



**POLITECNICO  
DI TORINO**

**Master of Science in Textile Engineering**

# **Functionalization of Textile Fibers with Hydrogel**

**Final Project Work**

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# Abstract

Hydrogels have been part of study for more than half century, but the development of new procedures and technologies, expanding the interest of scientists and biomedical researchers for the use of hydrogels. Hydrogels with specific characteristics are remarkable, they comprise of a self-reliant, three dimensional (3D) viscoelastic network of water-swollen, which allows the dispersion and connection of molecules and cells. Great attention of scientific community has recently been drawn for the use of hydrogels in the large production of biomedical applications, for example, wound mending, cartilage/bone recovery and the sustained drug delivery. Hydrogel products constitute a group of biopolymeric hydrogel, among which the hydrophilic structure of polysaccharides renders them skills of absorbing water in their three-dimensional networks without suffering disintegration. Extensive employment of these products in various mechanical and environmental regions of use is viewed as of prime significance. Hydrogels used for the purpose of incorporation, crosslinking parts, stimuli-responsive attributes and particle size in the functionalization of textile materials. A more inside and out knowledge on the impact of hydrogel molecule size is given, where macro-gels, micro-gels and nano-gels are considered for textile functionalization. In addition to the applications of macro-, micro- and nanogels to textile materials, the applications of hydrogel microspores (PNIPAAm) and the copolymer hydrogels are sensitive to temperature, environment and stimuli in hydroscopic, deodorant and delivery fabrics respectively and their planned usages.

**Keywords:** Hydrogel, Stimuli-responsive Hydrogels, micro and nanogels, PNIPAAm, Smart Textile, Preparation, Functionalization, Applications



# Summary

<b>Chapter 1 Introduction</b>	<b>9</b>
<b>Chapter 2 Prreparation of Hydrogel</b>	<b>14</b>
2.1 Copolymerization .....	14
2.2 Cross Linking .....	14
2.2.1 Compound Cross Linking .....	15
2.2.2 Physial or Ionic Cross linking.....	15
2.3 Chemical Hydrogels .....	15
2.4 Physical or reverssible Hydrogels.....	15
2.5 Conventional Hydrogels .....	16
<b>Chapter 3 Characterization of Stimuli-Responsive Hydrogels</b>	<b>19</b>
3.1 Nature of Polymers .....	20
3.2 Types of Cross Linking .....	20
3.3 External Stimuli.....	22
3.4 Hydrogel Particle Size .....	23
<b>Chapter 4 Stimuli-Responsive Hydrogels For Textile Functionalization</b>	<b>25</b>
4.1 Working Principle of hydrogel On Textile Material .....	26
4.2 Chemical Structures and Synthesis Condition of Hydrogels.....	28
<b>Chapter 5 Hydrogel Applications in Different Fields</b>	<b>34</b>
5.1 Hydrogel Application in Textile Modification.....	36
5.2 Temperture-Sensitive Hydrigel Applications .....	37
5.3 Temperature-Sensitive Hygroscopic Textile .....	38
5.4 Environmental-Sensitive Hydrogels in Deodorant fibers.....	44
5.5 Environmental-Sensitive Hydrogels in Nutrient/Drug Delivery fibers .....	46
<b>Chapter 6 Hydrogel Uses</b>	<b>49</b>

6.1 Hydrogel Used In Medical Field .....	49
6.2 Use of hydrogel to Increase comfort .....	51
6.3 Hydrogel use For Protective Properties of textile Material.....	52
6.4 Use of Hydrogel For Filtratio .....	52
<b>Chapter 7 Conclusion</b>	<b>54</b>
<b>Bibliographic References</b>	<b>56</b>



# Chapter 1

## Introduction

Polymer science is a continual development. This leads to the introduction of materials with unique properties. Amongst these, hydrogels play a particular role and have gained interest from the scientific community.[1] This is still true today, while the first synthetic hydrogel, cross-linked poly (2-hydroxyethyl methacrylate), was developed by Wichterle and Lim in the 1960's. It found use in contact lenses.[2]

In 1968, it was predicted that the repulsion between the polymer network and a weak solvent (intramolecular condensation) can lead to a phase transition and a change in the degree of swelling. Ten years later, Tanaka observed and explained the collapse of the polymer network in polyacrylamide gels. The existence of a critical point when the length of the polymer segment reaches a certain value has been confirmed in theoretically and experimentally. Following from this discovery of the phenomenon of "volume phase *transition*", hydrogels have taken on an important role in functional material research.[3]

It is interesting to note that hydrogels have been the first bio-materials certified for use in the human body. Progress in polymer science has allowed new approaches for the production of hydrogels and has led to new, more attractive properties. Today, hydrogels cover a large spectrum of applications going from agriculture to the medical field.[4]

Hydrogels are three-dimensional, hydrophilic, polymeric frameworks skilled in holding a great deal of water or natural fluids. Or then again as it were, Hydrogels are 3D cross section polymers that, because of the nearness in them of hydrophilic practical gatherings, swell up to a few times of their unique volume in fluid media. Various properties of hydrogels make them sensible for biomedical applications that require contact with living tissue. Hydrogels are fit for engrossing and holding a lot of water. The delicate, rubbery consistency of swollen hydrogels limits frictional aggravation of encompassing cells and tissue and might be manufactured in an assortment of shapes and geometries.[5]

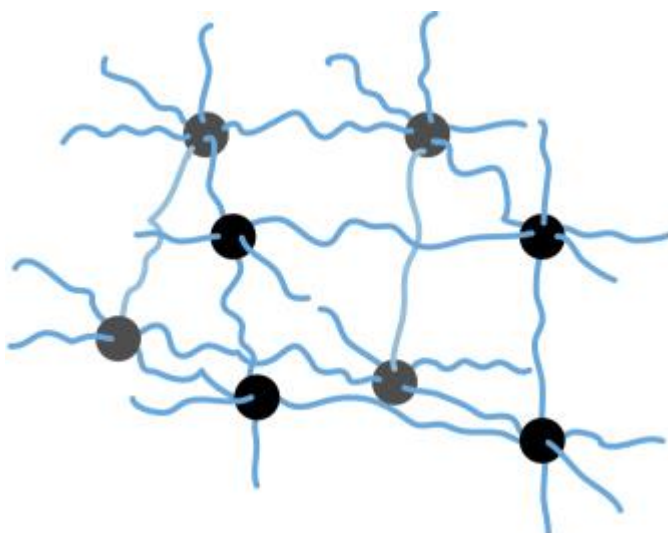
Hydrogel imperative trademark is their capacity to answer to outside physical/synthetic/mechanical boosts with an auxiliary change (for example distortion, swelling, separation of intentional gatherings). This capacity is misused inside the readiness of "canny" materials having beyond any doubt discretion systems. On the off chance that these gels moreover contain for example semiconducting metal particles, the response instigated by the revision inside the ecological parameter may happen amid an adjustment in the conduction of the nanoparticle-containing composite, since, looking on the degree of swelling, the particles captured inside the gel draw closer along or more distant separated. These properties might be all around connected in sensors. amid this case, the conduction of composite relies upon the scale, volume division and dispersity of the metal nanoparticles in line with percolation hypothesis.[2]

Keen hydrogel systems with various misleadingly and in a general sense responsive moieties show responsiveness to outside lifts including temperature, pH, ionic obsession, light, appealing fields, electrical fields, and engineered substances. Polymers with different responsive properties have likewise been developed flawlessly consolidating two additional lifts responsive frameworks. Sharp polymer hydrogels change their helper and volume organize advance as a response to external updates coming about in an gigantic potential for coherent discernments and for various advanced mechanical applications..[6]

Hydrogel can be characterized into two particular classifications, the characteristic and the engineered hydrogels. Common hydrogels incorporate collagen, fibrin, hyaluronic corrosive, materiel, and subsidiaries of normal materials, for example, chitosan, alginate and aptitude strands. They remain the most physiological hydrogels as they are parts of the extracellular matrix (ECM)in vivo. Two essential drawbacks of customary hydrogels, in any case, make their last microstructures and properties difficult to control reproducibly between trialsue. To begin with, the fine subtleties of their mechanical properties and their reliance on polymerization or gelation conditions are regularly ineffectively comprehended.[7]

Second, because of their regular inception (cow-like fibrinogen, rodent tail collagen, their organization may shift starting with one cluster then onto the next. Interestingly, engineered hydrogels, for example, Poly(ethylene glycol) diacrylate, poly(acrylamide)

Poly vinyl liquor are progressively reproducible, in spite of the fact that their last structure can likewise rely upon polymerization conditions unobtrusively, with the goal that a thorough control of the planning convention, including temperature, and condition control, might be vital. As a rule, manufactured hydrogels offer greater adaptability for tuning concoction piece and mechanical properties; clients can, for instance differ the focus or atomic load of the forerunner, or change the level of cross linkers. They can similarly be picked or tuned to be hydrolysable or biodegradable over factor time allotments. Hydrogels might be artificially steady or they may corrupt and in the long run crumble and break up. They are called «reversible» or «physical» gels when the systems are held together by sub-atomic entrapments or auxiliary powers including ionic, H-holding or hydrophobic powers. Physical hydrogels are not homogeneous, since bunches of molecular traps, or hydrophobic partner or amusingly related spaces, can make in homogeneities.[2]



**Figure 1: 3D Dimensions of Hydrogels[2]**

Free chain closures or chain circles likewise speak to transient system surrenders in physical gels. At the point when a polyelectrolyte is joined with a multivalent particle of the contrary charge, it might shape a physical hydrogel known as an inotropic hydrogel, alcium alginate is a case of this kind of hydrogel. Hydrogels are designated "changeless" or "compound" gels when they are covalently-cross connected systems. The manufactured hydrogels of Wichterle and Lim depended on copolymerization of HEMA with the cross linker EGDMA. Substance hydrogels may likewise be created by crosslinking of water-dissolvable polymers, or by change of hydrophobic polymers to

hydrophilic polymers in addition to crosslinking isn't fundamental. Now and again, contingent upon the dissolvable synthesis, temperature and solids fixation amid gel development, stage partition can happen and water-filled voids or macrospores can frame. In synthetic gels, free chains end speaks to gel organize "abandons" which don't add to the versatility of the system. Other system abandons are chain circles and traps, which additionally don't add to the changeless system flexibility.

Hydrogels are characterized in **Figure 1** as three-dimensional polymers ready to swell in water or in a natural liquid while saving their shape. Hydrogels are cross-connected, hydro extending polymer structures.[2]

Hydrogels can retain from 10% to a huge number of times their dry load of water. The capacity they have to assimilate water comes from their hydrophilic groups (such as -OH, -CONH-, -NH<sub>2</sub>, -COOH, and CH<sub>3</sub>OH) useful gatherings connected to the carbon polymer chain. [8]

In addition, their difficulty for dissolving originates from the cross-connecting of the chains of the network. The nearness of synthetic or physical cross-linking assures a network structure and guarantees the physical integrity of the system. This is justified by the specific character of hydrogels that are insoluble in water when they find themselves in an aqueous medium.[9]

During the swelling, the polymer chains separate up to a limiting value, determined by the properties of the solvent in which the hydrogels are placed and the length of the polymer chains. In swollen state, there are weak interactions between the chains, while in a dehydrated or retracted state, the polymer chains of the hydrogel network are close together. One of the important parameters influencing the swelling behavior of hydrogels is their level of cross-connecting.[8]

Strongly cross-linked hydrogels have a more compact and close-knit structure and swell less compared to a network that is looser (fewer cross-linking nodes). In addition, the chemical structure of polymers forming hydrogels equally determines their swelling properties.

The nearness of hydrophilic gatherings on the polymer chains of the hydrogel network increases the rate of swelling contrasted with systems containing hydrophobic gatherings. Hydrophobic gatherings form aggregates, destabilizing the structure of the

hydrogel within the sight of water and hence minimize their introduction to water molecules. [10]

What differentiates hydrogels from other polymer materials, is their unique properties such as their rubbery and supple behavior, their low interfacial energy with water, and their highly charged structure in water.[10]

Hydrogels are generally biocompatible materials, in view of their high-water, their composition and their mechanical behavior which is close to that for an extra cellular matrix of natural origin. Apart from biocompatibility, the water content also affects other properties such as permeability, and surface and mechanical properties.[2]

## Chapter 2

# Preparation of Hydrogels

The properties of the hydrogel network are closely linked to the conditions in which the hydrogels are synthesized. The formation of the hydrogel network, dictated by the choice of characteristics to achieve depending on the targeted applications, always pose problems for scientists as certain properties of the network are incompatible. There are several techniques and procedures used for the preparation of hydrogels. The most widespread synthesis path is by radical copolymerization between acrylamide-based monomers with a divinyl based monomer, playing the role of cross-linking agent, in aqueous solutions.[11]

There are 2 general approaches in the synthesis of hydrogels:

### 2.1 Copolymerisation

Copolymerisation/Cross-linking between one or several monomers and a multifunctional monomer that acts as a cross-linking agent.[5]

This is the most common approach. It involves the initiation of a polymerization reaction by a chemical initiator. The polymerization response should be possible in mass, in arrangement or in suspension. In solution, the monomers are mixed with the cross-linking agent and the polymerization/cross-linking reactions are initiated thermally, using a UV lamp or by a redox initiator system. Polymerization in suspension gives rise to the formation of spherical hydrogel microparticles, with a size of between 1  $\mu\text{m}$  and 1 mm. Dispersion of a monomer solution in a non-solvent lead to fine droplets is obtained in the presence of a stabilizer. The polymerization is initiated by the formation of free radicals obtained by thermal decomposition.[9]

### 2.2 Cross-Linking

Cross-linking of the linear polymer and a combination of monomer and linear polymer chains. Two methods of cross-linking are possible: chemical or physical cross-linking.

### **2.2.1 Compound Cross-Linking**

It includes radical polymerization, the chemical reaction of complementary groups, recourse to enzymes or to high energy irradiation. Reactions by radiation use electron bombardment, gamma ( $\gamma$ ), X, or ultraviolet (UV) rays to excite a polymer and to produce a cross-linked structure. When cross-linking is produced by the use of chemical compounds, the system must include at least one dual-function cross-linking agent able to react with the functional groups on the polymer chains. It thus produces a bridging between 2 polymer chains. Among the most common cross-linking agents, are *N,N'*-methylene bisacrylamide, divinyl benzene, and ethylene glycol dimethacrylate.[2]

### **2.2.2 Physical or Ionic Cross-Linking**

This is a simpler and ecological process. Unlike cross-linking by covalent bonds, no auxiliary molecule such as a catalyst is employed and the use of toxic cross-linking agents is avoided. It is important to underline the difference between chemical and physical hydrogels.[5]

## **2.3 Chemical Hydrogels**

They are qualified as permanent, are polymers for which the cross-linking is produced by covalent bonds. The nearness of useful gatherings, for example, – OH, – COOH, on the polymer chain can be utilized to shape covalent bonds between the polymer chains by corresponding responses between amine/carboxylic corrosive, isocyanate/OH or by the arrangement of a Schiff's base. Chemical hydrogels are mainly inhomogeneous, because of the presence of zones of weak swelling in water with an elevated cross-linking density. Sometimes a phase separation can occur in these hydrogels, creating empty zones filled with water or "micropores".[2]

## **2.4 Physical or Reversible Hydrogels**

These are characterized by the presence of molecular entangling and/or secondary forces including ionic forces, hydrophobic forces or forces due to hydrogen bonding. All these collaborations are reversible and can be perturbed by changes in physical conditions or by the demand of stresses. Inhomogeneities in physical hydrogels come

from entangled molecular networks, in areas linked ionically or hydrophobically or from the ends of the dangling chains or ringed sub-structures.[5]

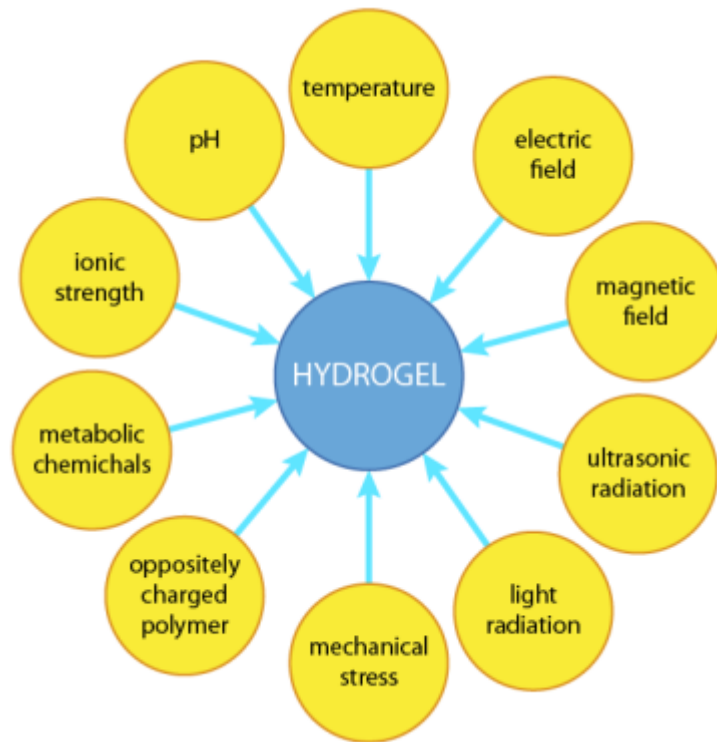
Physical and chemical hydrogels are displayed in several forms: solid and molded, compacted powder, microparticles, coatings, membranes, sheets, encapsulated solids or liquids.[2]

## 2.5 Conventional Hydrogels

They are not sensitive to changes in the environment, as opposed to **stimuli-responsive hydrogels** which can sense an external stimulus. The difference between conventional hydrogels and stimuli-responsive hydrogels depends upon the constituent polymers. Stimuli-responsive hydrogels contain smart polymers. These smart polymers have the ability to respond to small changes in their physiological or biological environment by changes in volume, that is, swelling or shrinking. They form systems for which slight variations in thermodynamic parameters (pressure, temperature, concentration, solvent, etc...) induce considerable modifications of the physical and chemical properties of the macromolecules (solubility, structure, shape, size) and of the stability of solutions.[5]

The volume phase transition takes place depending upon the hydrophobic/hydrophilic equilibrium reaching the level of the molecular structure of the polymer. Stimuli-responsive hydrogels contain more charged or less charged hydrophobic domains. Conventional hydrogels are generally not charged.[12]





**Figure 2: Parameters affecting on hydrogel[2]**

The sensitivity of "smart" polymers that form hydrogels determines the sensitivity of the whole network. Temperature, pH, and the electrical are probably the most exploited stimuli for controlling the swelling behavior of smart hydrogels. The following table represents several representative polymers that respond to these three stimuli and are able to form hydrogels that are sensitive to stimuli.[13]

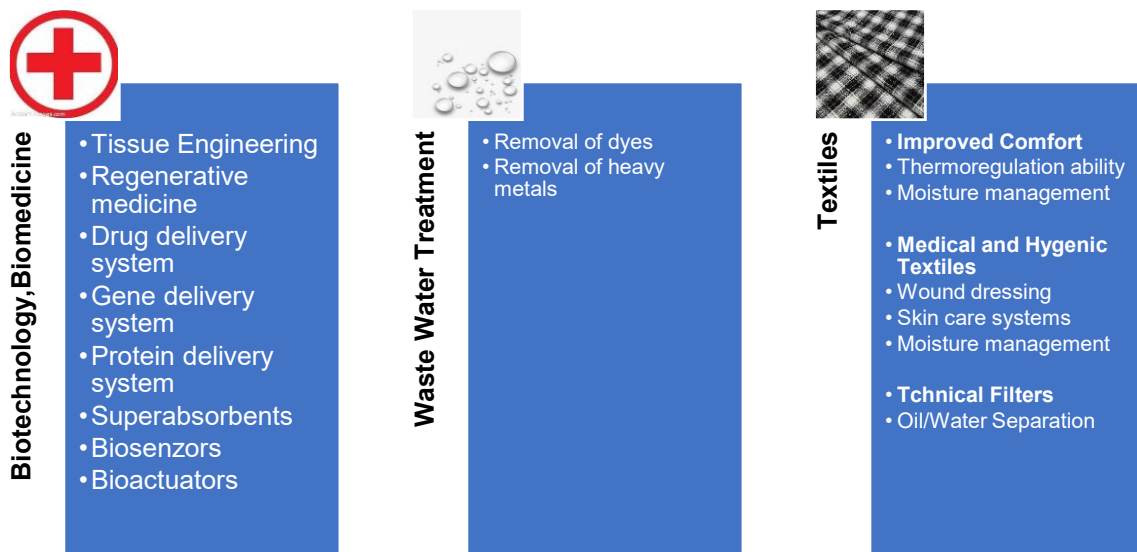
**Table 1: Sensitivity of Smart polymer**

<b>Thermo-sensitive</b>	<b>Sensitive to pH</b>	<b>Sensitive to electrical signals</b>
Poly(N-isopropylacrylamide)	Poly(acrylic) acid	Poly(2-arylamido-2-methylpropane sulfonic co-n-butyl methacrylate) acid
Poly(methacrylate of butyl-co-acrylamide)	Poly(methacrylic) acid	Poly(2-acrylamido-2-methylpropane sulfonic) acid
Poly(N,N-dimethylacrylamide)	Poly(metacrylate diethyl amine)	Xanthane gum grafted poly(acrylamide)
Block copolymer of poly(ethylene oxide) poly(propylene) oxide	Poly(N,N'-diethylaminoethyl methacrylate)	Poly(acrylic acid/poly vinyl sulfonic) acid
Poly(ethylene glycol)-poly(lactic-co-glycolic) acid-poly(ethylene glycol)	Poly(vinylacetate diethyl aminoacetate)	Poly(vinyl) alcohol
Xyloglucane	Chitosan	Agarose

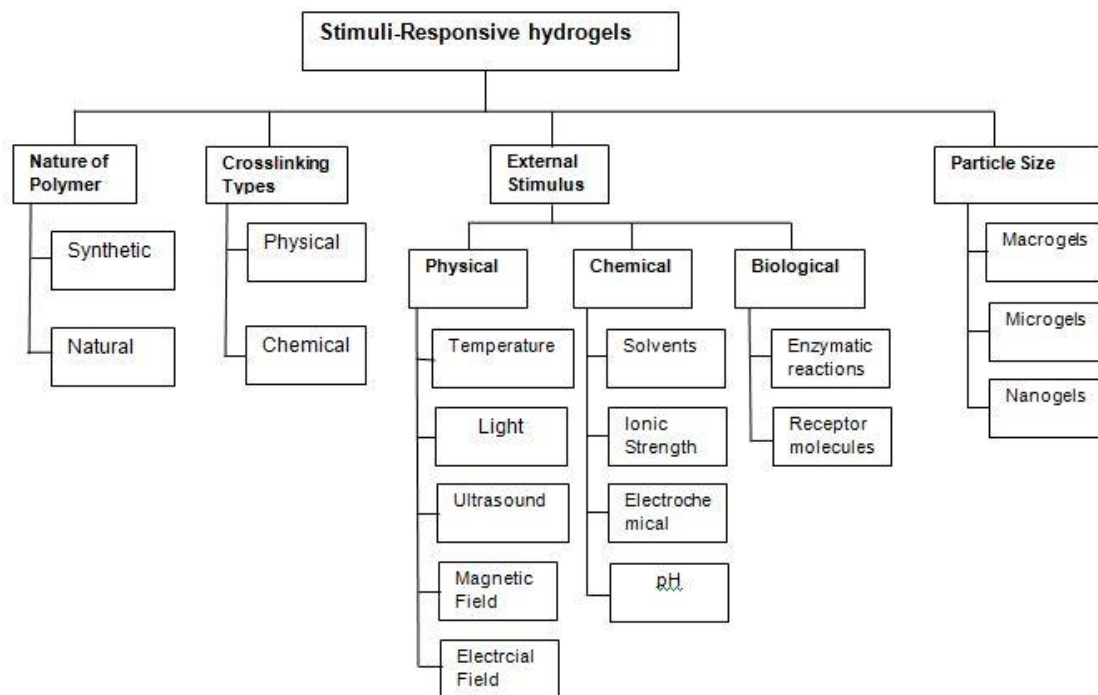
# Chapter 3

## Characterization of Stimuli Responsive Hydrogels

Hydrogels are generally arranged in writing as per the nature/wellspring of a polymer, sort of crosslinking, outer boosts that trigger stage progress and the extent of hydrogel particles (Figure 2).[14]



**Figure 3: Schematic outline of utilization fields of improvements responsive hydrogels**  
[14]



**Figure 4: Classification of Stimuli-Responsive Hydrogels**[14]

### 3.1 Nature of Polymers

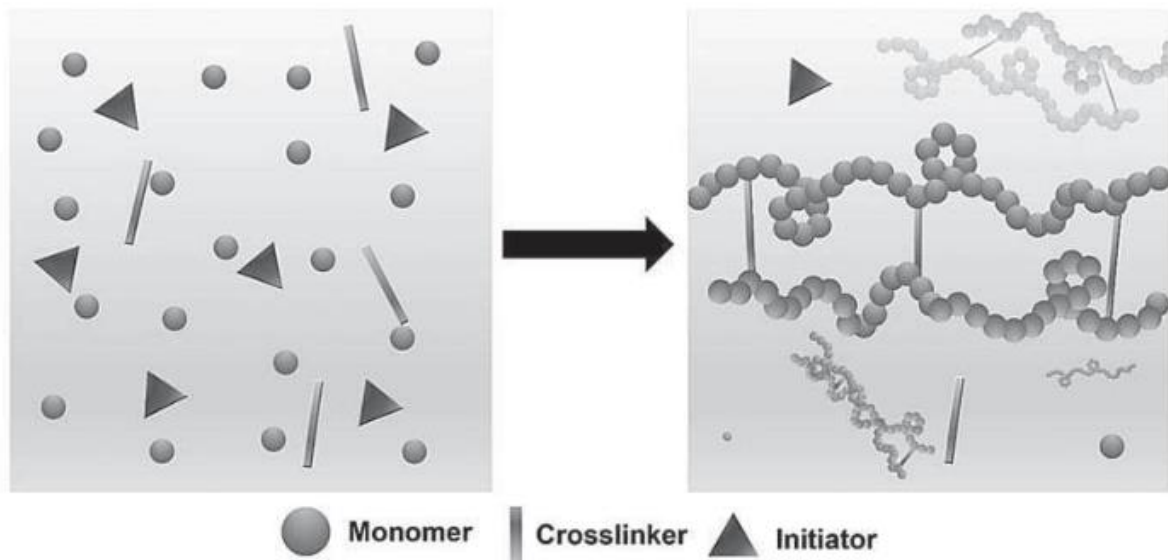
Polymers that structure upgrades responsive hydrogels can be of normal or designed origins. Trademark polymers, which join proteins, for instance, gelatin and polysaccharides (for instance chitosan, alginate, and  $\kappa$ -carrageenan), are named "green-adroit" polymers with low noxious quality and biocompatibility. As opposed to normal polymers, produced polymers are phony and are incorporated by substance polymerization procedures. Likely the most generally used polymers join poly(N-alkyl substituted acrylamides), poly(N-vinylalkylamides), poly(N, N-diacylamino ethyl methacrylate's).[14]

### 3.2 Types of Cross Linking

The crosslinking of the polymer sort out occurs in the midst of hydrogel preparation: in the midst of the method of gelation, polymer stays begin to crosslink and structure greater, extended, yet in the meantime dissolvable, polymers. Mixes of such poly-disperse extended polymers are ordered "sol". [15] the further ensnarement of

polymers prompts the course of action of an affirmed "gel", where the crosslinking of totally spread polymers occurs. Their dissolvability well ordered decreases with the extending catch of the polymer mastermind. This change is implied as the "sol-gel advance", while the essential time when a gel shows up is known as the "gel point". Hydrogels are named physically or falsely cross linked gels regarding the sort of crosslinking. In physically cross linked gels, polymer frameworks are formed by methods for physical joint efforts between macromolecular chains, for instance, van der Waals powers, ionic affiliations, hydrogen bonds or hydrophobic interactions. [16] Physically cross linked hydrogels can be solidly or sadly cross linked. Determinedly physically cross linked hydrogels structure strong convergences between polymer ties and are undifferentiated from falsely cross linked hydrogels. Strikingly, weakly physically cross linked gels are associated by momentary convergences between polymer chains.[15]

In this manner, they have a restricted life expectancy and are always showing signs of change. Physically cross-connected hydrogels are valuable for various biotechnological and biomedical applications in light of the fact that their polymerization procedure is done without the nearness of natural crosslinking agents. [16] On the other hand, artificially crosslinked hydrogels structure solid covalent bonds between polymer chains, which make them profoundly steady. Covalent bonds between polymer chains can be set up if the responding polymers contain practical side gatherings, for example, OH, COOH or NH<sub>2</sub> in their structure [17]. They have great mechanical properties and have a generally long debasement time. In the arrangement of artificially crosslinked hydrogels, natural crosslinking specialists and initiators are typically present in the polymerization procedure. [18] However, there are additionally forms in which natural crosslinkers are not utilized. Hydrogels can be orchestrated through radical polymerization, polymerization started by UV light, chemical catalyzed responses, and  $\gamma$ -beam or electron pillar illumination. At the point when presented to  $\gamma$ -beam or electron shaft radiation, radicals structure long polymer chains in a watery arrangement. The radiolysis of a water particle results in the arrangement of hydroxyl gatherings, which can respond with polymer chains to prompt the development of macroradicals. This permits the development of covalent bonds with a crosslinked structure without the expansion of a natural crosslinker.[16]



**Figure 5: schematic outline of the planning of artificially cross connected hydrogels [14]**

### 3.3 External Stimuli

In view of the source of the boosts to which hydrogels react, we can recognize physical, compound and natural improvements. Physical upgrades incorporate temperature, light, ultrasound, attractive fields, and electrical fields, while concoction improvements incorporate solvents, ionic quality, electrochemical fields, and pH.[19] Furthermore, organic boosts allude to the usefulness of atoms, for example, enzymatic responses and the distinguishing proof of a receptor particle. Hydrogels that react to numerous improvements can be incorporated when joining distinctive responsive polymers. Table 2 outlines outer improvements and their impact on the component of swelling and contracting of various kinds of hydrogels. For shrewd material functionalization, temperature and pH-responsive hydrogels are the most considered, as these two upgrades are noteworthy in physiological terms.[18] Temperature-and pH-responsive hydrogels can associate with the client specifically since those two improvements can happen either through an adjustment in temperature of the prompt surroundings of material or through changes in the pH of the skin or substantial discharges, for example, sweat, blood, and urine.[20] Hydrogels dependent on temperature-responsive polymers have a basic arrangement temperature, which can be distinguished as a lower basic arrangement temperature (LCST) or an upper basic

arrangement temperature (UCST). A LCST is described by contracting, which implies that a polymer shows up in one stage underneath the basic temperature and experiences stage partition when the temperature transcends the LCST, while a UCST is portrayed by swelling as the temperature rises, implying that stage division happens at lower temperatures, and a change to the monophasic structure happens with rising temperature. At the point when a temperature-responsive polymer is in a monophasic state, hydrophilic associations are transcendent, while hydrophobic cooperation win when the conditions make a biphasic state.[17]

Polymers that react to natural pH are polyelectrolytes with acidic or fundamental pendants, which can get or transmit protons in light of upgrades from the earth. As the pendants protonate or deprotonate at an uncommon pH, for example at pKa or PHb, the electrostatic shock among ionic gatherings produces osmotic weight, prompting an adjustment in the volume of a polymer. Polymers receptive to pH can be polyanions, which swell at rising pH esteems, or polycations, which swell at falling pH esteems.[18]

### **3.4 Hydrogel Particle Size**

Hydrogels can also be characterized by their particle size; macro-, micro- and nanogels can be formed. [22] Micro gel particles range in size from a micrometer or more, whereas micro gel particles have a diameter of 100nm to 1 $\mu$ m, forming colloid ally stable, water-swell able polymer networks.

Little hydrogel particles make a more noteworthy surface to volume proportion, which is reflected in shorter reaction times and expanded surface per unit. Since the elements of responsive hydrogel particles and the rate of the volume stage progress are conversely proportional,[23] little molecule sizes are likewise reflected in points of interest of more noteworthy command over the swelling and ensnarement and arrival of captured dynamic substances as a result of the more noteworthy explicit surface region of hydrogel nanoparticles.[19]

**Table 2: External Stimulus.Types and Mechanism**

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



# Chapter 4

## Stimuli Responsive Hydrogels for Textile

### Functionalization

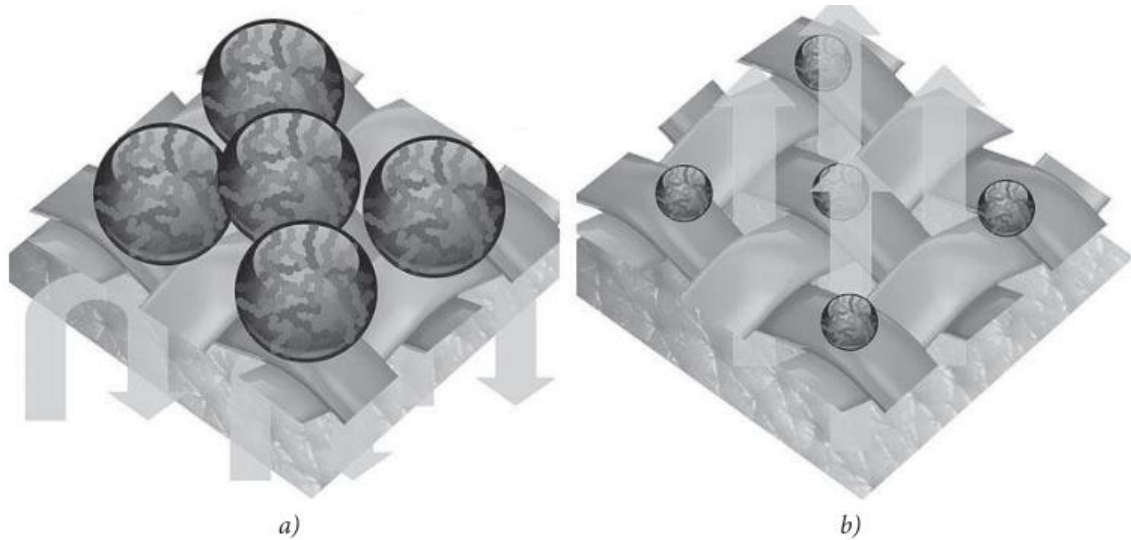
Hydrogels of improvements responsive polymers speak to a critical gathering of elite hydrated polymers that can react to various upgrades from the earth. Their hydration properties empower hydrogels to assimilate and hold expansive amounts of water or different watery arrangements in their three-dimensional polymer systems. [24] Namely, they can hold at any rate of 20% water with respect to their dry weight. [25] Because the crosslinking of the polymer organize keeps the disintegration of hydrogels in water, they swell, which causes an immediate increment in their volume. the swelling of a hydrogel is specifically influenced by water-polymer associations, which thus are influenced by the hydrophilicity of polymers: the higher the polymer hydrophilicity, the more grounded the water-polymer cooperations. The water in a hydrogel can be joined as free or bound water. Free water is situated at the peripheral layer and can be effectively expelled by means of mechanical pressure or centrifugation. Water joined to the polymer chain is called bound water and structures hydrogen bonds with polar gatherings of the polymer. This water must be evacuated at high temperatures, else, it remains some portion of the hydrogel structure. Interstitial water is physically ensnared inside hydrated polymer chains. In conclusion, semi-bound water has qualities of both bound water and free water. The swelling limit is dictated by the space inside the polymer organize, while the swelling procedure relies upon the rate of unwinding of polymer chains and on the rate of the dispersion of water molecules.[26] The exceptional property that recognizes upgrades responsive hydrogels from non-responsive hydrogels is their responsiveness to insignificant changes in natural conditions (temperature, pH, ionic quality, electric and attractive! driven, light, and so on.), which trigger the ingestion and arrival of water from the polymer arrange. This prompts a reversible volume change of the polymer to arrange from a swollen hydrogel to a fallen gel. The volume stage progress of a hydrogel is ascribed to an adjustment in polymer-dissolvable collaborations incited by outer improvements. To be specific, if an outer upgrade adjusts the polymer structure from a hydrophilic to a hydrophobic state, water will be discharged from the hydrogel to its environment, and the

dehydrated hydrogel will shrink as a result .[20] Since changes in a polymer structure are reversible, a hydrogel will come back to its underlying state when the outer upgrade is missing. Besides, the progress from hydrogel to arrangement can likewise be activated by outer boosts. Nonetheless, these auxiliary changes are less vital for material utilizations of hydrogels. [25] Their unrivaled boosts responsive properties result in the work of art! the cation of hydrogels as biomimetic "keen" polymer frameworks, the utilization of which is developing exponentially in different application fields (Figure 3). Hydrogels have just been built up in biotechnology and biomedicine, where they generally fill in as platforms for tissue designing; medication, quality and protein conveyance frameworks; superabsorbent; and biosensors and bio actuators.[9] Due to their contracting capacity, upgrades responsive hydrogels have turned out to be basic in nature, where they are utilized as adsorbents in wastewater treatment for the powerful expulsion of colors and substantial metals, and for the modification of wastewater from contamination brought about by oil.[14] Stimuli-responsive hydrogels likewise present incredible potential and openings in the field of materials, where they are connected to various material substrates to make new shrewd functionalities, including thermoregulation and dampness the board for solace enhancement, and the controlled arrival of dynamic substances for wound dressing or healthy skin. Hardly any survey articles have been composed to date on the point of hydrogels for use in materials, concentrating on the utilization of hydrogels for therapeutic materials and materials for expanded comfort.[28] To provide new knowledge in the use of hydrogels for chemical modification of textile materials.[14]

#### **4.1 Working Principle of Hydrogels on Textile Materials**

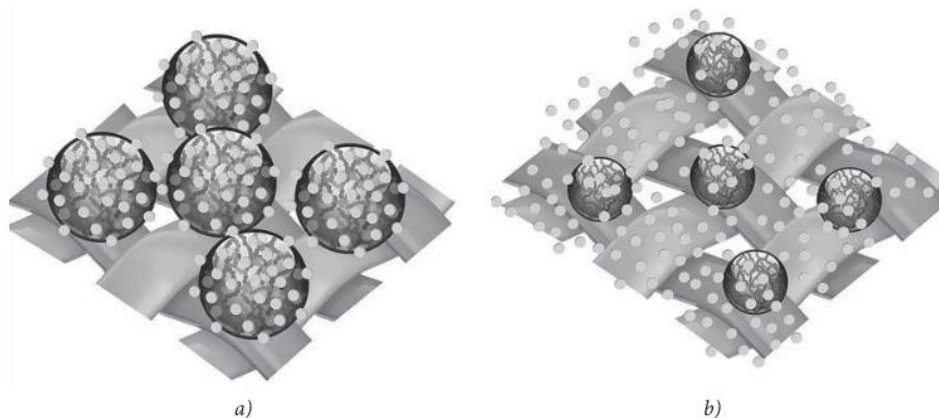
To accomplish comfort enhancement, the dynamic adjusting of body dampness and temperature by a material is urgent (Figure 6). An improvements responsive hydrogel present on material strands can cooperate with the client by recognizing and reacting to changes in natural conditions. At the point when an outer boost manages the swelling of a hydrogel, the porosity of the material declines. Such a marvel causes body vapors maintenance and therefore heat collection on the skin's surface (Figure 6a). Interestingly, when an outer upgrade manages the contracting of a hydrogel structure, texture porosity expands, in this manner giving breathability to the material

and more noteworthy body vapors and warmth progress from the skin's surface through the material to its environment (Figure 6b) .[21]



**Figure 6: Stimuli responsive hydrogels for textile functionalization**[14]

Boosts responsive hydrogels can likewise be used for the controlled arrival of dynamic substances from therapeutic and clean materials (Figure 7), which are utilized for quickened wound mending or healthy skin. Hydrogels assimilate dynamic fixings within the sight of natural conditions that manage their swelling. Dynamic substances can be held in a hydrogel structure (Figure 7a) until ecological conditions trigger shrinkage (Figure 7b). The reversible swelling and contracting of a hydrogel activated by an outer improvement gives the slow and controlled arrival of dynamic substances into the earth just under explicit conditions.[14]



**Figure 7 stimuli responsive hydrogels**

## 4.2 Chemical Structures and Synthesis Conditions for Textile material

For savvy material functionalization, temperature-responsive polymers, i.e., poly(N-isopropyl acrylamide) (poly-Nipa Am), poly(vinyl liquor) (PVA), poly (ethylene glycol) (PEG) and poly(vinyl caprolactam) (Figure 7), and pH-responsive polymers, i.e., chitosan (Cs), poly(acrylic corrosive) (PAA), poly(methacrylic corrosive) (PMAA) and poly(allylamine) (poly-ALA) (Figure 8), are utilized for their planning. Table 3 condenses the united states of the miniaturized scale and nano gels that were utilized for the material application. [30] It is obvious from the table that hydrogels are utilized in homopolymeric and copolymer shapes. The last incorporate blends of Nipa Am with chitosan, ALA, MAA or N-aminoethyl methacrylate (AEMA). Hydrogels have been orchestrated utilizing different strategies, for example, sans surfactant scattering copolymerization with an ordinary blending method, blending with the assistance of an ultrasound shower, copolymer amalgamation, coupling of a triblock copolymer, surface-started particle exchange radical polymerization (ATRP), free extreme polymerization and precipitation polymerization.[14] In many cases, sans surfactant scattering polymerization is utilized to combine both microgels and nano gels. In the sans surfactant scattering polymerization of hydrogels dependent on poly (N-substituted acrylamides, for example, poly-Nipa Am, the nearness of N,N'- methylene bisacrylamide (BIS) as a crosslinker is fundamental, despite the fact that copolymerization without the option of BIS has additionally been performed.[20] To start the response, N,N,N'- ammonium persulphate (APS) is included. APS changes monomers to free persulfate radicals, trailed by a response with polymer chains and non-enacted polymers, prompting the arrangement of a gel. [2] Potassium persulfate (KPS), which produces sulfate radicals through warm disintegration, can be utilized rather than APS, bringing about the negative surface charge of microgel particles brought about by the nearness of sulfate groups. [31]

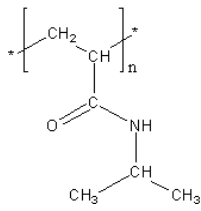
The use of driving forces, for instance, N'- tetramethylethylenediamine (TEMED) can be seen in poly-Nipa Am/chitosan nanogel association to enliven the course of action of free radicals. In the precipitation polymerization of hydrogels reliant on poly-Nipa Am, BIS was incorporated as the crosslinking pro. In any case, TEMED was used in the blend with APS to begin an anionic microgel, while a cationic microgel was begun

by UV light. [32] A Nano gel dependent on poly-NIPAAm and poly-ALA was combined utilizing a similar strategy, where monomers were weakened with SDS and stop defrosted multiple times. KPS was added to start polymerization. The nearness of chitosan in the union of a poly-NIPAAm-based hydrogel balanced out Nano gel particles and went about as a surfactant, avoiding molecule coagulation. [14]

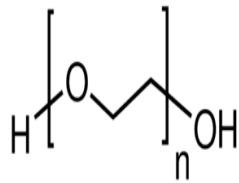
An expansion in the chitosan-to-poly-Nipa Am proportion diminished the measure of orchestrated particles of the nanogel. Besides, by expanding the temperature to 80°C, the nanoparticles of poly-NIPAAm/chitosan hydrogels could be framed without the expansion of an impetus or surfactant. Thusly, particles with a distance across of 81.2 nm were obtained. [33] Other microgels utilized for material adjustment have been founded on carboxymethylcellulose (CMC) in mix with fumaric corrosive as a crosslinker [91], di-phenylalanine, CMC and hydroxyethyl cellulose and poly (ethylene glycol) (PEG) and poly(caprolactone) (PCL). On account of the combination of nanogels, PVA-,  $\beta$ -cyclodextrin ( $\beta$ -CD)-, hydrophobized-pullulan-and collagen-bearing pullulan-based polymers have been utilized. Because of the particular idea of every polymerization or copolymerization, an itemized correlation among small scale and nanogel blends can't be made. The combination procedure, the amount of the crosslinker and initiator, temperature, time, mixing speed, and the nearness of surfactants and co-monomers straightforwardly influence the extent of hydrogel particles. [34]

As a rule, the nearness of a crosslinker causes the development of littler hydrogel particles than without a crosslinker. The amalgamation temperature and size of the particles are contrarily relative, as microgels are framed close room temperature and temperatures for microgel union increment to 50°C all things considered, despite the fact that they may ascend as high as 70°C, 80°C or even 85°C. Nanogels are generally arranged at temperatures of 70°C. Amalgamation time is definitely abbreviated by diminishing the hydrogel molecule measure from a large scale to small scale to nanogel. Littler hydrogel particles can be made through the expansion of a surfactant, for example, sodium dodecyl sulfate (SDS), which settles polymer particles right on time amid the polymerization response. The molecule estimate diminishes with an expansion in surfactant fixation. Hydrogel molecule sizes can likewise be diminished through the expansion of ionizable anionic co-monomers. [35]

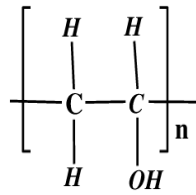
Poly(N-isopropylacrylamide)



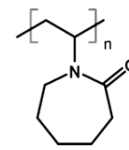
poly ethylene glycol



polyvinyl alcohol

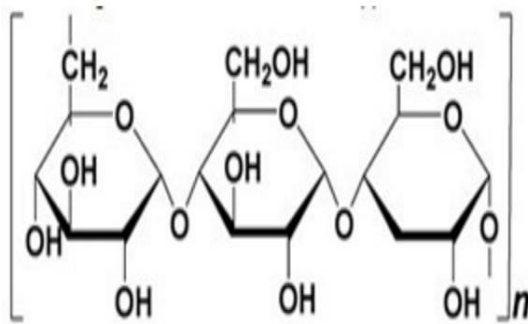


polyvinyl caprolactam

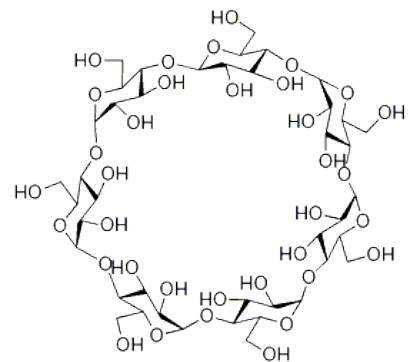


**Figure 8: Structure of Temperature-responsive polymers**

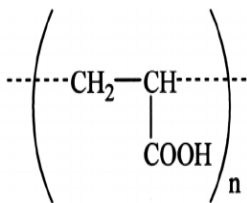
Pullulan



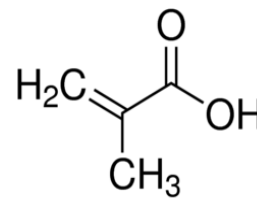
β-cyclodextrin



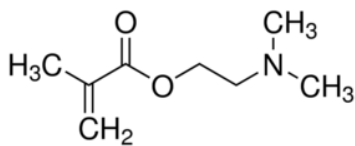
poly acrylic acid



poly methacrylic acid



poly(2-(di,methylamino)ethyl methacrylate)



**Figure 8: Structures of pH-responsive Polymers**

**Table 3: Fields of Hydrogel and Particles on a Substrate are crucial to achieve [14]**

Polymer/Monomer	Crosslinker	Initiator/Catalyst	Hydrogel particle size	Synthesis procedure	Synthesis conditions
NiPPAm, chitosan				Surfactant free dispersion copolymerization	
NiPPAm, AA and chitosan	BIS	APS		Surfactant free dispersion copolymerization	65°C, 4h and room temperature, 12h
NiPPAm and ALA	Ethylene glycol diacrylate	Sodium persulfate	72nm	Precipitation polymerization in the presence of surfactant (SDS)	70°C, 4h
NiPPAm and MAA	BIS	APS, MAA	180–220nm	Free radical polymerization in the presence of surfactant (SDS)	70°C, 4h
NiPPAm and AEMA	Azobisisobutyronitrile (AIBN)	/	810nm	Free radical polymerization in ethanol	70°C, 24h

2_dimethyaminnoethyl methacrylate (DMAEMA)	A solution of methanol/ H <sub>2</sub> O N, N, N,N'' Pentamethyl diethylenetriamine, copper bromide, DMAEMA	Bromoisobutyryl bromide	Not stated	Surface initiated atom transfer radical polymerization	60°C
Poly (ethylene glycol) Polycaprolactone Poly ethylene glycol (PEG-PCL-PEG)	Hexamethylene diisocyanate (HMDI)	/	Not stated	Coupling MPEG and PCL with HMDI as a chemical linker	85°C,5h
CMC	Fumaric acid	/	Not stated	FA Crosslinking of CMC hydrogel	Room temperature 5mins,30mins and 1 hour
CMC and hydroxyethyl cellulose	Citric acid	/	Not stated	Graft copolymerization	80°C,24h
PVA,PVA and Glycerol	/	/	10-50nm	Fructose-induced reduction of silver nitrate within PVA gel	60-90°C
PAA	BIS-AAM	Photo and thermo initiated	Not stated	Free radical polymerization	Annealing 110°C,60mins,induction of reactive group,.10 mins,UV illumination,1h



PDMAEMA	BIS	2,2 diethylene tophenone(DEOP )	Not stated	Free radical polymerization	Room temperature,12h
PNiPAAm	BIS	APS	Not stated	Free radical polymerization	70°C,2h

## Chapter 5

# Hydrogel Applications in Different Textile Fields

The use of textile materials to carry and release medicine is an old concept as that applied to wound dressing. Transdermal drug release has multiple advantages compared to other solutions, so much so that it is most often presented in the form of a cutaneous patch that can be easily removed, immediately and efficiently stopping the effects of the medicine. However, the creation of textiles carrying drugs that can be delivered transdermally is a complex process. This implies the control of the release and the bio-availability of the drug.[22]

The choice of textile substrates for the application of a hydrogel as a means of transdermal delivery system is related to the natural origin of the materials. Knowing that there will be contact with the skin, a cotton support appears as the most opportune choice given its aesthetic and physical properties combined with its natural and biodegradable origin. As for textile structures, knitwear has a high porosity, and offers a high ability to deliver a medicine (in the case of medical bandages), while nonwovens are omnipresent in the production of medical and surgical textiles, due to their short, flexible, versatile and low-cost fabrication cycles.[23]

The theoretical possibilities to design smart clothing for the controlled transdermal delivery of medicines are numerous. When the medicine to be delivered is a hormone (corticoids for patients suffering from neurodermitis or insulin for diabetics), an antiseptic substance or a local anesthetic, the crucial step in the release system from the point of view of the textile is to develop polymer materials in which the medicine can be encapsulated. Among the myriad of new multifunctional polymers, thermosensitive hydrogels have a promising future in this type of application.[24]

Textile materials can be made thermo-sensitive by applying on them polymers having this property. The interest in developing such textiles is varied: this goes to the protection of divers by bringing them an improved thermal insulation, passing by the

treatment of wounds and the controlled release of medicines, this latter point being one of the most fascinating and difficult to design.

The application of linear PNIPAAm (poly(N-isopropylacrylamide)) to textile materials has been more studied than that of hydrogels based on PNIPAAm. It is important to note that the latter make reference to hydrogels having an interpenetrating or semi-interpenetrating network structure with linear or cross-linked PNIPAAm.[25]

Very often, researchers base their work on grafting reactions. Jiaquin et al. have used a cellulose cotton cloth as a textile support to graft on linear PNIPAAm. They have used a process of pre-irradiation in air by radiation followed by immersion of the treated tissue in a grafting solution (solution of NIPAAm (N-isopropylacrylamide)). They concluded that the principal active particles having initiated the reaction were imprisoned in the interface between amorphous and crystalline zones of the cellulosic cotton. It is important to note that the thermo-sensitivity of grafted cloth has been obtained at 35.4°C, that is to say, at a temperature close to PNIPAAm alone.[26]

The research group of Gupta et al. has taken a similar approach with a polyester cloth and where the grafting reaction comprised a copolymerization of NIPAAm monomers and acrylic acid. The system thus obtained was potentially usable as a thermo-sensitive cloth patch for the release of an antibiotic (tetracycline hydrochloride) at a temperature greater than its critical low temperature zone (around 37°C).

In place of an irradiation process, an initiator such as ammonium persulphate can be used to graft by copolymerization of free radicals between the NIPAAm and an anionomer of vinyl saturated polyurethane on a nonwoven material comprised of 70% of cellulosic fibres and 30% polyester. The researchers claim a particular elasticity and a high degree of swelling for this system. The sensitive temperature falls at around 33°C and the potential applications concern plasters for wounds or cosmetic treatments.[27]

Polymerization by photo-induced grafting constitutes another method of preparing a thermo-sensitive grafted hydrogel on a nonwoven support. Chen et al. have grafted a hydrogel of PNIPAAm onto a film of ethylene polyterephthalate (EPT) and onto a nonwoven surface. Their study showed that a bond between the PNIPAAm hydrogel and the ETP film (as well as for a polypropylene surface) was improved by an argon-based plasma treatment. This is probably due to proxy groups on the polymer surface induced by the plasma treatment. The procedure involves the plasma treated fabrics

being placed in a mixture containing NIPAAm, a cross-linker, MBAAm (N,N-methylene bis-acrylamide), an initiator, APS (ammonium persulfate), and a catalyst, TEMED (N,N,N',N' tetramethylene diamine), then being irradiated by a high pressure mercury lamp.[25]

Among these previously cited examples, the textile structures containing hydrogels are obtained by the formation of hydrogel films on the surface of the fabric. However, studies dealing with hydrogels in the form of nano or micro-particles are rare. Kulkarni et al. have prepared them based on a co-polymer of PNIPAAm and of chitosan by a method of emulsion without a surfactant. The hydrogel nanoparticles, 200 nm in diameter, were bound by covalent bonds to cotton fabric using carboxylic acid as a cross-linking agent. The method of applied binding used was by a pad-dry, where the rate of loss of water was controlled by the pH and by the temperature.[28]

## **5.1 Fields of Hydrogel Application in Textile Modifications**

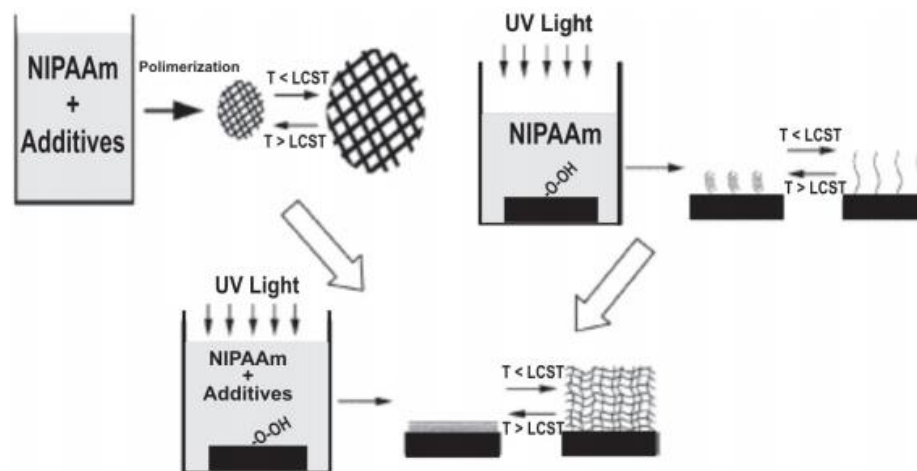
Stimuli-responsive hydrogels can be applied to textile substrates in the form of a solution, microcapsules, foam or gel .[29] Pad-dry-cure coating is the most common and the most accessible procedure from a technological point of view. When designing synthetic fibers, a hydrogel can be incorporated into fibers during the spinning process. 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.[30] The initial chemical composition of fibers 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, different approaches were 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 fiber, but also mechanical textile properties such as the cross-sectional shape of a fiber and fiber diameter, weave pattern, thickness etc.[31] 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 .[32] The

material technology approach, which is crucial for achieving improved textile comfort, requires the minimal effect of a hydrogel on the physic-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 Fiber surfaces to serve as bonding points between a hydrogel and substrate. Furthermore, the etching effect of plasma increases the roughness of the Fiber surface as well as the specific surface area of Fibres, resulting in the greater uptake of a hydrogel .[33] 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 stillness of the fabric. The most recent research is therefore focused on the synthesis and application of nanogels. Nanogels combine the characteristics of hydrogels and nanoparticles 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. 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 .[32]

## **5.2 Temperature Sensitive Hydrogels Applications**

Poly (N-isopropyl acrylamide) (PNIPAAm) is an intensively investigated temperature-sensitive polymer which has a simultaneously hydrophilic and hydrophobic structure (see Figure 7), and demonstrates a low critical solution temperature (LCST) at about 32 oC.[34] In an aqueous solution, the macromolecular chains of PNIPAAm experience reversible solubility and exhibit a significant hydration-dehydration change in response to temperature stimulus. Due to its sharp temperature-induced transition and well-

defined LCST, which is close to body temperature, the PNIPAAm (and in particular the PNIPAAm hydrogel) has been widely applied to temperature-sensitive drug delivery systems, separation membranes, and tissue engineering scaffolds. Recently, scientists have made many attempts to develop stimuli-sensitive textiles, or so-called smart textiles, by grafting the copolymerization of environment-responsive polymers (ERP) onto the surface of fabrics .[35] Among the ERPs used for this purpose, PNIPAAm has attracted considerable attention, and research into it may lead to novel temperature-sensitive smart fabrics. In view of the great potential applications of smart fabrics in many areas, we will review the recent achievements in smart fabrics, mainly covering Chinese and Japanese work on the application of PNIPAAm and its copolymer hydrogels The Application of Temperature-Sensitive Hydrogels to Textiles. The temperature sensitive delivery behavior of vitamin E from the poly(2-ethoxyethyl vinyl ether)/poly(hydroxyethyl vinyl ether) copolymer (EOVE200-HOVE40) is briefly introduced, and its potential application in cosmetic and pharmaceutical fields is also considered.[26]



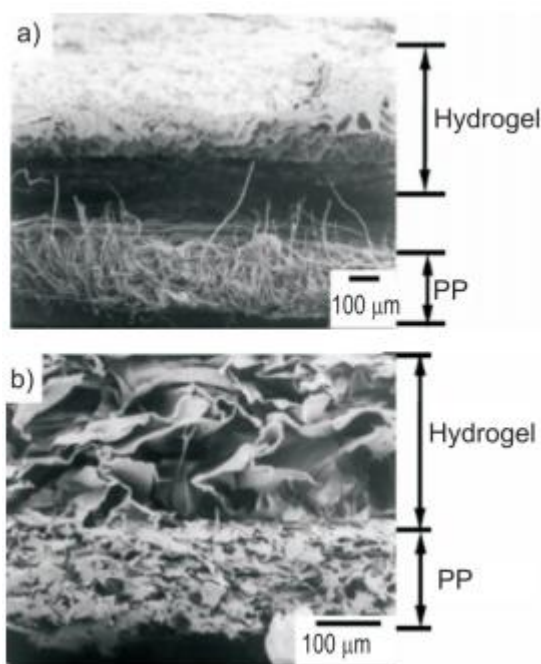
**Figure 9: Schematic description of photo-induced grafting polymerisation of NIPAAm gel onto PET film and the PP nonwoven fabrics surface.[26]**

### 5.3 Temperature-Sensitive Hygroscopic Textiles

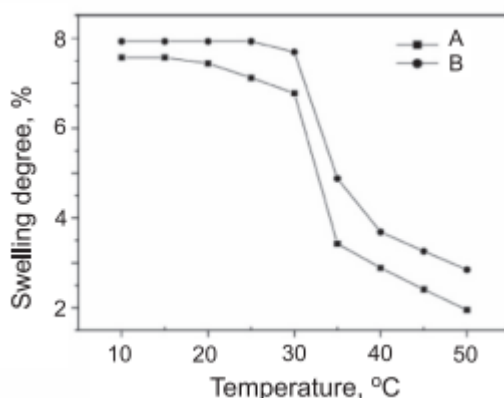
Environment-sensitive polymer hydrogels can be grafted or adsorbed onto the surface of polymer fibres. When the hydrogel is exposed to external stimuli, it will display swelling/shrinkage or hydration/dehydration properties, and cause changes in the water vapor transmission rates (WVTR), permeance and permeability of the fabrics. Chen et al. have grafted a PNIPAAm hydrogel onto nonwoven fabrics by photo-

induced graft polymerization and studied the fabrics' temperature-responsive characteristics. In their work, a temperature-sensitive PNIPAAm hydrogel was grafted onto a plasma-activated polyethylene terephthalate (PET) film and a polypropylene (PP) nonwoven fabric surface.[26] Factors affecting the formation of a PNIPAAm hydrogel by photo-induced graft polymerization were investigated in terms of the type of additives. The additives used were ammonium persulphate (APS as initiator), N,N,N',N'-tetra-methylethylene-diamine (TEMED as promoter), and N,N'-methylene-bisacrylamide (MBAAm as cross linking agent). The results indicated that the additives of APS, TEMED, and MBAAm were beneficial in promoting the grafting yield. These grafted hydrogels exhibited a lower critical solution temperature (LCST) of about 32 °C, indicating that the temperature-sensitive behavior of the bulk PNIPAAm hydrogel was maintained. Plasma pre-treatment has also been studied. A pre-treatment with the use of argon plasma was carried out, and a subsequent photo-induced surface graft polymerization was employed to graft NIPAAm. A schematic diagram of the photo-induced grafting polymerization is presented in Figure 9. Their experimental results indicated that such a pre-treatment can improve the binding ability between the hydrogel and matrix (see Figure 10), increase graft density, and endow the grafting PP with good permeability. After freeze-drying, a hydrogel with pore structure can be obtained. It can be seen from the swelling-deswelling curves that the PNIPAAm displayed similar temperaturesensitiveness with/ without grafting on the PP nonwoven fabrics surface (see Figure 11).[36] Thus, grafting almost does not alter the LCST of PNIPAAm. The PNIPAAm-g-PP nonwoven fabrics may be used in smart fabrics with a function of temperature-sensitive water vapour permeability. Kubota et al. synthesized cellulosic adsorbents (CR-CMC) by photo grafting acrylic acid (AA) onto fibrous carboxymethyl cellulose in the presence of N,N-methylenebisacrylamide (MBAAm) as a crosslinked agent. The CMC sample was firstly pre-treated with hydrogen peroxide in the presence of sulphuric acid to prepare CMC peroxides, and next AA and NIPAAm monomers were photo grafted onto the CMC surface. The peracid on the pre-treated CMC was decomposed as a polymeric photo initiator in the following grafting process. Two types of preparation methods, the one-step method and the two-step method, were used in this work (Figure 14). For the one-step method, NIPAAm and AA were photo grafted simultaneously onto the CMC in the presence of the MBAAm crosslinked agent. For the two-step method, AA was first coupled on the

CMC in the presence of MBAAm, and then PNIPAAm was photo grafted. The relationship between water absorbency and the temperature of these two samples is compared in Figure 11. It is obvious that the water absorbency of the latter method is much greater than that of the former. The latter samples also displayed a notable temperature-sensitive behavior. The CR-CMC prepared by the two-step method may be used as smart fabrics with a function of temperature sensitive water absorbance.[26]



**Figure 10. SEM Images of PNIPAAm-g-PP nonwoven fabrics (after freeze drying); (a) without pretreatment (b) with Argon plasma pretreatment [37].**

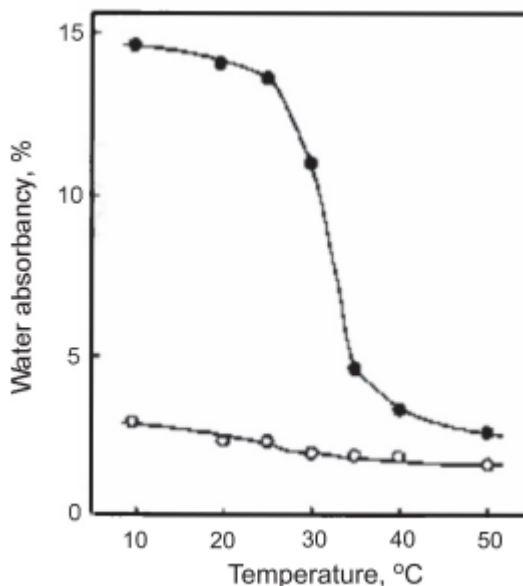


**Figure 11. Temperature effect on the swelling degree of PNIPAAm; (A) without grafting, (B) grafted on the PP Fabrics surface [37].**

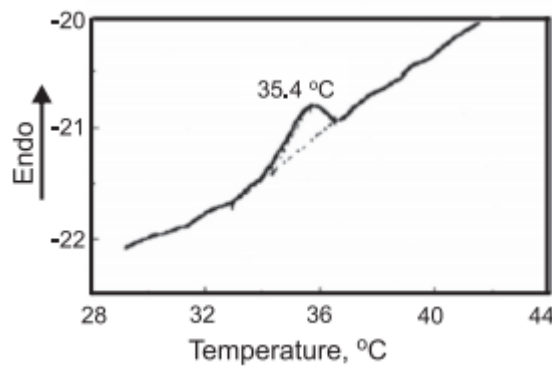
NIPAAm was also grafted onto the surface of cotton fibres by using the <sup>60</sup>Co irradiation method. The DSC results indicated that the PNIPAAm-g-cotton still maintains its



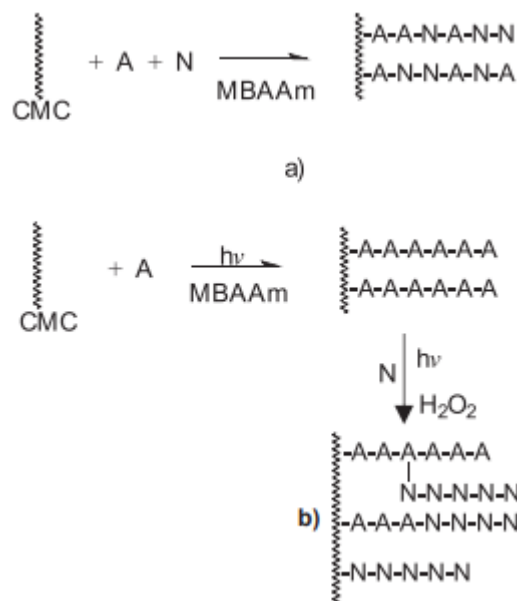
temperature-sensitivity. The phase transition temperature of PNIPAAm-g-cotton is around 35 centigrade, near to the body temperature (Figure 7). This research may be applied to developing environmentally responsive fabrics. Apart from the grafting methods mentioned above, ammonium cerium (IV) nitrate (CAN) can also be used to initiate the grafting reaction onto the cellulose fabric surface. The ordered crystalline and orientation structure of cotton cellulose was destroyed by pre-treatment by boiling in an NaOH solution and ZnCl<sub>2</sub> solution at room temperature respectively. The pre-treated cotton cellulose was introduced into 10 ml of 20mM CAN for 15 min, wiped with tissues for the removal of extra CAN, and then immersed in 5 ml of an NIPAAM/ MBAAm solution for 30 min. The copolymerization was performed under N<sub>2</sub> protection for 48h,; the grafting yield can reach up to 400% by using this grafting technology. Figure 8 shows the SEM images of a cellulose-supported PNIPAAm hydrogel. The smooth thick Figure 3. SEM Images of PNIPAAm-g-PP nonwoven fabrics (after freeze drying); (a) without pretreatment (b) with Argon plasma pretreatment. Figure 11. Temperature effect on the swelling degree of PNIPAAm; (A) without grafting, (B) grafted on the PP Fabrics surface. Figure 11. Photo grafting mechanism of AA and PNIPAAm binary monomer; a) one-step and b) two-step (A: Acrylic acid, N: NIPAAm) [38].



**Figure 12. Relationship between water absorbency and temperature in (○) one-step and (●) two-step prepared samples [39]**



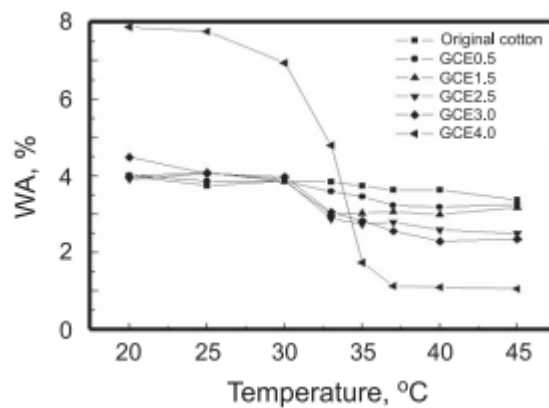
**Figure 13. DSC curves of PNIPAAm-g-cotton in wet condition.[26]**



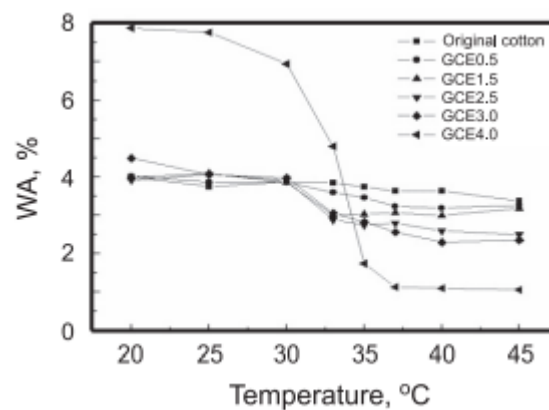
**Figure 14. Photografting mechanism of AA and PNIPAAm binary monomer; a) onestep and b) two-step (A: Acrylic acid, N: NIPAAm ) [39].**

Hydrogel layers were coated on the surface of the cellulose, making the fibres nearly invisible. The onset temperature of the phase-transition is between 28 °C and 40 °C, and the swelling degree of the hydrogel decreased with the increase in temperature. Shrinkage of the cellulose-supported hydrogel is observed near the phase transition temperature. The cellulose-supported thermo-sensitive hydro-gel is potentially useful in wound-dressing materials and nutrient controlled release cosmetics.[38] In order to create a dual temperature/ pH-sensitive hydrogel grafted fabric, our groups synthesized a vinyl-capped polyurethane an ionomer (VPUA), which was then grafted onto the nonwoven cotton cellulose together with NIPAAm by random copolymerization initiated by ammonium persulphate (APS). The DSC result of the PNIPAAm-co-VPUA free hydrogel displayed a typical endothermic peak at about 33 °C, close to the low critical solution temperature (LCST) of pure PNIPAAm, suggesting

that the incorporation of PU did not affect the thermal transition of PNIPAAm. The cotton cellulose grafted by PNIPAAm/ VPUA hydrogel also showed a similar phase transition temperature. At the same time, the water absorbency of the grafted cellulose can be tuned by adjusting the environmental temperature (Figure 15). Apart from the temperature sensitivity, the grafted cotton cellulose has pH sensitivity as well. It can be seen from Table 4 that the water absorbency considerably decreases in acid and increases in alkali media respectively, compared to that in a neutral medium.[26] The temperature-controlled release behavior of the PNIPAAm/VPUA hydrogel-grafted fabric was also studied in our research. Vitamin C was used as a model nutrient in this investigation. The preliminary results displayed that the release of vitamin C can be controlled by varying the surrounding temperature. The cumulative release amount of vitamin C was higher at 37 °C than at 20 °C, since at the elevated temperature the PNIPAAm network collapsed, squeezing more of vitamin C out of the gel (Figure 15).



**Figure 15. The variation of water absorbency as a function of temperature.**



**Figure 16. The cumulative release amount of vitamin C as a function of time determined at different temperatures; (GCE51: NIPAAm/PU feeding ratio was 5/1, monomer concentration 5.0% wt).[26]**

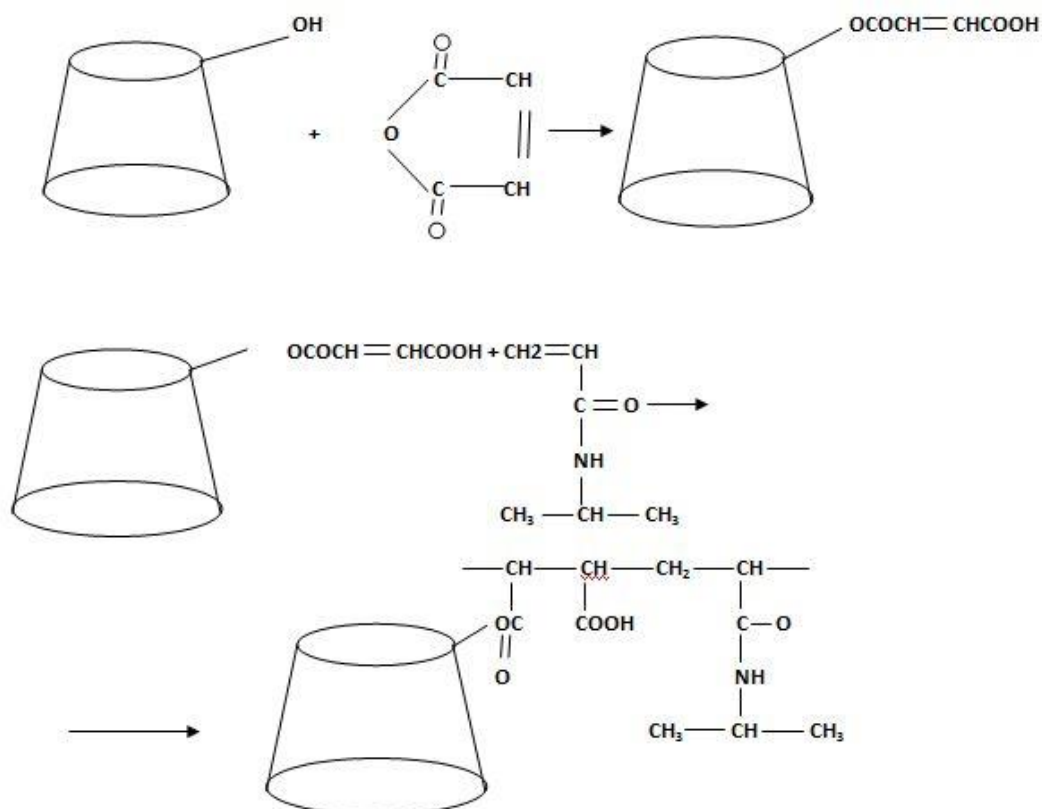
## 5.4 Environmental Sensitive Hydrogels in Deodorant Fibers

Water absorbency determined in different media pH:

PH	Original Cellulose	GEC0.5	GEC1.5	GEC2.5	GEC3.0	GEC4.0
1.0	1.98	2.46	2.46	1.98	2.71	10.68
7.0	2.17	2.62	2.60	2.60	3.25	15.89
13.0	2.40	2.78	2.77	3.23	3.34	22.49

**Table 4: Fibres and Textiles in Eastern Europe**

$\beta$ -cyclodextrin ( $\beta$ -CD) is a cone-shaped molecule. The  $\beta$ -CD is hydrophilic at the outer surface of the cavity thanks to the existence of many hydroxyl groups, while it is hydrophobic in the cavity. So  $\beta$ -CD is soluble in water, and a variety of hydrophobic guest molecules can be encapsulated in its non-polar cavity. This characteristic has been widely applied in the fields of drug-controlled release, separation and adsorption. This exhibits the molecular structure of  $\beta$ -cyclodextrin. Lee et al. [23] used formic acid as a catalyst to copolymerize N-methylal-acrylamide (NMA) and  $\beta$ -cyclodextrin( $\beta$ -CD) (CD-NMA). The CD-NMA was grafted onto cotton fibres by using CAN as an initiator. Figure 19 shows the effect of the reaction temperature on the graft yield. It demonstrates that a temperature of 40 °C is the optimum temperature; above this temperature value, the graft yield decreases.[26] The optimum graft yield can be acquired from adjusting the grafting time, reaction temperature, and CAN concentration. CD-NMA-grafted cellulose fibres can be used in the aroma finishing of cotton. The fragrance of CD-NMA-grafted cellulose fibres treated with vanillin was retained even after prolonged storage, initially at room temperature for 7 days, following holding at 80 °C for 7 days. In contrast, the untreated cotton fibres only retain the fragrance for less than two days (see Table 2).



**Figure 17. Synthesis route of PNIPAAm/ $\beta$ -CD copolymer [24].**

It is noted that the CD-NMA-attached cotton fibres only release the vanillin in a passive mode. Recently, Liu et al. have synthesized a novel hydrogel, poly(isopropyl acrylamide-co-maleic anhydride- $\beta$ -cyclodextrin), with pH and temperature sensitivity plus a molecular inclusion function. This novel hydrogel was obtained using free radical polymerization in an aqueous solution. Firstly, a reactive  $\beta$ -CD based monomer carrying vinyl carboxylic acid functional groups was synthesized via the reaction of  $\beta$ -CD with maleic anhydride (MAH) in N, N-dimethylformamide (DMF) at a temperature of 80 °C. The poly(NIPAAm-co-MAH- $\beta$ -CD) was obtained by copolymerization of the monomer with N-isopropyl acrylamide (NIPAAm). Figure 14 shows the synthesis route.[26] The equilibrium swelling ratio (ESR) of hydrogel is affected by pH and temperature, as shown in Figure 18. Obviously, the equilibrium swelling ratio of hydrogel increased with the increase in pH. At a certain pH, the equilibrium swelling ratio decreased with the rising temperature. The equilibrium swelling ratio dropped drastically near the phase transition temperature. The temperature/pH dual-sensitive hydro-gel has a great potential application in the field of smart fabrics. If a

temperature/pH dual-sensitive hydrogel is grafted onto the fiber's fabric's surface, the fabric will achieve environmental sensitivity. It is anticipated that the fragrance molecules included in the  $\beta$ -CD are capable of releasing in a sustainable fashion by changing the temperature or pH. Novel deodorant fabrics could be developed by loading the fragrance molecules into the  $\beta$ -CD.[26]

### 5.5 Environmentally Sensitive Hydrogels in Nutrient/Drug Delivery Fabrics

One special property of environment sensitive hydrogel lies in its being an open thermodynamic system. When the external environment changes a little, the volume of the hydrogel will swell or shrink drastically.[40]

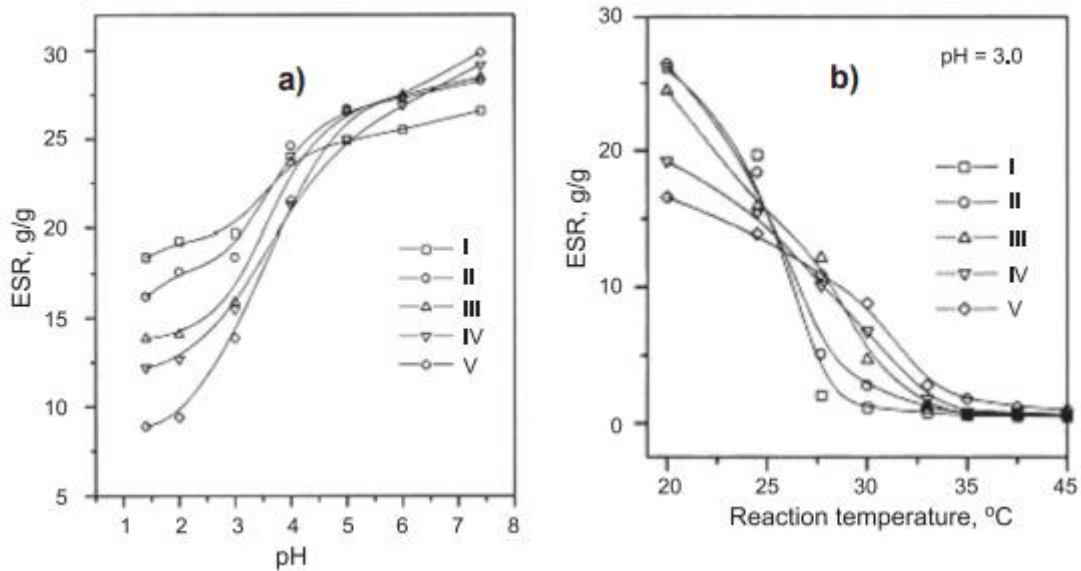


Figure 18. Influence of pH (a) and temperature (b) on the equilibrium swelling ratio of PNIPAAm-CD hydrogel; hydrogel's chemical composition of NIPAAm/MAH $\beta$ -CD(%wt): (I)(99.3/0.7); (II) (98.6/1.4); (III) (98.2/1.8); (IV) (97.6/2.4); (V) (96.2/ 3.8) [41].

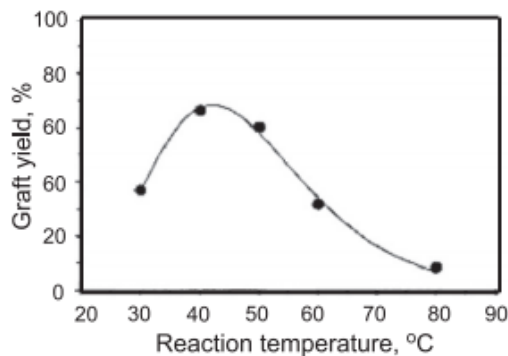
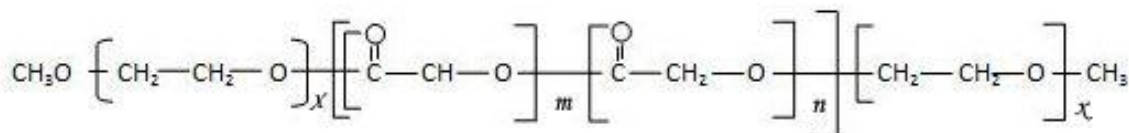


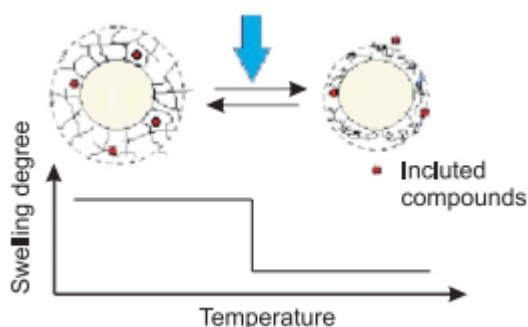
Figure 19. Effect of the reaction temperature on the grafting yield[26]

This characteristic phenomenon enables a drug or nutrient loaded in the hydrogels to be released in a controlled manner. The following temperature-sensitive copolymer hydrogel was frequently used as a controlled release system (Figure 20).



**Figure 20. Poly(ethylene oxide-co-propylene oxide-co-polyethylene oxide) (PEOPPO-PEO).[26]**

The release of vitamins, Chinese herbs, and therapeutic medicine has been widely used in the fields of therapy, health care and cosmetics. Ishida et al. synthesized a temperature-sensitive copolymer (EOVE200- HOVE400) consisting of poly (2-ethoxyethyl vinyl ether) (EOVE200) and poly (hydroxyethyl vinyl ether) (HOVE400). Here poly (hydroxyethyl vinyl ether) (HOVE400) was a hydrophilic segment. The temperature-sensitive segment EOVE200 caused a hydrophilic-hydrophobic transition at the lower critical solution temperature (LCST), while the hydrophilic segment HOVE400 was indifferent to temperature. The transition temperature of the 20% wt. EOVE200-HOVE400 was 20.5 °C.[26]



**Figure 21. Controlled release behaviour of reversible temperature-sensitive hydrogel layer on fibre surface[26]**

It was apparent that there was no release of vitamin E from EOVE200-HOVE400 at 30 °C owing to the gelation of the solution. When the temperature was reduced to 10 °C, vitamin E was released from EOVE200-HOVE400, since the gel had converted to sol. If EOVE200- HOVE400 is grafted onto the surface of fabrics, a novel fabric with a function of temperature-tunable release of nutrient or drug will be created (see Figure 21).

If a temperature-sensitive hydrogel is grafted on the nonwoven fabrics, the nutrient or medicine can be encapsulated in the hydrogel. The release of a nutrient or herbs can be controlled by temperature changes. Another advantage of this technology is that the mechanical performance of the temperature-sensitive hydrogel can be improved. Such temperature-sensitive hydrogel-modified fabrics may be used in the cosmetic and pharmaceutical field.[26]



## Chapter 6

# Uses of Hydrogel in Different Applications

### 6.1 Medical Applications

Overall, microgels 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 stillness does not play a significant role.[14] In one instance, smart wound dressings based on polyNiPAAm microgels and its copolymers were bound to textile substrates by graft copolymerization, which involves generating free radicals on a substrate and subsequently polymerizing monomers directly on a textile surface. Poly-Nipa Am was copolymerized with polyurethane and grafted on a cellulose non-woven textile, or with N,N-methylene bisacrylamide (BIS) and grafted to a cellulose support .[42] Photo-induced graft copolymerization of poly-Nipa Am on previously plasma-treated textile substrates has also been carried out through copolymerization with polypropylene (PP) , with the addition of chitosan and with a polyethylene terephthalate (PET) film . Microgels based on carboxymethyl chitosan (CMCh) and PVA, CMC and fumaric acid, CMC and hydroxyethyl cellulose derivatives, self-assembling di-phenylalanine, glycol and  $\epsilon$ -caprolactone, collagen, and polyacrylic acid and  $\beta$ -cyclodextrin 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 polymerization, or in combination with 1,2,3,4-butanetetracarboxylic acid to chemically bind a microgel with the functional groups of a textile substrate.[43] To improve its mechanical properties and decrease its tendency to coagulate, poly-NIPAAm has been synthesized in combination with other polymers such as the copolymer 2-aminoethyl methacrylate. To achieve a sterile wound environment, different antimicrobial agents have been added to microgels such as silver in various forms, zinc oxide and a biocidal agent based on quaternary ammonium salts [43]. 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 at 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 stabilized 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.[44] Temperature-responsive poly-Nipa Am-co-allylamine (PNIPAM-co-ALA) nanogels with incorporated silver nitrate have also been grafted onto non-woven polypropylene fabric to designing a smart wound dressing. Nanogel particles had a diameter of 72nm at temperatures above the LCST of the poly-Nipa Am, at which bacterial growth was prevented. Nanogels can be incorporated into the structure of fibres via electrospinning by adding nanogels to a spinning mass. Composite poly(caprolactone) micro fibres 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  $\mu$ m and the nanogel particles were located in the cores of the fibres, while fibres spun using CH/DMF had a diameter of 1  $\mu$ m 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 nano fibres were produced for use in tissue engineering. Nanogels composed of hydrophobized-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 electro spun from poly(acrylic acid) (PAA) crosslinked with  $\beta$ -cyclodextrin ( $\beta$ -CD) and thermally treated for stabilization[45]. Fibres ranged in size from 100 nm to several microns and were used as carriers of silver nanoparticles. A highly biocidal textile surface was achieved.[45]

## 6.2 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 polymerization 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. [14] Chemical activation was achieved through carboxymethylation and amination. 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 fiber 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 fiber 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[46]. Application of the PNCS microgel in combination with crosslinking agents, i.e. 1,2,3,4-butanetetracarboxylic acid (BTCA) and N,N'-methylenebisacrylamide, 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 fiber 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.[14] 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 .[47]

### **6.3 Use of Hydrogels for Protective Properties of Textile Materials**

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 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  $\beta$ -cyclodextrin ( $\beta$ -CD) was loaded with an insecticide, permethrin, where the size of the nanogel particles reached 100-200 nm.[48]

### **6.4 Use of Hydrogels for Filtration**

Textile materials functionalized 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. 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. Super hydrophilic to superhydrophobic transition was achieved through the application of stimuli-responsive hydrogels based on poly-Nipa Am or PAA. The poly-Nipa Am hydrogel was

coated on elastic polyurethane to achieve temperature-responsive switchable superhydrophilicity to super hydrophobicity with the LCST of poly-Nipa Am i.e., 32°C. This textile composite exhibited excellent water/oil separation properties, mechanical strength and elasticity. The hydrogel was prepared by dissolving poly-Nipa Am and BIS in APS and was spun into a micro Fiber mat by force spinning.[49] Sidorenko and his team synthesized 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 behavior is reversible upon drying.[50]

## Chapter 7

# Conclusion

Hydrogels are still fascinating material for scientists and biomedical researchers. Hydrogels are unique, they consist of a self-supporting, water-swollen three-dimensional (3D) viscoelastic network which permits the diffusion and attachment of molecules and cells. Hydrogels have recently drawn great attention for use in a wide variety of biomedical applications such as cell therapeutics, wound healing, cartilage/bone regeneration and the sustained release of drugs. But commercial hydrogel products in tissue engineering and drug delivery are still limited.

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 behavior 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.

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 stillness of a functionalized textile substrate greatly increases after the deposition of stimuli-responsive hydrogels. The use of appropriate sooners 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 Fibers 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 optimization 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 functionalized fabric is needed. From an economical point of view, the costs of textile functionalization 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 optimization 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 functionalized 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-functionalized textiles will focus on the Synthesis and incorporation of Nano-sized hydrogels into different textile materials. Application and combination of different stimuli responsive hydrogels to achieve simultaneous worn comfort along with proactive protection. 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 functionalized textiles and the bioaccumulation of hydrogel compounds and Optimization of synthesis methods to minimize production costs.

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