Superabsorbent Hydrogel Composites with a Focus on Hydrogels Containing Nanofibers or Nanowhiskers of Cellulose and Chitin

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ABSTRACT: The development of superabsorbent hydrogels (SHs) is a very important issue in both academic and industrial fields because of their applications in several technologies. The impressive number of publications dealing with SH confirms this statement: a quick search in the ISI (Web of Science) database under the words *superabsorbent hydrogels* revealed more than 600 articles published, with about 80% of those published in last decade. Current studies on the development of SHs have focused on the formulation of highly functional materials with enhanced properties for suitable applications in different fields. In light of this, the incorporation of microsized or nanosized materials in SH formulations has been explored as a very attractive strategy for tailoring desired properties. In this review, we discuss relevant aspects of the current knowledge of SHs and nanocomposite polymer hydrogels, mainly those based on chitin and cellulose nanocrystals (fibers and/or whiskers), bringing to light some structure–property relationships and future trends. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

INTRODUCTION

Continuous claims in the development of different technologies that improve society's welfare motivate and instigate researchers to constantly overtake the boundaries of knowledge in every scientific aspect. Hydrogels, crosslinked polymeric chains that are able to swell in aqueous solutions and retain their three-dimensional (3D) features without dissolving, are good examples of such evolution. Since their first appearance back in 1960,[1] hydrogels have advanced from simply inert to complex, stimuli-responsive materials (e.g., hydrogels displaying significant volume changes in response to variation in pH, ionic strength, temperature, magnetic field, specific molecules, and light); they present great prospects in a wide range of applications, such as tissue engineering,[2] soil conditioning,[3] wound dressing,[4] sensors,[5] contact lenses,[6] drug-delivery systems,[7] separation science,[8] and hygienic products.[9] A quick search in the ISI (Web of Science) database under the topic *hydrogel* reveals more than 30,000 articles published over the last 50 years [ca. 80% in the last decade, including the articles related to the superabsorbent hydrogel (SH) class] and illustrates the importance, in both the academic and technologic fields, of such a class of material.

Reports on hydrogel composites in the scientific literature have increased extraordinarily in the last decade.[10] The incorporation of microsized and nanosized materials in the hydrogel formulation has significantly improved their response to external stimuli and their mechanical[11] and thermal properties.[12]

In addition to the good review articles focused on SHs and their different aspects, properties, and applications,[13–16] in this review, we intend to gather relevant aspects of the current knowledge of SHs and nanocomposite polymer hydrogels (NPHs). Herein, the main attention is given to the SHs and to NPH-based on chitin nanofibers (CHNFs), cellulose nanofibers (CNFs), chitin nanowhiskers (CHNWs), and cellulose nanowhiskers (CNWs) as fillers to bring light to some structure–property relationships and future trends.

Responsive Hydrogels

Responsive hydrogels, also called *smart hydrogels*, present great applicability in several different fields because they are able to change their volume size, swelling, optical, electrical, and magnetic properties in response to external stimuli.[17] For example, molecularly imprinted hydrogels based on poly(*N*-isopropyl acrylamide) (PNIPAAm) that show temperature-responsive features were developed for application in cytochrome C and

lysozyme recognition.[18] These imprinted hydrogels showed a higher affinity and binding capacity than the nonimprinted hydrogels; this encourages their application in sensor devices and controlled released systems. Polysaccharide-based hydrogels filled with magnetite nanoparticles (diameter ≈ 50 nm) showed potential to be applied as remotely controlled devices for curcumin delivery.[12] Chitosan-*graft*-poly(acrylic acid) (PAAc)/nontronite clay hydrogel composites were found to be responsive to both pH and salt changes.[19] Such work shows that the charge screening effect caused by extra cations in the swelling medium decreases the osmotic pressure and, by consequence, the water uptake capacity. Another article described an original glucose-responsive hydrogel prepared by immobilization of the glucose/galactose binding protein within an polyacrylamide (PAAm) hydrogel network.[20]

SHs

SHs are slightly crosslinked networks that are able to absorb the amounts of aqueous solutions from 10% up to thousands of times its own dry weight.[21] Although SHs were first reported in 1961 by the U.S. Department of Agriculture,[22] SHs are still a topic of great interest nowadays. It is important to be aware that SHs are distinct from superporous hydrogels; they reach late equilibrium conditions in minutes, and the swelling kinetics are independent on the final size of the material.[15] SHs have been explored as soil conditioners and in hygienic products early on. However, the potential applications of SHs in the biomedical and other fields have considerably increased in recent years. Zohuriaan-Mehr et al.[16] recently pointed out in a review article many applications of SHs, including medical and pharmaceuticals uses, fiber and textiles, agricultural, separation and water treatment, electrical and civil constructions, and dewatering of fuels and coal.

Carboxymethylcellulose (CMC)- and cellulose-based SHs were developed to act as a carrier in drug-release systems.[23] It was shown that the release of bovine serum albumin is dependent on amount of CMC present in the hydrogel formulation, and the swelling properties were influenced by the presence of salt. Cellulose-based SHs prepared by the crosslinking of CMC and hydroxyethyl cellulose with divinyl sulfone as a crosslinker and poly(ethylene glycol) (PEG) as a spacer were used for edema treatment.[24] The experimental data showed that the water uptake capacity was strongly affected by the molecular weight and concentration of the spacer. Biocompatibility assays showed that such hydrogels did not affect the cell viability of the macrophages or the induced inflammatory response. SHs based on sodium acrylate loaded with silver nanoparticles showed bacterial activity against *Candida albicans* and showed great potential for use in wound dressings.[25]

Cell-compatible hydrogels have found promising application profiles, especially in tissue engineering.[26] Such materials are designed with a strategy of coordinated control over the physical properties and bioactivity to influence specific interactions with cellular systems. Important discoveries in stem cell research, cancer biology, and cellular morphogenesis have been realized with model hydrogel systems based on these designs. Basic and clinical applications for hydrogels in cell therapy, tissue engineering, and biomedical research continue to drive paradigms on design improvements through the use of performance-based and engineered materials, which can be considered important issues for future targets in this field. In this direction, Hubbel et al.[27] used collagen gels and exploited the PEG-based hydrogel system to systematically study the effect of specific extracellular microenvironments on the behavior of primary human fibroblasts in a 3D network. They found that the proliferation profiles of fibroblasts from different patients cultured within collagen gels (3D) differed significantly from their observed behavior on two-dimensional (2D) tissue culture plastic. Additionally, using a biomimetic PEG-based matrix, they showed that cell proliferation in 3D could be selectively manipulated via alteration of the gel characteristics. An important review in this subject was also published by DeForest and Anseth;[28] in their review, the authors pointed out the current understanding of cell–material interactions in 2D and discussed recent and future efforts and the challenges in works extended to 3D cell culturing.

PREPARATION OF SHs

Despite the existence of several suitable strategies for preparing SHs, in general, three of them are most used: (1) polymerization of synthetic monomers, (2) polymerization of functionalized polymers (synthetic or natural), and (3) copolymerization by functionalized polymers, oligomers, and monomers. The majority of preparation occurs via the free-radical polymerization pathway by different initiation forms. In this section, we discuss the more frequently used strategies for preparing SHs.

Polymerization of Synthetic Monomers

Vinyl monomers, such as methacrylates, acrylates, and acrylamides (AAm's), have been often reported in SH preparation[29,30] because of their hydrophilic character. Free-radical polymerization is perhaps the most well-used method of polymerization and, as the name implies, occurs via a free-radical reaction, where the carbon–carbon double bonds of the vinyl monomers are evolved with the continuous addition of monomer units into a growing free-radical chain.[31] The mechanism, kinetics, and other details of such reactions are not discussed in this review but can be found in textbooks of polymers.[32–34]

Free-radical formation can be initiated by the use of γ radiation.[35–37] However, it is well known that γ-ray sources and apparatus are not available in many laboratories, and this limits γ-radiation application. The preparation of hydrogels by the thermal generation of free-radical compounds is a suitable method to overcome such a drawback.[38–40] One good example of a compound able to generate free radicals by thermal activation is persulfate. When persulfate is used, the reaction should be performed around 70°C or higher, temperatures in which the thermal decomposition of persulfate into free radicals often occurs. However, in specific cases, the temperature required to obtain the hydrogel needs to be lower, for instance, in the obtainment of thermally sensitive hydrogels such as PNIPAAm. Often PNIPAAm hydrogels are obtained below their lower critical solution temperature, that is, at about 32–33°C.[36] This can be achieved by the use of a catalyst, N,N',N'-
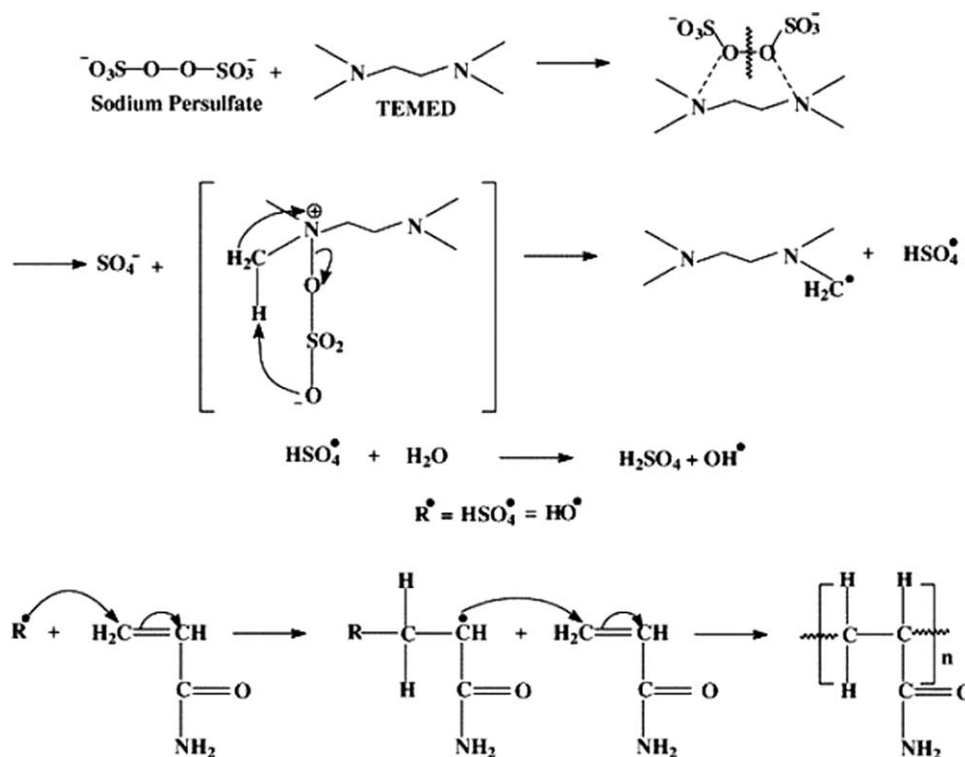
Figure 1. Synthesis strategy of the hydrogels and semi-IPN hydrogels based on PAAm with the persulfate–TEMED system at room temperature. Reprinted with permission from ref. 41. Copyright 2004 Elsevier.

tetramethylethylenediamine (TEMED). TEMED allows the decomposition of persulfate into free radicals at low temperatures because it accelerates the homolytic scission of persulfate moieties in aqueous media.[41] However, the reaction with the persulfate–TEMED system needs to occur in the absence of O_2 because of the high reactivity of persulfate–TEMED intermediates to O_2. Figure 1 presents the mechanism proposed by Feng et al.[42] for the radical formation on a system constituted of sodium persulfate and TEMED by a redox process.[41,42] There have been plenty of studies targeting the preparation of SHs in which the persulfate–TEMED system was used, although there are lot of different strategies that can be used to prepare SHs without the use of the persulfate–TEMED pathway.

The crosslinking agent has a critical role in hydrogel preparation mainly if only monomers are used as basic compounds for polymerization. In this case, the crosslinking agent has to possess a functionality higher than 2.[31–33] Marandi et al.[43] used formaldehyde as a crosslinking agent to obtain PAAm-based SHs. The as-prepared hydrogels were further saponified in a NaOH aqueous solution at a high temperature to achieve high swelling capacities. During the saponification reaction, ammonia gas was produced from the hydrolysis of the amide groups. The release of ammonia produced pores in the hydrogel structure, a fact that substantially increased their swelling performance.[43] SHs based on poly(aspartic acid) with high swelling ratio properties were also prepared by a crosslinking reaction with polysuccinimide.[44]

Hydrogels with semi-interpenetrating networks (semi-IPNs) with enhanced swelling ratios have been prepared with different polymers, including starch, carrageenan, and PAAm, incorporated into their formulation. For instance, the swelling ratio of hydrogels based on polysuccinimide was significantly enhanced compared to that of the control when PAAm was added to the hydrogel formulation.[45]

Polymerization of Functionalized Polymers

Biopolymers such as polysaccharides correspond to the majority of the natural-based SHs because of their exceptional properties, that is, biocompatibility, biodegradability, renewability, and nontoxicity. The water solubility of polysaccharides is due to the presence of polar functional groups, such as hydroxyls and carboxyls, on polymer chains; these groups can be used as reactive sites for the SH preparation.[46,47] Biodegradable SHs have been prepared by the etherification of cellulose with succinic anhydride, which could absorb 400 times its dry weight of water.[48] Other SHs were prepared from CMC and cellulose in an NaOH/urea aqueous solution by crosslinking with epichlorohydrin.[23] Demitri et al.[49] focused on the preparation of SHs derived from cellulose and two cellulose derivatives, CMC and hydroxyethyl cellulose. The use of citric acid as a crosslinking agent helped to overcome drawbacks such as the toxicity and high costs associated with other synthetic crosslinkers and was used for a thermally activated reaction. An esterification mechanism based on anhydride intermediate formation was proposed to explain the reaction of cellulose derivative polymers with citric acid.[49] Fujioka et al.[50] reported the preparation of novel SHs by the reaction between guar gum and sodium alginate (SA) with 4-dimethylaminopyridine as an esterification promoter and water or dimethyl sulfoxide as the solvent; this was followed by

neutralization with an NaOH aqueous solution. Recently, biodegradable SHs were prepared by the esterification reaction of chitin[51] and starch[52] with SA with 4-dimethylaminopyridine as the esterification agent.

The interaction between carboxylic and amine groups is another alternative for crosslinking in the synthesis of SHs based on alginate and aqueous multivalent amines (e.g., ethylenediamine, L-lysine, chitosan).[53] The hydrogel having the highest water absorbency was obtained with the sample with a chitosan feed ratio to SA of 100 mol %; it reached 410 g/g in pure water and 100 and 80 g/g in 0.9 and 3.5% NaCl solution, respectively. The absorbent capability of the SHs decreased significantly in the presence of salts. Poujavadi et al.[54] proposed a parameter that easily measures the effect of salts on the water absorbency capacity by correlating the hydrogel swelling in pure water and that in a salt aqueous solution.

Guilherme et al.[55] obtained brain-resembling SH composites via the UV-induced copolymerization crosslinking of vinyl-modified starch with acrylic acid (AAc) monomers and N,N-dimethyl acrylamide in the presence of Fe_3O_4 particles. Paulino et al.[56] developed a system to remove methylene blue dye from water using SHs formed by PAAc, PAAm, and chemically modified gum arabic. The fast swelling properties of this system were further studied by Favaro et al.[57] In these cases, the synthetic routes were simple because of the incorporation of glycidyl methacrylate (GMA) into the gum arabic structure to form a methacrylated product in an appropriate solvent and with TEMED as a catalyst. Cashew gum was also methacrylated,[58] with the SH preparation targeted by copolymerization with AAm and further hydrolysis. The as-obtained SHs swelled almost 2000 times in relation to its dry weight. The reaction mechanism for inserting GMA onto different polymer backbones as function of the reaction media pH was investigated in depth by Reis et al.[59] It was shown that in acidic conditions (pH 3.5), GMA reacted with carboxylic and hydroxyl groups through an epoxide ring-opening mechanism. However, under alkaline conditions (pH 10.5), GMA was hydrolyzed and reacted with hydroxyl groups by both epoxide ring opening and transesterification mechanisms, in which the first was preferred.

Copolymerization of Functionalized Polymers, Oligomers, and Monomers

Usually, most SHs are prepared from a copolymerization process[60–62] with functionalized polymers and oligomers or monomers. Several researchers have developed SHs through the copolymerization of AAc on biopolymers by free-radical pathways in the presence of N,N-methylene bisacrylamide (MBAAm) as a crosslinker. From this perspective, Bao et al.,[63] prepared SHs by the copolymerization of AAc/AAm/2-acrylamido-2-methyl-1-propanesulfonic acid onto sodium CMC in the presence of montmorillonite. Sadeghi et al.[64] obtained SHs based on the biopolymer carrageenan via graft copolymerization with AAc in the presence of kaolin powder. Pourjavadi et al.[65,66] obtained SHs based on alginate in the presence of kaolin and also novel protein-based SHs by graft copolymerization with AAc monomers. In other studies, SHs were developed by the crosslinking of AAc-graft-copolymerized onto silk sericin.[67,68]

SHs based on PAAm and polyacrylonitrile (PAN) were also investigated.[69] The physical mixture of the copolymers of PAAm and PAN was hydrolyzed with an NaOH solution to prepare SHs based on the copolymer PAAc-co-PAN. The nitrile groups of PAN were completely converted to a mixture of hydrophilic carboxamide and carboxylate groups during the basic hydrolysis, which was followed by the in situ crosslinking of the PAN chains by starch alkoxide ions. Pourjavadi and Hosseinzadeh[69] used acrylonitrile, AAc, and AAm monomers to develop hydrogels with excellent superabsorbent properties using a two-stage methodology. In the first stage, the copolymerization reaction of the AN and AAm monomers with ammonium persulfate as a free-radical initiator was performed. In the second stage, the resulting copolymer was hydrolyzed to produce carboxamide and carboxylate groups; this was followed by the in situ crosslinking of the PAN chains.

Hydrogels in nanoscale dimension (or nanogels) with excellent swelling properties can be prepared by inverse miniemulsion (IME) polymerization. Attention has been paid to the development of multifunctional nanogels with this strategy.[70–72] Because all droplets formed in IME remain as particles (nanoreactors) upon polymerization, this method allows one to perform a variety of reactions based on the chemical composition and physical and chemical properties of the monomers present in the dispersed droplets containing hydrophilic moieties to get novel architectures.[73,74] In a recent study,[75] AAc monomers stabilized around gelatin macromolecules inside droplets were polymerized with ammonium persulfate and TEMED in a 1:5 molar ratio and were crosslinked with MBAAm to form semi-IPN nanogels; these were sequentially crosslinked with glutaraldehyde to form interpenetrating networks (IPNs). Transmission electron microscopy (TEM) images recorded from these IPN nanogels showed that they possessed nonuniform surfaces; this suggested a phase-separation phenomena between the two polymer networks. With different strategies, SHs can be made in the form of membranes, particles (on the macroscale, microscale, and nanoscale) with or without a controlled pore geometry.[76]

SH COMPOSITES CONTAINING MICROSIZED AND NANOSIZED PARTICLES

SHs are mostly prepared with vinyl monomers, such as acrylates and/or polysaccharides, because of their hydrophilic character, but generally, they form materials with poor mechanical properties.[77] The improvement of the mechanical properties of hydrogels has been done through three main strategies: (1) increasing the crosslinking density, (b) crosslinking the hydrogel surface, and (3) incorporating microsized and/or nanosized particles into the hydrogel matrix.[10] This section deals with the main properties presented by SHs having microsized and/or nanosized particles incorporated into the hydrogel 3D matrix.

SHs with Microsized or Nanosized Particles: Main Properties
Some studies have shown that the incorporation of microsized and nanosized particles, for example, clays, nanofibers (NFs) or nanowhiskers (NWs), and inorganic particles, such as magnetite, into the hydrogel matrix is a suitable strategy for overcoming challenges related to the poor mechanical properties and for

improving other properties (e.g., thermal stability, water uptake capacity, release rate). For instance, the incorporation of Laponite into PNIPAAm-based hydrogels improved the mechanical properties of the composite material related to the neat PNIPAAm.[78] That study changed the paradigm in the field and became a reference work in the use of nanostructured particles to improve the mechanical properties of hydrogels. The incorporation of industrial waste materials, such as rice husk ash (RHA), is a good alternative in the formation of SHs with improved features and follows current environmental concerns.[79]

SHs with Microsized or Nanosized Particles: Application

The incorporation of microsized and nanosized particles into the 3D matrix can improve some existing hydrogel properties and provide some new features; this allows tailoring of the superabsorbent material for specific applications. The incorporation of microsized and nanosized particles could be a versatile method for the further encapsulation of different solutes (e.g., drugs, fertilizers, essential oils) and therapeutic agents (e.g., antimicrobial and growth factors)[80] and for enabling hydrogels to absorb some water contaminants (e.g., dyes, heavy metals).[81] With such considerations taken into account, it is reasonable to say that in the last decade, a well-established research field focusing on SH composites has been continuously explored.

Since the first generation of SHs containing microparticles and nanoparticles, the use of clays such as montmorillonite, bentonite, kaolinite, and sepiolite, have been explored because of their hydrophilic characteristics, availability, and low cost of production.[10] The incorporation of raw clays was the first strategy used to form this kind of composite.[82] Wei et al.[83] presented one of the first studies on the incorporation of mineral clay micropowders into a hydrogel matrix. In that study, the authors incorporated different kinds of raw clays into a starch-*graft*-PAAm matrix and evaluated the influence of the clays (kind and amount) in the swelling properties. Despite the improvements provided by the clay incorporation, its dispersion inside the hydrogel matrix was not satisfactory. So, an alternative to solve this problem was to modify the clays with hydrophilic intercalants, which enhanced the clay dispersion and the swelling properties and allowed the crosslinking of the clays to organic matrices. Guilherme et al.[84] designed a hydrogel consisting of dispersed vinyl montmorillonite crosslinked to a maltodextrin-*co*-dimethyl acrylamide matrix. The authors observed an excellent dispersion in the modified montmorillonite at the matrix even after the hydrogel was swollen, and the water absorption mechanism became more dependent on the polymer relaxation for those mineral-filled hydrogels.

Metal nanoparticles have also been used in the preparation of SH composites.[25] Silver nanoparticles have been extensively incorporated into SH matrices because of their well-known antibacterial activity. Magnetic materials, such as magnetite $\{[Fe^{3+}]_1(Fe^{2.5+})_2O_4\}$ or maghemite (γ-Fe$_2$O$_3$), have been widely incorporated into different hydrogel matrices to provide a quick response after external stimuli, generated by the use of applied magnetic field, were applied.[85] Among the several inorganic fillers applied to form SH composites, the ashes obtained from the incineration of rice husk (RHA), an industrial waste byproduct,

is a very promising candidate.[86] RHA is primarily composed of silica mineral. Some studies show that this material presents interesting features in the adsorption of metal ions, heavy metals such as lead and mercury, and also some dyes. Rodrigues et al.[87] investigated the potential of RHA incorporated into a chitosan-*graft*-PAAc matrix. The swelling properties of those SH composites were dependent on the ash structure (amorphous or crystalline) and the amount of ash incorporated. Shen et al.[88] added graphene oxide (GO) into a PAAm-based hydrogel formulation to modify their mechanical and thermal properties. The original PAAm hydrogels are commonly crosslinked by MBAAm (PAAm–MBAAm hydrogel), generally exhibit unsatisfactory mechanical properties, and are often brittle. After GO was added to the PAAm–MBAAm hydrogel, Shen et al.[88] observed that GO/PAAm–MBAAm hydrogels become very tough and exhibited fairly good tensile properties. The mechanical and thermal properties of the GO/PAAm–MBAAm hydrogels were significantly affected by the shifting of the GO or MBAAm content in the hydrogel formulation. This was probably caused by the microstructure, which was related to the specific combination of GO sheets and MBAAm, and acted as a multifunctional crosslinking agent in the GO/PAAm–MBAAm hydrogels. However, the hydrogel without GO (PAAm–MBAAm hydrogels) presented a higher equilibrium swelling ratio than the corresponding GO/PAAm–MBAAm hydrogels.

Microparticles and nanoparticles have been incorporated into hydrogel matrices for uses in the pharmaceutical field to enhance the drug-release rate and act as carriers for biological components (e.g., growth factors).[89] Hezaveh and Muhamad[90] observed that the incorporation of silver and magnetite nanofillers into modified κ-carrageenan hydrogels improved drug release in the intestine and minimized it in the stomach. The experimental data showed that the nanofiller loading could significantly improve the release at the specific target.

In the environmental field, hydrogels with microparticles and nanoparticles have been designed to act in water desalinization and remediation. In a recent study, Wang et al.[91] investigated the ability of chitosan-*graft*-PAAc/vermiculite hydrogel composites to remove Pb(II) and Cd(II) ions from aqueous solutions The maximum Pb(II) adsorption capacity was 63.27%, whereas the maximum Cd(II) adsorption capacity was 86.26%. Mahdavinia et al.[92] designed a hydrogel composite based on AAm–carrageenan containing Laponite clay; it was tested in the removal of crystal violet, a cationic dye, from water. The experimental data showed that the maximum adsorption capacity of crystal violet was about 79.8 mg/g of hydrogel composite.

The technological field related to electronics has just started to show interest in SH composite materials. SHs containing metallic nanoparticles have been studied for application as conductive materials. Golikand et al.[93] prepared a conductive hydrogel composite containing zinc nanoparticles. The experimental data showed that the zinc–hydrogel composite had good conductivity.

NFs AND NWs FROM CHITIN AND CELLULOSE

As natural polymers, chitin and cellulose are biodegradable, biocompatible, renewable, and affordable. Cellulose has been used
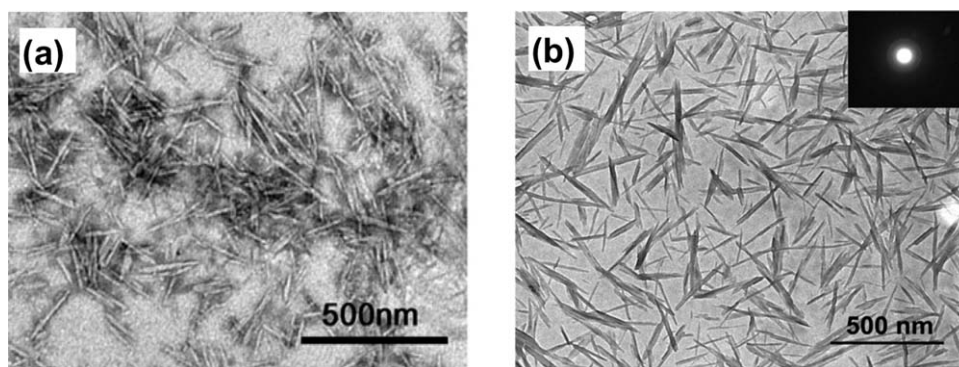
Figure 2. Micrographs by TEM of the obtained CNWs[117] by hydrolysis with (a) H_2SO_4 (Reprinted with permission from ref. 117. Copyright 2013 Elsevier.) and (b) dilute suspension of CHNW[118] (Reprinted with permission from ref. 118. Copyright 2003 American Chemical Society). The inset shows the typical electron diffractogram recorded on chitin fragments.

for decades in many different fields, including the paper and fabric industries,[94] gun powder and propellants,[95] and food additives.[96] More recently, cellulose has found applications in the nanomaterials field[97] and in the production of bioethanol.[98,99] Cellulose presents three hydroxyl groups in each sugar residue, and as a linear polymer, the interchain H-bond interactions occur at a high level. As a consequence, cellulose is found in nature as a highly crystalline polymer with crystallinities that vary depending on the source.[100] The high crystallinity renders cellulose insoluble in most common solvents and, therefore, prevents many of its potential applications.[101] Similarly to cellulose, chitin is a very crystalline polymer presenting a restricted solubility as well. From a structural point of view, the chitin molecule is compared to cellulose with the hydroxyl group at carbon 2 substituted by an acetylamide group; this confers to chitin about 7 wt % nitrogen.[102]

So far, different approaches have been reported in the preparation of CHNFs, CNFs, and CNWs;[103,104] these include acid hydrolysis,[105,106] oxidation by 2,2,6,6-radical tetramethylpoperidine-1-oxyl,[107,108] and mechanical defibrillation.[109,110]

Despite some confusion that has been noticed in the literature regarding the nomenclature of polysaccharide nanocrystals, recent review articles have brought clear definitions. According to Khalil et al.'s[103] definition, the term *whiskers* is used to designate elongated crystalline rodlike nanoparticles, whereas the designation *nanofibrils* should be used to designate long, flexible nanoparticles consisting of alternating crystalline and amorphous strings.

CNWs and CHNWs are generally obtained from acid hydrolysis and are 2–20 nm wide and 0.2–1 μm long, depending on the source.[97] CNFs often present diameters in the range 10–30 nm and are derived from 30–100 extended cellulose chains.[111,112]

Chitin and cellulose have crystalline and amorphous domains. The amorphous regions act as structural defects and are responsible for transverse cleavage when subjected to hydrolysis in an acid medium. So, by this process, colloidal particles, commonly referred as NWs and nanocrystals, can be obtained from chitin and cellulose.[97,112–116] Depending on the hydrolysis conditions,

including the concentration and type of acid, time, temperature, and polysaccharide source, CNFs, CNWs, CHNFs, and CHNWs with different features can be obtained. Figure 2 shows TEM images recorded from CNWs obtained by hydrolysis with H_2SO_4[117] and a diluted suspension of CHNWs.[118] The inset shows a typical electron diffractogram recorded from the chitin fragments.

SH COMPOSITES CONTAINING CNFs, CNWs, AND CHNWs

As mentioned in the last section, the preparation of hydrogel-containing microsized and/or nanosized particles is a very interesting strategy for obtaining properties not found in hydrogel matrices without such particles. This kind of material is the so-called NPH. The target of this strategy is to obtain a hydrogel with very high swelling capabilities and good mechanical properties. Often, conventional hydrogels do not possess these properties at the same time. Highly swelled SHs normally present poor mechanical properties. In sequence, we describe some important works in this field and highlight the main results and applications.

Spagnol and coworkers[11,119,120] incorporated CNWs in different superabsorbent matrices to produce materials with interesting liquid uptake capacities and stimuli-sensitive properties. Additionally, Zhang et al.[121] prepared supramolecular hydrogels based on cyclodextrin/polymer with CNWs and CHNWs incorporated into their formulation. Their goals were to enhance the mechanical strength and regulate the drug-release behavior. The structures and properties of the resulting NPHs were characterized by X-ray diffraction analysis, scanning electron microscopy (SEM), and rheological tests. The elastic modulus of the NPHs climbed because of the reinforcing function of the CNWs and CHNWs. The modulus of this type of NPH was 50 times higher than that of the native hydrogel. In addition, the presence of NWs increased the stability of the hydrogel framework and inhibited the diffusion of bovine serum albumin, which served as a model protein drug in the NPH and showed prominent sustained release profiles. Finally, but equally important, is the fact that incorporating CNWs did not lead to additional cytotoxicity of the NPH compared to the native hydrogel. The
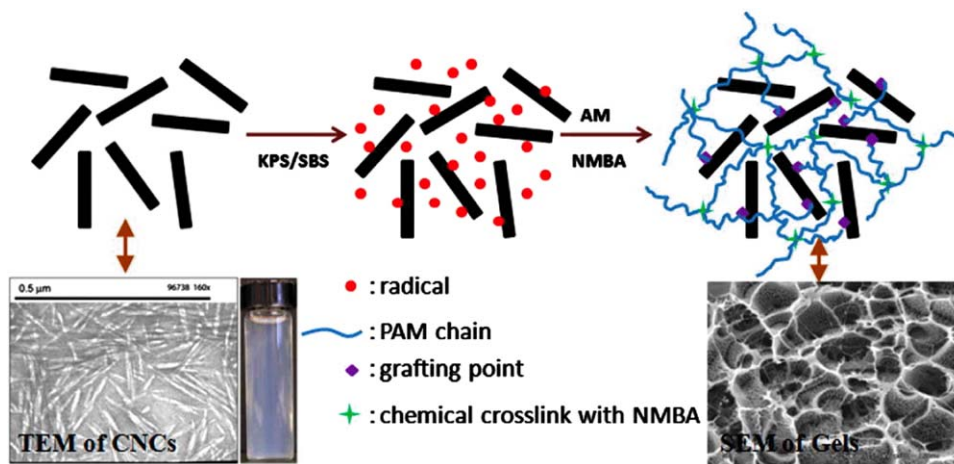
Figure 3. Scheme of the gelation mechanisms of the PAAm–CNF nanocomposite hydrogels. Reprinted with permission from ref. 122. AM - Acrylmide; NMBA - N,N′-methylenebisacrylamide; KPS - Potassium persulfate; SBS - Sodium Bisulfate. Copyright 2011 Elsevier. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shear-thinning property characteristic of this NPH contributed to its potential as an injectable biomaterial.

Zhou et al.[122] prepared NPHs based on PAAm reinforced with cellulose nanocrystals (CNCs) by an *in situ* free-radical polymerization. Their aim was to investigate the nanocomposite chemical structure, morphology, swelling, and compression strength properties. The potential application of such nanocomposites was both traditional bone-defect repair and bone tissue engineering. A possible mechanism route for preparing NPHs was proposed in that article, as shown in Figure 3. The results show that CNCs accelerated the formation of the hydrogels and increased the effective crosslinking density; that is, it was suggested that the CNCs acted as a multifunctional crosslinking agent. Furthermore, compared to neat PAAm hydrogels, the NPHs exhibited a significant improvement in the strength (by compression tests) and storage and loss moduli (by oscillatory tests); these improvements were attributed to the good dispersion of CNCs in the PAAm matrix and allowed enhanced interfacial interaction between the two components. The 6.7% w/w loading led to maximum mechanical properties for the NPH among the used CNC contents.

In another work from the same research group, Zhou et al.[123] used dynamic rheology to characterize the *in situ* polymerization process of NPHs of PAAm and CNCs (NWs, and NFs) and to explore the mechanism of gelation. They investigated the influence of the chemical crosslinker concentration, polymerization temperature, initiator concentration, and CNC aspect ratios on the mechanical properties of the NPHs. The results show that CNCs accelerated the onset of gelation and acted as a multifunctional crosslinker for the network of gels. The NPH possessing 5 wt % CNC exhibited an enhancement in the mechanical properties; this indicated that the CNCs not only reinforced but also toughened the PAAm matrix. The elastic modulus increased with increasing crosslinker concentration, polymerization temperature, and CNC aspect ratios but decreased with increasing initiator concentration. In addition, the onset of gelation decreased with increasing crosslinker con-

centration, polymerization temperature, and initiator concentration. CNCs with lower aspect ratios reduced the onset of gelation and promoted the sol–gel transition of the NPHs; this suggested that CNCs with a higher relative surface and surface charge had the ability to facilitate the formation of the network. A possible mechanism of such an NPH formation is shown in Figure 4, and variable effects were proposed in that article.

Yang et al.[124] prepared NPHs with PAAm-containing CNCs by a combination free-radical polymerization and self-assembled CNC polymer particles in the absence of chemical crosslinks. The influences of the CNCs on the swelling degree and mechanical properties were the main focus evaluated in that study. Even in the absence of chemical crosslinks, the NPHs exhibited bulk swelling without any apparent dissolution or mass loss; this suggested that such CNCs acted as extra crosslink points within the 3D polymer matrix. The equilibrium swelling ratios of the NPHs were strongly dependent on the CNC content, and a decrease in the swelling ratio occurred with increasing content of CNCs. This suggested the existence of physical and chemical interactions between the polymer matrix and the CNCs. Also, an increase in the CNC content from 0.2 to 3 wt % led to an increase of two orders of magnitude in the hydrogels' elastic (Young's) modulus; this indicated that the CNCs mainly determined the rubbery elasticity of the systems. In addition, the addition of a small fraction of CNCs led to a significant increase in Young's modulus. The authors suggested that the low density of crosslinks, the homogeneous network structure, and the multifunctionality of CNCs within the primary chains promoted the remarkable strength of the hydrogels. As shown in Figure 5, the covalent bonds between the CNCs and PAAm via silane bridges induced the formation of an elastic network, whereas the polymer chains' dynamic relaxation and CNC orientation process led to viscoelastic properties.[124] Before deformation, the PAAm chains were probably attached to the surface of CNCs via covalent and hydrogen bonds. It was stated that during deformation, the initial coiled chains presented stretched and unfolded conformations, which were related to the unique
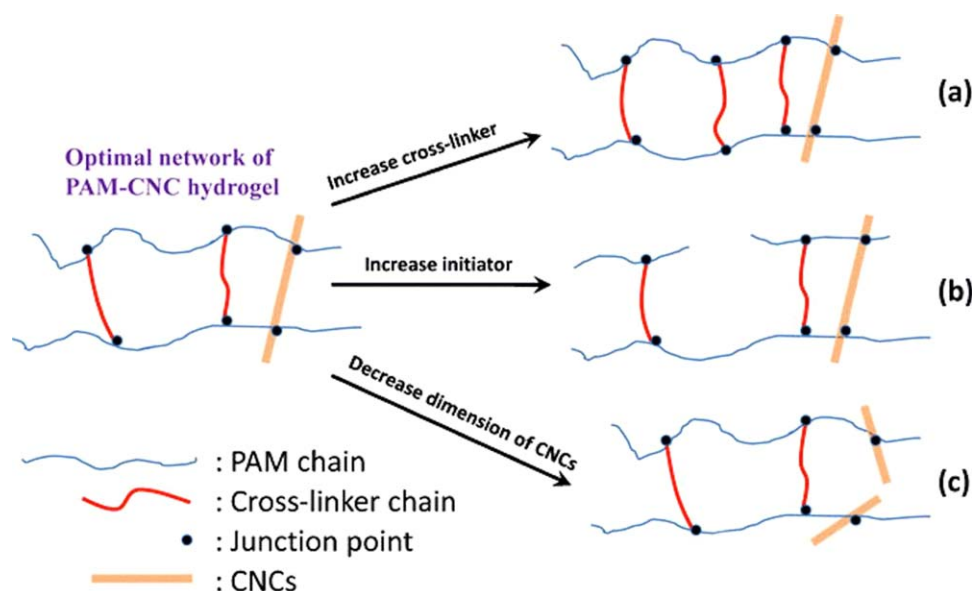
Figure 4. Scheme of the effects of the (a) crosslinker, (b) initiator, and (c) CNC dimension on the network microstructure of the PAAm–CNC hydrogels. Reprinted with permission from ref. 123. Copyright 2011 Elsevier. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

energy release process. These findings provided new perspectives for understanding the relations between the network structures and mechanical properties and create another facile method for the preparation of high-performance hydrogels for applications such as artificial muscles, sensors, and other environmentally friendly materials.[124]

NPHs based on PAAm–methylcellulose (MC) reinforced with natural cellulose microfibers (CMFs) and CNFs were prepared by Aouada et al.[125] with free-radical polymerization. They focused on the investigation of the morphology, swelling degree, and mechanical properties. The presence of the CNFs provoked pronounced changes in the hydrophilic, mechanical, structural, and morphological properties without diminishing their thermal stability. Morphological analyses by SEM showed significant

decreases in the pore size and formation of the 3D well-oriented porous microstructure as the CNFs were added to hydrogels; this suggested the existence of stronger interactions between the CNFs and network hydrogel. Moreover, the addition of CNFs improved the mechanical properties and some structural network properties of the NPHs without negative impacts on the thermal and hydrophilic properties. A possible mechanism for the formation of the microcomposite and NPHs was proposed for this system, as shown in Figure 6.[125]

NPHs based on PAAm reinforced with natural chitosan nano-fibers (CHSNFs) were prepared by Zhou and Wu[126] via *in situ* free-radical polymerization. The structure of the NPHs and their properties, including strength, morphology, and rheological properties, were the main issues on which the authors
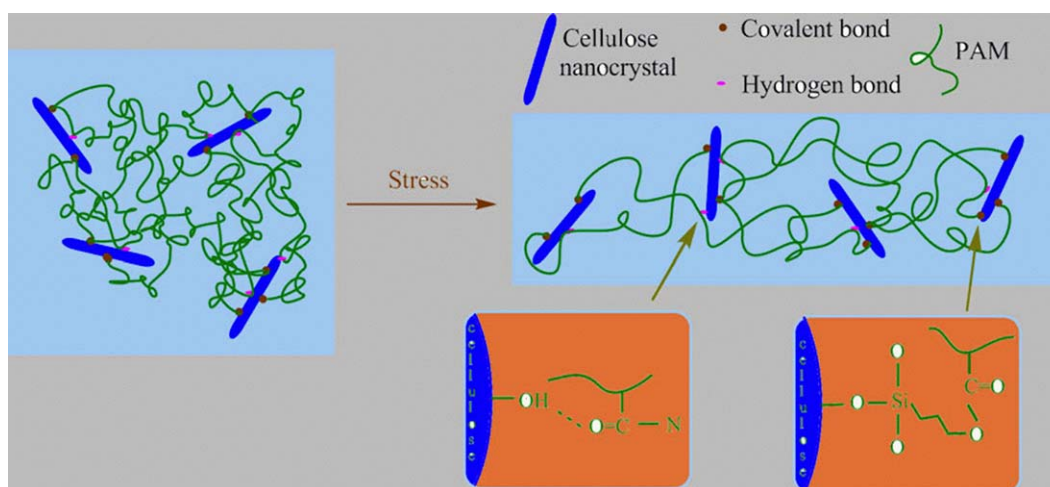

Figure 5. Schematic illustration of the structural changes during network deformation in the CNC–PAAm hydrogels. Reprinted with permission from ref. 124. Copyright 2013 Springer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
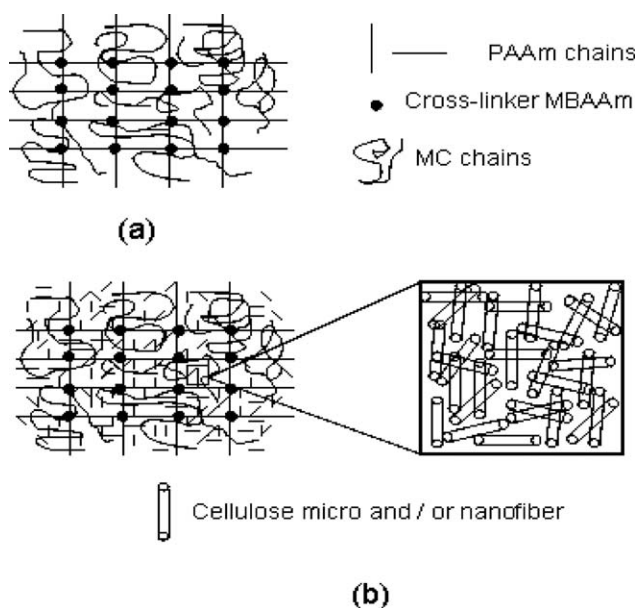
Figure 6. (a) Formation of the crosslinked network structures based on PAAm and MC with MBAAm and TEMED as the crosslinker and catalyst agent, respectively. (b) CNCs anchored to the PAAm–MC hydrogels. Reprinted with permission from ref. 125. Copyright 2011 American Chemical Society.

focused. The compression strength and the loss and storage moduli of the PAAm–CHSNF-based NPHs were significantly higher than those of the neat PAAm hydrogels and the corresponding semi-IPN PAAm/chitosan hydrogels, which were both used for comparison. The authors pointed out that the combination of covalent and hydrogen bonds between the PAAm and CHSNFs led to stronger interactions on the PAAm–CHSNFs interface as compared to the neat PAAm or to semi-IPN PAAm/chitosan systems. In this case, the presence of CHSNFs decreased the swelling ability of such NPHs; this indicated that the CHSNFs acted as a multifunctional crosslinker and reinforced the hydrogel system. The 1.5 wt % loaded CHSNFs showed the best combined swelling and mechanical properties for the hydrogels. A possible mechanism for the formation of NPHs was proposed, as shown in Figure 7.[126]

Chemically modified CNWs have been used to prepare hydrogels with enhanced properties. For instance, Dash et al.[127] pre-

pared a renewable and biocompatible hydrogel with superior mechanical properties consisting of a gelatin matrix crosslinked with oxidized CNWs. The oxidized CNWs were prepared by use of periodate in the absence of light at room temperature and were further used as a crosslinking agent for obtaining this type of NPH. The increase in the hydrogel rigidity not only affected the local chain dynamics but also reduced the gel swelling; the gel showed a relatively reduced water uptake ability compared to the neat gelatin. An improvement in the NPH storage modulus of about 150% compared to that of the neat gelatin was observed. Chemical crosslinking also increased the resistance of the gels toward thermal degradation above the melting temperature of the gelatin, as observed by thermal scanning experiments.[127]

Borges et al.[128] evaluated the swelling and compressive mechanical behavior, morphology, and biocompatibility of composite hydrogels based on Tween 20 trimethacrylate (T3), N-vinyl-2-pyrrolidone, and nanofibrillated cellulose (CNFs). The chemical structure of T3 was verified by Fourier transform infrared spectroscopy and ^{1}H-NMR, and the degree of substitution was found to be around 3. Various concentrations of CNFs (0.2–1.6 wt %) were used to produce composite hydrogels that showed lower swelling ratios than the neat ones for a given T3 concentration. The neat and composite hydrogels exhibited a typical nonlinear response under compression. The authors observed that all of the composite hydrogels showed an increase in the elastic modulus compared to that of neat hydrogel of about threefold to eightfold; the elastic modulus reached 18 kPa at 0% strain and 62 kPa at 20% strain for the hydrogel with the highest CNF content. The authors pointed out that all of the hydrogels presented porous and homogeneous structures, with interconnected pore cells around 100 nm in diameter, and verified that the hydrogels were biocompatible. They demonstrated that the composite hydrogels reinforced with CNF might have been viable as nucleus pulpous implants because of their adequate swelling ratio, which could restore the annulus fibrous loading, and their increased mechanical properties, which could possibly restore the height of the intervertebral discs, a very important issue in biotechnological applications.

A hydrophobic superabsorbent matrix was also produced through the use of cellulose-fibril-based hydrogels. Korhonen et al.[129] prepared highly porous nanocellulose aerogels by freeze
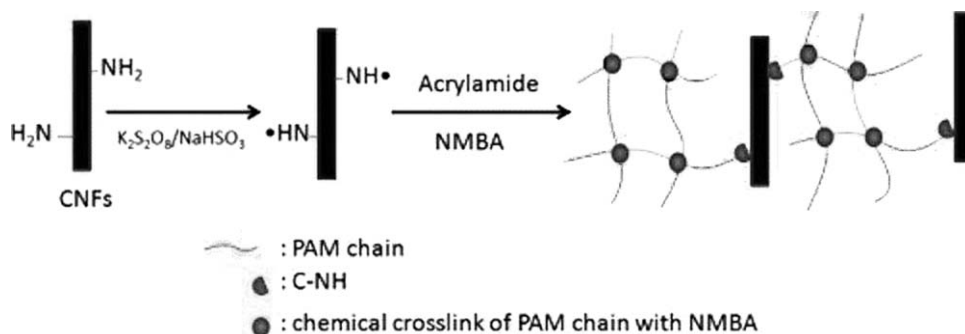

Figure 7. Schematic diagram showing the covalent bonding mechanism in the PAAm–CNF nanocomposite hydrogels. Reprinted with permission from ref. 126. Copyright 2011 Elsevier.

drying from CMF hydrogels. The authors showed that through the functionalization of the native CMFs of the aerogel with an oleophilic coating, such as TiO_2, a selectively oil-absorbing material capable of floating on water was achieved. Because of their low density and ability to absorb nonpolar liquids and oils up to nearly all of their initial volume, the surface-modified aerogels allowed the collection of organic contaminants from the water surface. It was shown that the materials could be reused after washing, recycled, or incinerated with the absorbed oil. Because cellulose is renewable and titanium dioxide is not environmentally hazardous, that material showed potential for environmental applications.

PERSPECTIVES OF SHs CONTAINING CNC

In this review, we present a short discussion of the most general aspects in the incorporation of polysaccharide NWs and/or NFs into SH formulations to produce NPHs. This new class of superabsorbents materials has great application prospects in several fields. In addition, there are still a lot of subjects about the microsized and nanosized particles and their relation with the huge class of crosslinkable polymers (synthetic and natural) to be investigated and improved. More comprehensive studies will broaden the understanding of the structure–property relationship. Herein, some future trends in this field can be highlighted, among others, as follows:

1. The controlled surface chemical modification of particles (NWs or NFs) could provide better dispersion on different SH matrices. This could be also helpful for more intense and effective crosslinking effects of NWs or NFs because of the presence of groups at derivated-surface-enabling extracovalent bonds to the polymeric chains that form the SH matrices;
2. Nanogels with excellent water uptake capabilities (e.g., a thousandfold) may have their properties improved by particles (NWs or NFs) incorporated into the nanogel formulation prepared mainly by the IME method.
3. Hydrogels as NFs can be prepared by electrospinning techniques.[130] Surprisingly, only few works with nanoparticles such as NWs or NFs to produce SHs by electrospinning have been found in the literature to date. One can suggest that such particles may be introduced into the solution before the electrospinning experiments or after the experiments by the contact of fresh NFs with the suspension. The presence of microsized and nanosized particles (NWs or NFs) should tailor the polymer NFs to specific applications.

CONCLUSIONS

SHs are a hot issue in materials science. The number of publications announcing SHs based on a novel methodology or on new polymeric materials and SHs with new structures and properties has increased year by year. Recent studies have shown that the incorporation of microsized and/or nanosized materials into SH matrices improved the final properties of SH composites or NPHs to enhance the use and application of these kinds of materials. In this sense, the preparation of hydrogel-containing particles (NWs or NFs) is a very interesting strategy

for obtaining properties not found in the hydrogel matrix without such particles. There is no doubt that more comprehensive studies will further broaden the understanding of the structure–property relationships in this very important class of materials.

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