Hydrogels Embedded Nanocomposites & Their Applications

CHAPTER-I
1. Hydrogels, Hydrogels Embedded Nanocomposites & Their Applications.

Hydrogels are crosslinked polymer chains containing hydrophilic groups connected by physical or chemical bonds, and as one of the most intelligent materials by virtue of their exceptional properties, which absorb and retain large amounts of water. Hydrogels are hydrophilic polymeric networks that can imbibe a large amount of biological fluids including water and can swell several times of their dry volume. In the polymeric network hydrophilic groups or domains are present which are hydrated in an aqueous environment thereby creating the hydrogel structure. As the term, ‘network’ implies, crosslinks have to be present to avoid dissolution of the hydrophilic polymer chains/segments into the aqueous phase. Hydrogels can also be described in a rheological way. Aqueous solutions of hydrophilic polymers at low or moderate concentrations, where no substantial entanglement of chains occurs, normally show Newtonian behaviour. On the other hand, once crosslinks between different polymer chains are introduced, the so obtained networks show viscoelastic and sometimes pure elastic behavior. Because of their water absorbing capacity, hydrogels are not only the subject of investigation of researchers interested in aspects of swollen polymeric networks, but have also found widespread application in different technological areas. These materials are used for contact lenses, protein separation, matrices for cell-encapsulation and devices for the controlled release of drugs and proteins. There are a variety of excellent books and review papers that describe the fundamental aspects and application areas of hydrogels [1–9]. As mentioned, crosslinks have to be present in a hydrogel in order to prevent dissolution of the hydrophilic polymer chains in an aqueous environment. A great variety of methods to establish crosslinking has indeed been used to prepare hydrogels. Their ability to absorb water in large amount is due
to the presence of hydrophilic functional groups such as -OH, -CONH-, CONH₂, -COOH, and 
-SO₃H [1] in their networks. To qualify as hydrogel a polymer in practical sense, the dry 
material should spontaneously imbibe about twenty times its own weight of aqueous fluid. 
While undergoing this phenomenon of volume change of 2000 percent, the swelling 
material retains its original identity.

The first generation of hydrogels with swelling capacity up to 40-50% appeared in the late 
1950s and were mainly based on polymers derived from hydroxyalkyl methacrylate and 
related monomers. These hydrogels were used in developing contact lenses which marked 
a revolution in ophthalmology. The need to improve these lenses, and the emerging of 
other medical problems resulted in the development of a second generation of hydrogels 
with swelling degrees of 70-80% which widened the scope of their application.

Hydrogels are most commonly obtained by free radical crosslinking polymerizations 
of hydrophilic acrylate or methacrylate monomers with small quantities of crosslinking 
agents containing two (or more) polymerizable double bonds. Examples of typical 
crosslinking agents include N,N¹-methylenebis-acrylamide, triallylamine, 
ethyleneglycoldiacrylate, tetraethyleneglycoldiacrylate, trimethylolpopane-triacrylate and 
the methacrylate analogs of the aforementioned acrylates. Hydrophilic esters of acrylic or 
methacrylic acid (such as 2- hydroxyethyl methacrylate and its analogs) have been 
extensively polymerized using the above reagents to form hydrogels which typically 
exhibited a maximum swelling of 40-50 wt% water. The unique set of properties exhibited 
by the hydroxyethyl(meth)acrylate hydrogels have lead to their extensive application in a 
host of biomedical materials and devices.
Gel is a general term which describes the state of matter which is neither film, solid nor totally liquid but possesses some characteristics of all. Depending upon the nature of the liquid, we can have hydrogels or organogels. When entrapped fluid is water, the system is called a hydrogel and when it is an organic solvent, we call it an organogel. Organogels are not versatile and hence are not as popular as hydrogels. This is because of the chemistry of organogels which are usually nonionic and nonaqueous and has their own limitations. In comparison, hydrogels can be neutral or ionic and can tolerate hydrophobic segments too. Moreover, the special features of the water as a solvent makes a whole spectrum of chemical reactions possible. Added to this, are the successful attempts to use the hydrogels as models for biological tissues [10, 11]. Both chemical and physical methods have been used to create hydrogels. In chemically linked gels, covalent bonds are present between different polymer chains. In physically crosslinked gels, dissolution is prevented by physical interactions, which exist between different polymer chains.

In the dehydrated state, a hydrogel is hard and glassy, but swells in water to form a soft elastic material. The extent to the network

Whether the hydrogels are of natural or synthetic origin all hydrogels share some common properties:

1. High water content.

2. Permeability to a variety of molecules including their macromolecules if pore size permits.

3. Potentially good biocompatibility.

Hydrogels can also be designed with controllable responses so as to shrink or expand with changes in external environmental conditions [1]. The extent of swelling or deswelling in
response to the changes with external environment of the hydrogel could be so drastic that
the phenomenon is referred to as volume collapse or phase transition [2-3]. Hydrogels
respond uniquely to changes in external environmental conditions such as ionic strength
[4], electromagnetic radiation [5], pH [3-7], and temperature [8-12]. Other important
conditions such as the type of salt used for the preparation of buffer [13,14], the solvent
used as the medium [15], photoelectric stimulus [16] and the external stress [17,18] also
influences the hydrogel’s performance. These unique properties make hydrogels as
excellent candidates for numerous applications in biomedical, pharmaceutical, agricultural
and consumer-oriented fields.

1.1. Applications of Hydrogels

Hydrogels are used in many potential applications due to their excellent high water
absorbency, water retention and environmental sensitive nature. These hydrogels are
widely used in many products such as disposable diapers, feminine napkins, soil for
agriculture and horticulture, gel actuators, water-blocking tapes for biomedical
applications, and as absorbent pads. Some of the applications of hydrogels are described
below.

1.1.1 Agricultural and Horticulture Applications

Hydrogels are commonly utilized in agricultural field mainly as water storage granules
[19]. The need to improve the physical properties of soil to increase the productivity in the
agricultural sector was visualized in 1950s [20]. This led to the development of water-
soluble polymers such as PVA, PEG and PAM to function as soil conditioners followed by
the introduction of water-swellable polymeric hydrogels in the early 1980s. Water-
swellable hydrogels from crosslinked PAM, crosslinked polyacrylates and copolymers of acrylamide and acrylates for such applications have been reported [21].

Soils containing moist hydrogels as conditioners increases water-holding capacity of the potting media by 50 to 100 %. The increased water supply enhances the germination process by reducing the relative amount of water loss via evaporation and drainage. Swellable hydrogel delivery systems are also commonly utilized for controlled release of agrochemicals and nutrients of importance in agricultural applications to enhance the plant growth with reduced environmental pollution. A number of researchers have reported the versatility of polymeric hydrogels in agricultural applications.[22].

1.1.2. Hydrogels as Construction materials

Other applications are being developed based on the ability of these polymers to absorb water and salt solutions. For example leaking of water is often a problem in major construction projects. A sealing composite that swells slightly in water can be prepared by blending the hydrogel with rubber. Because of the incompatibility of the rubber and the hydrogel polymer, appropriate modification of the interface of the polymer phase is critical to the success of this material. The sealing composite is used between the concrete blocks for the construction of walls. When water contacts the composite, the sealant swells slightly, making an impermeable barrier for further penetration of water. Such a composite was used in the construction of the Channel linking England to France [23].

1.1.3. Hydrogels as water blocking tapes

Similarly, leaking of water is also detrimental to the performance of fiber optic communication cables and power transmission cables. Water-blocking tapes prevent intrusion of water [24]. The tape is prepared by applying a dispersion of hydrogel in a
polymeric binder onto a nonwoven fabric which provides flexibility. Because the cables are exposed either to seawater or ground water containing divalent cations, superabsorbents incorporating sulfonate functional groups rather than carboxylic acid groups- are preferred for this application [25].

1.1.4. Hydrogels as feminine napkins and baby diapers

Hydrogel polymers are expanding into many product areas. Personal hygiene products, however, use more than 95% of the 350,000 metric tons of hydrogel manufactured per year in the world. The principal use in disposable diapers is due to their thinner capacity by the introduction of hydrogel polymers. The Polymer absorbs liquid that was held previously in open spaces between the fibers of cellulose fluff. The cores of early polymer containing diapers contained about 12 % superabsorbent polymer. Current diapers are designed to incorporate up to 60% of superabsorbent polymer in addition to thinner size of diapers for infants, and also the superabsorbent polymers are used in feminine napkins.

1.1.5. Gel actuators and Sensors

Gel actuators are an active area of research related to hydrogels; these materials are used as artificial “muscles” in robots to provide motion to mimic human musculature. Variation of the swelling conditions is used to control the actuator. For example, changing the temperature, light intensity, electric filed strength, or composition (pH, salt concentration) of the swelling fluid can change the extent of swelling and cause the gel to move in response to the change in volume [26].
1.1.6. Medical Waste Treatment

Hydrogels are widely used in medical waste management. They can solidify the waste fluids and retain it even under significant pressure. This solidification of medical waste has a lot of advantages to the end user such as reduction in biohazard handling, ease of disposal and cost saving. Also, hydrogels have an application in hot and cold pads. When used in wound dressing it absorbs blood and exudates thereby enabling a clean and hygienic dressing.

1.1.7. Artificial snow

Artificial snow made up with hydrogel is used in an indoor ski centre near Tokyo. The snow is made by swelling the polymer with 100 times its mass of water and freezing it in a place with the cooling system. The frozen gel layer is groomed to yield snow with a realistic feel, similar to powder snow [27]. By using these polymers, the temperature of the air in the building can be at least 10 °C higher than with conventional artificial snow, increasing comfort for the skiers.

1.1.8. Hydrogels in vegetable and fruit storage buildings

At high humidity, hydrogel absorbs and releases moisture more effectively than silica gel. This property can be used for example, to prevent damage from moisture condensation on walls and ceilings in humid buildings. Since powdered products are difficult to apply in such cases, sheets and fibers have been developed. Simple laminates of polymer hydrogels are incorporated between two tissue layers as absorbent pads for meat and poultry packages. Sheets are made by polymerizing monomers directly onto nonwoven fabrics. These are used in vegetable and fruit storage buildings to maintain a constant humidity and
to prevent spotting of the produce caused by dripping of the condensed water from surface of the structure [23].

1.1.9. Hydrogels for pharmaceutical applications

Hydrogels have been attempted extensively to achieve ideal drug delivery systems with desirable therapeutic features [28]. The unique attractive physicochemical and biological characteristics of hydrogels, along with their huge diversity, have led to considerable attention to these polymeric materials as excellent candidates for delivery systems of therapeutic agents [29-31]. Pharmaceutical hydrogels have been categorized according to a variety of criteria mainly including, route of administration [32-36], type of material being delivered [37,30], release kinetics [38], etc. Therefore, a common classification system for the therapeutic hydrogel formulations might not be found within the literature. Nonetheless, a classification based on the route of administration of the hydrogel drug delivery systems [39], seems to include in the vast area of these therapeutic materials. Accordingly, the pharmaceutical hydrogels can be classified as: i) oral hydrogel systems [40], ii) transdermal and implantable hydrogel systems [41], iii) topical and transdermal hydrogel systems [42], iv) hydrogel devices for gastrointestinal (GI) drug delivery [43], and v) hydrogel-based ocular delivery systems [44]. Furthermore, hydrogel-based formulations applied via other routes are also significant. In this regard, novel approaches to improve bioavailability through nasal [45] and vaginal [46] routes using hydrogels have been presented.
1.1.10. Other applications of Hydrogels

Hydrogels are used as thickening agents (e.g., starch and gelatin) in foods. The addition of hydrogel-forming agents to incontinence products increases the fluid uptake and ensures improved retention capacity.

Hydrogels are used in photographic technology because they are light permeable and can also store light sensitive substances. In electrophoresis and chromatography, the separation and diffusion characteristics of the gel structure are exploited. Hydrogels, thus applied, operate within only a very limited range of swelling.

1.2. HYDROGEL MAGNETIC NANO COMPOSITES

Inorganic-polymer nanocomposites have recently gained importance and drawing the attention of many researchers. Several kinds of small inorganic particles have been coated with a layer of polymer or encapsulated in a polymer matrix. If these inorganic particles possess functions such as magnetic susceptibility, electrical conductivity, catalytic activity, or electro activity, it may be possible to form functional composites from them. These organic-inorganic hybrid materials present the properties of both the inorganic nanoparticles and the polymer by combining thermal stability, mechanical strength, or electronic and optical properties with flexibility and the ability to form films [47].

In biomedical applications also, it is necessary to cover inorganic magnetic particles with an organic material, such as polymers. In recent years, polymer-based magnetic nanocomposites have gained an increasing interest because of their potential applications. A variety of functional polymers including derivatives of polystyrene, poly(vinylpyridine), polyimine, poly (vinyl alcohol), poly(pyrrole), poly(aniline), and poly(vinyl-pyrrolidone) have been used in the preparation of nanocomposites. In addition
to their biocompatibility, magnetic polymer nano-particles should fulfill some criteria to fit further biomedical applications: no sedimentation (stable latexes), uniform size and size distribution, high and uniform magnetic content, super paramagnetic behaviour, no toxicity, no metal-ions (e.g., cobalt and iron) leakage, etc.

Polymer magnetic nanocomposites with a distinct inorganic core and an organic shell usually are the result of covering of magnetic nanoparticles via physical interactions with macromolecules as well as chemical reactions between the inorganic oxide surface and the organic material [48]. Such particles are well-known materials and have been widely studied due to their applications in diverse areas, such as tunneling magneto resistance [49-51], environmental remediation and biomedical arena [52]. These applications involve data storage, separation of enzymes and proteins, purification of nucleic acids [53], techniques of magnetic resonance imaging for cancer diagnostics [55] and cancer therapy through drug carriers that are magnetically controlled [55]. All these technological and medical applications require that the nanoparticles be super paramagnetic with sizes smaller than 20 nm and the overall particles size distribution be narrow so that the particles have uniform physical and chemical properties [56]

Different kinds of magnetic nanocomposites have been produced with both natural and synthetic polymers with the objective of incorporating groups on their surface, or modifying it, in order to carry out selective separation [57]. The incorporation of inorganic particles to polymers results in materials of higher mechanical strength [58-59] thermal stability [60] and superior optical [61], magnetic and electric properties [62]. Particles of nanometric dimensions (10-500 nm), such as nanocrystals [63], present high surface area,
promoting a better dispersion within the polymer matrix, allowing one to obtain interesting nanoparticulate materials with unique dimensional quantum effects, transport and magnetic properties. The controlled polymer synthesis in the presence of inorganic nanoparticles results in nanocomposite dispersions that have polymer matrices with very specific properties, combined with low production costs. The polymer matrix mainly determines the surface-related properties of these hybrid materials [64].

1.2.1 Polymer Hydrogels for Biomedical Applications

A biomaterial is a synthetic material used to replace a part of a living system or to function in intimate contact with a living tissue [65]. The word “biomaterial” is generally used to recognize materials for biomedical applications. Biomaterial saves lives, relieve suffering and improve the quality of life for a large number of patients every year. According to the applying of the materials in the body, biomaterials are classified into four groups: polymers, metals, ceramics and composites [66-67]. Polymeric biomaterials (PB) are polysaccharides (starch, cellulose, chitin, alginate, hyaluronate etc.) or proteins (collagens, gelatins, caseins, albumins) and/or synthetic and biodegradable polymers (Polyvinyl alcohol (PVA), Polyvinylpyrrolidone (PVP), Polyethylene glycol (PEG), Polylactic acid (PLA), Polyhydroxy acid (PHA) etc.).

Currently, applications of polymeric biomaterials are promising for drug delivery, tissue engineering, biotextiles etc. It also covers targeted drug delivery to the nervous system, gastrointestinal tract, and kidneys etc. PB also includes the modern textile-based biomaterials for surgical applications; novel techniques in biomimetic polymer preparation; contemporary uses for polymers in dental and maxillofacial surgery; and many more [68]. From a practical perspective, medical applications of polymers fall into
three broad categories: (i) extracorporeal uses (catheters, tubing, and fluid lines; dialysis membranes/artificial kidney; ocular devices; wound dressings and artificial skin), (ii) permanently implanted devices (sensory devices; cardiovascular devices; orthopedic devices; dental devices), and (iii) temporary implants (degradable sutures; implantable drug delivery systems; polymeric scaffolds for cell or tissue transplants; temporary vascular grafts and arterial stents; temporary small bone fixation devices, transdermal drug delivery) [69].

1.2.2 Polymer Silver Nano Particles

Silver nanoparticles are of interest because of their unique properties (e.g., size and shape depending optical, electrical, and magnetic properties) which can be incorporated into antimicrobial applications, biosensor materials, composite fibres, cryogenic superconducting materials, cosmetic products, and electronic components. Several physical and chemical methods have been used for synthesizing and stabilizing the silver nano particles. The most popular chemical approaches, including chemical reduction using a variety of organic and inorganic reducing agents, electrochemical techniques, physicochemical reduction, and radiolysis are widely used for the synthesis of silver nano particles. Recently, nano particle synthesis is among the most interesting scientific areas of inquiry, and there is growing attention to produce nano particles using environmentally friendly methods (green chemistry) [70]. Green synthesis approaches include mixed-valence polyoxometalates, polysaccharides, Tollens, biological, and irradiation method which have advantages over conventional methods involving chemical agents associated with environmental toxicity. Here in presents an overview of silver nanoparticle preparation by physical, chemical, and green synthesis approaches is presented. The aim of
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this overview is, therefore, to reflect on the current state and future prospects, especially the potentials and limitations of the above mentioned techniques for industries. Moreover, we discuss the applications of silver nanoparticles and their incorporation into other materials, the mechanistic aspects of the antimicrobial effects of silver nanoparticles.

Nanosilver particles have been applied to a wide range of healthcare products such as burn dressings, scaffold, skin donor and recipient sites, water purification systems, and medical devices [71-75]. Multipurpose systems are required to exhibit superior antibacterial activity toward germs on contact without releasing any toxic biocides. Ongoing research efforts, on three dimensional network hydrogels, suggest that huge free space is available between the cross-linked networks in the swollen stage and behaves as nanoreactors for generating the nano particles[76]. These hydrogel nanoreactors offer a platform for nucleation and growth of nanocrystals, which eventually lead to nano particle formation. Further, gel–nano particle systems have opened a new skylight for different applications in biomedical engineering and these approaches are most effective and safe because they are compatible with most of biological molecules, cells, tissues, etc [77].

1.2.3 Scope and Objectives of the Present Investigation

The nano particles offer the possibility of being targeted towards a specific target in the human body and remaining eventually localized by means of an applied magnetic field. For this the achievement of good homogeneous dispersions of the nano partilces in a polymer matrix is an important issue. Due to the peculiar characteristics of nano particals' they are suitable for many applications, such as controlled release of drugs, mechanical devices, artificial muscles, etc. The same materials also have many applications in Decease as
sensors, optical switches, and data storage systems. Such wide range of uses requires controlled size by employing different types of natural polymers. The literature survey reveals that from 1970 onwards the coating of polymers plays an important role in controlling the nano particle size. Therefore the present research work is focused on to control the size and shape of the particles and the matrix or the medium in which the particles are embedded. Generally in vivo application (like drug delivery, magnetic resonance imaging, and hyperthermia) requires the particles being biocompatible, stable and biodegradable. This is achieved by coating and embedding the particles in a suitable network like polysaccharides & protein (natural polymer) based hydrogel networks. Finally the developed nanoparticles are employed for different biomedical applications.

The objectives of this investigation are.

- To develop novel hydrogel nanocomposites using natural polymers.
- To develop temperature responsive hydrogel silver nanocomposites
- Particle size analysis of the nano particles as well as the hydrogel nanocomposites
- Swelling and deswelling studies of the hydrogel nano particles in different media
- Drug delivery studies of these nano particles
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