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Review article

UV curable PVA-based hydrogel systems: Properties, applications and future directions

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Abstract. Poly(vinyl alcohol) (PVA) based hydrogels have gained more interest in the field of biomaterials because of their many biomedical uses (*i.e.*, wound healing, drug delivery, and tissue engineering) and intrinsic physicochemical and biological characteristics. They can be made using a variety of synthetic techniques, but all of them are very time-consuming. Among them, photopolymerization also referred to as light-induced polymerization, has drawn a lot of attention because of its benefits, which include not requiring the use of solvents, easy and quick network formation, energy efficiency, quick processing, control over both space and time and reliability of crosslinking density and matrix strength. Ultraviolet (UV)-curable hydrogels containing PVA as a main component are gaining interest because of their excellent properties, including biodegradability, biocompatibility, less cytotoxicity and remarkable mechanical strength. This review highlights the significance of UV curable systems and their components, types, advantages and disadvantages of photoinitiators (PIs), UV curable monomers and their structures, properties of UV-cured PVA hybrid hydrogels, and their characterizations and applications in different fields. The photopolymerization mechanisms, tunable properties, and unique advantages of these hydrogels have been explored in detail. Furthermore, it sheds light on recent advancements in PVA-based hydrogels research and future exploration in this domain.

Keywords: *UV curable hydrogels, PVA, Bone tissue engineering, drug delivery, adsorption*

1. Introduction

UV curable poly(vinyl alcohol) based hydrogel systems are crucial because of their applications in catalysis [1], adsorption, drug delivery [2], ophthalmic material [3], cartilage repair [4, 5], bone regeneration [6], heart valves [7], repairing and reformation of tissues [6], and tendon repair [8]. Mainly, PVA hydrogels are utilized in biomedical field because of their excellent adhesive, biodegradable [9, 10], low cytotoxic [11], biocompatible [12] and mechanical properties [13, 14]. PVA can be linked with different synthetic (styrene, acrylamide, vinyl chloride, propylene, acrylates) and natural (cellulose, chitosan, sodium alginate, hydroxyapatite) components in order to form hydrogel system [15, 16]. PVA works as an artificial water-loving polymer which shows admirable water absorption properties due to the hydrophilic functionalities in its structure [17]. Different methods have been used to synthesize the PVA-based hydrogels including redox polymerization [18], freeze-thawing [19, 20] process and thermal [21] methods. All these methods possess some limitations as well. For example, in the freeze-thawing process, it is quite difficult to maintain –20 °C temperature for freezing hydrogel [22] and in thermal treatment, a high temperature is required [23].

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Similarly, hydrogels prepared through redox polymerization possess non-uniformity [24]. Due to these limitations, the UV-curing process is preferred as it shows some benefits like uniform gelation, facile curing and mild reaction conditions [24].

PVA itself does not possess any UV light absorbing properties, so it is linked with some photo-curable component to form UV curable hydrogels. Usually, UV curable monomers consist of vinyl, acrylate or methacrylate groups. Generally, acrylamide, Glycidyl methacrylate, 2-isocyanatoethyl methacrylate, acrylic acid and methacrylic acid monomers serve as pendent groups in PVA chains. These co-monomers along with different photoinitiators (PIs) (*i.e.* TPO, Irgacure-2959) help to form photo-curable PVA-based hydrogels [8]. For example, Qin *et al*. [25] prepared poly(vinyl alcohol)/poly(ethyleneglycol) diacrylate (PVA-PEGDA) hydrogel through UV light (λ = 365 nm) at room temperature by using PEGDA as a UV precursor. Similarly, Kamoun *et al*. [26] developed poly(vinyl alcohol)/glycidyl methacrylate (PVA-GMAA) hydrogel by UV irradiation method for various biomedical applications. PVA-based double network hydrogels can also be cured through photo-polymerization such as Liu *et al*. [27] prepared poly (vinyl alcohol)/poly(acrylamide-*co*-acrylic acid)/chitosan (PVA/(PAM-*co*-AA)/CTS) double network hydrogel by irradiation of UV light for 12 h for separation of oil/water mesh [27].

Many general reviews have been published on PVA-based hydrogels because of their unique characteristics compared to other synthetic polymers. Barbon *et al*. [28] presented the mechanical (elongation, compression, stress relaxation, friction behavior, creep test, tear test) and biomedical (biocompatibility, cytotoxicity) properties of PVA-based hydrogel systems in their review. Similarly, Qin *et al*. [29] reviewed the synthesis and mechanism of photo-curable hydrogels mainly for biomedical applications (*i.e.* tissue engineering). Moreover, they have studied the types, structures and properties of photoinitiators used in photopolymerization. Although these reviews are good they covered a broad range of properties of hydrogels prepared through thermal methods, freeze-thawing process and others. These reviews are not specific to PVA-based UV curable hydrogels. UV curable PVA-based hydrogel systems have gained importance because of the facile synthesis and exclusive properties of PVA polymer. Therefore, it is necessary to summarize the properties and significance of photo-curable PVA-based hydrogels. According to our knowledge, no one has described the latest progress on PVA-based photo-curable hydrogel systems.

In this particular review, the need of photo-curable systems, types of photoinitiators, UV curable monomers, PVA-based UV-cured hydrogel system with characterizations and applications are described.

2. Need of UV curable systems

Lasers, electron beams (EB), visible light, and UV radiation can all cause photo-induced polymerization. The photopolymerization method yields polymeric systems with a large range of industrial uses, including pressure-sensitive adhesives (PSAs), coatings, inks and photoresists. The UV-curing method is widely favored for its advantages, such as high chemical stability, excellent dimensional strength, low cost, rapid production in a small space, and curing without solvents at room temperature. UV-curing leads the way in thermoset production, revolutionizing the market with its fast curing time, minimal energy consumption, and solvent-free process [30]. UV curable radical polymerization emerges as a cost-effective, fast, and eco-friendly curing method compared to other curing processes [31]. These benefits include quick solidification, strong solvent resistance in cured films, lower volatile organic compound (VOC) emissions, greater ink flash points, and general environmental friendliness improvements. Additionally, it improves the dimensional properties of polymeric systems, which are particularly beneficial for the electronics industry [32].

2.1. UV curable monomers and their properties

UV curable inks, adhesives and coatings depend heavily on UV curable monomers. When exposed to UV radiation, they are made to withstand fast polymerization, which forms a solid crosslinked network. They are made up of monomers such as polyester acrylates, polyether acrylates, urethane acrylates, epoxy acrylates, and acrylated oils [33]. The polyfunctional monomers are the main constituents of photocrosslinkable systems. The UV curable monomers, their structures, cytotoxicity, advantages, disadvantages, and applications are summarized in Table 1.

Table 1. Monomers their structure, cytotoxicity, advantages, disadvantages, and applications in different fields.

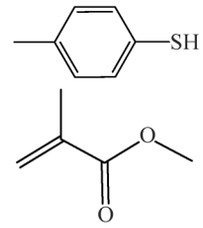
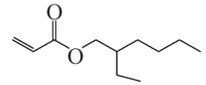
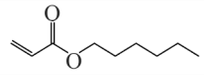
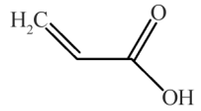
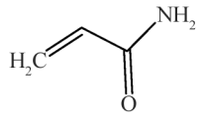
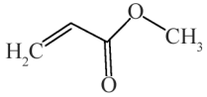
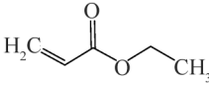
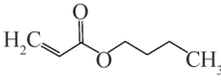
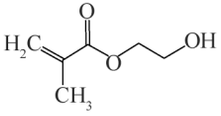
Monomer	Examples	Type	Structure	Cytotoxicity	Advantages	Disadvantages	Applications	References
Thiol/ene	Alkyl thiols, thiophenols, thiol propionates, and thiol glycolates	Radical type		Low cytotoxicity	Less air inhibition sensitivity, good yields, conversions, high reaction rates, high possibility of photo-initiation	Distinct odor, toxicity, short shelf life	Coatings, adhesives, sealants, printing plates, microcircuits, hydrogel formation	[34]
Acrylates	2-ethyl hexyl acrylate (EHA)	Radical type		Low cytotoxicity	Good flexing action	Volatile, slow cure and poor solvent resistance		[35]
	N-butyl acrylates (BA)	Radical type		Low cytotoxicity	Good viscosity reducer and flexing action	Volatile, low curing rates and bad solvent resistance		[36]
	Acylic acid	Radical type		May exhibit cytotoxic effects at higher concentrations and prolonged exposure	High reactivity	Corrosive	Polymerization reactions	[36]
	Acrylamide	Radical type			Fast curing rate	Potential neurotoxicity	Production of polymers, gels and adhesives	[36]
	Methyl acrylate	Radical type			Good reactivity	Flammable	Production of polymers, adhesives and coatings	[36]
	Ethyl acrylate	Radical type			Good balance of reactivity and volatility	Flammable	Polymers production, coatings and adhesives	[36]
	Butyl acrylate	Radical type			Good film forming properties	Flammable	Production of polymers, coatings and adhesives	[36]
	2-hydroxyethyl methacrylate	Radical type			Hydrophilic nature with good solubility in water	Can cause skin and eye irritation	Production of hydrogels, coatings and adhesives	[36]

Table 1. Continuously 1.

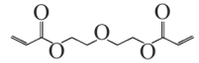
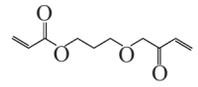
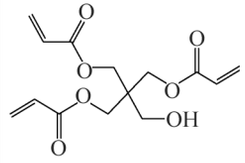
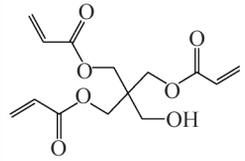
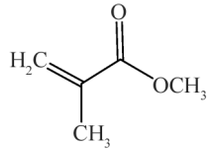
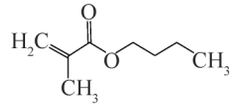
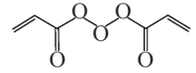
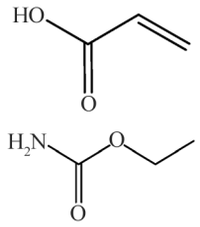
Monomer	Examples	Type	Structure	Cytotoxicity	Advantages	Disadvantages	Applications	References
Diacrylates	Diethyleneglycol diacrylate (DEGDA)	Radical type		Moderate cytotoxicity	Relatively good viscosity reducer and low volatility	Suspected skin irritation		[36]
	1,4-butanediol diacrylate (BDDA)	Radical type		High cytotoxicity	Good viscosity reducer	Adverse dermatitis and toxicity properties		[37]
Triacrylates	Pentaerythritol triacrylate (PETA)	Radical type		Low cytotoxicity	Rapid cure	Eye irritation and carcinogenic	Printing inks, adhesives, and coatings	[38]
Tetracrylates	Pentaerythritol tetraacrylate	Radical type		Low cytotoxicity	Low volatility	Eye irritant and suspected to be carcinogenic	Printing inks, adhesives, and coatings	[38]
Methacrylates	Methyl methacrylate	Radical type		Low cytotoxicity	Improved chemical resistance, hardness	Higher shrinkage, potential for cracking	Dental materials, optical coatings, adhesives	[35]
	Butyl methacrylate	Radical type		Low cytotoxicity	Good film forming properties	Moderate volatility and flammability	Production of polymers, coatings, and adhesives	[35]
Epoxy acrylates	Epoxy resins and acrylates			Low cytotoxicity	High chemical resistance, excellent adhesion	Higher viscosity, longer curing times	Coatings for metals, plastics, composites	[39]
Urethane acrylates	Urethane resins and acrylates			Low cytotoxicity	Good flexibility, chemical resistance, adhesion	Higher cost, potential for moisture sensitivity	Automotive coatings, furniture finishes, adhesives	[33]

Table 1. Continuously 2.

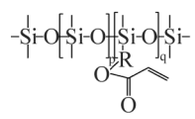
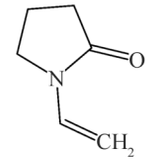
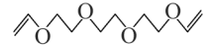
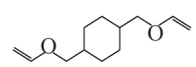
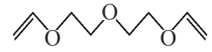
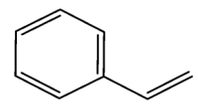
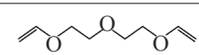
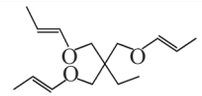
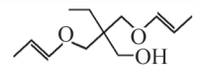
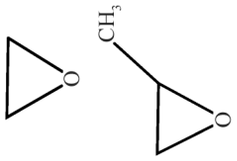
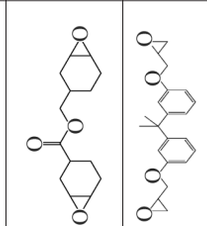
Monomer	Examples	Type	Structure	Cytotoxicity	Advantages	Disadvantages	Applications	References
Silicone acrylates	Silicone and acrylates			Low cytotoxicity	Excellent heat resistance, water repellency, anti-corrosion	Higher cost, potential for lower mechanical strength, unpleasant odor	Release coatings, electronic encapsulation, Hydrophobic materials synthesis	[40]
Vinyl ethers	*N*-vinyl pyrrolidone	Radical type		Low cytotoxicity	Low toxicity and high flexibility when cured		Hair care products, such as hairsprays, gels, and styling products	[32]
	Triethylene glycol divinyl ether (TEGDE)	Radical type		Low cytotoxicity	High diluting power and less toxic	Boiling temperature is low	Crosslinking agents, Adhesives and Sealants, Ion Exchange Resins	[32]
	1,4-cyclohexanedimethanol divinyl ether	Radical type		Low cytotoxicity	Large diluting power and low toxicity	Eye irritation and toxic		[41]
	Diethylene-glycol-divinyl-ether (DEGDE)	Radical type		Low cytotoxicity	High diluting power and low toxicity	Eye irritant	Crosslinking agents, Adhesives and Sealants, Ion Exchange Resins	[42]
	Styrene	Radical type		Moderate cytotoxicity	Excellent flexibility, Good weather resistance, Low cost	Slowly cure, together with volatility problems and the small number of monomers available	Used in the wood finishing industry	[35]
	Diethyleneglycol divinyl ether	Ionic type		Low cytotoxicity	Fast photopolymerization	Inconvenient and expensive synthesis		[42]
Propenyl ethers	Trimethylolpropane tripropenyl ether	Ionic type		Low cytotoxicity	Good reactivity			[43]
	Trimethylolpropane dipropenyl ether	Ionic type		Low cytotoxicity	Good reactivity			[43]

Table 1. Continuously 3.

Monomer	Examples	Type	Structure	Cytotoxicity	Advantages	Disadvantages	Applications	References
Epoxides	Ethylene oxide and propylene oxide	Cationic type		Low to moderate cytotoxicity	Good chemical resistance, High mechanical strength, Versatile formulation options	lower propagation rate constant, potential for skin sensitization, longer curing times, potential for bisphenol A (BPA) leaching	Organic and polymer syntheses, bactericide, diluents, coatings, adhesives and electrical packaging, automotive	[35]
	3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane	Ionic type		Low cytotoxicity	Low shrinkage, chemical and thermal resistance	Fragility and low toughness		[32]
	Diclycidylether derivative of bisphenol A (ADE)	Ionic type		Low cytotoxicity	Small shrinkage, thermal and chemical resistance	Fragility and low toughness		[32]

2.2. Mechanism of photopolymerization

UV curable hydrogel systems are mainly obtained by the photopolymerization of acrylates, methacrylates and vinyl groups. These components can show maximum absorption in UV region. The polymerization of these monomers can be done by using different mechanisms such as 1) free-radical curing mechanism and 2) ionic curing mechanism. Both mechanisms impart unique characteristics to photocurable components in order to form the hydrogel systems [44].

2.2.1. Free radical photopolymerization mechanism

The use of UV curable resins is widespread because of their high reactivity, quick curing time and variety of monomers. Three primary components are typically found in the feed mixture for acrylate-based resins: photoinitiator, which creates free radicals when exposed to UV light; functionalized prepolymers, which form the polymer chain structure; and monomers, which function as reactive diluting agents that control the viscosity of the system [45]. A free radical mechanism is used in photopolymerization to employ a broad variety of commercially accessible monomers. A free radical polymerization process consists of four fundamental steps: a) initiation, b) propagation, c) chain transfer and d) termination. Free radical active centers are created as the reaction starts, and these centers start the propagation chain. Propagation adds monomer units one after the other, increasing the polymer structure. Then, chain transfer stops the polymer from expanding and starts the creation of a new polymer. Lastly, termination stops the polymer's development by ending the active centers [32]. The free radical photopolymerization mechanism is summarized in the Figure 1.

Free radicals photopolymerization involves the use of a variety of monomers such as acrylates (2-hydroxyethyl methacrylate, butyl acrylate, ethyl acrylate, methyl acrylate, acrylamide, acylic acid, *n*-butyl acrylates (BA), diacrylates (diethylene glycol diacrylate (DEGDA), 1,4-butanedioldiacrylate (BDDA), tricrylates (*i.e.* pentaerythritol triacrylate (PETA)), tetraacrylates (pentaerythritol tetraacrylate), methacrylates (methyl methacrylate, butyl methacrylate), epoxy acrylate (EA), and urethane acrylate (UA). These monomers offer a diverse selection to meet specific application requirements and enable the

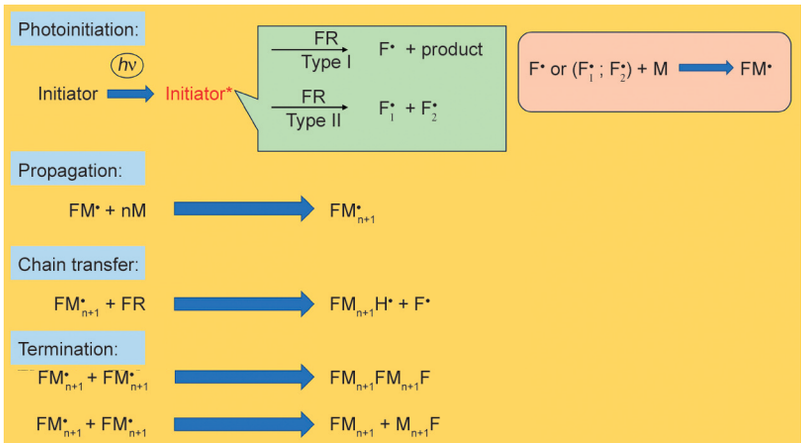


Figure 1. Free radical polymerization mechanism of a monomer (M) with photoinitiator (F). The reaction initiates with the generation of a radical specie which combines with monomer to form reactive specie (FM•) [42].

formulation of customized hydrogel systems. A number of considerations are made when choosing a monomer for a certain application or manufacturing technique, including how it will affect viscosity, curing rate, film characteristics, contraction during polymerization process, cost, lifespan, turbulence, odor, and cytotoxicity.

From above described monomers, acrylates are the most extensively employed due to their versatile properties and compatibility with different resin systems. Acrylates offer a broad range of options for achieving desired performance in formation of photo-polymerized hydrogel systems. The reaction mixture's viscosity is directly influenced by the monomer's chemical structure, which also affects the polymerization process's termination and propagation phases. As a result, the particular structures of the monomers utilized have a noteworthy impact on the finished material's qualities.

2.2.2. Ionic photopolymerization mechanism

Although ionic UV curing techniques are becoming more and more popular in specialized domains due to their unique benefits over free radical polymerization, free radical UV curable polymerization has been widely used in commercial applications. Advantages of ionic curing systems include low sensitivity to water, no inhibition of oxygen, and the capacity to polymerize heterocyclic monomers like oxiranes and vinyl ethers that do not polymerize by free radical processes. Some ionic systems can be formulated to allow for post-exposure curing, also known as dark curing. Ionic healing methods have these qualities, which make them extremely adaptable and useful for certain uses [46]. Cationic and anionic photopolymerization are two types of ionic curing processes, distinct from free-radical systems. While the remainder of the polymerization mechanism is identical, the main difference between anionic and cationic photopolymerization is the kind of photoinitiator utilized. Crivello developed the mechanism of cationic photopolymerization in the late 1970s [47] that involves the start of polymerization process by using photoinitiators capable of absorbing UV light. These photoinitiators generate reactive cations that serve as initiators for the polymerization reaction. This discovery opened up new possibilities for initiating polymerization processes and paved the way for advancements in cationic photopolymerization technology [48]. Different monomers, such as epoxy resins, epoxy-functionalized resins (ethylene oxide and propylene oxide), propenyl ethers, and other resins with vinyl ether groups, including diethylene glycol divinyl ether, are used in cationic photopolymerization. Because of their quick photopolymerization kinetics, vinyl ethers stand out among them and frequently surpass the comparable free-radical photopolymerization of acrylic monomers in terms of curing speeds. However, the synthesis of vinyl ether can be expensive. Propenyl ethers have good reactivity, making them an ideal alternative. Among the often used vinyl and propenyl ethers are diethyleneglycol divinyl ether, trimethylol propane tripropenyl ether, and trimethylol propane dipropenyl ether. Epoxides are a different type of monomers utilized in cationic photopolymerization. They offer excellent mechanical properties, little shrinkage, and exceptional resilience to heat and chemicals. However, epoxy-based systems can become brittle and have low robustness. Catalytic

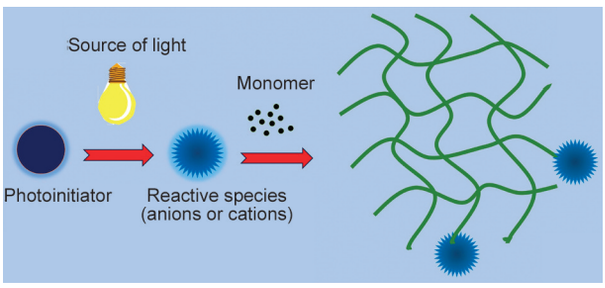


Figure 2. Schematic representation of ionic photopolymerization process.

photopolymerization uses epoxides such as diclycidyl bisphenol A (ADE) ether derivatives and 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate. In cationic photopolymer systems, these monomers aid in the creation of crosslinked networks with advantageous characteristics [49].

The process of anionic photopolymerization commences with the photo-induced formation of an active anion, which is then introduced to the monomers. The expanding anionic chain is repeatedly supplemented with monomers as the polymerization process moves forward. This is similar to the mechanism of cationic photopolymerization, in which reactive cations are produced from photoinitiators to initiate the process. [50]. A simple illustration of ionic photopolymerization mechanism is represented in Figure 2.

2.3. UV curable photoinitiators and their essentialities

Initiators contain a source of reactive species which are linked with a large number of monomers constituting polymeric substances. They create active sites such as free radicals and cations on the polymeric system. These active sites are the main reasons to initiate polymerization in the polymeric material. Each material comprises a specific type of initiator. There are basically two types of initiators used in polymerization, thermal initiators and PIs. Thermal initiators require heat to produce active sites and start polymerization. Common examples of thermal initiators include peroxides, persulfates and azo compounds.

Another different class of initiators, commonly known as PIs, are activated by light specifically UV light. Numerous efforts, consisting of a wide range of experiments, have been dedicated in the field of photosensitive (UV curing) systems to increase their functionality. Polymerizable medium, source of light and photo-initiating system are the main ingredients of any photopolymerization reaction. According to photolysis mechanism, a two-fold classification of photoinitiators exists: cationic and free radical photoinitiators.

The most researched type of PIs are free-radical PIs, sometimes referred to as classical PIs, whose reaction processes have been investigated [51]. Radical photoinitiators generate free radicals upon absorption of UV radiations. These absorbed radiations are used to trigger the chemical reaction. Based on polymerization, these free radicals photoinitiators are classified into the following types; type-I and type-II photoinitiators which are also named as cleavage and hydrogen abstraction photoinitiators, respectively, as shown in Figure 3. When exposed to UV light, type-I PIs cleave homolytically from a triplet state. These photoinitiators (alpha hydroxy ketones and phosphine oxides) breakdown the light photons into two radicals. On the other hand, type-II PIs, such as thioxanthones and benzophenones, generate radicals

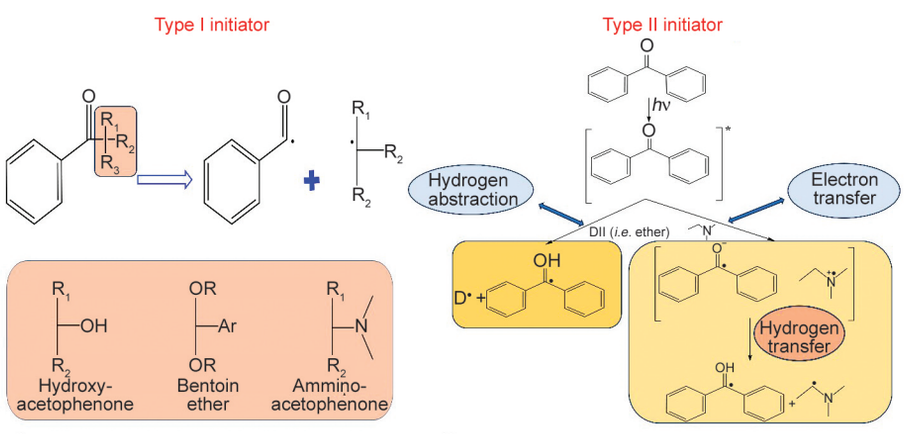


Figure 3. Schematic representation of photoinitiation process; a) mechanism of type-I photoinitiators and b) mechanism of type-II photoinitiators [55].

by the processes of electron/proton transfer or hydrogen abstraction using a co-initiator from the triplet state [52]. Secondary radicals are produced as a result of their need for a co-initiator like thiol, ester, or tertiary amine, ether, to extract hydrogen. Cationic PIs, on the other hand, are the second important type of PIs, such as salts of iodonium, diaryl iodonium, sulphonium, and that of triaryl sulphonium [53]. They generate acids (such as H^+) on the exposure of light. The rate of initiation (r_i) of polymerization is a direct function of the intensity of incident light (I_0) and the quantum yield (Q_i) at which the starting species forms and an exponential function of the amount of light absorbed (A) by the photoinitiator as described in Equation (1):

$$r_i = Q_i \cdot I_0 \cdot [1 - \exp(-A)] \quad (1)$$

The rate of initiation of photopolymerization increases with an increase in the intensity of incident light. Similarly, the concentration of PI can also control the depth of curing and hence directly affects the light of absorption (A) as in Equation (2) [35]:

$$A = \ell \cdot \varepsilon \cdot [\mathrm{PI}] \quad (2)$$

where ε symbolizes the photoinitiator absorptivity and ℓ denotes the sample thickness.

Several traits have to be considered when selecting a photoinitiator for a hydrogel to ensure its suitability for the specific application. Table 2 represents different photoinitiators used by different researchers of this field for the production of UV curable PVA-based hydrogels.

2.4. UV curable PVA-based hydrogel systems

UV curable PVA-based hydrogels present a promising avenue for advanced materials with diverse practical uses, showcasing their potential to contribute significantly to the scientific and industrial domains. Their tunable mechanical properties allow researchers to adjust the stiffness and strength of the hydrogels, making them suitable for mimicking the mechanical behavior of various tissues in applications like tissue engineering.

Moreover, due to their high water absorbency and biocompatibility, they are appropriate for healing wounds, drug delivery methods, as well as biological uses. The ability to incorporate bioactive molecules into the hydrogel matrix further enhances their potential as carriers for well-ordered drug release. PVA-based UV curable hydrogel systems are useful in responsive actuators and sensors outside of the biomedical industry because of their ready reactions to an applied stimulus. When ionic strength, pH value or temperature changes, these hydrogels can expand or contract, enabling them to convert environmental cues into mechanical motion. In essence, PVA-based UV curable hydrogels represent an exciting intersection of polymer chemistry, material science and biotechnology. Their synthesis and properties offer a versatile platform for creating smart materials that can address challenges in the fields of medicine and engineering [24, 26].

Some globally used PVA-based UV curable hydrogels, along with required photoinitiators, their characterization techniques and study outcomes, are enlisted in Table 3.

3. Applications of PVA-based UV curable systems

Hydrogels with high water absorption in aqueous media form the majority of soft tissues of all living organisms. Therefore, hydrogels are an ideal material for making scaffolds [73]. PVA is extremely biocompatible, hydrophilic and non-immunogenic. It has been used in many biomedical sectors, such as drug delivery, wound healing and hard and soft tissue engineering (TE), and the US Food and Drug Administration (FDA) authorized it for use in human clinical applications [9]. To be effectively used for soft TE applications, PVA must be modified since, like other synthetic polymers, it has a limited capacity to promote cell adhesion and proliferation. A particular Young's modulus in the 1–100 kPa range is typically needed for soft tissues, such as the liver, adipose tissue and skin [74]. UV curable PVA-based biomaterials have a long recorded history of use in a wide range of cutting-edge applications in the domains of biomedicine, biotechnology, pharmaceuticals, food production, industry and commerce because of their exceptional mechanical qualities and inherent biodegradability [75] as shown in Figure 4.

3.1. Drug delivery

Hydrogels offer the ability to regulate the release of therapeutic materials in both time and area, such as cells, macromolecules and small molecules. Hydrogels offer a platform for different kinds of physiochemical interactions with the encased medicines

Table 2. UV curable photoinitiators and their specific wavelength, along with advantages and disadvantages.

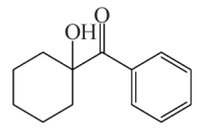
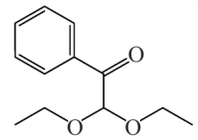
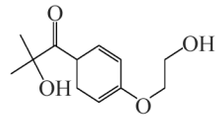
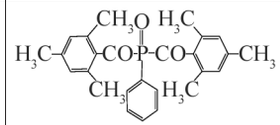
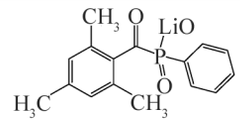
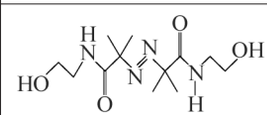
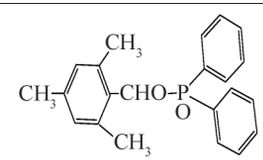
Photoinitiators	Type	Structure	Wavelength [nm]	Appearance	Cytotoxicity	Advantages	Disadvantages	References
Irgacure 184 (1-hydroxycyclohexyl phenyl ketone)	Type-I		333	White, non-yellowing		Highly efficient, good adhesive strength, coating material	Exhibits poor migration, most widely used in industry	[54]
DEAP (2,2-diethoxyaceto-phenone)	Type-II		230–260	Clear yellow	Medium	Good in surface drying, compatible with oligomers		[55]
Irgacure 2959 (4(2 hydroxyethoxy)phenyl(2 hydroxy-2 propyl)ketone)	Type-I		315–400	White powder	Low	Fast curing, water solubility is moderate, low immunogenicity, high rate of initiation, highly efficient	Human health effective wavelength range, slower polymerization reaction, low water solubility (<5 w%)	[56]
Irgacure 819-DW (phenyl bis(2,4,6 trimethylbenzoyl)phosphine oxide	Type-I		295–400	Pale yellow powder	Low	UV and visible light sources can be used, water solubility is good	Low initiating rate when ray comprises visible light	[57]
LAP (lithium phenyl 2,4,6 trimethyl benzoyl phosphonate)	Type-I		320–390	White to off-white	Very low	Spectral range is broader, superior water solubility, possible use in UV and visible light, preferred over Irgacure-2959 for biological purposes, cytocompatible	Molar extinction coefficient is low, initiation rate is less	[58]
α-hydroxy isobutyryl benzene	Type-II		365		Low			
VA086 (2,2 azobis[2 methyl-*N*(2 hydroxyethyl) propionamide]	Type-I		365–385	White-slightly yellow crystalline powder		Non-nitrile, non- ionic, introduce hydroxyl group into polymer terminal, less toxic, 90% cell survival, good water solubility	It can form bubbles by releasing nitrogen	[59]
TPO (diphenyl (2,4,6 trimethylbenzoyl)phosphine oxide	Type-I		350–400	White crystal light yellow to yellow to green		Does not require any co-initiator, color stability, can be polymerized in thick layers, high dental resin efficiency, optical fiber coating, soluble in methanol, high light curing speed	Toxic to aquatic organisms, cause infection if swallowed, possible risk or impaired fertility, incompatible with strong oxidizing agents	[60]

Table 2. Continuously.

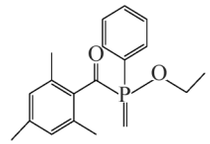
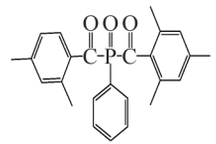
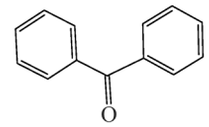
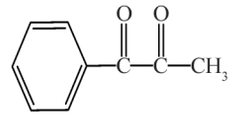
Photoinitiators	Type	Structure	Wavelength [nm]	Appearance	Cytotoxicity	Advantages	Disadvantages	References
TPOL omnirad (ethyl(2,4,6 trimethylbenzoyl)phenyl phosphinate)	Type-I			Yellowish	Low	Suitable for clinical practice, curing efficiency is very well and deep, cause polymerization in oligomers		[60]
BAPO (bisacylphosphine oxide)	Type-I		365–416		High	Higher mechanical resistance, good degree of conversion and polymerization rate, good water solubility-54 g/L	Poor solubility in some monomers, extinction coefficient is low especially in the range above 400 nm	[61]
BP (benzophenone)	Type-II		204–385	White crystal flake		Its photosensitizer is efficient and less expensive, good for coatings	Requires co-initiator (like methyldiethanolamine,trimethylamine) for polymerization, easily catch fire, can react with organic solvents	[62]
PPD (1-phenyl-1,2-propanedione)	Type-I and Type-II		300–400	Pale yellow		Good compatibility with resins, maximum absorption at 393 nm	Lower rate of polymerization, lower crosslink density	[63]

Table 3. PVA-based UV curable hydrogels and their study outcomes.

UV curable hydrogel	Photoinitiators	Characterization techniques	Studies	References
Polyethylene glycol diacrylate/poly(vinyl alcohol) (**PEGDA/PVA**)	Irgacure 2959	SEM, swelling test ESCA, FTIR	Large tensile strength (44.08 kPa), higher crosslinking density, rupture elongation (53.40%), low swelling	[25]
Poly (2-hydroxyethyl methacrylate)/poly(vinyl alcohol)-acrylamide (**PHEMA/PVA-AA**)	DEAP	DSC, ESCA, FTIR, H-NMR	Absorption peaks (1640, 1725 cm^{-1}), Young's modulus (PHEMA 3.9, co-A2H8 3.7, co-A1H9 6.3 MPa), water content (PHEMA 31.5%, co-A2H8 25.6%, co-A1H9 25.1%), tensile strain (PHEMA 43.4%, co-A2H8 13.1%, co-A1H9 11.9%), brittle	[55]
Magnetic beads poly(vinyl alcohol)/polyethylene glycol dimethacrylate (**MPVA/PEGDMA**)	Irgacure 2959	NMR, MTT assay, ATR-FTIR, DSC, SEM	Drug release (10 mg/hydrogel), C=O peak at 1723 cm^{-1} of ester group of PEGDMA and 1719 cm^{-1} of MPVA, OH group due to maleic anhydride, ester linkage confirmed by FTIR, stretching of O–H at 3289 cm^{-1}, C–H bending at 2909 and stretching of C–H at 1420 cm^{-1} respectively, high degree of swelling of PVA than PEGDMA, Young's modulus (4.36±0.68–7.59±0.39), tensile stress (1.04±0.28–2.08 ±0.56 MPa), dexamethasone drug release PVA 600 with ratio of 1 to 1 and PVA 600 with ratio of 1 to 4)	[8]

Table 3. Continuously.

UV curable hydrogel	Photoinitiators	Characterization techniques	Studies	References
Poly(vinyl alcohol/cellulose nanocrystals/ poly(2-hydroxyethyl methacrylate)/ poly(*N*′-methylene bisacrylamide) (**PVA/CNC(/poly HEMA/poly MBA)**)	Irgacure 2959	SEM, RTIR, TGA, DSC	Dual network (DN) hydrogels, water loss ration reduced from 90 to 79.0% and 80.5% for PVA/poly MBA/CNC, PVA/poly HEMA/CNC, respectively, PVA/poly MBA/CNC has macropores existed regularly in hydrogels, tensile strength of PVA/poly MBA/CNC increased to 1.1±0.12 MPa, tensile strength of CNC/PVA (0.32±0.06) MPa	[64]
Poly(vinyl alcohol)/gellan gums (**PVA/GG**)	Irgacure 2959	FTIR, XRD, DSC, SEM	Friction coefficient reduced to 80%, elastic modulus increased by 89%	[65]
PVA/alginate/PEGDA	Irgacure2959	SEM	At filament distances of 800 and 1000 μm disappearance of pores occurred, Young's modulus (6.77±0.40 MPa), swelling ratio (6.77%±0.38%)	[66]
Poly(vinyl alcohol)/poly(ethylene glycol) (**PVA/PEG**)		AFM, PCR	Ranges of stiffness from 20 kPa (soft) to 100 kPa (hard), RNA extraction, cell culture	[67]
Ethylene glycol acrylate methacrylate-dihydroxyphenylalanine/PVA (**EGAMA-DOPA/PVA**)		FTIR, H-NMR, RTIR, SEM	Peaks (C=O at 1725 cm^{-1}, C=C at 1635 cm^{-1})	[68]
Polyvinyl alcohol thrombin-receptor-agonist-peptide-6, polyvinyl alcohol-4-nitrobenzenediazonium (**PVA-TRAP6**, **PVA-NB**)		MTT assay, SEM, ROTEM, FACS	FACS analysis revealed that % of triggered platelets for PVA/TRAP6/P was ca. 55% high, 0.1% PVA/TRAP6 shorten coagulation time (CT) to Ca. 45% of the physiological CT, storage moduli was enhanced from 8, 22, 120 to 45 kPa when thiol to NB ratio was increased 0.4 to 1.2, swelling ratio changed from 130, 45, 10 to 17	[69]
Poly(vinyl alcohol) graft glycidyl methacrylate (**PVA-*g*-GMA**)	Irgacure-2959	FTIR, SEM, TGA	C–O stretching at 1091 cm^{-1}, the $R_2C{=}CH_2$ stretching at 1182 cm^{-1} and stretching of C–H band was detected at 2918 cm^{-1}, that of –OH groups at 3402 cm^{-1}, at 446 °C PVA lost its original weight (T50), degree of crosslinking and the adsorbed protein have been found to be inversely correlated	[26]
Radiopaque iodine-PVA	Irgacure-2959	Rheological characterization	For 10, 15 and 20% solutions shear viscosity was measured, samples of UV-cured and redox-cured has close resemblance, iodine increased the viscosity.	[70]
PVA/chitosan (CTS)	None	FTIR, SEM, DSC, XRD	Displayed the porous structure with much smaller pore sizes as compared to that of the hydrogel S20/30, the hydrogel S22/30 has dense porous structure	[71]
Maleilated chitosan/methacrylated poly (vinyl alcohol) (**MCS/MPVA**)	Darocur-2959	XRD, DSC	MCS/MPVA hydrogel showed pores sizes having range from 10 to 62 μm and this structure was compacted as MPVA content was increased, 0.169±0.011 MPa compressive modulus was measured and it was close to the modulus of articular cartilage which is 0.1–2.0 MPa, photo-crosslinked MPVA /MCS hydrogels were not toxic to L929 cells	[72]
PVA/Poly(acrylamide-*co*-acrylic acid) (**PVA/P(AM-*co*-AA)/CTS**)	2-hydroxy-2-methylpropiophenone	Compressive tests, SEM	HEPC/Gel holds excellent deformation aptitude, HEPC/Gel displays 164±20.67 kPa tensile strength and also having exceptional ductility (28±1.60 mm/mm), Young's modulus for HEPC/Gel was highest	[27]

Figure 4. Applications of UV curable PVA-based hydrogels in various fields.

because of their pliable nature, controlled degradation and ability to prevent delicate drugs from dissolving. It has been noted that medication distribution involves several scale processes, including network, mesh and molecule levels [76].

Usually, drug is loaded into hydrogel systems. Drug release can occur from deswelling of the hydrogel network or diffusion through the porous hydrogel network, depending on a number of parameters, including pH, temperature, and ionic concentration. Various mechanisms are involved in drug delivery, such as chemically controlled drug release, diffusion controlled and swelling controlled mechanisms [77], as shown in Figure 5. Among the various drug release mechanisms, chemically controlled mechanisms are indeed one of the most familiar and extensively studied. The general discussion on the mechanism of loading of drug and release of drug is beyond the range of this report. Our discussion is limited to the drug release from UV curable PVA-based hydrogels.

Mawad *et al.* [24] measured the release of minit by using PVA-based hydrogel functionalized with acrylamide groups. Model drugs, FITC Dextran (fluorescein isothyocyanate dextran) FD-20 (20 kDa) and FD-4 (4 kDa) were loaded in the hydrogels. Loaded-PVA

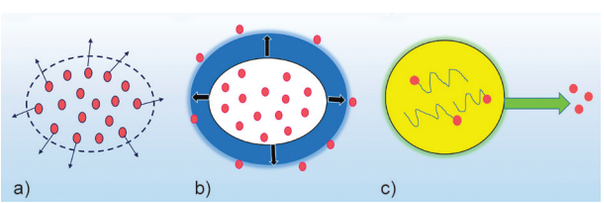


Figure 5. A schematic representation of the three ways by which hydrogels can release drugs; a) diffusion controlled, b) swelling controlled, and c) chemically controlled [80].

hydrogels were formed using 10 and 15 wt% solutions containing 0.125 wt% FD-20. After that, vortexing the liquids made sure they mixed properly. UV light caused the macromer solutions to crosslink. The hydrogels were weighed initially and after the loading of the drug. The discharge of FD-4 from 10 and 15 wt% UV cured hydrogel systems was accomplished using the same process. The drug release from each polyconcentration was evaluated using three separate assays, each with three duplicates. Research has been done to examine the release of large molecules present in PVA-based systems for the studying of crosslinking techniques and polymer concentration. Three parameters were deduced, namely the experimental diffusion coefficient, the release duration, and the percentage of total release. The results demonstrated that 40–50% of model drug with burst was released through hydrogel. The observed typical time for discharge of FD-4 was 7 h and for FD-20 was approximately 12–15 h in the case of 10 and 15 wt%, respectively.

The study conducted by Bourke *et al.* [78] in 2003 examined the discharge of platelet-derived-growth-factor (PDGF/ββ) for curing applications. In order to achieve this target, acrylamide-functionalized nondegradable PVA hydrogel was fabricated by UV crosslinking procedure. Because of its similar structure and molecular weight to PDGF, soybean-trypsin-inhibitor (STI) with 21 000 MW model drug was used for initial loading concentration and release studies. In addition, they created a delivery system for growth factors to study the behavior of PDGF/ββ with its release profile onto human dermal fibroblasts that are normally distributed. STI was added to 10, 15, and 20% PVA hydrogel at concentrations of 5–20 mg/mL. In 10% hydrogels, maximum release happened before 8 h, in 15% hydrogels, 24 h, and in 20% PVA hydrogels, 24 to 48 h. There was a noticeable increase in the percentage of protein as released from 57 to ~100% when 5 mg/mL protein loading concentration was raised to 20 mg/mL. In a similar vein, the percentage of released protein rose from 41 to 60% and from 42 to 76% for levels of 20 and 15%. According to the study, there are three adjustable key parameters to manage the release of protein from PVA hydrogels: solid content (how much solid material is in the gel), initial protein loading and by adding substances that like water (hydrophilic fillers). The experiment demonstrated that this gel could release PDGF/ββ for about 4 days, making

it a good option for delivering important proteins in the body. The combined results indicate that networks of polyvinyl alcohol (PVA) is useful for delivery systems, especially for the regulated proteins release with biological activity.

Killion *et al*. [8] determined drug release of dexamethasone (10 mg/hydrogel) by performing UV spectroscopy on swelling hydrogel composite. Maleic anhydride and PVA hydroxyl groups were reacted to create the hydrogel system that was utilized for the dexamethasone release investigations. Maleic PVA was combined with polyethylene-glycol-dimethacrylate (PEGDMA) at various molecular weights and concentrations (PEGDMA600 and PEGDMA1000) to enhance crosslinking. Experimental evidence has demonstrated that the medication was localized on the hydrogel's surface as a result of the hydrogel composite's quick swelling, which resulted in a first burst release within 24 h. The PEGDMA concentration regulated pore-size alterations, which affected the release of drugs of PVA 600 with 1 to 1 ratio and PVA 600 with 1 to 4 ratio. At different pore sizes and swelling of the hydrogels, the reported drug release profile was between 11 and 16 days. A higher initial water content in the hydrogel system before photopolymerization resulted in larger pores within the hydrogel, facilitating quicker drug molecule release from the composite.

3.2. Tissue engineering

Tissue engineering (TE) using hydrogels involves a carefully orchestrated process to regenerate damaged bone tissues. Hydrogels serve as the foundation for this approach. Initially, a suitable hydrogel material is chosen due to its biocompatibility and biodegradability. These hydrogels function as a scaffolding framework that emulates the extracellular matrix (ECM) found naturally in bone tissues [6]. Bioactive substances such as transforming growth factor-beta (TGF-β), vascular endothelial growth factor (VEGF), and bone morphogenetic proteins (BMPs) are added to the hydrogel matrix to improve the regeneration potential. These growth factors promote the necessary cellular processes for the development of new blood vessels and bones. Subsequently, the hydrogel scaffold is seeded with mesenchymal stem cells (MSCs), which are specialized bone-forming cells. These multipurpose cells are derived from bone marrow and adipose tissues, among other sources. Once seeded, the hydrogel scaffold provides cues that prompt MSCs to differentiate into osteoblasts, responsible for producing bone matrix. Furthermore, the hydrogel scaffold serves as a framework for osteoconduction, guiding the cells as they proliferate and form new tissues. Mechanical stimulation plays a crucial role in this process. Through dynamic culturing systems like bioreactors, mechanical forces are applied to the hydrogel scaffold, promoting cell proliferation, extracellular matrix synthesis and mineralization. This mimics the natural bone remodeling process and contributes to the development of mechanically robust bone tissues. Angiogenesis, the formation of new blood vessels, is also encouraged by hydrogel scaffold's architecture and the incorporated growth factors. A well-established blood supply is vital for delivering nutrients, oxygen, and removing waste as the tissues matures. As the time passes, osteoblasts continue to deposit mineralized extracellular matrix rich in calcium and phosphate. This matrix closely resembles native bone tissues, offering strength and stability. Throughout maturation, the tissues undergo remodeling, with osteoclasts breaking down older tissue while osteoblasts simultaneously deposit new matrix. Upon reaching the desired level of maturity, the scaffold can be transplanted or implanted into the patient's site of bone defect [79]. A simple illustration of bone tissue engineering (BTE) is illustrated in Figure 6. Surgical procedures guided by medical imaging techniques facilitate this step, with the ultimate goal of restoring function and improving the patient's quality of life. Through ongoing research and refinement, the methodology of tissue engineering using hydrogels continues to advance, holding immense potential for addressing various bone-related issues effectively [71, 80, 81].

Killion *et al*. [8] studied the innovative synthesis of photopolymerizable maleic acid-functionalized PVA. Maleic anhydride and polyvinyl alcohol (PVA) were combined in a formamide medium in a one-step process that was made possible by acid catalysis. Maleic anhydride acylated one out of every sixteen hydroxyl (OH) groups in PVA, according to NMR and infrared (IR) spectroscopy, which confirmed the synthesis. A material with moderate mechanical characteristics was produced by photopolymerizing the maleic PVA hydrogels. In response, efforts were made to improve the system's mechanical robustness by using Polyethylene Glycol (PEG). A comparative study was carried out comparing hydrogels with and

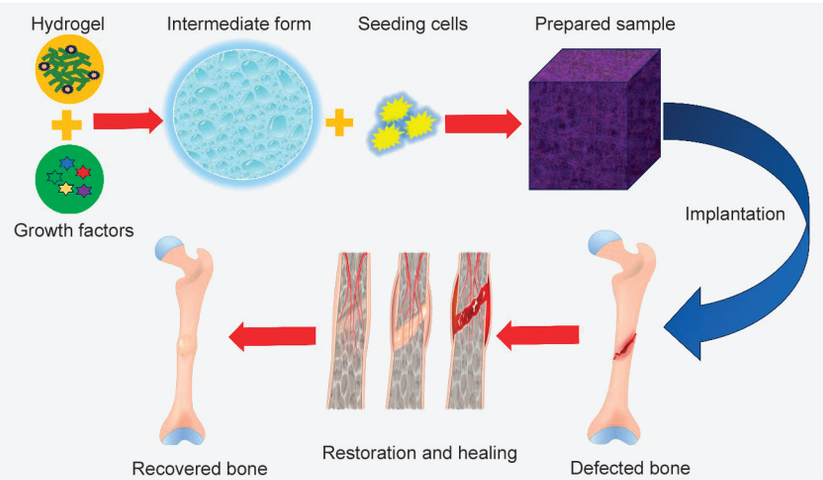


Figure 6. Schematic representation of regeneration of bone using hydrogel matrix incorporated with some growth factors and seeding cells.

without incorporated maleic PVA. Maleic PVA hydrogels showed significant improvements in stress at limit values and Young's modulus in compression tests compared to hydrogels containing regular PVA. Moreover, biocompatibility evaluations using the MTT test showed that the hydrogels were appropriate for promoting cell proliferation, making them potentially useful scaffolds for bone tissue regeneration.

Schmedlen *et al*. [82] investigated the utilization of photoactive PVA as scaffolds in tissue engineering applications. The benefit of *in situ* polymerization provided by these hydrogels allows for less intrusive implantation methods. These materials' mechanical properties may be adjusted to fit a variety of soft tissue applications. Specifically, when the polymer concentration increases, PVA hydrogels' Young's modulus and ultimate tensile strength increase. A detailed analysis showed the uniform placement of fibroblasts within PVA hydrogels that were 3 mm thick, and these cells remained viable throughout a two-week period while being cultured. Notably, the assessment of cell viability revealed uniform outcomes across the hydrogel thickness. Furthermore, cells that were encapsulated within the PVA hydrogels showcased the ability to create proteins found in the extracellular matrix. This was indicated by the generation of hydroxyproline. It was observed that with the addition of RGDS (arginyl glycyl aspartic acid) peptide, non-adhesive PVA hydrogels showed excellent cell adhesive properties. The cumulative findings emphasized the potential of photopolymerized PVA hydrogels as a promising option in tissue engineering applications.

Feng *et al*. [65] revealed that the incorporation of a minor proportion of gellan gum (GG) into PVA hydrogels imparted favorable effects on the enhancement of elastic modulus and reduction of friction. The introduction of GG demonstrated a notable elevation in elastic modulus, with a recorded value of 12.1±0.8 kPa with a GG content of 0.5%. Interestingly this modulus closely resembled the modulus of chondrocytes and the pericellular matrix situated around them (measured at 12±1 kPa). This highlights the significant promise of using this material for tissue engineering applications aimed at promoting chondrocyte growth and facilitating cartilage restoration. The enhancement in mechanical properties along with lowered friction coefficients showed their suitability to human knee joints. The addition of GG into PVA hydrogel the friction coefficient values reduced to almost $\mu \sim 0.012$, corresponding to an enhancement of mechanical strength up to 80%. This result showcased the ability of hydrogel systems to reliably endure shear stresses relevant to biomedical scenarios. This offered a conducive environment for sustained cell growth. Furthermore, their investigation revealed inverse relation between the applied load and the friction coefficient. This specific property of low-friction behavior remains steady across sliding speeds that mimic everyday human movements like walking and running. The harmonious convergence of desirable modulus and minimal friction attributes in PVA/GG hydrogels highlighted their viability not only in cartilage repair applications but also in extensive biomedical scenarios.

Goldvaser *et al*. [73] cured a PVA based methacrylate (PVA/MA) hydrogel before using it for tissue engineering (TE) applications. Vero cells were then used to measure cell viability and attachment, building on prior research by Lim *et al*. [83] found that while PVA/MA hydrogels were non-cytotoxic to Vero cells, very little cell adhesion occurred on the hydrogel surface. This was likely due to the presence of PVA, which can hinder cell attachment. To address the low cell adhesion observed by Lim *et al*. [83], Goldvaser *et al*. [73] modified the MA chains within the hydrogel by incorporating Arginine-Glycine-Aspartic acid (RGDS) sequences. This modification aimed to enhance cell attachment. To achieve this, they likely used a Cys-RGD (CRGD) peptide. The thiol group of the cysteine residue in CRGD can form a covalent bond with the vinyl group of the MA chain under UV light irradiation. Cell attachment was studied by varying concentrations of CRGD in PVA/MA hydrogel. It was observed that an increase in CRGD increased the cell attachment to hydrogel system. This enhanced cell attachment is likely due to the CRGD sequence acting as a ligand for integrin receptors on the cell surface. In the absence of CRGD, the cells have no specific binding sites on the hydrogel, resulting in minimal attachment. Zhou *et al*. [84] also observed similar results. They prepared a methacrylated PVA hydrogel loaded with hydroxyapatite (HA) to study the adhesion of mouse fibroblast cells (L929) to the hydrogel system. While PVA is a biocompatible polymer, unmodified PVA-based hydrogels (like PVA/MA) often exhibit poor cell adhesion due to their lack of inherent cell-binding motifs. To address this limitation, Zhou *et al*. [84] incorporated HA into the PVA/MA hydrogel. This modification aimed to improve cell adhesion and growth of L929 cells. The incorporation of HA significantly enhanced the adhesion and growth of L929 cells on the hydrogel system. This improvement likely resulted from HA's enhanced bioactivity, providing a more favorable microenvironment for cell attachment and proliferation.

Zhang *et al*. [85] investigated the effect of incorporating methacrylate silica nanoparticles (MSi) into a PVA-based methacrylate hydrogel (PVA-GMA). As expected, unmodified PVA-GMA hydrogels showed poor L929 cell adhesion likely due to their low stiffness and high hydrophilicity. In contrast, the MSi-loaded hydrogels promoted both cell adhesion and proliferation. This improvement might be attributed to the enhanced surface roughness and ligand presentation by MSi, providing a more favorable microenvironment for cell attachment and growth. These findings suggest that photo-crosslinked PVA-GMA-Si hydrogels hold promise for tissue engineering applications due to their ability to support cell functions.

3.3. Adsorption studies

Many sectors, including textile, paper, leather tanning, plastics, rubber, cosmetics, and printing, use synthetic dyes extensively. Their uniform color rendering, affordability, and exceptional durability are the reasons behind their widespread use. But throughout the dyeing process, some of these colors will unavoidably find their way into the wastewater stream. Because the resulting colored effluent is hazardous and carcinogenic, and because it may endanger aquatic ecosystems, it must be purified before being released into the environment. Of all the strategies that are accessible, adsorption has shown to be a particularly beneficial option when compared to traditional methods because of its high efficacy, low cost, and ease of operation. The utilization of hydrogels for adsorption phenomena constitutes a significant and extensively investigated area within the field of materials research. Hydrogels, characterized by their distinctive three-dimensional polymeric networks possessing inherent hydrophilic properties, have garnered substantial attention due to their pronounced capacity to selectively adsorb a wide array of solutes from aqueous solutions. This phenomenon is orchestrated through intricate physicochemical interactions that occur between the hydrogel matrix and the target adsorbate molecules. Notably, the phenomenon involves intricate physicochemical interactions, including physical forces such as van der Waals interactions, hydrogen bonding, and electrostatic attractions, which enable the mixing of adsorbate species into the porous hydrogel structure. Moreover, chemical interactions such as covalent bonds, ion exchange, and complexation further augment the potential for precise and tailored adsorption of specific molecular entities. The interplay between these mechanisms is inherently dependent upon influential variables, including pH levels, temperature, ionic strength, and the presence of competitive ions within the solution. Adsorption is like a sticky interaction between two things (like hydrogels and dyes); the surface of a material and other substances in its

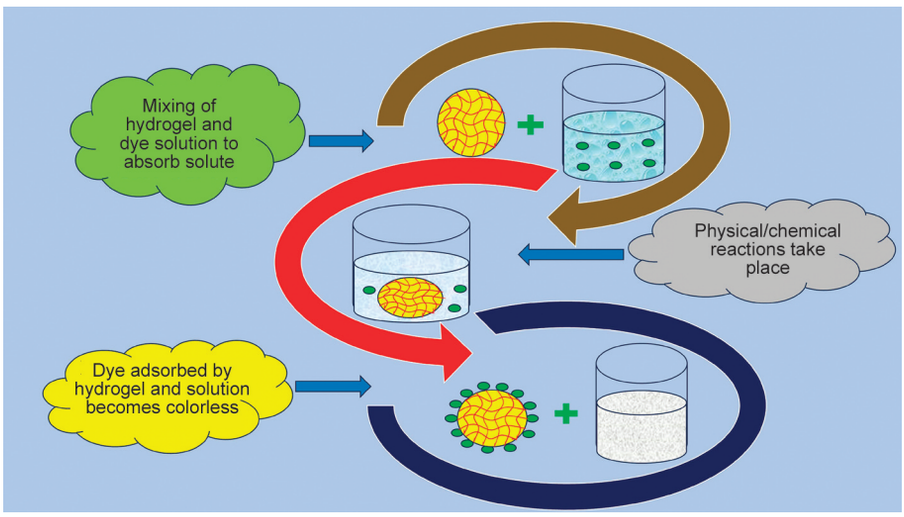


Figure 7. Removal of organic dyes from aqueous medium using PVA-based hydrogels as adsorbents.

surroundings. When materials come into contact, the outer layer of the material can attract and hold onto molecules or particles from the surrounding environment. Imagine a sponge soaking up water, but on a small scale. A simple illustration of the adsorption phenomenon is shown in Figure 7. Adsorption depends on factors like the type of material and the properties of the substances being adsorbed. Understanding how adsorption works is crucial in various fields, from cleaning up pollution to designing better products like filters and catalysts [64, 86].

Bai *et al*. [64] concentrated on the synthesis of inventive PVA/cellulose nanocrystals(CNC)-based hydrogels utilizing a photo-crosslinking approach in order to generate unique, environmentally friendly absorbent hydrogels. PVA/CNC matrices were used to create the hydrogel compositions, which are poly (2-hydroxyethyl methacrylate) (PVA/CNC/poly-HEMA) and PVA/CNC/poly(*N*′-methylenebisacrylamide) (PVA/CNC/poly-MBA). Notably, the hydrogel production method produced an easy-to-use and environmentally responsible method. The combination of crosslinking agents, namely HEMA and MBA, which initiate interpenetrating networks (IPNs) with PVA and CNC components, so improving the overall characteristics of the resultant PVA/CNC hydrogels, is what made these hydrogels unique. The strengthened contact between PVA and CNC resulted in the stimulation of a bond network by photo-crosslinking of HEMA or MBA inside the PVA/CNC hydrogels, which in turn led to the creation of the IPN structure. FTIR analysis provided support for the HEMA and MBA photo-crosslinking inside the PVA/CNC/poly-HEMA and PVA/CNC/poly-MBA hydrogels. Through the use of TGA, the adsorbent hydrogels' weight loss patterns were successfully described. The assessment of swelling capabilities and reswelling behavior confirmed the favorable performance of the synthesized hydrogels. Glass conical 100 mL flasks were used for adsorption testing, and they were shaken in a water bath at 200 rpm at 25 °C. Each flask contained 70 mg of dried materials mixed with a solution of either 60 mL xylenol orange (XO) or 60 mL methylene blue (MB). Three milliliters of the MB and XO solutions were used for UV-Visible measurements after the hydrogels reached adsorption equilibrium. The absence of binding sites in both PVA and PVA/CNC hydrogels was shown to be the reason for the poor adsorption capacity of pure PVA hydrogel for MB or XO. When compared to PVA/CNC/poly-HEMA and PVA/CNC/poly-MBA hydrogels, this is because of their thin porous walls, which result in a decreased availability of binding sites for MB or XO adsorption. Compared to the relatively less efficient pure PVA and PVA/CNC hydrogels, the PVA/CNC/poly-HEMA and PVA/CNC/poly-MBA hydrogels had a much higher removal efficiency because of their thick and significant IPN structure. Moreover, the PVA/CNC/poly-HEMA and PVA/CNC/poly-MBA hydrogels exhibit improved properties concerning swelling, reswelling, mechanical strength and thermal stability when compared to the PVA/CNC hydrogel. The PVA/CNC-based hydrogels' extensive range of characteristics highlights their suitability for use as dye carriers and materials for water management.

Kamoun *et al*. [26] prepared UV cured poly(vinyl alcohol)-grafted-glycidyl methacrylate (PVA-*g*-GMA)

hydrogel for different applications including adsorption studies of bovine serum albumin (BSA). They also observed the effect of GMA on crosslinking density and adsorption of BSA on hydrogel. PVA-*g*-GMA (with different concentrations of GMA) was dissolved in fixed quantity of PBS-BSA solution (7.4 at 37 °C) for nightlong. The difference in hydrogel weight after BSA adsorption was determined by subtracting the final measurement from the initial weight of the hydrogel samples. UV-VIS spectrophotometer (at 280 nm) was used in order to measure the exact amount of BSA adsorbed on hydrogel samples. They observed that change in concentration of GMA influenced the adsorption of BSA. The crosslinking density of hydrogel systems was increased with an increase in concentration of GMA. Increased crosslinking in the hydrogel system enhanced its hydrophobic nature, which led to a reduction in BSA adsorption. Indeed, the adsorption of BSA protein increased with a decrease in the concentration of GMA.

Kashi *et al*. [87] prepared PVA/AA hydrogel through UV curing for 3D printing. They also studied adsorption kinetics of 3D printed hydrogel capsules. Adsorption of Pb(*II*) ions from water was done by PVA/AA capsules. To investigate the effect of photoinitiator concentration on Pb(*II*) adsorption, they prepared capsules with varying photoinitiator concentrations during the printing process. PVA/AA-B0 (no photoinitiator), PVA/AA-B20 (20 mg photoinitiator) and PVA/AA (25 mg photoinitiator) hydrogel capsules were used for adsorption studies. These 3D capsules were added to a dispersion containing metal ions. The content of these metal ions was then studied using atomic absorption spectroscopy (AAS). Concentration of adsorbed Pb(*II*) was measured through Equation (3):

$$q = \frac{(C_0 - C_e)V}{m} \tag{3}$$

where q represent adsorbed Pb(*II*) in mg/g onto capsule's unit mass, C_0 and C_e describe the concentration of Pb(*II*) initially and after adsorption, respectively, m [g] denotes the mass of 3D printed capsule and V [L] is the volume of aqueous phase. To estimate the adsorption kinetics, hydrogel capsules were added to several colloidal dispersions containing Pb(*II*) ions at different concentrations (ranging from 100 to 600 mg/L). The contact time of the experiment varied from 0 to 60 min to investigate the adsorption equilibrium of Pb(*II*) ion adsorption by the hydrogel capsules. It was observed that the presence of other substances can disturb the adsorption rate. That is why they studied adsorption kinetics in the presence of other ions like cobalt(*II*), nickle(*II*) and iron(*III*). Contact time significantly impacted the adsorption of Pb(*II*) onto hydrogel capsules. As contact time increased, the rate of adsorption of Pb(*II*) also increased. The quickest adsorption times were observed for PVA/AA-B25 (2 min), PVA/AA-B20 (9 min), and PVA/AA-B0 (10 min), respectively. The faster adsorption rate observed for the 3D capsules could be attributed to their high porosity. In short, capsules with a high-porosity, spongy structure have been shown to exhibit enhanced adsorption capacity for Pb(*II*). The loading capacity of the capsules was also affected by the initial concentration of the Pb(*II*) solution. Higher initial concentrations of the adsorbate Pb(*II*) led to increased adsorption. PVA/AA-B25 and PVA/AA-B20 exhibited a higher adsorption capacity at lower initial Pb(*II*) concentrations compared to the control, PVA/AA-B0. The mechanism of Pb(*II*) adsorption was studied with the help of different adsorption isotherms, such as Langmuir and Freundlich equations. The adsorption of Pb(*II*) onto capsules was investigated using isotherms. The Freundlich isotherm best described this process, indicating multilayer adsorption and a non-uniform capsule surface. Additionally, the maximum adsorption capacity of the capsules for Pb(*II*) was determined by Freundlich isotherm [88, 89].

3.4. Food and packaging material

PVA-based hydrogel films are promising candidates for food safety and packaging materials due to their combination of desirable properties: excellent mechanical strength, good optical clarity, potential for antimicrobial activity, efficient film formation, water resistance, and biodegradability [90]. Packaging and food preservation increase the shelf life of the material. Various active components, like nutrients, antimicrobial agents, and antioxidants, can be incorporated into packaging materials to create superior functionality. Nutrients can extend shelf life by providing additional sustenance to the food product. Antimicrobial agents help prevent the growth of harmful bacteria and mold, further enhancing food safety. Finally, antioxidants can delay the oxidation process that leads to spoilage and quality loss in food items. In the past decade, many other researchers have

incorporated biodegradable materials with various natural preservatives to avoid environmental and health concerns. To improve biodegradability and other properties of hydrogels, various natural polymers such as chitosan (CS) and guar gum (GG') have been combined with PVA [91–93]. Such as, Bhat *et al*. [93] investigated PVA-based hydrogels crosslinked with chitosan, along with hydroxy citric acid (HCA), as a potential food packaging material. They investigated the influence of HCA on the properties of PVA/CS hydrogel films prepared with different PVA/CS ratios. Their findings suggest that HCA addition enhances both the mechanical properties and degradation temperature of the resulting PVA/CS-GG'-HCA films. Furthermore, these hydrogel films showed a decrement in permeability of water vapour and stop the growth of *E. coli* and *S. aureus* bacteria. Owing to all these properties, they suggested PVA hydrogel films as an excellent material for food packaging applications.

Similarly, Yun *et al*. [94] investigated a medium molecular weight chitosan (MCh)/(PVA) hydrogel system incorporating sulfosuccinic acid (SSA) as a crosslinking agent. This MCh/PVA-SSA hydrogel was prepared using a UV curing process for potential application as a food coating. They also observed non-UV cured films as well without SSA. Furthermore, hydrogel films were evaluated by its thermal, optical, and physical properties. These properties included swelling behavior, elongation at break (%*E*), tensile strength, biodegradability and absorption of water vapour. Subsequently, the hydrogel's potential as a food coating was investigated by applying it to apples. The effects of various plasticizers, including sorbitol (SO), xylitol (XL), and glycerol (GL), on the physical properties of films were also investigated. The results showed that UV cured films possessed thermal and optical properties as compared to non-UV cured films. The SO-containing films exhibited superior mechanical properties compared to those containing XL and GL. This enhanced tensile strength might be attributed to the presence of additional hydroxyl groups in sorbitol. These hydroxyl groups can potentially form more hydrogen bonds with PVA, CS and SSA, leading to a more robust network structure. Moreover, the effect of SSA on crosslinking was investigated. Hydrogel films without SSA exhibited slower curing compared to those containing SSA. This was confirmed by analyzing crosslinking density, solubility,

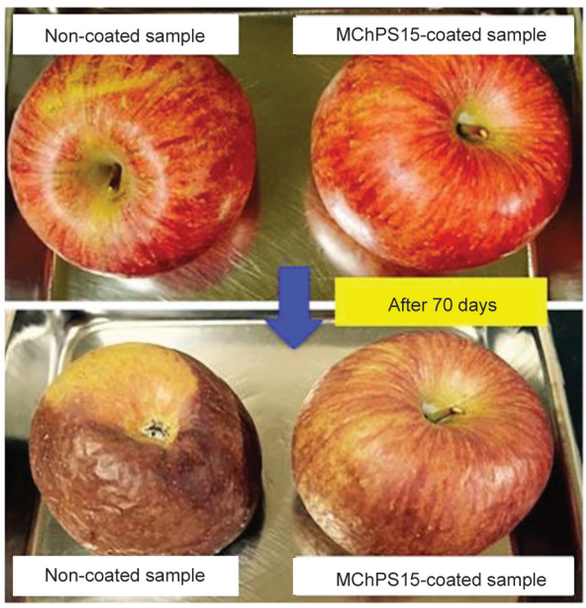


Figure 8. Coating of apple with MCh sample along with decomposition of uncoated sample. As reproduced with permission of reference [96].

and degree of swelling. The addition of SSA resulted in a decrease in the degree of swelling compared to hydrogels without SSA, indicating an increase in crosslinking density. Furthermore, with increasing UV curing time, the solubility decreased. This confirms that SSA not only enhances crosslinking density but also improves the water resistance characteristics of the hydrogel films. In line with the enhanced crosslinking density, films containing SSA exhibited a slower degradation rate under soil burial conditions. Building on these findings, they investigated the coating efficiency of Mch/PVA hydrogel solution on apples, as shown in Figure 8. An uncoated apple served as a control and degraded within 70 days, while the MCh/PVA-coated apple exhibited significantly extended shelf life, demonstrating the effectiveness of the coating in preserving the fruit. This way, PVA based hydrogels served as food and packaging applications [94].

4. Conclusions

In conclusion, this review has provided a comprehensive report of UV curable PVA-based hydrogels and their diverse applications in various fields, from biomedical to industrial applications. The photopolymerization mechanisms, tunable properties, and unique advantages of these hydrogels have been explored in detail. UV curable PVA-based hydrogels offer an exciting avenue for researchers and practitioners seeking innovative materials with tailored

properties and rapid crosslinking capabilities. As highlighted throughout this review, UV curable PVA-based hydrogels exhibit exceptional promise in drug delivery, tissue engineering and adsorption. Their biocompatibility, tunable mechanical properties and ease of fabrication make them valuable candidates for addressing specific application requirements. Furthermore, their response to UV irradiation provides precise control over gelation and crosslinking, enhancing their utility in various manufacturing processes.

UV curable PVA-based hydrogels have emerged as a capable material for of 3D printing, particularly within bioprinting and tissue engineering. However, their continued development and integration into these fields are met with several intricate challenges that researchers and industry professionals must address to harness their full potential. Firstly, one of the primary challenges lies in refining the material properties of PVA-based hydrogels. These hydrogels need to closely mimic the mechanical, structural, and biological attributes of native tissues. Researchers are actively working to enhance their strength, elasticity, and biocompatibility to make them more suitable for tissue regeneration and other medical applications. Biocompatibility and cytotoxicity represent another critical hurdle. Ensuring that UV curable PVA hydrogels are entirely biocompatible and devoid of harmful cytotoxic elements is imperative, particularly when they are intended for use in implantable medical devices or as scaffolds for tissue engineering. Rigorous biocompatibility testing and the development of cytotoxicity moderation strategies are ongoing areas of focus. Moreover, in case of UV cured 3D printing offers significant advantages but faces challenges that limit its broader application. These challenges can be categorized into material and process limitations. Material limitations include improper dispersion of fillers leading to inconsistencies and incompatibility between resin components, hindering printability and desired properties. Process limitations involve balancing factors like curing time for complete polymerization, viscosity and surface tension impacting printability, density control for applications like scaffolds, and contact angle affecting adhesion between resin and the printing platform. Additionally, achieving uniform curing can be hindered by uneven UV light absorption, necessitating functionalities that promote consistent light penetration.

Another challenge arises when using non-curable components alongside UV curable resins. While these components offer desired functionalities, they can be toxic and require post-printing evaporation. Unfortunately, this evaporation process can disrupt the structure of the cured hydrogel, impacting pore size and surface morphology. Researchers are actively addressing these challenges to achieve:

– Improved biocompatibility by minimizing the use of toxic materials while maintaining desired properties.
– Enhanced printability through optimized resin properties for efficient printing.
– Precise control over structure for achieving uniform curing and desired pore size and surface characteristics for specific applications.

Overcoming these challenges will unlock the full potential of UV-cured 3D printing in various fields, including bioprinting for tissue regeneration, functional and sustainable food packaging development, and designing controlled-release drug delivery systems. Continuous research and innovation are key to making UV-cured 3D printing a more versatile and robust technology [32, 95–97].

List of abbreviations

PVA	Poly(vinyl alcohol)
UV	Ultraviolet
BTE	Bone tissue engineering
PI	Photoinitiator
PVA-*g*-GMa	Poly(vinyl alcohol) graft glycidyl methacrylate
SbQCNC	Stibnite quantum dots carbon nanocomposites
HA	Hydroxyapatite
P(AM-*co*-AA)	Poly(acrylamide-*co*-acrylic acid)
PVA/CTS	Poly(vinyl alcohol)/chitosan
PVA-TRAP6	Polyvinyl alcohol thrombin-receptor-agonist-peptide-6
PVA-NB	Polyvinyl alcohol-4-nitrobenzenediazonium
EGAMA-DOPA	Ethylene glycol acrylate methacrylate dihydroxyphenylalanine
PVA-AA	Poly(vinyl alcohol)/acrylamide
MPVA	Magnetic beads poly(vinyl alcohol)
PEGDA	Poly(ethylene glycol) diacrylate
TPO	Diphenyl(2,4,6-trimethyl benzoyl) phosphine oxide

GMAA	Glycidyl methacrylate
PAM-*co*-AA	Poly(acrylamide-*co*-acrylic acid)
CTS	Chitosan
EB	Electron beam
PSAs	Pressure-sensitive adhesives
VOCs	Volatile organic compounds
EHA	2-ethyl hexyl acrylate
BA	*N*-butyl acrylates
DEGDA	Diethyleneglycol diacrylate
BDDA	1,4-butanediol diacrylate
PETA	Pentaerythritol triacrylate
CNC	Cellulose nanocrystals
TEGDE	Triethylene glycol divinyl ether
CHDMDE	1,4-cyclohexanedimethanol divinyl ether
DEGDE	Diethylene-glycol-divinyl-ether
ADE	Diclycidylether derivative bisphenol A
EA	Epoxy acrylate
UA	Urethane acrylate
r_i	Initiating rate
Irgacure-184	1-hydroxy cyclohexyl phenyl ketone
DEAP	2,2-diethoxyaceto-phenone
Irgacure-2959	(4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-Propyl)ketone)
Irgacure-819-DW	Phenyl bis(2,4,6-trimethylbenzoyl)phosphine oxide
LAP	Lithium phenyl-2,4,6-trimethylbenzoyl phosphonate
VA-086	2,2-Azobis[2-methyl-N-(2-hydroxyethyl) propionamide]
Omnirad TPO-L	Ethyl(2,4,6-trimethylbenzoyl)-phenyl phosphinate)
BAPO	Bisacylphosphine oxide
BP	Benzophenone
PPD	1-phenyl-1,2-propanedione
FTIR	Fourier transform infrared
XRD	X-ray diffraction
TEM	Transmission electron microscopy
SEM	Scanning electron microscopy
FDA	Food and drug administration
TE	Tissue engineering
FITC	Fluorescein isothyocyanate
PDGF/ββ	Platelet-derived growth factor
TI	Trypsin inhibitor
PEGDMA	Polyethylene glycol dimethacrylate
ECM	Extracellular matrix
BMPs	Bone morphogenetic proteins
VEGF	Vascular endothelial growth factor
TGF-β	Transforming growth factor-beta
MSCs	Mesenchymal stem cells
MCS	Maleilated chitosan
MPVA	Methacrylated poly(vinyl alcohol)
NMR	Nuclear magnetic resonance
IR	Infrared
PEG	Polyethylene glycol
MTT	3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide
RGDS	Arginyl glycyl aspartic acid
GG	Gellan gum
Poly-HEMA	Poly(2-hydroxyethyl methacrylate)
Poly-MBA	Poly(*N*′-methylene bisacrylamide)
IPNs	Interpenetrating networks
RTIR	Real-time infrared
TGA	Thermo-gravimetric analysis
MB	Methylene blues
XO	Xylenol orange
GG’	Guar gum
HCA	Hydroxycitric acid
SSA	Sulfosuccinic acid
SO	Sorbitol
XL	Xylitol
GL	Glycerol
TE	Tissue Engineering
BSA	Bovine Serum Albumin
PBS	Phosphate-buffered saline
AAS	Atomic Absorption Spectroscopy
MA	Methacrylate
CRGD	Cys-RGD
MSi	Methacrylate functionalized silica nanoparticle

Acknowledgements

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