A Review on Polysaccharide Based Nanocomposite Hydrogel Systems Fabrication Using Diverse Reinforcing Materials

Nisha Sharma1,*, Vikrant Singh Rana2,3
1Assistant Professor, Department of Physical Sciences, Sant Baba Bhag Singh University, Jalandhar, Punjab, India
2Research Scholar, Department of Physical Sciences, Sant Baba Bhag Singh University, Jalandhar, Punjab, India
3Assistant Professor, Department of Chemistry, Sri Guru Gobind Singh Khalsa College Mahilpur, Hoshiarpur, Punjab, India

Abstract

In the current scenario, materials with better physicochemical properties are desirable to achieve quality life and sustainability. Polysaccharide/biopolymeric based hydrophilic systems owing to their inherent properties, especially hydrophilicity, nontoxicity and biocompatibility have extended their approach in every strata of biomedical sciences and replaced synthetic polymers upto great extent. Despite this, they have also experienced certain demerits due to their biological origin. Functionalization of polysaccharide based hydrophilic polymer with reinforcing materials/modulators, especially in nano-dimensions, is one of such approach getting much attention in current scenario. Although great deal of work has been published in nanocomposite hydrogels but least attention was paid for polysaccharide based nanocomposite hydrophilic systems. Present study is an attempt to compile a brief account of fabrication of polysaccharide based nanocomposites using metallic nanoparticles, metallic oxides, CNT and graphene, and clay as nanofillers with improved physicochemical as well as biological properties.

Keywords: Hydrogel, nanocomposite hydrogel, functionalization, reinforcing materials, physicochemical properties, nanofillers, sustainability

*Author for Correspondence E-mail: nishi.hpu@gmail.com

INTRODUCTION

Since last century, polysaccharide based hydrophilic systems have revolutionized all sectors viz. biomedical, drug delivery, environmental and advanced industrial sectors due to their unique characteristics such as hydrophilicity, swelling ability, biodegradability, nontoxicity and biocompatibility. Apart from these properties, they possess certain demerits such as uncontrolled swelling profile, poor mechanical and tensile strength, and poor stability which limit their use for advanced applications where such behavior is desirable. From time to time, different strategies have been adopted to overcome such drawbacks. Composite hydrogels, graft copolymerization, and various other chemical treatment strategies have been adopted from time to time. Fabrication of nanocomposite filled hydrophilic system is one of the most fascinating and advantageous approaches due to improved behavior of gel system without compromising the base properties of the system. Biopolymeric nanocomposite hydrogels are a class of homogeneous natural polymeric network prepared by reinforcement of the polymer matrix with nanoparticles imparting high tensile strength and high toughness compared to conventional hydrogel [1-5]. Natural, synthetic and combination of natural and synthetic polymers are used to form nanocomposite hydrogel matrix. Nanocomposite hydrogel can also be defined as water swollen materials composed of polymer matrix and nanoparticles, both organic and inorganic, metals, metal oxides, with clay as reinforcing
materials into a biopolymeric base matrix. These materials improve the behavior of material in different aspects. Reinforcing materials are primarily in nano-scale dimensions and possess special characteristic attributes to their size which in turn modulate behavior of polymeric matrix. There are primarily covalent or physical interactions which bind the gel system and reinforcing materials together. There is a clear distinction among composite and nanocomposite hydrogels as the reinforcing material used in composite need not necessarily to be of controlled size but in nanocomposite, reinforcing material must have nano-scale dimensions and should have some distinct inherent behavior due to their size [6].

In literature, various polysaccharides such as alginate [7], chitosan [8-10], carrageenan [11, 12], cellulose and modified cellulose [13-15], gum acacia [16], guar gum [17, 18], xanthan gum [19, 20], starch and modified starch [21, 22], tragacanth gum[23, 24], and gum karaya [25, 26] have been modified using diverse class of reinforcing materials. Present study is intended to compile a brief account on different types of polysaccharides and different reinforcing materials used for synthesis of nanocomposite systems for advanced applications.

Characteristics of Nanocomposite Hydrogels

Polysaccharides based nanocomposite hydrogels possess mixture of properties such as biodegradability, biocompatibility, permeability, hydrophilicity, non-toxic, and non-immunogenic behavior owing to natural polymeric matrix and new/improved properties attributed to nanoparticles included with in which in turn increase the horizons of polysaccharide nanocomposite hydrophilic systems. They also possess ease of surface modification as compared to synthetic polymer matrix [27-29]. Nanocomposite hydrogels have enhanced mechanical strength, multifunctionalities [30] and multi-responsiveness [31] with zero dimensional scale, like fullerenes enhance mechanical strength of gel and impart photo responsiveness [32]. One-dimensional nanomaterials such as single wall and multiwalled carbon nanotubes when embedded in hydrogel networks improve their mechanical, thermal and electric properties [33, 34]. Two-dimensional graphene sheets when embedded in biopolymeric matrix improve specific surface area, mechanical stiffness, optical behavior and gas permeability [35]. Similarly, three-dimensional nanoparticles, when incorporated, improve basic characteristics of polymeric systems, are also used in printing technology.

TYPES OF BIOPOLYMERIC NANOComposite HYDROGELS ON THE BASIS OF REINFORCING MATERIALS

Metal Nanoparticles Based Nanocomposite Hydrogels

Metal nanoparticles are most demoralized reinforcing materials used for the fabrication of nanocomposite hydrogels. Most common metallic nanoparticles such as Ag, Au, Cu, Pt, Ce and Fe have been used for the synthesis of polysaccharide based nanocomposite hydrogels [36-41].

In literature, a great deal of work is dedicated for the incorporation of silver ion as nanoparticle owing to inherent antimicrobial property of silver thus helpful for the synthesis of biomedical systems. During fabrication of metallic nanoparticle embedded gel systems, different reducing systems are desirable as auxillary stabilizing systems such as strong reducing agents like sodium borohydride. Natural polysaccharide itself also acts as reducing and stabilizing system due to presence of different functionalities on the backbone. Plant extracts are also applicable as reducing systems. Ag-sodium alginate nanocomposite hydrogels when fabricated through single step green synthesis using *Mukia maderaspatana* plant extract as a reducing agent show improved chemical and physical properties [42]. Rao *et al.* have incorporated silver nanoparticles inside xanthum gum and chitosan based polysaccharide matrix without the use of any chemical reducing agent. Polysaccharide chain itself stabilizes the nanoparticle through ionic and dipole-dipole interaction [43]. Silver nanoparticles can also be incorporated through
redox polymerization using vinylic monomers and N’N’, Methenamine bisacrylamide as crosslinking system in to a tragacanth gum based hydrogel matrix. Leaf extract of *Terminalia chebula* acts as reducing medium and nanoparticles were also stabilized as a result of hydrogen bonding with the functional groups present on the hydrogel matrix. These functionalities also attribute to swelling behavior of hydrogel networks [44]. Carboxymethyl tamarind (CMT) acts as reductant and capping agent for the amalgamation of silver nanoparticles. Base concentration of CMT and silver nitrate modulates the physical and chemical properties of the prepared nanocomposite hydrogel [45]. Chitosan-PVA polymer matrix embedded with Ag nanoparticles has been fabricated through freeze thaw method using glutaraldehyde as crosslinker. NaBH₄ acts as reducing agent to convert silver ions in to silver nanoparticles. Concentration of the glutaraldehyde controls the size of silver nanoparticles. There is strong interaction among silver nanoparticles and polymer matrix which is reflected in terms of declined swelling capacity of the hydrogel [46]. Kristic et al. have also fabricated silver nanoparticles embedded chitosan/PVA polymer matrix by gamma irradiation. The nanoparticles were stabilized by interaction with the functional groups present on the polymer network. Composition of feed matrix system strongly influences the size and stability of nanoparticles which in turn control the physicochemical characteristics of the system [47].

In one pot reaction by Abdullah et al., Ag nanoparticles could be included inside guar gum in the presence of epichlorhydrin. The resultant nanocomposite films have low water permeability and were used in food packaging [48]. Polysaccharide embedded nanoparticles could be achieved through electrospinning method. Vellora et al. Have prepared Ag nanoparticles through chemical reduction of silver nitrate and subsequently embedded into Gum Karaya/PVA matrix by electrospinning. 80:20 ratio of PVA/Chitosan fabricated membranes display excellent physicochemical properties as well as with good antibacterial activity [49]. Djerahov fabricated Chitosan/Ag nanocomposite films using D-(+)-raffinose as reducing and stabilizing agent. These films have good mechanical strength in aqueous solution.

There is narrow size distribution of nanoparticles with excellent homogeneity in shape as compared to silver nanoparticles prepared by other methods [50]. Ag nanoparticles can be incorporated into starch/PVA films fabricated through solvent casting method using UV light as reducing system. Elasticity modulus and tensile strength values have been enhanced at low silver concentration and decreased at high silver concentration [51]. Singh et al. have fabricated gum tragacanth, acacia gum, PVA and polyvinyl pyrollidone (PVP) based hydrogels films through radiation induced crosslinking method. Ag nanoparticles have been incorporated through swelling equilibrium method using NaBH₄ as reducing agent. These hydrophilic networks have been used in wound dressing. Ag nanoparticles increase antioxidant properties along with inherent antimicrobial behavior. Concentration of acacia gum controls the release of the silver nanoparticles from the hydrogel network and thus facilitates release of silver ions for extended period of time [52]. Au nanoparticles when incorporated into chitosan polysaccharide matrix loaded with curcumin an anticancer drug resulted into a pH responsive gel networks [53]. Alginate/Acrylamide hydrogels loaded with iron nanoparticles results into photo-responsive hydrogels. The appearance of orange color indicated the incorporation of ferric ions into the hydrogel network. The photochemical treatment changed the microscopic and macroscopic behavior of the hydrogel [54]. Al-Enizi et al. prepared Cu nanoparticles embedded cellulose gum matrix using hydrazine as reducing system. Copper nanoparticles are stabilized through the interaction between the hydroxyl and carboxyl group functionalities of the gel matrix. Storage modulus of the nanocomposite hydrogel was found to be higher than loss modulus [55]. Gold alginate bio-nanocomposites have also been synthesized through impregnation of alginate films with HAuCl₄ followed by reduction with glucose. Polymer concentration affects the thickness, amount of
Au\(^{3+}\) trapped, and volume fraction of Au (0) [37]. Laudenslager et al. have synthesized Au, Ag and Pt nanoparticles integrated native chitosan and carboxymethyl chitosan based nanocomposite gel matrix using NaBH\(_4\) as reducing system. Nanoparticle aggregation takes place inside carboxymethyl chitosan as compared to native chitosan where uniform distribution is obtained [39].

### Metal Oxides Based Nanocomposite Hydrogels

Metal oxides are other reinforcing materials used for nanocomposite fabrication. They possess unique characteristics i.e. thermal stability, optical and photo-responsive behavior and when incorporated in nanodimensions into a polymeric matrix, inculate same behavior into the gel system. ZnO nanoparticles based chitosan matrix can be synthesized through single step in-situ sol-gel method. ZnO drastically improves the thermal stability of Chitosan/ZnO as compared to chitosan hydrogel [56]. Chitosan/PVP nanocomposite films have been fabricated through incorporation of AgO nanoparticles by sodium citrate reduction. Concentration of AgO influences the size of nanoparticles inside the gel matrix without affecting the swelling ability [57]. TiO\(_2\)/Collagen-Chitosan scaffolds fabricated through freeze drying process, by Keke et al., possess good stability and permeability as compared to scaffold without TiO\(_2\) nanoparticles [58]. ZnO incorporated PVA/Starch/Chitosan hydrogel membranes have been synthesized by freezing thawing cycle. These membranes have good flexibility, porosity, adequate mechanical strength and tear resistance [59]. Pectin grafted poly-2-acrylamide-2-methyl-propane sulphonic acid-co-acrylamide/ZnO nanocomposite hydrogel through microwave irradiation method. ZnO nanoparticles increased the absorption capacity of the polymeric hydrogel [60]. In literature, Guar Gum/Al\(_2\)O\(_3\) and Guar Gum/CuO nanocomposites were synthesized by sol-gel method. The red shift shows strong interaction between polymer matrix and aluminium oxide nanoparticles [61, 62]. CuO based nanoparticles show negligible cytotoxicity and good thermal stability and prove to be good candidates for controlled drug release system [62]. Sahoo et al. have synthesized Guar Gum coated iron oxide (Fe\(_3\)O\(_4\)) nanocomposites through coprecipitation method. These were good adsorbents for removal and enrichment of organic dye Congo red from aqueous medium [63].

Iron oxide, apart from acquiring nanodimensions, also possesses magnetic behavior and is sensitive to the external magnetic field. When incorporated into a gel matrix inculates magnetic responsive behavior into parent matrix. Co-precipitation method is the conventional method adopted for synthesis of magnetic nanoparticles and possesses high magnetic sensitivity against external field. Pourjavadi et al. have fabricated magnetic nanocomposite hydrogels of starch-graft-poly (acrylic acid) in the presence of Fe\(_3\)O\(_4\)/SiO\(_2\) nanoparticles through in situ cross linking polymerization. Fe\(_3\)O\(_4\)/SiO\(_2\) nanoparticles decline the water holding capacity of nanocomposite hydrogel as compared to nonmagnetic hydrogel because Fe\(_3\)O\(_4\)/SiO\(_2\) nanoparticles act as auxiliary crosslinkers as well as copolymers [64]. Polyelectrolytic Xanthan gum/Chitosan/Fe\(_3\)O\(_4\) based magnetically responsive bio-nanocomposite hydrogels have been fabricated through in situ ionic complexation using D- (+)-glucuronic acid and δ-lactone as a green acidifying agent. Functional groups present on gel network contribute to the improved stability of magnetic nanoparticles. Cell adhesion, storage modulus and mechanical properties were improved by incorporation of Fe\(_3\)O\(_4\) magnetic nanoparticles [65]. Maghemite (Y' - Fe\(_3\)O\(_4\))/Iota carrageenan based magnetic nanocomposite hydrogels have been designed by Maciel et al. The nanocomposites display good ferromagnetic behavior, spherical morphology, good thermal stability, good swelling ability and particle size of 710 μm [66]. Iota-carrageen and Y'-Fe\(_3\)O\(_4\) magnetic nanocomposites were synthesized by Raman et al. through sonication. The electrostatic interaction between the sulphate groups of carrageenan and Y'-Fe\(_3\)O\(_4\) stabilized the nanoparticles. The sulphate groups present on the carrageenan were also responsible for the improved physical properties [66, 67].
Nanoparticle concentration strongly influences the surface charge, gel forming ability and magnetic properties of nanocomposites which further can be exploited to fit into appropriate applications [67]. Cobalt ferrite (CoFeO₄) nanoparticles coated with 3-amino propyl trimethoxy silane could be easily loaded on to carboxy-methylcellulose to obtain nanocomposite hydrogels [68]. Bisht et al. used supercritical carbon dioxide assisted green chemical technology to synthesize starch/Fe₃O₄ nanocomposites. Magnetic nanoparticles have crystalline structure with size of 16 nm range and nanocomposites possess good adsorption capacity as compared to nanoparticles alone [69]. Fe₃O₄ enclosed nanocomposite hydrogels were obtained in the presence of chitosan matrix using an in situ co-precipitation method in alkali medium. High chitosan concentration prevents formation of iron oxide nanoparticles, instead ferric hydroxide was formed. The presence of magnetic nanoparticles increased elastic modulus of chitosan ferrogels [70].

**Cellulose Nano Crystals (CNC) and Cellulose Fibres Based Nanocomposite Hydrogels**

In literature, Cellulose nanocrystals and cellulose fibres have been exploited as reinforcing materials for the synthesis of polysaccharide based nanocomposite hydrogels. Rao et al. have prepared CNC reinforced xanthum gum/chitosan bionanocomposites using D-(+)-Glucuronic acid and 6-Lactone as green acidifying agents. These nanocomposite hydrogels have improved mechanical properties, good biocompatibility and good porous structure when compared with the xanthan gum and chitosan hydrogels without CNC. Porosity of gel networks attributes to the electrostatic interaction and hydrogen bonding between the functional groups present on the CNC and the polysaccharides. CNCs display their characteristic behavior in the concentration range of 2 to 10% [71]. Cellulose fiber (*Grewia optiva*) reinforced nanocomposite blend films of starch/PVA have been fabricated by casting method using citric acid as plastisizer and glutaraldehyde as crosslinker. These is clear improvement in physicochemical properties such as mechanical properties, tensile strength, elongation percentage, degree of swelling, biodegradability and cell adhesion of nanocomposite blend films as compared with starch/PVA blend films without reinforcing material *Grewia optiva*. Mixing time, concentration of citric acid, glutaraldehyde and *Grewia optiva* control all their physicochemical properties [72]. Similar behavior is also observed in PVA (polyvinyl alcohol)/chitosan/CNC bionanocomposite films. The tensile strength shows drastic increase from 98.4 to 395 MPa when CNC content increased from 0 to 1 weight%. The oxygen permeability of the CNC reinforced blend films increases due to the formation of pores [73]. These properties favor their use in fabrication of wound dressing scaffolds. CNC/Halloysite reinforced nanocomposite scaffolds of sodium alginate and xanthum gum as hydrogel matrix have been synthesized by freeze drying. Incorporation of CNC and halloysite show improved mechanical, compressive and thermal properties of these scaffolds when compared with those without CNC/Halloysite but in turn decline the water holding capacity. The compressive properties of nanocomposite scaffolds were improved in both wet and dry state [74].

**Carbon Nanotubes (CNT)/Graphene Oxide (GO)/Graphene Based Nanocomposite Hydrogels**

Different forms of carbon in the form of graphene, graphene oxide and carbon nanotubes (CNT) are also used as reinforcing materials for nanocomposite hydrogel fabrications. All these forms have excellent properties such as high electrical conductivity at room temperature, long term environmental stability, good electrochemical activity and biocompatibility. CNTs, when incorporated into polysaccharide matrix, modulate their inherent properties [75]. CNTs/graphene need functionalization through chemical or radiation treatment to improve their binding affinity to polysaccharide systems [75]. Bibi et al. have incorporated 7-irradiated carbon nanotubes into silane crosslinked chitosan/PVA polymer matrix to prepare a green nanocomposite. CNTs improve physical
properties but drastically decrease the swelling profile of hydrogel systems [76]. This behavior favors their use as implants where stability is the more crucial property to be kept in consideration. Acrylic acid functionalized \( \kappa \)-carrageenan hydrophilic networks when reinforced with multiwalled carbon nanotubes (MCNT) improve swelling and adsorption behavior. Concentration of reinforcing material influences the adsorption capacity. The adsorption capacity decreased with decrease in pH, increase in MCNTs concentration beyond .04%, in agitation time of more than 90 min [77]. GO/Cellulose Nano Crystals and GO/Urea cellulose nanocomposites display improved viscosity, thermal stability, mechanical strength and tensile strength [78, 79]. GO/Chitosan nanocomposite has strong interaction between the functional groups of two components and thus increases mechanical strength in both wet and dry state, storage modulus and thermal stability [80]. Starch/Graphene nanocomposite films when prepared through solution castings have improved tensile strength with increase in the graphene content and decline in moisture uptake [81].

Clay Nanocomposite Hydrogels
Clay also acts as an excellent reinforcing material for the synthesis of nanocomposites. Montmorillonite [82], saponite [83] and hectorite [84] are clays most commonly used in synthesis of nanocomposites. \textit{In situ} polymerization [85], solution dispersion [86] and fusion intercalation [87] are some methods adopted for synthesis of polysaccharide/clay nanocomposite hydrogels. Silane modified nanoclay when crosslinked with functionalized starch (starch phthalate) notably improve the compressive modulus and strength of hydrogel upto twice by the addition of nanoclay. The increase in the mechanical properties was due to interaction between the amine groups present on the nanoclay and the hydroxyl and ester groups present on the modified starch [88]. Zhang \textit{et al.} prepared superabsorbent hydrogels by graft polymerization of acrylic acid and AMPS (2-acrylamido-2-methyl propane sulphonic acid) onto xylan and montmorillonite, an inorganic clay. These superabsorbents have high compressive modulus, swelling capacity and multistimuli responsive behavior as well as tolerance to salt due to the incorporation of ionic and nonionic groups [89]. Menon \textit{et al.} have incorporated nanoclay cloisite into the guar gum grafted with polyacrylic acid semisynthetic matrix through microwave irradiation. Cloisite improved mechanical properties and thermal stability of the nanocomposite. Swelling capacity of cloisite embedded nanocomposite was maximum when the concentration of cloisite was 2%. With further increase in the clay concentration the swelling capacity declines as the clay itself starts acting as auxiliary crosslinker [90]. Guar gum/montmorillonite enclosed nanocomposites have improved mechanical, tensile strength and adsorption properties [91]. Silane modified nanoclay has also been used to prepare acrylic acid grafted guar gum nanocomposites through microwave irradiation. These prepared nanocomposites were pH sensitive and have good swelling capacity [92]. Guar gum-g-poly (sodium acrylate)/Na-montmorillonite superadsorbent nanocomposites were also prepared by grafted polymerization in aqueous medium. Montmorillonite was exfoliated and evenly dispersed in guar gum-g-poly (sodiumacrylate) matrix [93]. Starch, xanthum gum and nanoclay (sodium montmorillonite) based biodegradable nanocomposite films can also be synthesized by extrusion using glycerol as plasticizer. Nanoclay addition generates more transparent and resistant films with lower water permeability and lower water sorption capacities and xanthum gum addition improves the elongation properties of starch films [94].

Polysaccharide based nanocomposite hydrogels have applications in the field of wound dressing [43, 44, 46, 49, 52, 58, 95, 96], drug delivery [53, 71, 91, 97-99], tissue engineering [65, 88, 100], bioremediation of toxic metal ions and dyes [101-103], biosensors and photocatalysis.

CONCLUSION
Reinforcing materials such as metallic nanoparticles, metal oxides, CNTs, clay and cellulosic fibres improve physical properties, especially mechanical and tensile behavior, which favors their applicability as tissue
engineering materials. At the same time these materials also incorporate antibacterial, antimicrobial, antioxidant, optical and electrical properties in polymeric matrix which pave the way to apply such advanced materials to biomedical applications with ease. Nanocomposite hydrophilic systems have drastically improved and provided new route for current biomedical research as they have resulted into double potential hydrophilic systems.

REFERENCES


74. Kumar A, Rao KM, Han SS. Development of Sodium Alginate-Xanthan Gum Based


Cite this Article