing, characterised in that it comprises the process steps of mixing hexadecyl acrylate, one or more hydrophilic monomers miscible with hexadecyl acrylate, and one or more photoinitiators miscible with hexadecyl acrylate, and depositing the

mixture by a vat photopolymerisation technique, and impregnating the deposited structure with water.

8. A hydrogel production method according to claim 7, characterised in that the hydrophilic monomer is selected from acrylic acid, methacrylic acid, N-N-di methylacrylamide, 3-trimethylammonium propyl (meth)acrylamide, N-(3-(dimethylamino)propyl)acrylamide, n-propylacrylamide, n-tert-butylacrylamide or a mixture thereof.

9. A hydrogel production method according to claim 8, characterised in that acrylic acid is used as the hydrophilic monomer and acrylic acid is mixed with hexadecyl acrylate such that hexadecyl acrylate comprises between 10 and 75% by mole.

10. A hydrogel production method according to claim 8, characterised in that a mixture of methacrylic acid and dimethylacrylamide is used as the hydrophilic monomer and the hydrophilic monomer is mixed with hexadecyl acrylate such that hexadecyl acrylate comprises between 10 and 75% by mole.

11. A hydrogel production method according to claim 7, characterised in that the photoinitiator is selected from 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 2,4,6-trimethylbenzoylpenylethoxyphosphine oxide, 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone, bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, 2-methyl-4'-(methylthio)-2-morpholinopropiophenone, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, 2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one, 4-benzoyl-4'-methyl diphenyl sulphide, 4,4'-bis(diethylamino)benzophenone, 4,4'-bis(N,N'-dimethylamino)benzophenone or a mixture thereof.

12. A hydrogel production method according to claim 11, characterised in that 1.5 to 3.5 % by weight of photoinitiator is used.

13. A hydrogel with shape memory and self-healing, suitable for additive manufacturing, comprising a hydrophobic monomer and copolymers of one or more hydrophilic monomers miscible with the hydrophobic monomer formed in the presence of one or more photoinitiators miscible with hexadecyl acrylate, and characterised in that the hydrophobic monomer is hexadecyl acrylate.

14. A hydrogel according to claim 13, characterised in that the copolymers of the hydrophilic monomer with hexadecyl acrylate also contain water.

15. A hydrogel according to claim 13, characterised in that the hydrophilic monomer is acrylic acid, methacrylic acid, N-N-dimethylacrylamide, 3-trimethylammonium propyl (meth)acrylamide, N-(3-(dimethylamino)propyl)acrylamide, n-propylacrylamide, n-tert-butylacrylamide or a mixture thereof.

16. A hydrogel according to claim 15, characterised in that the hydrophilic monomer is acrylic acid and the mixture of acrylic acid and hexadecyl acrylate comprises between 10 and 75% by mole of hexadecyl acrylate.

17. A hydrogel according to claim 15, characterised in that the hydrophilic monomer is a mixture of methacrylic acid and dimethylacrylamide, and the mixture of the hydrophilic monomer and hexadecyl acrylate comprises 10 to 75% by mole of hexadecyl acrylate.

Figure 1

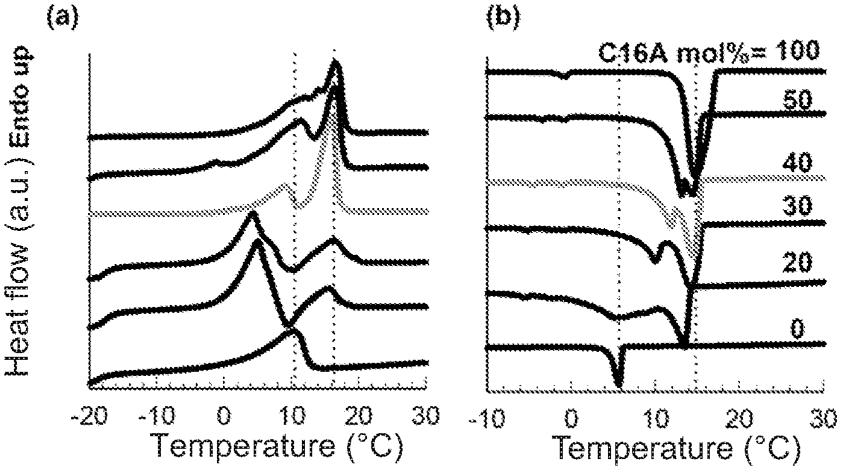


Figure 2

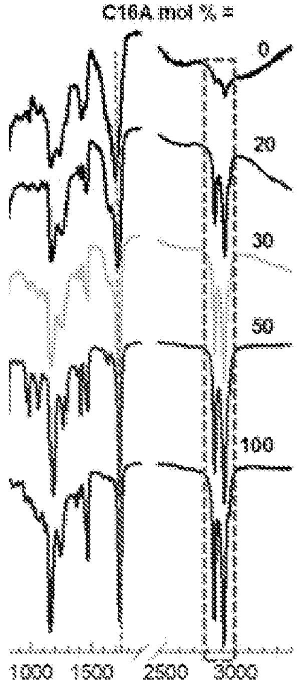
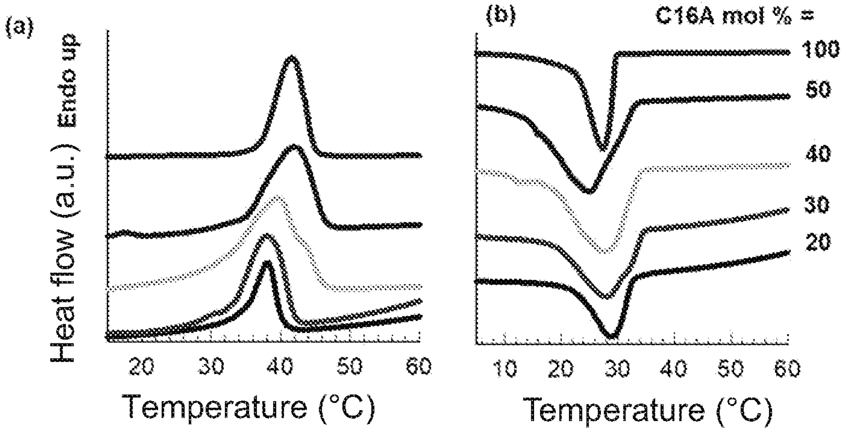


Figure 3



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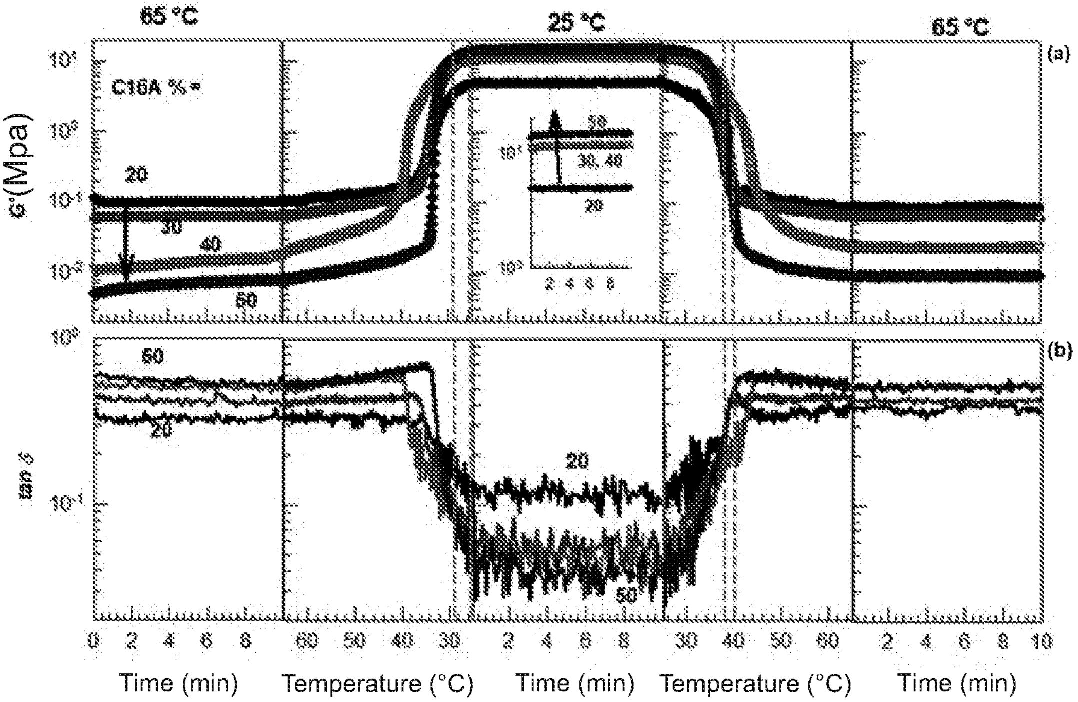
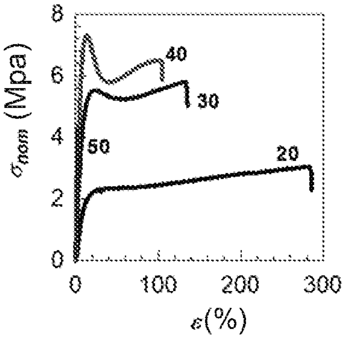


Figure 5



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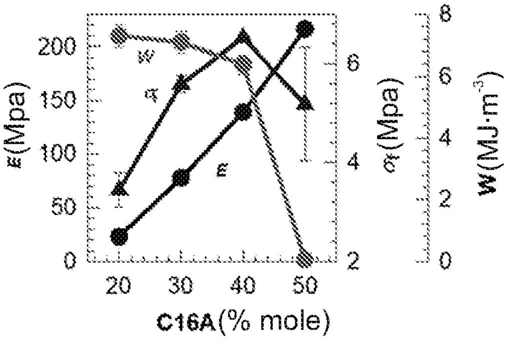


Figure 7

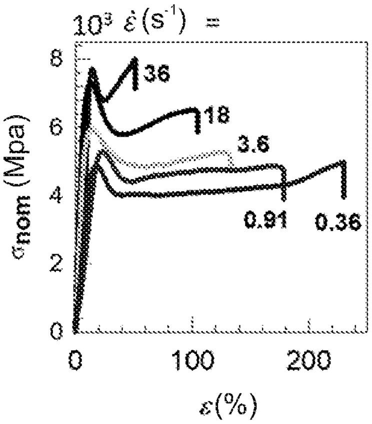


Figure 8

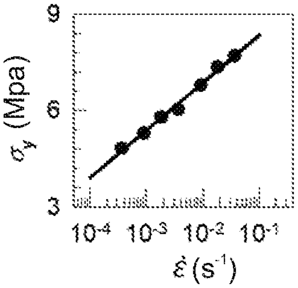


Figure 9

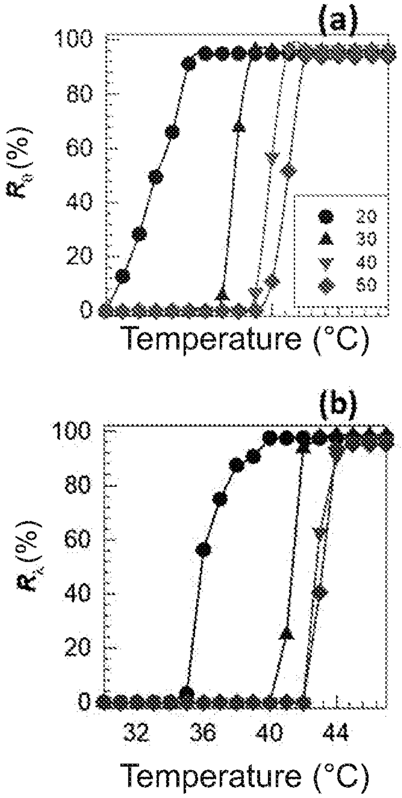


Figure 10

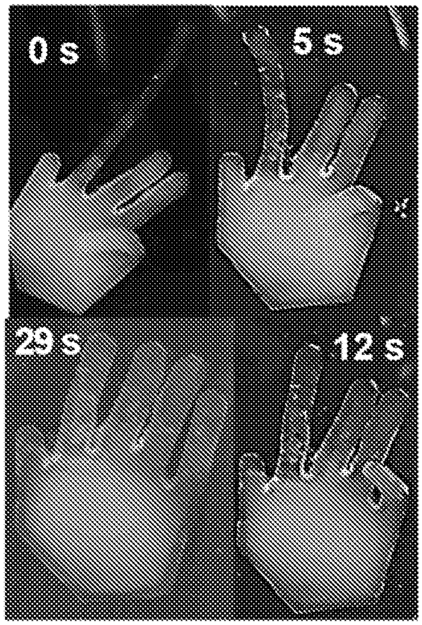


Figure 11

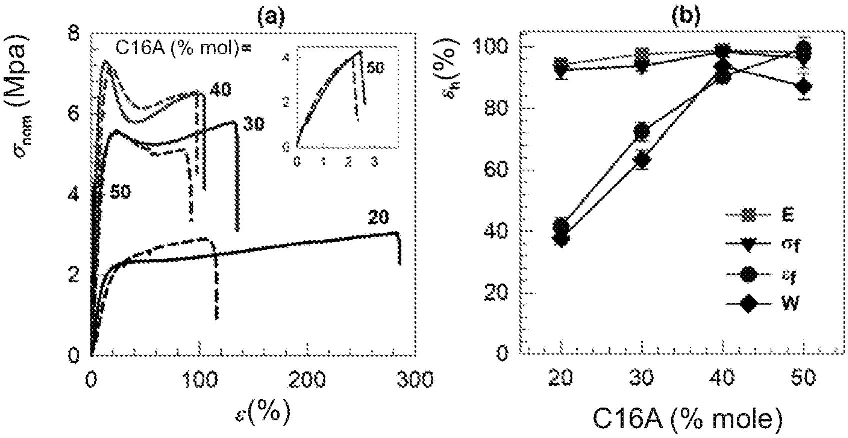


Figure 12

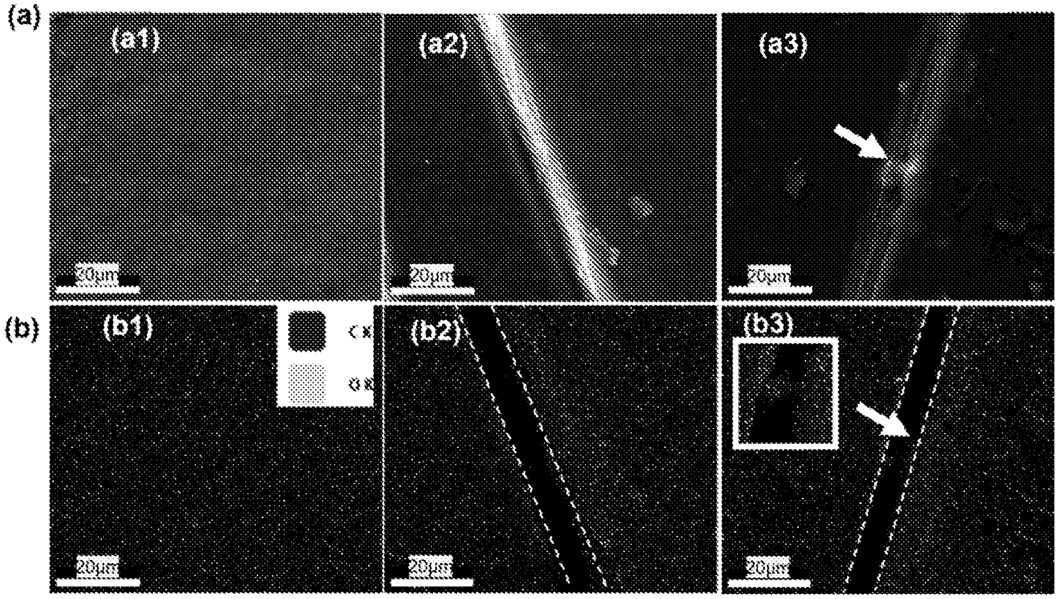


Figure 13

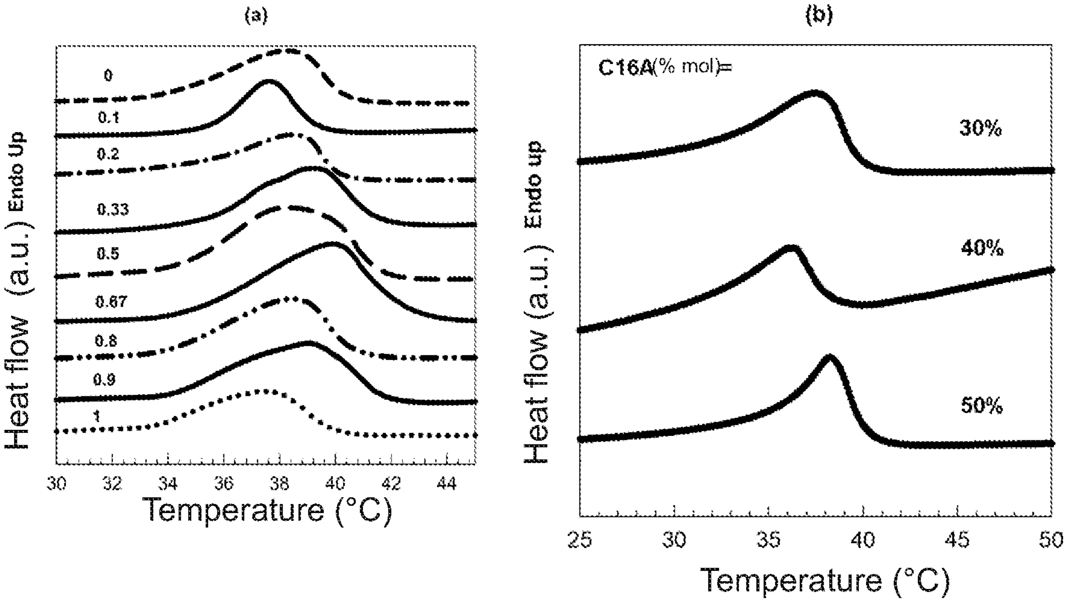


Figure 14

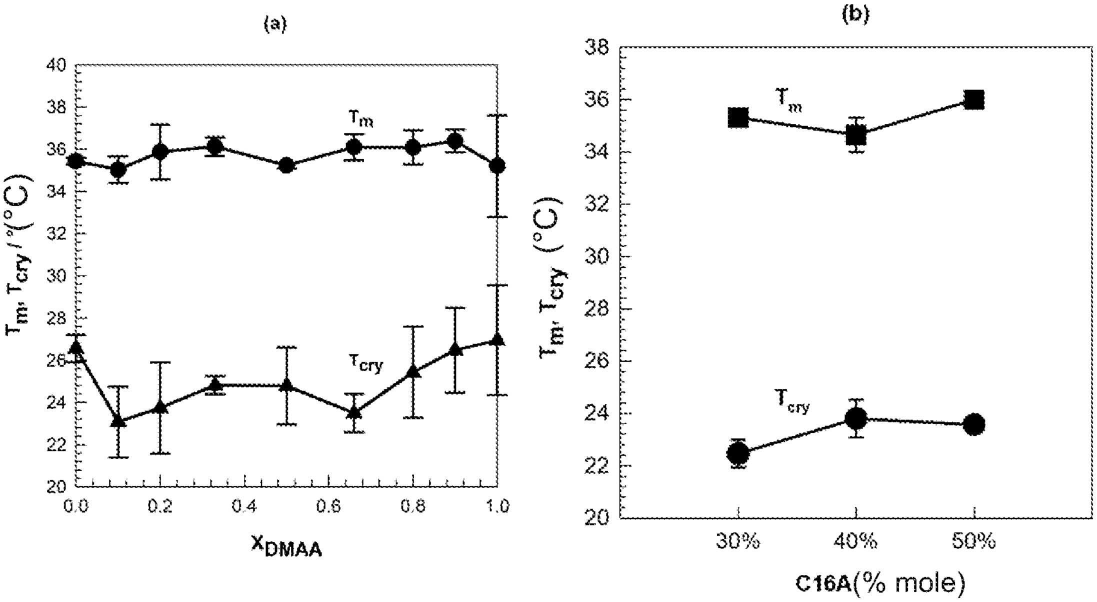


Figure 15

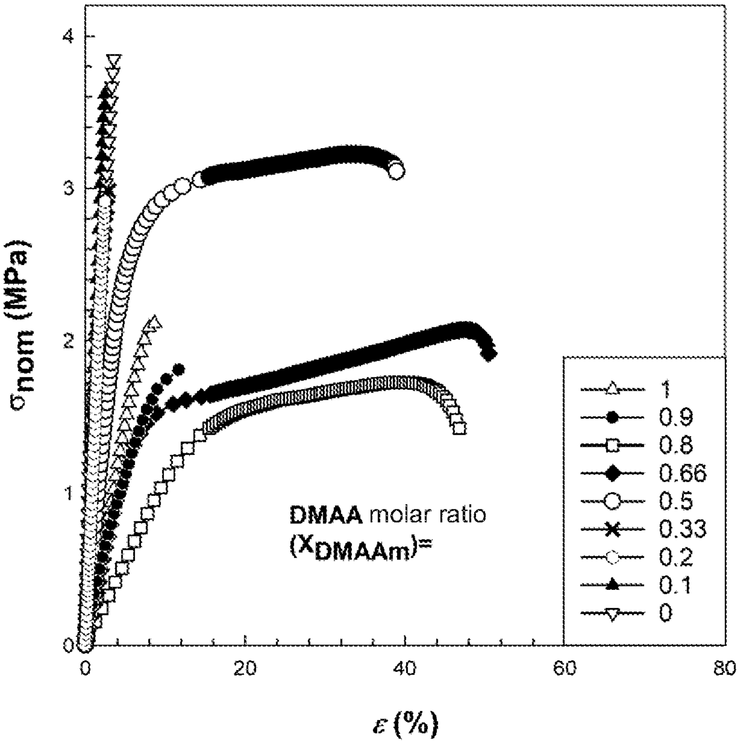


Figure 16

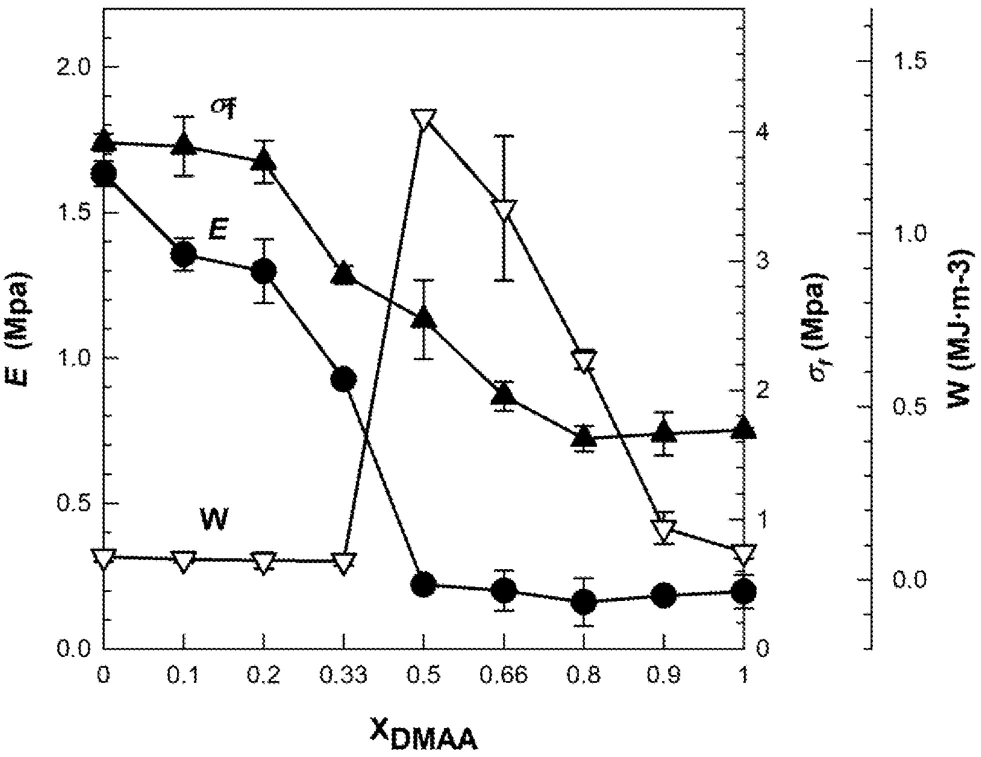
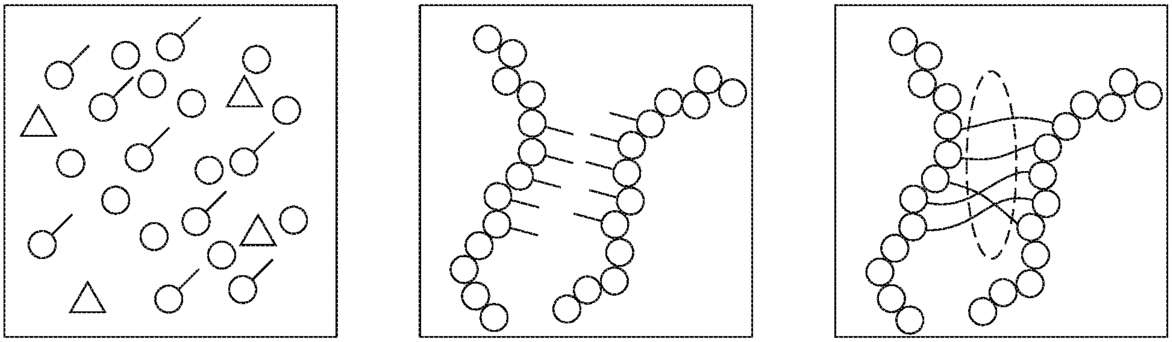


Figure 17

(a) (b) (c)



INTERNATIONAL SEARCH REPORT

International application No.

PCT/TR2024/050687

A. CLASSIFICATION OF SUBJECT MATTER

C08F 2/48(2006.01)i; ***C08F 220/18***(2006.01)i; ***C08F 220/56***(2006.01)i; ***C08J 3/075***(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F; C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published patent and utility model applications of Turkey, 2005-2024.

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO Abstract & Fulltext Databases, Google Scholar.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Abdullah, T., & Okay, O. (2023). 4D printing of body temperature-responsive hydrogels based on poly (acrylic acid) with shape-memory and self-healing abilities. ACS Applied Bio Materials, 6(2), 703-711. [2023-01-26]	1-3, 5-9,11-16
Y		4,10, 17
Y	CN 104151584 A (UNIV ZHEJIANG) 19 November 2014 (2014-11-19) Whole document	4,10,17
A	CN 108409989 A (UNIV ZHEJIANG) 17 August 2018 (2018-08-17) Whole document	1-17
A	CN 104497219 A (UNIV SOUTH CHINA TECH) 08 April 2015 (2015-04-08) Whole document	1-17
A	CN 113997650 A (XIAMEN TIANCE MATERIAL TECH CO LTD) 01 February 2022 (2022-02-01) Whole document	1-12

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

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“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search **13 August 2024**	Date of mailing of the international search report **20 September 2024**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/TR2024/050687

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN 104151584 A	19 November 2014	CN 104151584 B	01 February 2017
CN 108409989 A	17 August 2018	CN 108409989 B	06 September 2019
CN 104497219 A	08 April 2015	CN 104497219 B	05 April 2017
CN 113997650 A	01 February 2022	NONE	