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Stimuli-responsive Hydrogels for Textile Functionalisation: A Review

Hidrogeli, občutljivi na dražljaje, za funkcionalizacijo tekstilij

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Abstract

This article reviews hydrogels used for the functionalisation of textile materials. Hydrogels are reviewed according to their reason for incorporation, aspects of crosslinking, stimuli-responsive characteristics and particle size. A more in-depth focus on the effect of hydrogel particle size is provided, where macrogels, microgels and nanogels for textile functionalisation are considered. The advantages and disadvantages of each size group are presented. Furthermore, the correlation between synthesis conditions and the sizes of hydrogel particles is discussed, in addition to the applications of macro-, micro- and nanogels to textile materials and their intended uses.
Keywords: smart textiles, stimuli-responsive hydrogels, microgels, nanogels, preparation methods

Izvleček

V preglednem članku so predstavljeni hidrogeli, ki se uporabljajo za funkcionalizacijo tekstilnih materialov. Hidrogeli se uvrščajo glede na vzrok za aplikacijo, način zamreženja, glede na odzivne lastnosti in velikost delcev. Podrobneje se članek osredotoča na vpliv velikosti delcev hidrogela, kjer se za funkcionalizacijo tekstila uporabljajo makrogeli, mikrogeli in nanogeli. Predstavljene so prednosti in slabosti vsake velikostne skupine, prav tako pa je opisana povezava med pogoji sinteze in velikostjo delcev hidrogela, aplikacija makro-, mikro- in nanogelov na tekstilni material ter njihova predvidena uporaba.
Ključne besede: pametne tekstilije, hidrogeli, odzivi na dražljaje, mikrogeli, nanogeli, metode priprave

1 Introduction

Hydrogels of stimuli-responsive polymers represent an important group of high-performance hydrated polymers that can respond to different stimuli from the environment. Their hydration properties enable hydrogels to absorb and retain large quantities of water or other aqueous solutions in their three-dimensional polymer networks [1–4]. Namely, they can retain at least 20% water relative to their dry weight [5]. Because the crosslinking of the polymer network prevents the dissolution of hydrogels in water, they swell, which causes a direct increase in their volume. The swelling of a hydrogel is directly affected by water-polymer interactions, which in turn are affected by the hydrophilicity of polymers: the higher the polymer hydrophilicity, the stronger the water-polymer interactions. The water in a hydrogel can be incorporated as free or bound water. Free water is located at the outermost layer and can be easily removed via mechanical compression or centrifugation. Water attached to the polymer chain is called bound water and forms hydrogen bonds with polar groups of the polymer. This water can only be removed at very high temperatures, otherwise it remains part of the hydrogel structure. Interstitial water is physically entrapped within hydrated polymer chains. Lastly, semi-bound water possess characteristics of both bound water and free water. Swelling capacity is determined by the space within the polymer network,

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while the swelling process depends on the rate of relaxation of polymer chains and on the rate of the diffusion of water molecules [6–7].

The unique property that distinguishes stimuli-responsive hydrogels from non-responsive hydrogels is their responsiveness to minimal changes in environmental conditions (temperature, pH, ionic strength, electric and magnetic field, light, etc.), which trigger the absorption and release of water from the polymer network. This induces a reversible volume change of the polymer network from a swollen hydrogel to a collapsed gel. The volume phase transition of a hydrogel is attributed to a change in polymer-solvent interactions induced by external stimuli. Namely, if an external stimulus alters the polymer structure from a hydrophilic to a hydrophobic state, water will be released from the hydrogel to its surroundings, and the dehydrated hydrogel will shrink as a result [8]. Since changes in a polymer structure are reversible, a hydrogel will return to its initial state when the external stimulus is absent. Furthermore, the transition from hydrogel to solution can also be triggered by external stimuli. However, these structural changes are less important for textile applications of hydrogels [5].

Their superior stimuli-responsive properties results in the classification of hydrogels as biomimetic "smart" polymer systems, the use of which is growing exponentially in various application fields (Figure 1). Hydrogels have already been established in biotechnology and biomedicine [9–12], where they mostly serve as scaffolds for tissue engineering [13]; drug, gene and protein delivery systems [14]; superabsorbents; and biosensors and bioactuators [3]. Due to their reversible swelling/shrinking ability, stimuli-responsive hydrogels have become essential in ecology, where they are used as adsorbents in wastewater treatment for the effective removal of dyes and heavy metals [15–24], and for the filtration of wastewater from pollution caused by oil [24–26].

Stimuli-responsive hydrogels also present great potential and opportunities in the field of textiles, where they are applied to different textile substrates to create new smart functionalities, including thermoregulation and moisture management for comfort improvement, and the controlled release of active substances for wound dressing or skin care.

Few review articles have been written to date on the topic of hydrogels for use in textiles [27–32], focusing on the use of hydrogels for medical textiles and textiles for increased comfort. To provide new knowledge in the use of hydrogels for chemical modification of textile materials, this article focuses on the comprehensive study of the hydrogel particle size in relation to synthesis conditions and the field of application.

2 Classification of stimuli-responsive hydrogels

Hydrogels are usually classified in literature according to the nature/source of a polymer, type of crosslinking, external stimuli that trigger phase transition and the size of hydrogel particles (Figure 2).

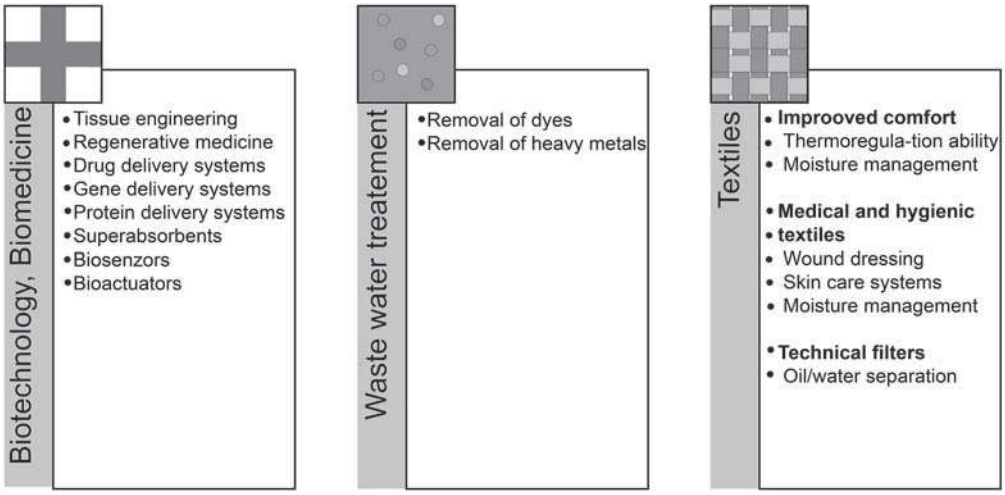


Figure 1: Schematic illustration of application fields of stimuli-responsive hydrogels

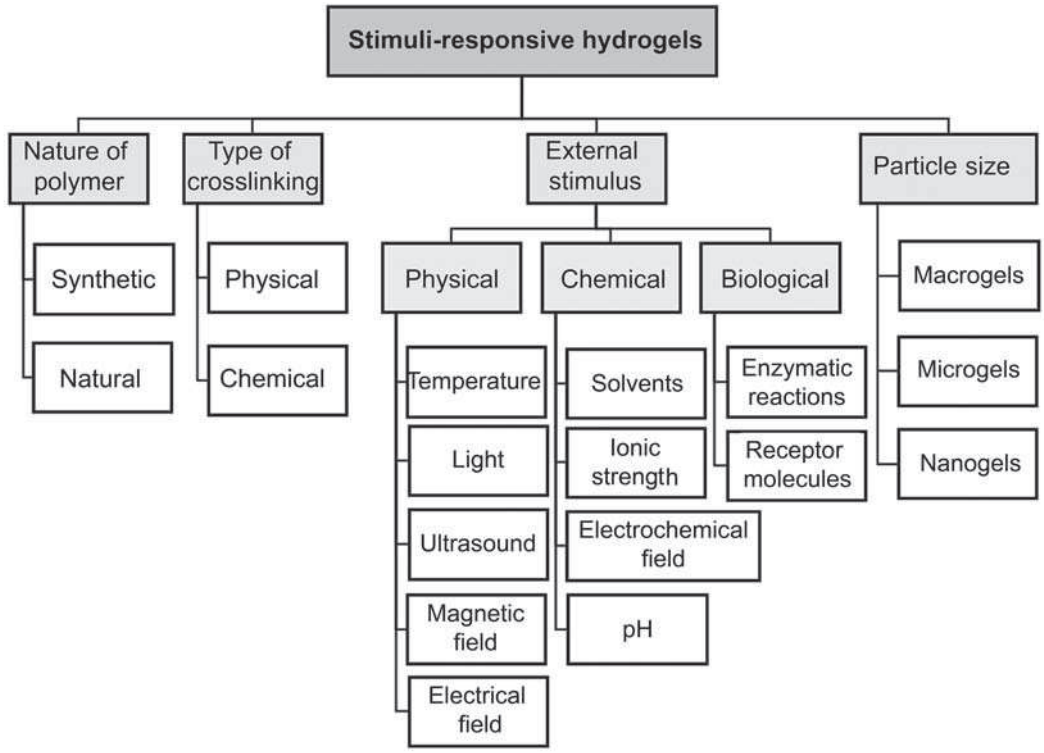


Figure 2: Schematic illustration of stimuli-responsive hydrogel classification

2.1 Nature of polymers

Polymers that form stimuli-responsive hydrogels can be of natural or synthetic origins. Natural polymers, which include proteins such as gelatine [33] and polysaccharides (e.g. chitosan, alginate and κ-carrageenan [34]), are classified as "green smart" polymers with low toxicity and biocompatibility. Unlike natural polymers, synthetic polymers are artificial and are synthesised by chemical polymerisation methods. Some of the most commonly used polymers include poly(N-alkyl substituted acrylamides), poly(N-vinylalkylamides), poly(N,N-diakylamino ethylmethacrylates) [33].

2.2 Type of crosslinking

The crosslinking of the polymer network occurs during hydrogel preparation: during the process of gelation, polymer chains begin to crosslink and form larger, branched, but still soluble, polymers. Mixtures of such poly-disperse branched polymers are called "sol". The further entanglement of polymers leads to the formation of a so-called "gel", where the crosslinking of fully branched polymers occurs. Their solubility gradually decreases with the increasing entanglement of the polymer network. This transition is referred as the "sol-gel transition", while the critical point at which a gel first appears is called the "gel point" [8].

Hydrogels are classified as physically or chemically crosslinked gels with regard to the type of crosslinking. In physically crosslinked gels, polymer networks are formed via physical interactions between macromolecular chains, such as van der Waals forces, ionic interactions, hydrogen bonds or hydrophobic interactions [9, 35–37]. Physically crosslinked hydrogels can be strongly or weakly crosslinked [38]. Strongly physically crosslinked hydrogels form strong junctions between polymer chains and are analogous to chemically crosslinked hydrogels. In contrast, weakly physically crosslinked gels are linked by temporary junctions between polymer chains. They therefore have a limited life span and are constantly changing [8]. Physically crosslinked hydrogels are useful for numerous biotechnological and biomedical applications because their polymerisation process is carried out without the presence of organic crosslinking agents [38].

On the other hand, chemically crosslinked hydrogels form strong covalent bonds between polymer chains [5], which make them highly stable. Covalent bonds between polymer chains can be established if

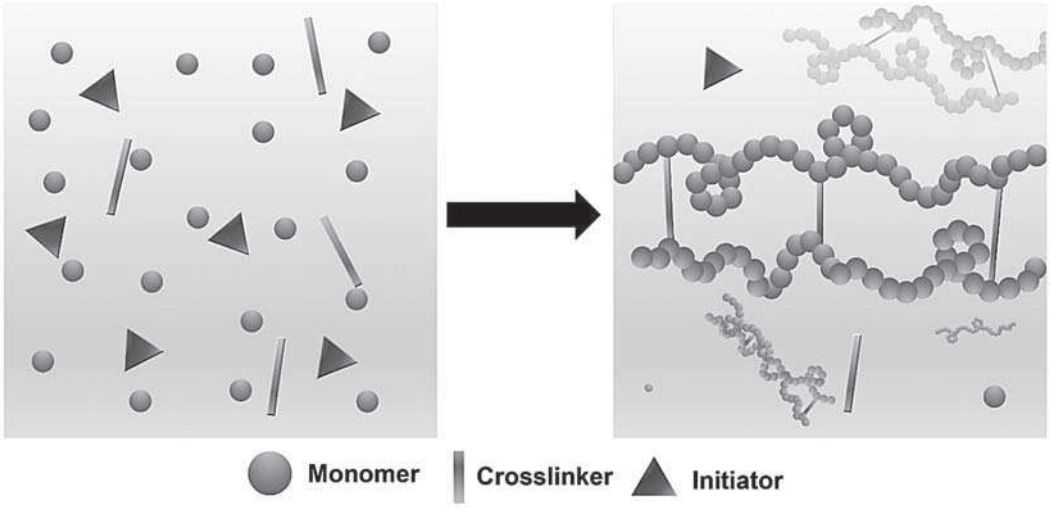


Figure 3: Schematic illustration of the preparation of chemically crosslinked hydrogels [2]

the reacting polymers contain functional side groups such as OH, COOH or NH_2 in their structure [39]. They possess good mechanical properties and have a relatively long degradation time [40–43]. In the preparation of chemically crosslinked hydrogels, organic crosslinking agents and initiators are usually present in the polymerisation process (Figure 3) [2]. However, there are also processes in which organic crosslinkers are not used [38, 44–46]. Hydrogels can be synthesised through radical polymerisation [38], polymerisation initiated by UV light [47], enzyme-catalysed reactions [48], and γ-ray [46] or electron beam [45] irradiation. When exposed to γ-ray or electron beam radiation, radicals form along polymer chains in an aqueous solution. The radiolysis of a water molecule results in the formation of hydroxyl groups, which can react with polymer chains to lead to the formation of microradicals. This allows the formation of covalent bonds with a crosslinked structure without the addition of an organic crosslinker [38, 44].

2.3 External stimuli

Based on the origin of the stimuli to which hydrogels respond, we can distinguish between physical, chemical and biological stimuli [1, 5]. Physical stimuli include temperature [49], light [50], ultrasound [51], magnetic fields [52] and electrical fields [53], while chemical stimuli include solvents [54], ionic strength [55], electrochemical fields [56] and pH [54]. Furthermore, biological stimuli refer to the functionality of molecules such as enzymatic reactions [57] and the identification of a receptor molecule [58]. Hydrogels that respond to multiple stimuli can be synthesised when combining different responsive polymers. Table 1 summarises external stimuli and their effect on the mechanism of swelling and shrinking of different types of hydrogels.

For smart textile functionalisation, temperature- and pH-responsive hydrogels are the most studied, as these two stimuli are significant in physiological terms [1, 5, 59, 60–61]. Temperature- and pH-responsive hydrogels are able to interact with the user directly, since those two stimuli can occur either through a change in temperature of the immediate surroundings of a textile material or through changes in the pH of the skin or bodily excretions such as sweat, blood and urine [62].

Hydrogels based on **temperature-responsive** polymers possess a critical solution temperature, which can be identified as a lower critical solution temperature (LCST) or an upper critical solution temperature (UCST) [63]. An LCST is characterised by shrinking, which means that a polymer appears in one phase below the critical temperature and undergoes phase separation when the temperature rises above the LCST, while a UCST is characterised by swelling as the temperature rises, meaning that phase separation occurs at lower temperatures, and a change to the monophasic form occurs with rising temperature. When a temperature-responsive polymer is in a monophasic state, hydrophilic interactions are predominant, while hydrophobic interactions prevail when the conditions create a biphasic state [26, 64].

Table 1: External stimuli and their effect on the mechanism of swelling and shrinking of different types of hydrogels [67]

External stimulus	Type of hydrogel	Responsive mechanism
Temperature	Temperature-responsive hydrogels	Change in temperature causes a change in polymer-polymer and water-polymer interactions, which affects the swelling and shrinking of a hydrogel
Ultrasound	Hydrogels based on ethylene-vinyl alcohol	Ultrasonic waves cause an increase in temperature, which leads to the swelling and shrining of a hydrogel
Electric current	Hydrogels based on polyelectrolytes	Electric current charges the membrane, which leads to the swelling or shrinking of a hydrogel
Ionic strength	Ionic hydrogels	A shift in ionic strength causes a change in the concentration of ionic groups within the hydrogel, causing the swelling and shrinking of a hydrogel
Chemical species	Hydrogels with electron-acceptor groups	An electron-donor compound causes the formation of an electron donor-acceptor complex, which affects the swelling and shrinking of a hydrogel
pH	pH- responsive hydrogels	Change in pH causes weakly acidic or basic groups within the polymer to receive of transmit protons, which affects the swelling and shrinking of a hydrogel
Enzymatically degradable substrate	Hydrogels with immobilised enzymes	Enzymatic degradation occurs in the presence of a substrate, which creates products that affect the swelling and shrinkage of a hydrogel

Polymers that respond to environmental **pH** are polyelectrolytes with acidic or basic pendants, which can receive or emit protons in response to stimuli from the environment. As the pendants protonate or deprotonate at a specific pH, i.e. at pK_a or pH_b, the electrostatic repulsion among ionic groups produces osmotic pressure, leading to a change in the volume of a polymer. Polymers responsive to pH can be polyanions, which swell at rising pH values, or polycations, which swell at falling pH values [38, 65–66].

2.4 Hydrogel particle size

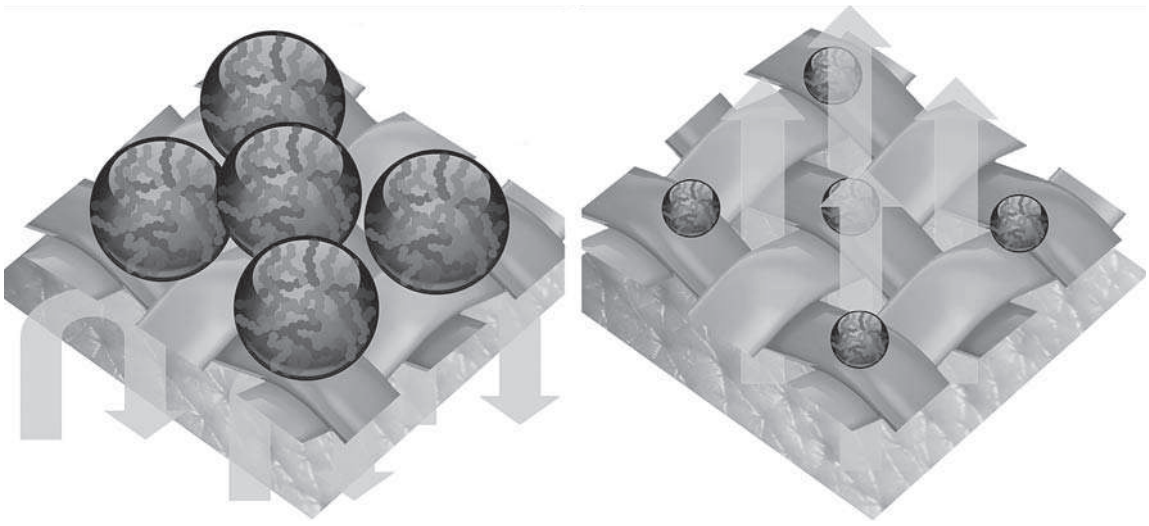
Hydrogels can also be characterised by their particle size; macro-, micro- and nanogels can be formed [68–71]. Macrogel particles range in size from a micrometre or more, whereas microgel particles have a diameter of 100nm to 1µm, forming colloidally stable, water-swellable polymer networks. Nanogels occur in a size of <100nm, although the definition in the relevant literature is often expanded to hydrogel particles with sizes of up to 200nm [68] or even higher [69], thus overlapping with the size range of microgels.

Smaller hydrogel particles create a greater surface to volume ratio, which is reflected in shorter response times and increased surface per unit. Since the dimensions of responsive hydrogel particles and the rate of the volume phase transition are inversely proportional [66], smaller particle sizes are also reflected in advantages of greater control over the swelling and entrapment and release of entrapped active substances because of the greater specific surface area of hydrogel nanoparticles [71].

3 Stimuli-responsive hydrogels for textile applications

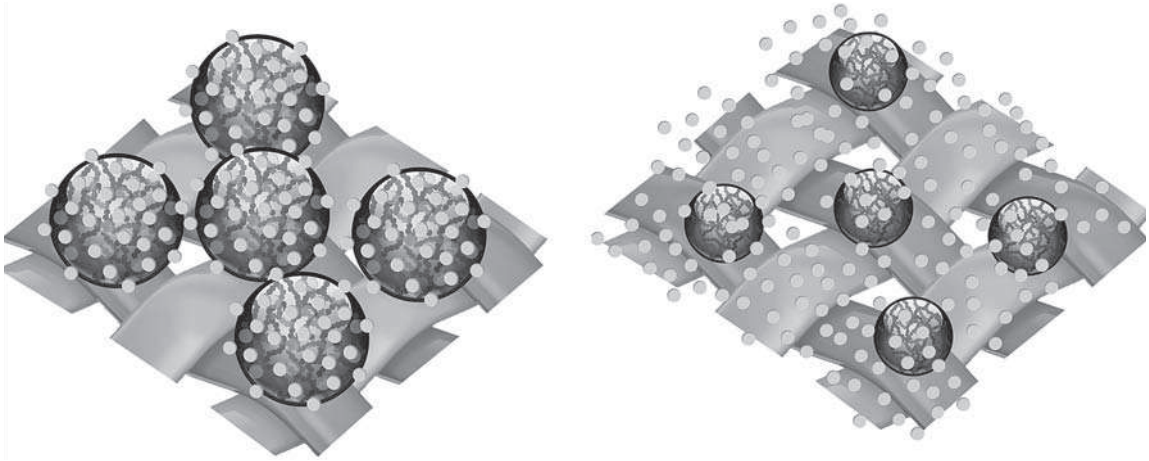
3.1 Working prunciple of hydrogels on textile materials

To achieve **comfort improvement**, the active balancing of body moisture and temperature by a textile is crucial (Figure 4). A stimuli-responsive hydrogel present on textile fibres can interact with the user by detecting and responding to changes in environmental conditions. When an external stimulus dictates the



a) *b)*

Figure 4: Schematic illustration of body moisture and temperature balancing by a hydrogel present on a textile surface: (a) body heat retention through a textile, if a hydrogel is in a swollen (hydrophilic) state, (b) release of body heat through the porous structure of a textile, if a hydrogel is in a shrunken state (b)



a) *b)*

Figure 5: Schematic illustration of the controlled release of active substances from a hydrogel: (a) retention of active substance in a swollen hydrogel, (b) release of active substance from a shrunken hydrogel

swelling of a hydrogel, the porosity of the textile material decreases. Such a phenomenon causes body vapour retention and consequently heat accumulation on the skin's surface (Figure 4a). In contrast, when an external stimulus dictates the shrinking of a hydrogel structure, fabric porosity increases, thus providing breathability to the textile and greater body vapour and heat transition from the skin's surface through the textile to its surroundings (Figure 4b) [59].

Stimuli-responsive hydrogels can also be utilised for the controlled release of active substances from **medical and hygienic textiles** (Figure 5), which are used for accelerated wound healing or skin care. Hydrogels absorb active ingredients in the presence of environmental conditions that dictate their swelling. Active substances can be retained in a hydrogel structure (Figure 5a) until environmental conditions trigger shrinkage (Figure 5b). The reversible swelling and shrinking of a hydrogel triggered by an external stimulus provides the gradual and controlled release of active substances into the environment only under specific conditions.

3.2 Chemical structures and synthesis conditions of hydrogels

For smart textile functionalisation, temperature-responsive polymers, i.e., poly(N-isopropylacrylamide) (poly-NiPAAm), poly(vinyl alcohol) (PVA), poly (ethylene glycol) (PEG) and poly(vinyl caprolactam) (Figure 6), and pH responsive polymers, i.e., chitosan (Cs), poly(acrylic acid) (PAA), poly(metha-crylic acid) (PMAA) and poly(allylamine) (poly-ALA) (Figure 7), are used for their preparation.

Table 2 summarises the synthesis conditions of micro- and nanogels that were used for textile application. It is evident from the table that hydrogels are used in homopolymeric and copolymeric forms. The latter include combinations of NiPAAm with chitosan [59, 72–79], ALA [80], MAA [81] or N-aminoethyl methacrylate (AEMA) [82]. Hydrogels have been synthesised using various techniques such as surfactant-free dispersion copolymerisation with a conventional stirring technique [59, 72–77], mixing with the help of an ultrasound bath [78–79, 83], copolymer synthesis [82], coupling of a triblock copolymer [61], surface-initiated atom transfer radical polymerisation (ATRP) [26], free radical polymerisation [81] and precipitation polymerisation [76]. In most cases, surfactant-free dispersion polymerisation is used to synthesise both microgels and nanogels. In the surfactant-free dispersion polymerisation of hydrogels based on poly(N-substituted acrylamides) such as poly-NiPAAm, the presence of N,N'-methylenebisacrylamide (BIS) as a crosslinker is essential [59, 72–78, 79–81, 84–85], although copolymerisation without the addition of BIS has also been performed [78]. To initiate the reaction, N,N,N'-ammonium persulphate (APS) is added. APS transforms monomers to free persulfate radicals, followed by a reaction with polymer chains and non-activated polymers, leading to the formation of a gel [2]. Potassium persulfate (KPS), which produces sulphate radicals through thermal decomposition, can be used instead of APS [78, 86], resulting in the negative surface charge of microgel particles caused by the presence of sulphate groups [87]. The use of catalysts such as N'-tetramethylethylenediamine (TEMED) can be seen in poly-NiPAAm/chitosan nanogel synthesis [79] to accelerate the formation of free radicals.

In the precipitation polymerisation of hydrogels based on poly-NiPAAm, BIS was added as the crosslinking agent. However, TEMED was used in combination with APS to initiate an anionic microgel, while a cationic microgel was initiated by UV irradiation [88]. A nanogel based on poly-NIPAAm and poly-ALA was synthesised using the same procedure, where monomers were diluted with SDS and freeze-thawed three times. KPS was added to initiate polymerisation [80]. The presence of chitosan in the synthesis of a poly-NIPAAm-based hydrogel stabilised nanogel particles [79] and acted as a surfactant, preventing particle coagulation [59]. An increase in the chitosan-to-poly-NiPAAm ratio decreased the size of synthesised particles of the nanogel [89]. Furthermore, by increasing the temperature to 80°C, the nanoparticles of poly-NIPAAm/chitosan hydrogels could be formed without the addition of a catalyst or surfactant. In this way, particles with a diameter of 81.2 nm were obtained [90].

Other microgels used for textile modification have been based on carboxymethylcellulose (CMC) in combination with fumaric acid as a crosslinker [91], di-phenylalanine [83], CMC and hydroxyethyl cellulose [92] and poly (ethylene glycol) (PEG) and poly(ε-caprolactone) (PCL) [61]. In the case of the synthesis of nanogels, PVA- [93], β-cyclodextrin (β-CD)- [94], hydrophobised-pullulan- [95] and collagen-bearing pullulan- [96] based polymers have been used. Due to the specific nature of each polymerisation or copolymerisation, a detailed comparison between micro- and nanogel syntheses cannot be made.

The synthesis process, the quantity of the crosslinker and initiator, temperature, time, stirring speed, and the presence of surfactants and co-monomers directly affect the size of hydrogel particles [70]. In general, the presence of a crosslinker causes the formation of smaller hydrogel particles than in the absence of a crosslinker. The synthesis temperature and size of the particles are inversely proportional, as macrogels are formed near room temperature [97–100] and temperatures for microgel synthesis increase to 50°C [78, 80] on average, although they may rise as high as 70°C [82], 80°C [26] or even 85°C [61]. Nanogels are usually prepared at temperatures of 70°C [80–81, 101]. Synthesis time is drastically shortened by reducing the hydrogel particle size from macro- to micro- to nanogel. Smaller hydrogel particles can be created through the addition of a surfactant such as sodium dodecyl sulphate (SDS), which stabilises polymer particles early during polymerisation reaction [80–81]. The particle size decreases with an increase in the surfactant concentration [86]. Hydrogel particle sizes can also be reduced through the addition of ionisable anionic co-monomers [86].

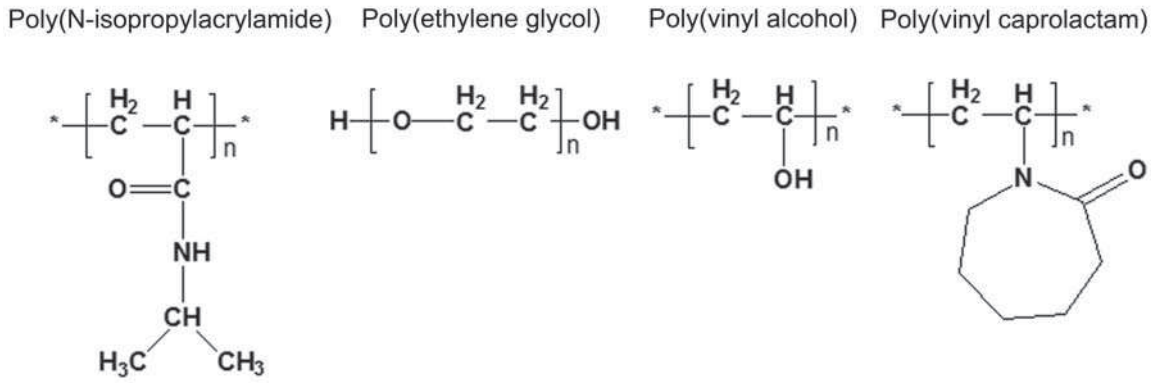


Figure 6: Structures of temperature-responsive polymers used for stimuli-responsive hydrogels for textile modification

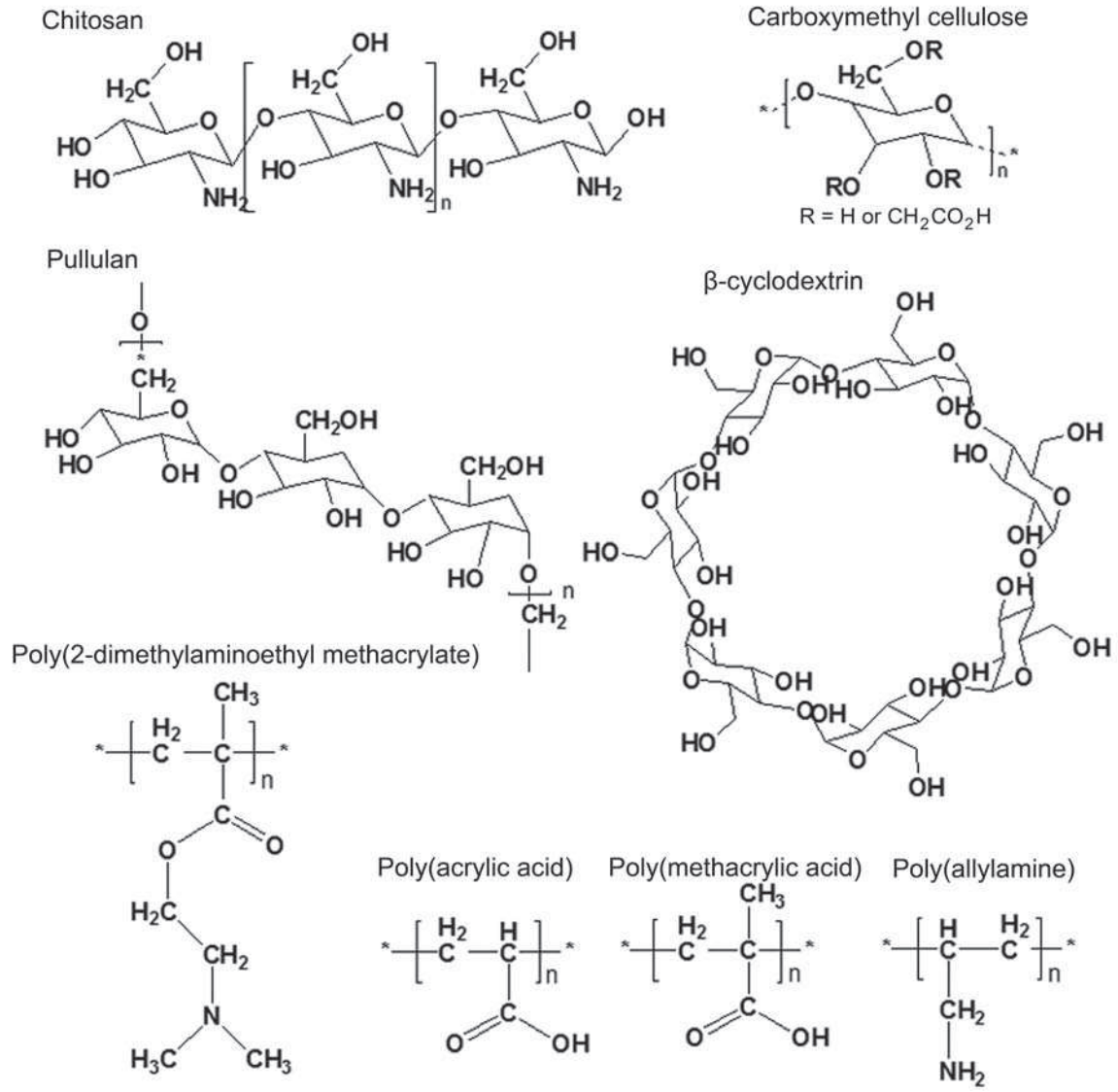


Figure 7: Structures of pH-responsive polymers used for stimuli-responsive hydrogels for textile modification

Table 2: Components, size of micro- and nanogel particles and synthesis conditions of hydrogels for use in textiles

Polymer/monomer	Crosslinker	Initiator, catalyst	
NiPAAm, chitosan	BIS	APS	
	BIS	KPS	
	BIS	APS, TEMED	
NiPAAm, AA and chitosan	BIS	APS	
NiPAAm and ALA	ethylene-glycol diacrylate	sodium persulfate	
NiPAAm and MAA	BIS	APS, MAA	
NiPAAm and AEMA	Azoisobutyronitrile (AIBN)	/	
2-dimethylaminoethyl methacrylate (DMAEMA)	A solution of methanol/H_2O, *N,N,N′,N′,N″*-pentamethyldiethylenetriamine, copper(I) bromide, DMAEMA	Bromoisobutyryl bromide	
poly (ethylene glycol)-polycaprolactone-poly(ethylene glycol) (PEG-PCL-PEG)	Hexamethylene diisocyanate (HMDI)	/	
CMC	Fumeric acid	/	
di-phenylalanine (F2) 9-fluorenylmethoxy- Carbonyl (Fmoc)	phosphate buffer saline (PBS) tablets solution	/	
CMC and hydroxyethyl cellulose	Citric acid	/	
PVA, PVA and glycerol	/	/	
β–CD	Isocyanate-terminated star-shaped poly(ethylene oxide-*stat*-propylene oxide)	/	
Acryloyl group modified cholesterol-bearing pullulan (CHPOA)	Penta erythritol tetra (mercaptoethyl) polyoxyethylene (PEGSH)	/	
PAA	BIS-AAM	Photo- and thermo-initiated	
PDMAEMA	BIS	2, 2′-diethoxyacetophenone (DEOP)	
PNiPAAm	BIS	APS	

3.3 Fields of hydrogel application in textile modification

Stimuli-responsive hydrogels can be applied to textile substrates in the form of a solution, microcapsules, foam or gel [105]. Pad-dry-cure coating is the most common and the most accessible procedure from a technological point of view. When designing synthetic fibres, a hydrogel can be incorporated into fibres during the spinning process [95, 106–107]. Regardless of the application procedure, a uniform distribution and the minimum thickness of hydrogel particles on a textile substrate are crucial to achieving the free swelling of hydrogel particles in their hydrophilic state [59].

The initial chemical composition of fibres dictates their hydrophilicity or hydrophobicity, which greatly affects the uptake of the functional finish. Stimuli-responsive hydrogels, however, do not form covalent bonds with a textile substrate. Because chemical and physical compatibility between a textile substrate and the applied hydrogel greatly affect the durability of the applied hydrogel [108], different approaches were

	Hydrogel particle size (shrunken)	Synthesis procedure	Synthesis conditions	Literature
	180nm	Surfactant-free dispersion copolymerisation	50°C, 3h	[72–47, 76]
	150nm		70–50°C, 100min	[78]
	85.2nm		70°C, 4h	[101]
	1.5μm	Surfactant-free dispersion copolymerisation	65°C, 4h and room temperature, 12h	[85]
	72nm	Precipitation polymerisation in the presence of surfactant (SDS)	70°C, 4h	[80]
	180–200nm	Free-radical polymerisation in the presence of surfactant (SDS)	70°C, 4h	[81]
	810nm	Free-radical polymerisation in ethanol	70°C, 24h	[82]
	Not stated	Surface-initiated atom transfer radical polymerisation	60°C	[26]
	Not stated	Coupling mPEG and PCL with HMDI as a chemical linker	85°C, 5h	[61]
	Not stated	FA crosslinking of CMC hydrogel	room temperature, 5min, 30min and 1h	[91]
	Not stated	Self-assemble polymerisation	Room temperature, 30min	[83]
	Not stated	Graft copolymerisation	80°C, 24h	[92]
	10–50nm	Fructose-induced reduction of silver nitrate within PVA gel	60–90°C	[93]
	50–200nm	Water-based organic, solvent-free polymerisation	Room temperature, 24h	[94]
	30nm	Self-assemble polymerisation	37°C, 1h	[96]
	Not stated	Free-radical polymerisation	Annealing 110°C, 60 min, introduction of reactive groups 10 min, UV –illumination, 1h	[102]
	Not stated	Free-radical polymerisation	Room temperature, 12h	[103]
	Not stated	Free-radical polymerisation	70°C, 2h	[104]

used in the application of stimuli-responsive hydrogels on textile materials, and are described in more detail in the following paragraphs. Not only the chemical composition of a fibre, but also mechanical textile properties such as the cross sectional shape of a fibre and fibre diameter, weave pattern, thickness [109–110] etc. greatly affect the moisture and water vapour transmittance of a fabric, and could affect the responsive properties of hydrogel functional fabrics.

According to the smart textile functionality provided by a hydrogel, there are two application approaches: **material technology** and **biotechnology** [59]. The material technology approach, which is crucial for achieving improved textile comfort, requires the minimal effect of a hydrogel on the physico-mechanical properties of textile materials, as well as the durability of a hydrogel on a textile surface. Both factors are directly related to the conditions of hydrogel synthesis, the hydrogel particle size and the application technique. To increase the durability of hydrogel coatings, hydrogels are applied in combination with crosslinking agents or to previously

activated fibres. The latter can be achieved through a low-temperature plasma treatment that provides new functional groups on fibre surfaces to serve as bonding points between a hydrogel and substrate. Furthermore, the etching effect of plasma increases the roughness of the fibre surface as well as the specific surface area of fibres, resulting in the greater uptake of a hydrogel [100]. The hydrogel particle size has a significant effect on the mechanical properties of a textile material. The presence of microgels on a textile substrate increases the stiffness of the fabric [74]. The most recent research is therefore focused on the synthesis and application of nanogels [81, 93–94, 101, 111]. Nanogels combine the characteristics of hydrogels and nanoparticles [111] and result in a minimum effect on the mechanical properties of a textile substrate. An applied nanogel coating is a homogenous, thin gel layer or particles, and therefore has a minimum effect on the performance and haptic properties of a textile substrate [94].

The biotechnology approach is more common in the preparation of medical and hygienic textiles with an incorporated hydrogel. In such cases, a textile substrate serves as a carrying material that contributes to the improvement of the mechanical properties of a hydrogel when it is in its hydrophilic, swollen state. Accordingly, the biocompatibility of a textile substrate and the maximum responsiveness of a hydrogel are crucial, while the effect of a hydrogel on the mechanical and physical properties of a textile substrate is less important [59].

3.3.1 Use of hydrogels for medical application

Overall, macrogels are not as common in the textile field due to their effect on the mechanical properties of textile materials, although they can be useful when stiffness does not play a significant role. In one instance, smart wound dressings based on poly-NiPAAm macrogels and its copolymers were bound to textile substrates by graft copolymerisation, which involves generating free radicals on a substrate and subsequently polymerising monomers directly on a textile surface. Poly-NiPAAm was copolymerised with polyurethane and grafted on a cellulose non-woven textile [97], or with N,N-methylene bisacrylamide (BIS) and grafted to a cellulose support [98]. Photo-induced graft copolymerisation of poly-NiPAAm on previously plasma-treated textile substrates has also been carried out through copolymerisation with polypropylene (PP) [99], with the addition of chitosan [100] and with a polyethylene terephthalate (PET) film [99].

Microgels based on carboxymethyl chitosan (CMCh) and PVA [112], CMC and fumaric acid [91], CMC and hydroxyethyl cellulose derivatives [92], self-assembling di-phenylalanine [83], glycol and ε-caprolactone [62], collagen [30], and polyacrylic acid and β-cyclodextrin [107] have been used. Poly-NIPAAm-based microgels have been by far the most studied because of the LCST of the polymer, which is in the body temperature range. Microgels based on poly-NIPAAm have been applied to textile substrates alone through graft polymerisation [113], or in combination with 1,2,3,4-butanetetracarboxylic acid [78] to chemically bind a microgel with the functional groups of a textile substrate. To improve its mechanical properties and decrease its tendency to coagulate, poly-NIPAAm has been synthesised in combination with other polymers such as the copolymer 2-aminoethyl methacrylate [82]. To achieve a sterile wound environment, different antimicrobial agents have been added to microgels such as silver in various forms [91], zinc oxide [114] and a biocidal agent based on quaternary ammonium salts [113].

Nanogels have been used in the field of medical textiles as smart coatings for wound dressings, tissue engineering and for the delivery of active substances. Smart wound dressings using nanogels have been created through the application of pullulan nanogel, carrying collagen onto a NanoClik membrane made of silicone [96]. That coating promoted wound healing and protected the wound from infection. Hence, bioactive molecules or proteins could potentially be incorporated into its structure. The average particle size of a nanogel was 30nm. In a different study, polyvinyl alcohol (PVA) nanogels were applied to a cotton fabric into which silver nanoparticles were inserted. The hydroxyl groups of the PVA stabilised the silver nanoparticles to prevent their agglomeration and further growth. A significant reduction in bacteria and more rapid wound healing were thus achieved. The size of nanogel particles was 10–50nm [93]. Temperature-responsive poly-NiPAAm-co-allylamine (PNIPAM-co-ALA) nanogels with incorporated silver nitrate have also been grafted onto non-woven polypropylene fabric for the purpose of designing a smart wound dressing. Nanogel particles had a diameter of 72nm at temperatures above

the LCST of the poly-NiPAAm, at which bacterial growth was prevented [80].

Nanogels can be incorporated into the structure of fibres via electrospinning by adding nanogels to a spinning mass. Composite poly(caprolactone) microfibres have been spun with a nanogel composed of poly(vinyl caprolactam) and 2-(methacryloyloxy) ethyl acetoacetate (PVCL/AAEM) copolymers [106]. For this purpose, two different solvent systems were used, methanol/toluene (Me/Tol) and chloroform/dimethylformamide (Ch/DMF), which led to the different morphological characteristics of spun fibres. Namely, fibres spun using Me/Tol had a diameter of 3 mm and the nanogel particles were located in the cores of the fibres, while fibres spun using CH/DMF had a diameter of 1 μm with nanogel particles on the surfaces of the fibres. The size of hydrogel nanoparticles in a dry state was 100nm. In another study, polysaccharide and gelatin nanofibres were produced for use in tissue engineering [95]. Nanogels composed of hydrophobised-pullulan were added to a spinning mass. Fibres with a 200 to 300 nm diameter included 60–80nm nanogel particles. Hence, hydrogel-like sub-micron fibres were electrospun from poly(acrylic acid) (PAA) crosslinked with b-cyclodextrin (β-CD) and thermally treated for the purpose of stabilisation [107]. Fibres ranged in size from 100 nm to several microns and were used as carriers of silver nanoparticles. A highly biocidic textile surface was achieved.

3.3.2 Use of hydrogels for increased comfort

Both nanogels and microgels can be used for improved comfort. To achieve dual temperature- and pH-responsiveness and thus increased comfort, poly-NIPAAm has been applied in combination with chitosan (PNCS microgel). Surfactant-free emulsion polymerisation was used to prepare a microgel with a particle size of 200 nm. Furthermore, a PNCS microgel was applied to different textile substrates, namely cotton, polyester and polyamide. To achieve chemical bonding of the PNCS microgel and consequently greater durability, the microgel was applied to previously chemically or physically activated fibres or in combination with crosslinking agents [59]. Chemical activation was achieved through carboxymethylation and amination [72–73].

While carboxymethylation included the application of monochloroacetic acid to form carboxymethyl groups, amination of the cotton fabrics was performed by dyeing cotton fabric with a reactive dye followed by reduction, thereby forming amino groups on the fibre surface. It was concluded that the pH responsiveness of the previously aminated, PNCS microgel-coated fabric was superior, while the temperature responsiveness of both previously activated fabrics was comparable. Oxygen, nitrogen and argon low-temperature plasma were used for the physical activation of cotton fabrics, not only to increase the number of functional groups on the fibre surface but also to increase the roughness of the fibres through a plasma etching effect, thus achieving a greater contact surface between the fibres and the microgel particles, and consequently greater adhesion of the PNCS microgel [115]. Application of the PNCS microgel in combination with crosslinking agents, i.e. 1,2,3,4-butanetetracarboxylic acid (BTCA) [74–75] and N,N'-methylenebisacrylamide [84–85], has also been studied. In the case of BTCA, a PNCS microgel was applied to a cotton fabric, where the acid reacted with hydroxyl groups of the cellulose and chitosan through the formation of ester bonds and with the free amino groups of chitosan through the formation of amides. When the PNCS microgel was applied in combination with the N,N'-methylenebisacrylamide crosslinker, a polyester fabric previously treated with acrylic acid was used. Crosslinking was achieved through UV irradiation in the presence of a benzophenone photo initiator. In a different study, the successful application of a PNCS microgel on PES fabric was achieved by using sol-gel technology, where a polysiloxane matrix was formed on the fibre surface in which microgel particles were physically incorporated. The matrix was formed using a vinyltrimethoxysilane sol-gel precursor in combination with hydrophilic silica nanoparticles. Due to the elastic properties of the polysiloxane matrix, the microgel particles could swell and shrink without any restrictions, while its presence increased the washing fastness of the hydrogel coating [76–77].

Nanogel coated fabrics with smart thermoregulation have been tailored using a temperature- and pH-responsive nanogel based on poly-NIPAAm and chitosan (PNCS), which was incorporated onto cotton fabric in combination with a BTCA crosslinker. The nanogel swelled at lower pH values and temperatures and shrank at higher temperatures and pH values. The addition of BTCA reduced the swelling ability slightly [79].

3.3.3 Use of hydrogels for protective properties of textile material

Textiles with protective properties can be obtained by adding different active substances into nanogel structures. A non-woven textile was coated with a nanogel based on poly-NIPAAm and methacrylic acid (MAA) incorporating silver nanoparticles into its structure [81] to achieve antimicrobial properties. The nanoparticles were inserted during or after synthesis, but prior to application to textiles; less agglomeration and smaller silver nanoparticle sizes were found when they were added during synthesis. The nanogel particle size was between 180 and 200nm. To achieve insecticidal properties with wool and other keratin fibres, a nanogel composed of highly functional β-cyclodextrin (β-CD) was loaded with an insecticide, permethrin, where the size of the nanogel particles reached 100-200 nm [94].

3.3.4 Use of hydrogels for filtration

Textile materials functionalised with stimuli-responsive hydrogels can be used as filtration systems, namely for oil and water separation. Such materials could help clean the ocean in the case of a catastrophic event. An extensive review article was written on this topic by Wang [116]. To achieve water/oil filtration, a temperature- and pH-responsive PDMAEMA hydrogel was applied to a stainless steel mesh to achieve active separation of water from oil/water mixtures at controlled pH values and temperatures. When the temperature was below 55°C and pH values were less than 13, water was able to pass through the textile material, and oil was inhibited. When the temperature rose above 55°C and pH levels rose above 13, the hydrogel particles shrank, and water and oil could transit through the fabric [103]. Superhydrophilic to superhydrophobic transition was achieved through the application of stimuli-responsive hydrogels based on poly-NiPAAm or PAA. The poly-NiPAAm hydrogel was coated on elastic polyurethane to achieve temperature-responsive switchable superhydrophilicity to superhydrophobicity with the LCST of poly-NiPAAm i.e., 32°C. This textile composite exhibited excellent water/oil separation properties, mechanical strength and elasticity. The hydrogel was prepared by dissolving poly-NiPAAm and BIS in APS, and was spun into a microfibre mat by force spinning [104]. Sidorenko and his team synthesised two PAA hydrogels and a tailored hydrogel array of isolated rigid setae hybrids etched to silicon to achieve smart wetting ability. One hybrid acts superhydrophobic before exposure to water and transforms to a hydrophilic state in the presence of water, while the second surface acts in the opposite manner. The wetting behaviour is reversible upon drying [102].

4 Conclusion

Stimuli-responsive hydrogels are an important group of materials with potential applications in various fields. They can be classified by their mode of crosslinking (chemical/physical) and their responsive characteristics, where they divide into physical (temperature, light, ultrasound, magnetic and electric field), chemical (pH, solvent and ionic strength) or biological (functionality molecule, e.g. enzymatic reactions) stimuli responsiveness. The stimuli-responsive behaviour of a hydrogel to a specific stimulus or a combination of different stimuli results in a reversible volume change of the hydrogel (i.e. swelling or shrinking) as a result of its transition from a hydrophilic to a hydrophobic state or vice versa. An important classification of hydrogel materials is based on their size, where macro- (>1mm), micro- (100nm–1μm) and nanogels (<100nm) can be synthesised. Due to the high degree of hydration and their three-dimensional structure, which resembles natural tissues, and their biocompatibility, hydrogels are already well-established in the fields of biotechnology, biomedicine and pharmacy, and textiles.

Textile material can serve as a reinforcement material to macrogels, where the primary textile properties play a minor role. In contrast, micro- and nanogels are used when hydrogels are being used as the active finish of a textile material, to provide a minimum effect on the original properties of the textile material. A temperature-responsive hydrogel based on poly-NiPAAm and chitosan was most commonly used for textile functionalisation. To reduce the size of hydrogel particles, shorter synthesis times and higher temperatures are needed. To achieve nano-sized hydrogel particles, appropriate synthesis is needed, depending on the monomers used. With the commonly used dispersion polymerisation technique, the key to reducing the size of hydrogel particles lies in stabilising the precursor particles early in the polymerisation reaction, either by the addition of a surfactant, catalyst or an ionisable anionic comonomer, or by increasing the temperature.

5 Future aspects of hydrogels applied in textiles

Although important pioneering research work has already been performed regarding the applications of hydrogels for smart textiles [67, 102], there are still many topics that remain largely unexplored and therefore present challenges for researchers. They address issues regarding technology, as well as issues concerning the safe handling of such smart textiles in terms of their potential toxicity to health and the environment. Accordingly, some of the major research problems that need to be resolved in the future are the impaired handling properties of a textile material. The stiffness of a functionalised textile substrate greatly increases after the deposition of stimuli-responsive hydrogels. The use of appropriate softeners should thus be considered. The stability of a hydrogel on textile material also needs to be further improved. Accordingly, some progress has been made with the use of crosslinking agents, and through the chemical activation of fibres and the physical entrapment of hydrogel particles. However, to achieve increased washing durability with a minimum effect on the stimuli responsiveness of a hydrogel, further focus on the optimisation of application parameters is needed. In the field of medical textiles, more in-depth understanding of the controlled release of active substances from the structure of hydrogel particles, the effect of released compounds on the wearer and thus the potential cytotoxicity assessment of the functionalised fabric is needed. From an economical point of view, the costs of textile functionalisation using stimuli-responsive hydrogels must also be considered. Because the price of hydrogel-based finishes varies greatly depending on the chemicals used and on the complexity of the synthesis, further production optimisation will be needed to achieve the successful transfer of such stimuli-responsive finishes from a laboratory scale to industry in order to meet the demands of cost production on the one hand and the desired level of profit on the other. Last but not least, the effects of hydrogel based finishes on humans and the environment are also crucial. Depending on their origin, polymers composing stimuli-responsive hydrogels could be more or less cytotoxic. Because studies of the potential risk of newly developed compounds on human health and the environment still lag behind studies regarding their functionality, further focus regarding the toxicity of functionalised smart textiles during their use or after their disposal is needed in order to make a proper risk-benefit assessment.

Research in the field of hydrogel-functionalised textiles will therefore focus on the following:

- Synthesis and incorporation of nano-sized hydrogels into different textile materials;
- Use of hydrogels as carriers for different active agents;
- Application and combination of different stimuli-responsive hydrogels to achieve simultaneous worn comfort along with proactive protection;
- Improvement of durability and washing fastness of hydrogel coatings, in terms of maintaining stimuli-responsive characteristics;
- Reduction of the effect on the mechanical properties of textile materials;
- Health and environmental effects of hydrogel-based finishes, by addressing problems of toxic side effects, as well as the biodegradability of disposed functionalised textiles and the bioaccumulation of hydrogel compounds; and
- Optimisation of synthesis methods to minimise production costs.

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